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OPTIMIZATION OF ACTIVATED CARBON PREPARATION PROCESS FROM SESAME (*SESAMUM INDICUM)* HUSKS AND ITS APPLICATION FOR ADSORPTION OF Cr(VI) IONS FROM AQUEOUS SOLUTION

BY

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List of Acronyms and Abbreviations

AC	Activated Carbon
ANOVA	Analysis of Variance
ASTM	American Society for Testing Material
BBD	Box Behnken Design
CA	Concentration of Activating Agent
CT	Carbonization Temperature
C.V	Coefficient of Variations
Df	Degree of Freedom
GAC	Granular Activated Carbon
HT	Holding Time
IR	Impregnations Ratio
MC	Moisture Content
PAC	Powdered Activated Carbon
RSM	Response Surface Methodology
SH	Sesame Husk
SHAC	Sesame Husk Activated Carbon
VC	Volatile Content

Abstract

The demand for activated carbon is increasing owing to the increased utility of the carbon materials in pollution control. As a result, cost of activated carbon is also growing depending on the application. Designing ways for the production of activated carbon through economic ways is the need of the hour. A range of low cost, easily available, carbon rich and low ash precursors and sources are being explored for the production of carbon materials. This research has presented sesame (*Sesamum indicum*) husks as row material for preparation of low cost activated carbon and assessed its potential application for adsorption of Cr(VI) from aqueous solution. Process variables for sesame husk activated carbon preparation were optimized response surface methodology (RSM). The effect of activating agent concentration, impregnation ratio, carbonization temperature and holding time were analyzed as main factor variable based on BBD. Adsorption % of Cr(VI) was used as response variable. The statistical significance of the model was investigated by ANOVA. The optimum condition during sesame husk based activated carbon preparations was found 30min, 614.7^0C, 1M, 1w/w and 76.41 for holding time, Carbonization Temperature, Concentrations of Activating agent, Impregnations Ratio and Adsorptions % respectively at pH 2, amount of adsorbent dosage of 0.5g in 100mL solutions and temperature of 25^0C. Characterization result shows sesame husk can be used as row material for productions of activated carbon with comparable property with other reported activated carbons. The optimum pH value for the adsorptions of was determined to be 2, at which the Cr(VI) removal of were determined to be approximately 76%. The uptake of chromium from solution by SHAC increased with contact time and attained equilibrium at 360min for all of the temperatures studied. The adsorptions kinetics of pseudo-first order and pseudo-second-order rate equations were tested on the kinetic data and the adsorptions process was found to follow pseudo-second-order rate kinetics for all temperature. The Langmuir and Freundlich isotherm models were applied to the experimental equilibrium data depending on temperature at 30, 40 and 50^oC, and the isotherm constants were determined by using linearized correlations coefficient. Equilibrium data were represented better by the Freundlich model than the Langmuir model. Freundlich equations was found to fit the equilibrium data for Cr(VI) adsorption with monolayer capacity of 18.34, 17.54 and 16.01 at 30, 40, and 50^0C respectively.

1 Introductions

1.1 Background

Increased industrializations and human activities have made an enormous impact on the environment through the disposal of waste containing heavy metals, as e.g., electroplating and leather industries. The discharge of industrial wastewater and domestic wastes to surface waters has caused substantial adverse effects on aquatic life, and it has indirectly affected the people who depend on the surface waters. Industrial wastewater frequently is laden with toxic heavy metals, and significant amounts of which are deposited into the natural aquatic and terrestrial ecosystems. It is well known that heavy metals can damage nerves, the liver, and bones, and that they block functional groups of essential enzymes. Out of the various toxic pollutants chromium and its compounds are considered as the most dangerous inorganic water pollutants Sekarathil Anuradha Jabasingh and Pavithra (2010).

Activated carbon is used in a number of industrial applications including separations and purifications technologies, catalytic processes, biomedical engineering, and energy storage, among others (Gonzalez-Serrano, Cordero, Rodriguez-Mirasol, Cotoruelo, & Rodriguez, 2004; Guo, Xu, Chen, & Lua, 2005; Luo, Zhou, Liu, & Xia, 2008; J. L. Song, Feng, Zhao, Zheng, & Zhu, 2010). The extensive applications of activated carbon is mainly due to its wide availability, high performance in adsorptions processes, surface reactivity and the versatility to modify its physical and chemical properties for synthesizing adsorbents with very specific characteristics (Durán-Valle, 2012; Joao Valente Nabais, Peter Carrott, M.M.L. Ribeiro Carrott, Vania Luz, & Ortiz, 2008).

The removal of ions from industrial wastewater is an important problem to be solved. Chromium, which is on the top-priority list of toxic pollutants defined by the US Environmental Protections Agency (EPA), exists usually in both trivalent and hexavalent forms in aqueous systems. The two-oxidation states of chromium have different chemical, biological, and environmental characteristics. Cr (III) relatively insoluble and is considered as an essential trace nutrient for human and animals, while , in turn, Cr(VI) is highly toxic(Bhattacharya, Naiya,

Mandal, & Das, 2008). Because of its mutagenic and carcinogenic properties, it includes skin irritations to lung cancer, as well as kidney, liver, and gastric damage for humans. The hexavalent form is 500 times more toxic than the trivalent. It is toxic to micro-organism, plants, animals and humans. Chromium is considered as priority pollutants because of their high toxicity at low concentrations(Sekarathil Anuradha Jabasingh & Pavithra, 2010).

Heavy metals are, among pollutants, the worst group of and Cr(VI) ions are considered to be highly toxic, often present in industrial wastewaters as chromate and dichromate ions. For instance, the discharge of ions into aquatic ecosystems has become a matter of concern in all the tannery area in Ethiopia over the last few decades. This pollutant is introduced into aquatic systems significantly from the effluents of leather processing units as a result of chrome tanning of leather. The tanning process is one of the largest polluters of chromium all over the world. Most of the tanneries in Ethiopia adopt the chromium tanning process because of its processing speed, low costs, and light color of leather and greater stability of the resulting leather. In the chromium tanning process, the leather takes up only 60–80% of applied chromium, and the rest is usually discharged into the sewage system causing serious environmental impact. The maximum levels permitted in wastewater are 5mg/L for trivalent chromium and 0.05mg/L for hexavalent chromium. With this limit, it is essential for industries to treat their effluents to reduce the Cr to acceptable levels. Due to more stringent environmental regulations, most of the mineral processing plants, metal-finishing industries, and tannery industries are facing now a days the difficult problem of disposal of wastewater produced in huge quantities, laden with Cr. The tolerance limit for discharge into inland surface waters is 0.1mg/L, and in potable water, it is 0.05mg/L (Kobya, 2004; Selen·, Özer·, & Özer, 4 July 2014).

In this context, most studies on chromium involve reductions of ions to less toxic and less mobile forms such as Cr (III) ions. In this regard, the increasing awareness of accumulations of heavy metals in the environment also led to a request for new and improved cleaner technologies to overcome metal pollutions. Several technologies have been used for the removal of chromium from industrial wastewater, including electrochemical precipitations, ions exchange, evaporations, reverse osmosis, chemical oxidations or reductions, electro-dialysis, ultrafiltrations, solvent extractions, applications of membrane technology, adsorptions /sorptions

(Selen· et al., 4 July 2014). An innovative heavy metal removal process called adsorptions gained enormous impetus. Among the methods mentioned above, adsorption is preferred from an economic perspective due to the relative simplicity of its operations and the availability of various inexpensive adsorbents. Adsorptions is the binding and concentrations of heavy metals from aqueous solutions (even very dilute ones) by certain types of agro waste or it can also be defined as the ability of materials to accumulate heavy metals from wastewater through physicochemical pathways of uptake. Most of the other technologies suffer from drawbacks such as high operational costs and incomplete removal or the disposal of the residual metal sludge. Adsorption by activated carbon is one of the effective techniques for ions removal from wastewater because of the high surface area, highly porous character, and relatively low cost of the adsorbent. Activated carbon is especially known for the effective removal of organic chemicals, inorganic and heavy metal ions pollutants from wastewater in the laboratory as well as in various industries. Activated carbon can be prepared by a physical activation or chemical activation process. Physical activation consists of two steps: a carbonaceous material is carbonized under the oxygen-free atmosphere (carbonization process) and then activated with an activating gas such as CO_2 and H_2O (activation process). In chemical activation, both carbonization and activation processes occur simultaneously at a lower temperature and a shorter time than that in physical activation. Therefore it saves time and energy. Moreover chemical activation is reported to give activated carbon with higher specific surface area and much better developed porosity than physical activation. In chemical activation, several types of chemicals are used as the activating agent including $ZnCl_2$, H_3PO_4, H_2SO_4 and KOH. Different activating agents provide activated carbons with different properties (Samorn Hirunpraditkoon, Nathaporn Tunthong, Anotai Ruangchai, & Nuithitikul*, 2011).

The major advantages of adsorptions over conventional treatment methods include: low cost, good efficiency, minimizations of chemical sludge, regenerations of adsorbents, and possibility of metal recovery. The adsorption process involves a solid phase (adsorbent or adsorbents) and a liquid phase (solvent, normally water) containing a dissolved species to be adsorbed (adsorbate, metal ions). Due to higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portions remaining in

the solutions. The degree of adsorbent affinity for the adsorbate determines its distributions between the solid and liquid phases. Mechanisms of metal adsorptions are essential to be understood first in order to successfully exploit the phenomenon and for regenerations of adsorbent materials in multiple reuse cycles. The complex nature of adsorbent materials makes this task particularly challenging. Agricultural by-products and some industrial wastes contain high carbon content and hence they could be used as starting/raw materials for the preparations of indigenously prepared activated carbons (IPACs). Although some attempts have already been made to economize the activated carbon (AC), the scope for minimizing its cost and development of alternative adsorbent materials to commercial activated carbon (CAC) by preparing IPACs from agricultural wastes is still open. The reported results revealed that carbons prepared from agricultural wastes exhibit a high adsorptions capacity, obeyed Langmuir and Freundlich isotherms, first order kinetic equations and found to be pH sensitive towards the removal of metal ions (N. KANNAN, 2009).

The major raw materials for productions of activated carbon are wood, coal, nutshells, and fruit stones. The main disadvantage of activated carbon is the weak mechanical properties of its surface and that it is easily burned at high operations temperature. Some low cost industrial and agricultural waste products activated carbons used for removing of hexavalent chromium ions such as groundnut husk, agro-waste, neem leaves, mud, bauxite, carbon nanotubes, coal, polyacrylamide-grafted sawdust, peat, hazelnut shells, teafactory waste, eucalyptus bark, beech-wood sawdust, nonliving microbial biomass, freshwater algae, clay minerals, pomegranate-husk carbon, sunflower stems, rice straw, zeolites, waste tires, sphagnum peat moss, sugarcane bagasse, wheat bran, sawdust, wheat bran, rice bran , sago waste, green coconut shell, hazelnut shell, olive stone, gingelly oil cake, and peanut shell have all been reported as useful for preparing adsorbents (Selen· et al., 4 July 2014).

Sesame (*Sesamum indicum*) husk is agricultural by-product and as such, it is a readily available and abundant natural material in Ethiopia that can be considered as a raw material to produce an effective adsorbent. There is also a lack in the mitigations of agricultural wastes in developing countries including Ethiopia so it very necessary to investigate this waste as a way of mitigations and as low cost adsorbent to minimize the import of commercial activated carbons. Sesame is

grown primarily for its oil-rich seeds. The leaves, husks and stems of this plant are disposed of as waste after removal of the seeds for oil extractions and export purpose. These wastes are burned at the farm land to control pastes as animals inter to the farm land to eat the waste they also excrete at the farm land. The excretion produces pastes(Maiti, , Ghosh, & A.Logeswari, 18 Dec 2007).

In this study, sesame husk was used as the starting material to prepare activated carbon. The sesame husk is inevitably generated with a significant amount. Converting this waste to activated carbon was adding more value to the product. Moreover it is renewable biomasses which are environmentally friendly. In present research modified sesame husk was used to develop activated carbon by chemical activations method using H_2SO_4 for the adsorptions of hexavalent chromium ions from aqueous solutions. The physicochemical mechanisms in the adsorptions are complex; no simple theory of adsorptions could adequately describe experimental results. Several groups of researchers described the kinetics of adsorptions in metal-adsorbent systems using various kinetic models. In recent years, the research attentions has been focused on agro and agro processing byproducts chemically modified low cost activated carbon methods for the treatment of effluents. Previous study on 'the Removal of Ions by Sesame (*Sesamum indicum*) Stems Dehydrated with Sulfuric Acid' mainly dealt with the adsorptions of ions not on the optimizations of activated carbon preparations(Selen· et al., 4 July 2014).

The search for the optimization of operation conditions for its production process is an important factor for tackling production cost. This includes identifying new row material with high carbon content and low cost. Researchers proposed number of lignocellulosic industrial and agricultural wastes. Those lignocellulosic wastes not only lessen its cost of productions, but also diminish environmental impact of agricultural and industrial wastes and avoid additional cost for waste management (Peláez-Cid & Teutli-León, 2012). Optimization of process parameter and the way to enhance the qualities of the carbon produced is also being studied to make its production more profitable, and, hence, solve specific environmental issues.

A sooner or later mass production of activated carbon from agricultural residue is inevitable, for its increased need for adsorption of pollutant from industrial wastewater. With this regard designing way for the production of activated carbon through economic way is the need of the

hour. Optimizing application of activated carbon in adsorption process through its proper design in the way to enhance the adsorptive efficiency of produced activated carbon is the other knowledge gap to be addressed, in making its application economically feasible and environmentally sustainable.

With this regard, not fully investigated yet, Sesame stem is one of those lignocellulosic precursor proposed for preparation of AC and shown promising result(Selen· et al., 4 July 2014). It is the major solid waste residue from the handling and processing of sesame. Since Ethiopia is one of major sesame producing countries in the world, large amount of sesame husk is produced as waste. No research found on how process parameters in preparation of sesame husk activated carbon interact and affect adsorption capacity or adsorption %, on chemical activation using H_2SO_4 in preparation of sesame husk activated carbon and on adsorption of Cr(VI) ions from aqueous solution using chemically activated H_2SO_4 modified sesame husk activated carbon. The behavior of adsorption system such as equilibrium isotherm, kinetic model and thermodynamic parameters were not reported yet.

In the present study, the response surface methodology (RSM) was adopted to optimize the variables affecting the preparations of activated carbon for adsorptions of ions from aqueous solutions. These methods are employed after a ‘‘vital few’’ controllable factors are identified. RSM is a collection of mathematical and statistical techniques for experimental design, model development, and evaluation of factors and optimization of conditions. Statistical optimization reflects the role of each of the components of the activated carbon (AC) preparation process. Optimization through Box-Behnken design and application of RSM is a common practice for optimizing the process parameters. Sesame stem was previously exploited for its ability to remove Cr(VI)(Selen· et al., 4 July 2014). RSM was earlier applied to optimize the removal of Cr(VI) by Mucor racemosus, The potential usage of the mucor biomass for biosorption has been studied and response surface approach for the biosorption of Cr(VI) Ions by Mucor racemosus was studied(Sekarathil Anuradha Jabasingh & Pavithra, 2010). However, no investigations have been carried out on the statistical optimization of operating conditions of AC preparation for the adsorption of Cr(VI) by sesame husk. The objective of the present work was to investigate the

optimum operating conditions during AC preparations on the enhancement of adsorptions % of Cr(VI) ions by sesame husk.

1.2 Problem Statement

The demand for activated carbon is increasing owing to the increased utility of the carbon materials in pollution control. As the applications of activated carbon are immense, the gap between demand and supply is ever widening. As a result, cost of activated carbon is growing. This is due to the use of non-renewable and relatively expensive starting material such as either coal based or petroleum pitch based which are prone to exhaustion and unjustified in pollution control applications (Tan, Ahmad, & Hameed, 2007). Their global distribution is also non uniform. This may in due course result in scarcity of the material in addition to becoming expensive. This situation necessitates the need for the exploration of new sources of carbon materials with desired physico chemical properties namely, high specific surface area, micro or meso porosity or both, depending on the end application, surface functionality, thermal stability, carbon purity, adsorptive capacity and chemical composition.

In their literature review of the last two decades (1992–2011) Peláez-Cid and Teutli-León (2012) indicated that worldwide researchers had proposed number of agricultural and industrial wastes as low cost sources to obtain raw materials for the production of activated carbon. These researchers have in mind not only to lessen its cost of production, but also to diminish environmental impact of agricultural and industrial wastes and to avoid cost of associated cost of solid waste handling (Peláez-Cid & Teutli-León, 2012).

At the present time, different industries are growing in Ethiopia due to governmental incentive given to investors. Among these industries the most polluter one is tannery industries which have primary treatment plant for general wastewater line only and does not have treatment for chrome and lime line. Due to the fact that the industries increase their capacity and to manufacture finished leather which results in increased wastewater effluent loading from the factories which affects the environment. To enhance efficiency wastewater treatment plant and safety discharge it to water bodies it is necessary to have low cost treatment technology which is adsorption.

Among of the industries found in Ethiopia most of them get their water utility from well (ground) water. Ground or well water contains different pollutants that can affect human health

as well as decrease performance of manufacturing equipments like boilers. So the ground water must be treated before it is being used.

Now a day, several water treatment techniques are developed to treat ground water. Among these, carbon filtration (activated carbon unit) is one of the well known treatment technique used especially in bottled water industries. Currently, Activated carbon is produced in large amount across the world. However, Ethiopia is one of the importers of activated carbon rather than producing it.

In Ethiopia some newly developed factories utilize activated carbon as one of their water treatment unit. These newly developed factories and indirectly Ethiopia incur great amount of money on importing activated carbon. As import data presented in table 1 indicates, utilization of activated carbon in Ethiopian industries is growing faster in recent years. As a result of this, production of activated carbon from a biomass waste can be seen as one way of reducing costs that will be incurred for importing activated carbon.

Although Ethiopia imports AC, it has potentially row materials to locally produce it. The incredible versatility of the product makes producing it possible in many different areas depending on what row material is available. Some of the row materials for activated carbon production are agricultural waste such as sesame husk, corn comb, coffee husk, spent grain, macadamia nutshell, etc.

Therefore, this research can be seen as one way of an import substitution of AC by producing it from locally available cheap biomass waste.

This research presented sesame husk as new low-cost, locally abundant material for production of activated carbon and investigated its application for adsorption of Cr(VI) from aqua solution. In this endeavor, first process parameters involved in preparation of sesame husk activated carbon by chemical activation using H_2SO_4, were optimized aiming reduction of its production cost. Then the characteristics of activated carbon prepared at predicted optimum operational parameters were analyzed. Finally application of sesame husk activated carbon for Cr(VI)

adsorption form aqua solution was investigated, and adsorption process is properly designed through accurate description of equilibrium isotherm and kinetic model.

1.3 Objectives

1.3.1 General Objective

To investigate optimum sesame husk based activated carbon preparation process, its characteristic and application in batch adsorption of Cr(VI) from aqua solution.

1.3.2 Specific Objectives

The specific objectives of this research are:

- ✓ Optimization of process parameters in preparation activated carbon from sesame husk by chemical activation using H_2SO_4.
- ✓ Characterize sesame husk based activated carbon produced at predicted optimum process conditions.
- ✓ Investigate application of sesame husk based activated carbon for adsorption of Cr(VI) from aqua solution.

1.4 Significance of the Study

The study was intended to develop low-cost adsorbent from agro-wastes/by products, to optimize the preparation conditions for optimum Cr(VI) ions adsorption from aqueous solutions using RSM and to application of sesame husk activated carbon for adsorption of Cr(VI)ions from aqueous solutions, industrial wastewater treatment process modifications, improve productivity, reduce pollutions loads and the effects that are chromium and agricultural byproducts, enhance the clean technology that is adsorption. Among many pollutants chromium is the concern because of it is not biodegradable and it is also a carcinogen.

This research therefore will contribute in triggering environmental awareness at all levels of governmental establishments, mitigate locally available agrowastes/byproducts, and minimize

the cost of industrial wastewater treatment and ground water treatment. Sesame husk was investigated locally available low cost agricultural waste adsorbent as an alternative of CAC by optimizing the preparation conditions and improved the efficiency of adsorbents activated carbon by chemical activations using H_2SO_4, for Cr(VI) ions adsorption from aqueous solutions. This will have a paramount significance in providing concrete evidence for development policy makers in assuring sustainability by mitigating the environmental threat/pollutions caused by inefficient industrial wastewater treatment.

2 Literature review

2.1 Chromium

Heavy metal discharge into the aquatic ecosystem is a matter of concern. Eleven metals such as lead (Pb), Chromium (Cr), mercury (Hg), uranium (U), selenium (Se), zinc (Zn), arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu),nickel (Ni), out of 20 classified metals as toxic, are emitted into the environment in quantities that pose risks to human health. Input of these trace metals into ecosystem are largely as a result of mining operations, refining ores, sludge disposal, fly ash from incinerators, processing of radio-active materials, metal plating, or manufacture of electrical equipment, paints, alloys, batteries, pesticides, and preservatives. Presences of heavy metals in environment become a major threat due to their bio-accumulating tendency and toxicity. Hence, it is necessary to remove these metals from industrial effluents before discharging aqueous waste into environment.

Chromium (VI) ions are highly toxic in nature. This is due to the fact that one of the reductions products of Chromium (VI) ions is Chromium (V) ions. Chromium (V) ions are a known carcinogen and will lodge in any tissue to form cancerous growths. There are reports that Chromium (V) ions are also a factor leading to premature senility in parts of Russia. The Chromium (VI) ions are a very strong oxidizing agent (therefore very fast in reacting, unlike Chromium (III) ions and likely to form complexes). Chromium (VI) ions are not a very stable state when compared to Cr (III) ions. Chronic inhalation of Chromium (VI) ions compounds increases the risk of lung, nasal and sinus cancer. Severe dermatitis skin ulcer can result from contact with Chromium (VI) ions compounds. It can cause mild to severe liver abnormalities. Chromium (VI) ions compounds are teratogenic to animals. Chromium (VI) ions are one such metal known to be carcinogenic and have an adverse potential to modify the DNA transcriptions process. It is also reported to cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage. Chromate (CrO_4^{-2}) is the prevalent species of ions in natural aqueous environments, and is the major pollutant from chromium related industries such as mining, iron sheet cleaning, chrome plating, leather tanning and wood preservations. Therefore, the reductions of amount of this metal from such effluents to a permissible limit before discharging them into streams and

rivers is very important for human health and environment. In this regard, several conventional wastewater treatment technologies such as ions exchange, chemical precipitations, evaporations, membrane filtrations, reverse osmosis, and electrodialysis were developed and are used successfully. Application of such traditional treatment techniques needs enormous cost and continuous input of chemicals which becomes impracticable and uneconomical and causes further environment damage. On the other hand, adsorption is an emerging technology for removal of heavy metals from industrial wastewater. The major advantages of this technique are the reusability of biomaterial, low operating cost and improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, and short operations time and no productions of secondary compounds which might be toxic.

2.2 Activated Carbon

Activated Carbon (AC) is the common term used for a group of absorbing substances of crystalline form, having a large internal pore structures that make the carbon more absorbent. The term of activated carbon is come from the word "carbon" and "active" which carbon mean raw material undergoes a carbonizations process (burning in high temperature) while active a material in carbon conditions undergoes activations process to open a pore surface area as maximum as can to increase adsorptions rate of activated carbon. Generally, the raw materials for the productions of AC are those with high carbon but low inorganic contents such as wood, lignite, peat and coal. Besides that, lots of agricultural waste and by product have successfully converted to AC for examples nutshell, paper mill sludge and peach stones(ROHAIDA & JAMALUDIN, 2010).

Activated carbon in its broadest sense includes a wide range of processed amorphous carbon-based materials. It is not truly an amorphous material but has a microcrystalline structure. Activated carbons have a highly developed porosity and an extended interparticulate surface area. Their preparation involves two main steps: the carbonizations of the carbonaceous raw material at temperatures below 800^0C in an inert atmosphere and the activations of the carbonized product. Thus, all carbonaceous materials can be converted into activated carbon, although the properties of the final product will be different, depending on the nature of the raw

material used, the nature of the activating agent, and the conditions of the carbonizations and activations processes.(R. C. Bansal & Goyal, 2005)

During the carbonizations process, most of the noncarbon elements such as oxygen, hydrogen, and nitrogen are eliminated as volatile gaseous species by the pyrolytic decompositions of the starting material. The residual elementary carbon atoms group themselves into stacks of flat, aromatic sheets cross-linked in a random manner. These aromatic sheets are irregularly arranged, which leaves free interstices. These interstices give rise to pores, which make activated carbons excellent adsorbents. During carbonizations these pores are filled with the tarry matter or the products of decompositions or at least blocked partially by disorganized carbon. This pore structure in carbonized char is further developed and enhanced during the activations process, which converts the carbonized raw material into a form that contains the greatest possible number of randomly distributed pores of various sizes and shapes, giving rise to an extended and extremely high surface area of the product. The activations of the char is usually carried out in an atmosphere of air, CO_2, or steam in the temperature range of 800^0C to 900^0C. This results in the oxidations of some of the regions within the char in preference to others, so that as combustions proceeds, a preferential etching takes place. This results in the development of a large internal surface, which in some cases may be as high as $250m^2/g$.(R. C. Bansal & Goyal, 2005)

Activated carbons have a microcrystalline structure. But this microcrystalline structure differs from that of graphite with respect to interlayer spacing, which is 0.335nm in the case of graphite and ranges between 0.34 and 0.35nm in activated carbons. The orientation of the stacks of aromatic sheets is also different, being less ordered in activated carbons. Electron Spin Resonance (ESR) studies have shown that the aromatic sheets in activated carbons contains free radical structure or structure with unpaired electrons. These unpaired electrons are resonance stabilized and trapped during the carbonizations process, due to the breaking of bonds at the edges of the aromatic sheets, and thus, they create edge carbon atoms. These edge carbon atoms have unsaturated valencies and can, therefore, interact with heteroatoms such as oxygen, hydrogen, nitrogen, and sulfur, giving rise to different types of surface groups. The elemental compositions of a typical activated carbon has been found to be 88% C, 0.5% H, 0.5% N, 1.0% S, and 6 to 7% O, with the balance representing inorganic ash constituents. The oxygen content

of an activated carbon can vary, however, depending on the type of the source raw material and the conditions of the activations process.(R. C. Bansal & Goyal, 2005)

The adsorptions % or adsorptions capacity of the adsorbents comes from the affinity of molecules, and is classified into physical adsorptions, chemical adsorptions, and catalytic actions. Generally, adsorbents are made of Fuller's earth and activated clays, aluminum oxide base materials, silica gel, ions exchangers, magnesia base materials, activated carbon, and so on. Activated carbon is the most common adsorbent in wastewater and waste gas because it is cheaper, easier to use, and recyclable. Activated carbon also has superior performance in dealing with organic and toxic waste, such as chrome, ozone, pesticides, aromatic series, and heterocyclic compounds. As a result, activated carbon is broadly applied for adsorptions in industry.(Chi Hslang Wang, Dec. 14, 2006)

Activated carbons are porous carbonaceous adsorbents. A large variety of organic solutes can be removed from water and wastewater by adsorptions onto activated carbon, and some inorganic solutes can also be removed by this means. The activated carbon adsorbs and retains solutes and gases, the amount of material adsorbed being potentially very large because of the great internal surface of activated carbon. Activated carbon has a high adsorptive surface area (500–1500m^2g^{-1}), while the pore volume ranges between 0.7 and 1.8cm^3g^{-1}. It is mainly used in the form of powdered activated carbon (PAC) or granular activated carbon (GAC)(Çeçen & Aktaş, 2011b).

2.3 Activated Carbon in Ethiopia

Many Ethiopian industries such as tannery industries and beverage and water factories etc. uses activated carbon as one means of treating their utility water which is obtained from the ground and surface water. For instance, mineral water manufacturers, tannery industries etc. in Ethiopia uses activated carbon to remove Oder, color, taste especially chromium, which is toxic waste from tannery industries. However, this activated carbon is not produced in Ethiopia rather it is mostly imported from South Africa, Sri Lanka, Netherland, Italy, China and UK.

Recent import data of activated carbon from ministry of industry of Ethiopia is given in Table 1

Table 1: Total activated carbon imported to Ethiopia from year 2007 to 2010 (ministry of industry, 2010)

Year	Amount of activated carbon (Kg)	Cost in birr (before tax)
2010	397,134.692	5,324,297.75
2009	7,905.43	263,781.95
2008	74,124.27	1,612,317
2007	7,380.00	289,665.75

2.4 Preparation of Activated Carbon

Commercially available activated carbons are prepared from materials having high carbon content such as coal, lignite, wood, peat, nut shell, coconut shell, lignin, petroleum coke, and synthetic high polymers. The manufacturing process comprises two phases, carbonizations and activations. The carbonizations process includes drying and heating to remove undesirable by-products such as tar and other hydrocarbons. The carbonaceous materials are then pyrolyzed and carbonized within a temperature range of 400–600^0C in an oxygen-deficient atmosphere. This removes the volatile low-molecular-weight fractions and causes the material to undergo an activations process. Activations can be achieved thermally by the use of oxidations gases such as steam at above 800^oC or carbon dioxide at higher temperatures. Chemical activations, on the other hand, involves impregnations of the raw material with chemicals such as sulfuric acid, phosphoric acid, potassium hydroxide, and zinc chloride(Khalili et al., 2002). The term activation refers to the development of the adsorptions properties of carbon. Micropores are formed during the activations process, the yield of micropore formations being usually below 50%. The raw material has a very large influence on the characteristics and performance of activated carbon obtained. Raw materials such as coal and charcoal have some adsorptions capacity, but this is greatly enhanced by the activations process. The common materials used in the productions of activated carbon and the basic properties of the activated carbons produced are summarized in Table 2((Inglezakis & Poulopoulos, 2006)).

Table 2: Basic properties of common materials used in the manufacture of activated carbon

Raw Material	Carbon (wt%)	Volatiles (wt%)	Ash (wt%)
Wood	40-50	55-60	0.3-1.1
Nut shells	40-45	55-60	-
Lignite	55-70	25-40	5-6
Coal	65-95	5-30	2-15
Petroleum coke	70-85	15-20	0.5-0.7

According to Hernández-Montoya, García-Servin, and Bueno-López (2012), the preparations of ACs from lignocellulosic materials involved two processes, the carbonizations and the activations, which can be performed in one or two steps depending on the activations method (physical or chemical, respectively). The carbonizations consists of a thermal decompositions of raw materials, eliminating non-carbon species and producing a fixed carbon mass with a rudimentary pore structure (very small and closed pores are created during this step).On the other hand, the purpose of activations is to enlarge the diameters of the small pores and to create new pores.

Specifically, when the carbonization is carried out in an inert atmosphere the process is called pyrolysis. According to the literature, the pyrolysis of lignocellulosic materials as coconut shells, coffee husk, olive stones, walnut shells, etc., gives rise to three phases: the char, oils (tars) and gases. The relative amount of each phase is a function of parameters such as temperature of pyrolysis, nitrogen flow rate and heating rate. For example, slow heating rates promote high yields of the carbon residue while flash pyrolysis is recommended for high liquid (oil) ratios (Mohamed, Mohammadi, & Darzi, 2010).

During the pyrolysis of lignocellulosic precursors, a rudimentary porosity is obtained on the char fractions as a consequence of the release of most of the non-carbon elements such as hydrogen,

oxygen and nitrogen in form of gases and tars, leaving a rigid carbon skeleton formed by aromatic structures (Hernández-Montoya et al., 2012).

All the available methods of activations can be classified in to two types, namely, physical activations or chemical activations depending on whether a gaseous or solid activating agent is used. Each of these methods has its own merits and demerits.

During physical activations, the agricultural and industrial waste (lignocellulosic) material as such or the previously carbonized materials can undergo gasifications with water vapor, carbon dioxide, or the same combustions gases produced during the carbonizations. Ammonium per sulfate, nitric acid, and hydrogen peroxide have also been used as oxidizing agents (Salame & Bandosz, 2001). Chemical activations consists of impregnating the agricultural and industrial waste (lignocellulosic) or carbonaceous raw materials with chemicals such as $ZnCl_2$, H_3PO_4, HNO_3, H_2SO_4, NaOH, or KOH. The carbonizations step and the activations step simultaneously progress in the chemical activations (Hayashi, Horikawa, Takeda, Muroyama, & Ani, 2002). Then, they are carbonized (a process now called "pyrolysis") and, finally, washed to eliminate the activating agent. The application of a gaseous stream such as air, nitrogen, or argon is a common practice during pyrolysis which generates a better development of the material's porosity. (M.P. Elizalde-González & Hernández-Montoya, 2007; Girgis, Yunis, & Soliman, 2002).

According to Hernández-Montoya et al. (2012) review chemical activations is the most used method for the preparations of ACs (~60%) from agricultural and industrial waste (lignocellulosic) precursors. Physical activations methods is used in 28% of the studies and a low quantity of studies combine both methods (i.e., physicochemical) to produce ACs. H_3PO_4 and $ZnCl_2$ are the two more employed activating agents in the impregnations of agricultural and industrial waste (lignocellulosic) materials (30% and 24 %, respectively), whereas alkaline reagents such as KOH, NaOH and K_2CO_3 have been considered because ACs with high specific surface can be obtained (1500-2500m^2g^{-1}). Physical activations of agricultural and industrial waste (lignocellulosic) precursors normally render carbons with lower specific surface area. However, when compared with chemical activations, this method is not corrosive and does not require a washing step (Hernández-Montoya et al., 2012).

2.5 Factors affecting activated carbon preparation

The properties of activated carbons as adsorbent are influenced basically by the following factors(Sanchez, 2011):

- ✓ Properties of the starting materials. The most common raw materials come from coal, organic polymers and lignocellulosic materials.
- ✓ Activations method: physical, chemical or a mixture of both.
- ✓ Carbonizations and activations conditions such as heating speed, time, temperature, etc
- ✓ Operations conditions such as impregnations ratio, impregnations time, and so on. Generally, operations conditions are influenced depending on the activations method.

Research has shown that carbon's properties such as specific surface area, porosity, density and mechanical resistance depend greatly on the raw material used. However, it may be possible to modify these parameters changing the conditions in the pyrolysis process of the lignocellulosic materials. In particular, the most important parameters to be considered while preparing activated carbons from lignocellulosic materials are described below(Sanchez, 2011).

2.5.1 Activating agent

The use of $ZnCl_2$ has declined because of the environmental pollutions problems with zinc disposal(Girgis et al., 2002). KOH and H_2SO_4 also have been used as activations reagents in the preparations of activated carbons with high specific surface. H_2SO_4 is the most commonly used chemical agent for synthesis of activated carbon.

In preparations of activated carbon, the lignocellulosic precursor is treated primarily with a chemical agent, such as H_3PO_4, H_2SO_4, HNO_3, NaOH, KOH or $ZnCl_2$ by impregnations or physical mixture and the resulting precursor is carbonized at temperatures between 400 and 800ºC under a controlled atmosphere.

In the last few years, the activations of lignocellulosic materials with H_2SO_4 has become an increasingly used method for the large-scale manufacture of ACs because the use of

this reagent has some environmental advantages such as ease of recovery, low energy cost and high carbon yield. H_2SO_4 plays two roles during the preparations of ACs:

- ✓ H_2SO_4 acts as an acid catalyst to promote bond cleavage, hydrolysis, dehydrations and condensations, accompanied by cross-linking reactions between sulfuric acid and biopolymers;
- ✓ H_2SO_4 may functions as a template because the volume occupied by sulfuric acid in the interior of the activated precursor is coincident with the micropore volume of the activated carbon obtained (Zuo, Yang, Liu, & Cai, 2009).

The chemical and physical properties of ACs obtained by chemical activations with H_2SO_4 are affected by the experimental conditions of preparations such as acid concentrations, time of activations, impregnations ratio, carbonizations temperature and heating rate. Also some recent works have shown that the atmosphere used in the carbonizations process has an obvious effect on the physicochemical properties of ACs (Zuo et al., 2009).

In the review of Hernández-Montoya et al. (2012) most literatures show the concentrations of acid is greater than 50% (w/w) and the activations temperature for 75 % of these studies is between 350 and 600 ºC. Carbons obtained with the highest phosphoric impregnations ratio (China Fir and avocado kernel seeds) are the materials with the largest S_{BET}(1785 and 1802 m^2g^{-1}). Additionally, the carbon obtained from Oil palm shell and activated using a rather low impregnations ratio (0.09) was one of the materials with a lower specific surface area (356 m^2g^{-1}).

2.5.2 Raw material

Activated carbons are manufactured from various carbonaceous substances of animal, vegetable or mineral provenience. Anthracite, petroleum coke, coal and waste products from lignocellulosic nature as wood, walnut shells, coconut or almond are frequently used as starting material. Anyway, any carbonaceous material can be suitable to be a good adsorbent but have to meet some requirements for being used commercially:

- ✓ Good availability

- ✓ Low cost
- ✓ The resulting activated carbon satisfies all kind of applications.

The starting material is amorphous and the porous structure is achieved during the activations. The compositions of the material will longer define the properties of the adsorbent. The literature shows differences between using coal or lignocellulosic materials as well as between lignocellulosic materials. Bansal et al (M. Bansal, Garg, Singh, & Garg, 2009) showed that the porosity developed from vegetable as raw material using physical or chemical activations was more heterogeneous than the ones prepared from coal(Sanchez, 2011).

The carbon derived from coconut shells (X. Song, Liu, Cheng, & Qu, 2010) have higher density and have a pore size distributions narrower, which makes these coals more suitable for the adsorptions of small molecules, useful in gas purifications applications(Sanchez, 2011).

The main properties of the activated carbons produced from lignocellulosic materials are:

- ✓ High temperature stability
- ✓ Resistance against acid attack
- ✓ Slightly hydrophilic
- ✓ Considerable mechanical strength
- ✓ Low economical cost due to the abundance of the raw material

Due to this reason, this work aims was to study the viability of manufacturing activated carbon from sesame husks, a lignocellulosic waste that comes from a sesame plants, which is the cover or shell above small oval white seeds of the sesame plant. Sesame, common name for a genus, containing about 15 species of herbaceous plants native to Africa and Asia, applied especially to one of its species that is widely cultivated for its seeds. The oil extracted from sesame seeds is used in cooking, as salad oil, and in making margarine. Commercially the plants are grown as annuals from seed, reaching a height of about 2 m (about 6 ft) in three to five months. The plants are cut and dried; as they dry, the seed capsules split open, and the seeds are easily extracted by shaking the plants upside down. Scientific classifications: Sesame is the

common name for the genus *Sesamum* of the family Pedaliaceae. The name is applied especially to the species *Sesamum indicum(Microsoft, 2009)*.

2.5.3 Heating Speed

Regularly, heating ramps with a low speed are used for preparations of activated carbon. This approach allows the complete combustions of material precursor and favors a better porosity development. Rapid heating during pyrolysis produces macroporous residue (Heschel & Klose, 1995).

2.5.4 Carbonizing Time and Holding Time

This parameter must be optimized to obtain the maximum porosity development while still minimizing the material's loss due to an excessive combustions. Bouchelta et al. (Bouchelta, Medjram, Bertrand, & Bellat, 2008) have shown that the yield percentage decreases with increase of activations temperature and hold time. Carbonizations times ranging from 1h (Rajeshwarisivaraj, Sivakumar, Senthilkumar, & Subburam, 2001) up to 14h have been used in charcoal productions.

2.5.5 Carbonizing temperature

It has the most influence over the activated carbon's quality during the activating process. It must be at least 400°C to ensure the complete transformations of organic compounds (present in agricultural and industrial waste (lignocellulosic) precursors) into graphene structures. The degree of specific surface area development and porosity is incremented on par with the carbonizing temperature(Rajeshwarisivaraj et al., 2001). During physical activations, carbonizations temperatures are greater than those needed for chemical activations (Lussier, Shull, & Miller, 1994). However, carbonizations temperatures used in activated carbon productions are generally greater than 400°C and temperatures ranging from 120 to 1000°C have been used.((Salame & Bandosz, 2001),(M.P. Elizalde-González & Hernández-Montoya, 2008),(M.P. Elizalde-González & Hernández-Montoya, 2007) and (Rajeshwarisivaraj et al., 2001)). It has been reported that carbon obtained from peach pits with temperatures below 700°C still have a high content of hydrogen and oxygen(MacDonald & Quinn, 1996).

2.5.6 Mass ratio of precursor and activating agent

The complete saturations of agricultural and industrial waste (lignocellulosic) precursor must be ensured to develop the adsorbent porosity with the minimum activating agent consumptions. This leads a minor consumption of chemical compounds and a better elimination of the excess during the carbon washing process. The effect of the increase in proportions of the impregnations over the carbon porous structure is greater than the one obtained with the increase of carbonizing temperature(Olivares-Marín, Fernández-González, Macías-García, & Gómez-Serrano, 2006).

2.5.7 Gas flow speed

It has been observed that during pyrolysis, the passing on an inert gas, such as N_2 or Ar, favors the development in the carbon's porosity. In this case, the flow and the gas type may affect the final properties of the activated carbon which is N_2. CO_2 flow-rate had a significant influence on the development of the surface area of oil palm stones (Lua & Guo, 2000).

2.5.8 Effect of washing process

During the lignocellulosic residue's pyrolysis, the presence of chemical activating agents generates carbons with a more orderly structure. The later eliminations of free chemical activating agents, by means of successive washings, will allow a better development of porosity.

2.6 Characteristics of Activated Carbon

Activated carbon is composed of microcrystallines that consist of fused hexagonal rings of carbon atoms, this structure being quite similar to that of graphite. The spaces between the individual microcrystallines are called pores. Micropores of activated carbon, where most of the adsorptions take place, are in the form of two dimensional spaces between two parallel crystalline planes. The diameter of the microcrystallines is roughly nine times the width of one carbon hexagon. Functional groups that terminate the microcrystalline planes interconnect the microcrystallines. Adsorption occurs on the planar surfaces of the microcrystallines and at the functional groups on the edges of the planes(Çeçen & Aktaş, 2011a).

Surface functional groups play an important role in the adsorptions of various organic molecules. For example, aromatic compounds can be adsorbed at the carbonyl oxygen on the carbon surface according to a donor–acceptor complexation mechanism. The carbonyl oxygen acts as the electron donor, while the aromatic ring of the solute acts as the electron acceptor. Adsorption also occurs by hydrogen bonding of the phenolic protons with surface functional groups and by complexation with the rings of the microcrystalline planes. Activated carbon may contain large quantities of minerals, mostly calcium, sulfate, and phosphate ions. These groups as well as the acidic or basic organic surface functional groups influence the activated carbon surface properties. Activated carbon also contains some ash derived from the raw material, the amount of ash ranging from 1% to 12%. The ash mainly consists of silica, alumina, iron oxides, and alkaline and alkaline earth metals. The ash in the activated carbon increases its hydrophilicity. This is advantageous when PAC is used for water treatment because PAC does not stick on the reactor walls if the ash content is high(Cecen, 2011).

2.6.1 Physical properties of activated carbons

2.6.1.1 Moisture content

Generally activated carbons are stored under dry conditions if not it might adsorb considerable moisture. Actually they may adsorb as much as 25 to 30% moisture and still appear dry. For many purposes, the moisture content does not affect the adsorptive power, but obviously it dilutes the carbon. However, an additional weight of moist carbon is needed to provide the required dry weight(Sanchez, 2011).

Table 3: Characteristics of activated carbons (shows the typical range of values for commercial activated carbons)(Sanchez, 2011)

Specific surface area, BET (m^2/g)		600 - 1500
Total pore volume (m^3/g)		0.6 - 1.8
Apparent density (g/cm^3)		0.3 - 0.7
Granularity (mm)	a: dust	0.05 - 0.1 (a)
	b: granular	0.1 - 2 (b)
Ash percentage (%)		2 – 10
Uniformity coefficient (grain)		1.1- 12

2.6.1.2 Ash content

The total amount of inorganic constituents will vary from one carbon to another depending on the source of materials and from activating agents added during manufacture. Ash content can lead to increase hydrophilicity and can have catalytic effects, causing restructuring process during regenerations. The inorganic material contained in activated carbon is generally in the range between 2 and 10% as can be seen in table 3.

2.6.1.3 Pore content

A pore is a kind of cavity which is linked to the surface of a solid and allows the connections of fluids into, out of, or through a material. Basically, the pores are classified in three groups according to the International Unions of Pure and Applied Chemistry (IUPAC) defining the diameter of the pore as:

- ✓ Micropores: D<2 nm
- ✓ Mesopores: 2<D< 50 nm
- ✓ Macropores: D >50 nm

Activated carbon is a mixture of the three size pores and each one has different functions. The micropores are the most important ones due to their high surface area which gives them the higher adsorptions capacity because of their smaller size; similar to the molecules that will be adsorbed. An activated carbon formed by numerous micropores in the same range of the

pollutant is expected to be efficient due to the enhancement of the adsorptions potential for such conditions. The adsorbent is filled completely because its behavior is similar to a low pressure liquid ($P/P^0<0.01$). Microporous carbons are characterized by the presence of small voids having accessible widths in the range of 0.04 to 2 nm and representing the adsorptive capacity. Micropores have the appropriate size to retain molecules such as lot of solvents and volatiles, compounds that usually generate odour, flavour. The mesopores have a double functions, at sufficiently high pressures, in the range from P/P0=0.20 till $P/P^o=0.95$, condensations take place forming a meniscus and, secondly, serve as a step towards the micropores. The typical molecules retained in these pores are those ones where the sizes are between the micropores and macropores range. Macropores are the big size pores and cannot be filled by capillary condensations. Their relative pressure is from P/P0=0.95 till $P/P^o=1.00$ and their main functions is to communicate the external surface of the activated carbon with the mesopores. Actually, the surface of the macroporous may be regarded as nonporous, though its importance lies in the liquid retentions that may occur. For that reason one of the main functions of the macroporous is to ensure that the adsorbate arrives quickly to the smaller size pores located deeper in the activated carbon. Nevertheless, macropores can also retain big molecules suc

h as humic acids, which are generated in decompositions of organic matter.

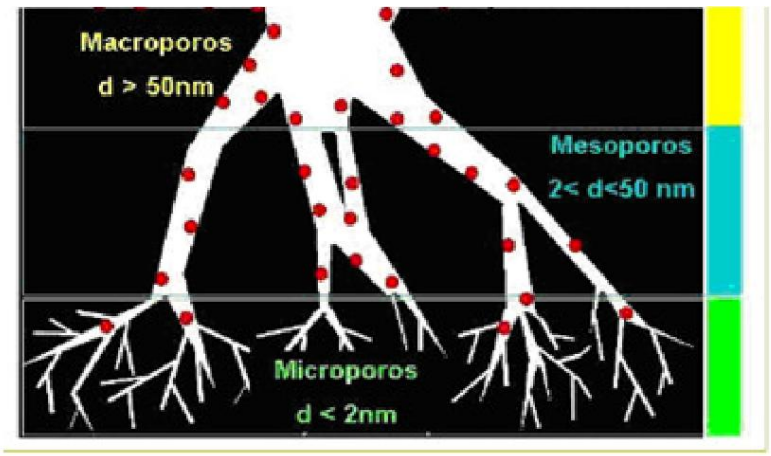


Figure 1: Representations of the three types of pores according to the IUPAC

Figure 1 is a representation of the transport of molecules being adsorbed at different points in relations to the pore diameter. In that sense, activated carbons show different properties depending on the raw material employed and the conditions of the activations and it would undoubtedly determine the adsorptions capacity that is usually attributed, besides to its surface area, for an appropriate internal pore volume that may be distributed in pores ranging in width from micropores to macropores. The porous structure can be characterize by various techniques such as adsorptions of gases as N_2, CO_2 or vapours as benzene, scanning electron microscopy (SEM) and transmissions electron microscopy (TEM).

2.6.1.4 Surface area

Activated carbons are widely known for the high specific surface area, which provides a well-developed porosity. The typical values ranged from 500m^2/g to 3000m^2/g and can be explained by the micropore structure. One can think that for a higher surface area, the adsorptions characteristics as adsorbent will be better because there will be more points where the adsorbates could be retained. However, depending on whether the adsorbate molecules size is bigger than some of the micropore size not all surfaces will be available for those molecules. At the same point the geometry of the adsorbate and the pore have to be taken into considerations as well(Sanchez, 2011).

2.6.2 Chemical properties of activated carbons

The physical properties and the chemical compositions of the starting material, as well as the methods and process conditions employed for activations, determine the pore size distributions and the adsorptions properties of the activated carbon . One of the parameters that differentiate one material from another is its compositions, i.e. lignin, cellulose and halocellulose. Materials with a greater content of lignin as grape seeds or cherry stones develop activated carbon with a predominance of macroporous, while other raw materials characterized by having a higher content of cellulose as apricot stones or almond shells produce activated carbons with a predominantly microporous structure. Furthermore of the porosity properties, the chemical surface characteristics of the solid develop specific surface complex which are also important in the adsorptive process.

The chemistry of the carbons takes places essentially on the edges of the graphitic sheets where a variety of oxygen groups or other induced chemically groups are found. One of the most important and studied is the oxygen complex; those ones are formed by the reactions between the carbon and the oxygen as well as reactions with oxidizing agents. Other compounds as hydrogen, nitrogen, phosphorous or sulphide could be mixed with carbon to form superficial complex but in a less quantity. The surface chemistry of an activated carbon is related to the presence of heteroatoms (oxygen, hydrogen, and nitrogen) within the carbon matrix resulting in superficial complex. Polar molecules are adsorbed weakly on the surface of the carbon, where the fixations of heteratoms in the carbon create functional groups as carboxylic acids, lactones, etc. which increases the affinity of polar molecules for the carbon surface. These heteroatoms found on an activated carbon surface are directly attributed to three factors: the starting material, method of activations and treatment conditions; and are chemically bonded to the carbon surface during the carbonizations and activations, forming carbon- heteroatom structures(Sanchez, 2011).

The surface chemistry of activated carbons determine their:

- ✓ Moisture content,
- ✓ Catalytic properties
- ✓ Acid-base character
- ✓ Adsorptions capacity

The efficiency of a carbon for removing a given pollutant depends on both its adsorptions capacity and its surface chemistry. Particularly, adsorptions of substances with high polarity and low molecular weight will be very complicated and will take place easily if the carbon is impregnated with specific chemicals or are used properly the catalytic properties of the carbon.

2.7 Cr(VI) adsorptions on low cost Activated carbon

The element chromium can exist in six valency states, 0, II, III, IV, V and VI, which represent the number of bonds an atom is capable of making. Metallic chromium Cr(0) does not occur naturally in the environment and Cr(II) is unstable and converted quickly to Cr(III). Cr(IV) and Cr(V) are also unstable and occur briefly as intermediates of conversions between Cr(III) and Cr(VI). Cr(III) and Cr(VI) are the environmentally important chromium species (A.M. Zayed & N.Terry, 2003). Chromium is most commonly found in nature as Cr(III), which is the most stable species. Most Cr(III) compounds are insoluble in water and Cr(III) is considered to be an essential trace element for human diets, although ingestions of large amounts can cause toxic effects (A.M. Zayed & N.Terry, 2003). The second most common and stable form of chromium in the environment is Cr(VI) compounds which are more toxic than Cr(III) due to their high water solubility and mobility (D. Mohan, C.U. Pittman, & P.H. Steele Jr., 2006).

Chromium is one of toxic pollutants discharge from industrial wastewater with concentrations varying from 5.2 to 208,000mg/L (Miretzky & Cirelli, 2010). Industrial sources of Cr(VI) include leather tanning, cooling tower blow down, plating, electroplating, anodizing baths, rinse waters, etc. (D. Mohan, K.P. Singh, & V.K. Singh, 2006; Mohan & Pittman Jr, 2006). Exposure to Cr(VI) may cause repository problems (asthma), internal hemorrhage, dermatitis, kidney and liver damage, dermatitis, and nausea. Skin and eye contact may cause nasal septum, ulcerations, irritations, severe burn and permanent damage to eye (Kara & Demirbel, 2012). The maximum allowable level for chromium discharge onto land surfaces is 0.1 and 0.05mg/L for drinking water (WHO, 2011).

A wide range of physical and chemical processes are available for the removal of Cr(VI) from effluents. A major drawback with those treatment systems is sludge productions, and, high operational cost and some of them are complicated for management. This actually makes the applications of these technologies to be limited only in developed countries. In response to this challenge a different attempt were undertaken to produce a media which was feasible and cost effective to use by the majority (Alebel Abebe Belay, 2010). With this regard, the prevalence of adsorptions separations in the environmental chemistry remains an aesthetic attentions and

considerations abroad the nations, owning to simplicity of design, ease of operations, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions (K. Foo & B. Hameed, 2010). Despite its prolific use in adsorptions processes, the biggest barrier of its applications by the industries is the cost-prohibitive adsorbent and difficulties associated with regenerations (Foo & Hameed, 2009). Realizing the complications, a growing exploitation to evaluate the feasibility and suitability of natural, renewable and low-cost materials as alternative adsorbents has been exerted.

Regarding Cr(VI) adsorptions a number of low cost materials such as olive bagasse (Demiral, Demiral, Tümsek, & Karabacakoğlu, 2008), modified tannery waste (Anandkumar & Mandal, 2011), sugar industrial waste (N.F. Fahim, B.N. Barsoum, A.E. Eid, & M.S. Khalil, 2006), maize bran(S.H. Hasan, K.K. Singh, O. Prakash, M. Talat, & Y.S. Ho, 2008), olive stones(A. A. Attia, S. A. Khedr, & S. A. Elkholy, 2010), sugar beet tailing (Dong, Ma, & Li, 2011), sawdust(Hamadi, Chen, Farid, & Lu, 2001), Rubber wood sawdust (Karthikeyan, Rajgopal, & Miranda, 2005) has been reported.

2.8 Types of Activated Carbon

2.8.1 Powdered Activated Carbon (PAC)

PAC is made up of crushed or ground carbon particles such that 95–100% of it will pass through a designated sieve of 0.297mm according to the American Water Works Associations Standard, or 0.177mm according to ASTM. PAC is generally produced from wood in the form of sawdust, the average particle size of PAC being in the range of 15–25mm. PAC finds wide applications in the treatment of both drinking water and wastewater. In wastewater treatment, it is either added to activated sludge or is contacted with wastewater in a separate unit. PAC may also act as a coagulant for colloidal fractions in the liquid phase. The regenerations of PAC can be rather difficult, because colloidal particles have to be separated from water before regenerations(Çeçen & Aktaş, 2011b).

2.8.2 Granular Activated Carbon (GAC)

GAC is usually in the form of crushed granules of coal or shell. GAC may also be prepared by granulations of pulverized powders using binders such as coal tar pitch. Unlike PAC adsorptions from the liquid phase, the rate-limiting step in GAC adsorptions from the liquid phase often becomes the intraparticle diffusions. GAC particles have sizes ranging from 0.2 to 5mm. GAC is designated by mesh sizes such as 8/20, 20/40, or 8/30 for liquid phase applications and 4/6, 4/8, or 4/10 for vapor phase applications. Particle sizes in the range of 12/42 mesh are advantageous for liquid phase adsorptions(Çeçen & Aktaş, 2011b).

2.9 Adsorption

Adsorptions is considered to be an important phenomenon in most natural physical, biological, and chemical processes, and activated carbon is the most widely used adsorbent material in water and wastewater treatment. Adsorption is the accumulations or concentrations of substances at a surface or interface. The adsorbing phase is termed the adsorbent, and the material being adsorbed called the adsorbate. Adsorptions can occur between two phases, namely liquid– liquid, gas–liquid, gas–solid, or liquid–solid interfaces. When activated carbon is used, the adsorbing phase is a solid. In activated carbon adsorptions, a hypothetical interfacial layer exists between the solid and fluid phases. This layer consists of two regions: that part of the fluid (gas or liquid) residing in the force field of the solid surface and the surface layer of the activated carbon.

Adsorptive surface reactions occur as a result of the active forces within the phase or surface boundaries. These forces result in characteristic boundary energies. The surface tensions developed at the surface of the liquid phase results from the attractive forces between the molecules of liquid. The liquid (solvent) molecules have a smaller attractive force for the solute molecules than for each other. Hence, a solute that decreases surface tensions is concentrated at the surface. The phenomenon of increased concentrations of the soluble material in a boundary or surface is commonly referred to as adsorptions. The term ‘adsorption’ refers to the process in which molecules accumulate in the interfacial layer, whereas desorption denotes the reverse.

Reductions and chemical precipitations has traditionally been the most used method. The most often used precipitations processes include hydroxide, sulphide, carbonate and phosphate precipitations techniques. The disadvantage of precipitations technique is the productions of sludge.

This process suffers from draw backs like incomplete removal, requirement of sizable quantities of treatment chemicals and productions of voluminous toxic sludge. It constitutes a solid waste disposal problem. Techniques like ions exchange and adsorptions with products obtained from naturally occurring materials like agro-wastes/byproducts activated carbon were considered as better alternatives. The exorbitant cost involved with ions exchange makes it prohibitive for wide applications. The presence of toxic heavy metals contaminated in aqueous streams, arising from the discharge of untreated metal containing effluent into water bodies, is one of the most important environmental issues. Their presence in aquatic ecosystem causes harmful effect to living organisms.

The low cost and extremely efficient adsorbents have the ability to bind various metals from aqueous effluents because of their cheap availability and relatively high surface area and high binding affinity. Numerous chemical groups may be responsible for chromium adsorptions by sesame husk, e.g. ligni-cellulose, carboxyl, sulphonate, hydroxyl and amino(Selen· et al., 4 July 2014).(Cecen & Aktas, 2011)

2.9.1 Types of adsorptions

In most types of water and wastewater treatment practice, two primary driving forces result in the adsorptions of a solute from a solution onto a solid phase. The first driving force is related to the lyophobic (solvent disliking) character of the solute. The most important factor for the intensity of adsorptions is the solubility of a dissolved substance. A hydrophilic substance likes the water system and tends to stay there. Hence, it is less adsorbable on a solid phase. Contrarily, a hydrophobic substance tends to be adsorbed rather than staying in water. Complex organic contaminants, such as humic acids have both hydrophobic and hydrophilic groups, so that the hydrophobic part of the molecule is adsorbed, whereas the hydrophilic part tends to stay in the solutions.

The second driving force for adsorptions is the affinity of the solute for the solid due to electrical attractions of the solute to the solid. This type of adsorptions can occur as a result of van der Waals attractions or chemical interactions with the adsorbent. These forces result due to the high affinity of the solute for the particular solid.

The adsorption induced by van der Waals forces is generally termed physical adsorptions or physisorptions, in which intermolecular attractions take place between favorable energy sites. Physisorptions is independent of the electronic properties of the adsorbate and adsorbent molecules. Exchange of electrons does not occur in physisorptions. The adsorbate is attached to the surface by relatively weak van der Waals forces. In physisorptions, multiple layers may be formed which have similar heats of adsorptions. As a rule, it is a reversible process that occurs at a lower temperature close to the critical temperature of an adsorbed substance. The adsorbate is less strongly attached to a specific site in physisorptions compared to chemical adsorptions. Therefore, physically adsorbed molecule is free to move within the interface.

In chemical adsorptions, or chemisorptions, the adsorbate undergoes chemical interactions with the adsorbent. Chemisorptions involve an exchange of electrons between specific surface sites and solute molecules, a chemical bond being formed. Chemically adsorbed adsorbates are not free to move on the surface or within the interface. Chemical adsorptions is characterized by a high adsorptions energy (tens of kcal mol1), since the adsorbate forms strong localized bonds at active centers on the adsorbent. Chemical adsorption is more predominant at high temperatures compared to physisorptions, because chemical reactions proceed more rapidly at higher temperatures. Generally, only a single molecular layer can be chemically adsorbed. Table 4 gives a comparison of physical and chemical adsorptions.

These two forms of adsorptions interact together in adsorptions. Adsorptions of organic molecules exhibit a large range of binding energies. Lower energies are usually associated with physisorptions, whereas higher energies are associated with chemisorptions. However, it is generally very difficult to distinguish between physisorptions and chemisorptions.(Cecen & Aktas, 2011)

Table 4: Comparison of physical and chemical adsorptions(Cecen & Aktas, 2011)

	Physisorption	Chemisorption
Coverage	Mono or multilayer	Monolayer
Nature of adsorption	Nondissociative and reversible	Often dissociative, may be irreversible
Specifity to adsorption sites	Nonspecific	Very specific
Temperature range	Near or below the condensation point of the gas	unlimited
Temperature dependence of uptake (with increasing T)	Decreases	Increases
Adsorption enthalpy	5–40 kJ mol^{-1}	40–800 kJ mol^{-1}
Kinetics of adsorption	Fast	Very variable, often slow
Desorption	Easy by reduced pressure or increased temperature	Difficult – high temperature is required to break bonds
Desorbed species	Adsorbate unchanged	Adsorbate may change

2.9.2 Advantages of Adsorptions

Adsorption is highly competitive with other presently available technologies and some of the key features as compared to conventional process include:

- ✓ Competitive performance
- ✓ Heavy metal selectivity
- ✓ Cost effectiveness
- ✓ Regenerative
- ✓ No sludge generations

Adsorption is particularly economical and competitive for environmental applications in detoxifying effluents from different industries.

2.9.3 Factors Affecting adsorptions capacity or adsorptions %

Activated carbon adsorption is not a uniquely homogeneous process, but is rather dependent on the various factors outlined below. These factors also play a significant role in the integrations of adsorptions with biological processes.(Cecen & Aktas, 2011)

2.9.3.1 PH

Organic molecules form negative ions at high pH values, positive ions at low pH values, and neutral molecules at intermediate pH values. Adsorption of most organic materials is higher at neutral conditions. In general, liquid phase adsorption of organic pollutants by activated carbon is increased with decreasing pH. This results from the neutralizations of negative charges at the surface of the carbon at low pH values. Neutralizations of negative charges reduce the hindrance to diffusions and leads to more active adsorptions sites. The extent of this effect varies with the type and activations technique of activated carbon. The differences in pH values may also arise due to acidic or basic surface functional groups on activated carbon. These groups could be freed by simple contact with distilled water rather than the fixed surface functional groups. An inverse relationship has previously been reported between adsorptions capacity and surface acidity.(Cecen & Aktas, 2011)

2.9.3.2 Temperature

Adsorption involves specific relations between the properties of activated carbon and the solute. Therefore, the quantitative effects of temperature are not the same with all carbons and solutes. The extent of adsorptions should increase with decreasing temperature because the adsorptions reactions are exothermic. However, increased temperature also increases the rate of diffusions of the solute through the liquid to the adsorptions sites, which eventually leads to increased adsorptions. An important difference in the adsorptions of solutes versus gases is found in the role of temperature. An increase in temperature increases the tendency of a gas to escape from the interface and thus diminishes adsorptions. However, in adsorptions from the liquid, the influence of temperature on solvent affinities is more dominant.(Cecen & Aktas, 2011)

2.9.3.3 Surface area of adsorbent

The extent of adsorptions is generally considered to be proportional to the specific surface area. Specific surface area is that proportions of the total surface area which is available for adsorptions. The more finely divided and more porous adsorbents would be expected to yield more adsorptions per unit weight of adsorbent. The surface can be characterized either as external when it involves bulges or cavities with width greater than depth or internal when it involves pores and cavities that have depth greater than width.(Cecen & Aktas, 2011)

2.9.3.4 Porosity of the adsorbent

The adsorptions performance is dependent on the conditions of internal surface accessibility. A very important and decisive property of adsorbent materials is the pore structure. The total number of pores and their shape and size determine the adsorptions capacity and even the rate of adsorptions. The significance of pores in adsorptions processes largely depends on their sizes. Most of the solid adsorbents possess a complex structure that consists of pores of different sizes and shapes. Total porosity is usually classified into three groups. According to the IUPAC recommendations, micropores are defined as pores of a width not exceeding 2 nm, mesopores are pores of a width between 2 and 50nm, and macropores are pores of a width greater than 50nm. The above classification is widely accepted in adsorptions literature. A further classification involves ultramicropores, which are pores of a width less than 0.7nm.

The mechanism of adsorptions on the surface of macropores does not differ from that on flat surfaces. The specific surface area of macroporous adsorbents is very small. Therefore, adsorption on this surface is usually neglected. Capillary adsorbate condensation does not occur in macropores. Macropores do not adsorb small molecules by volume but by surface. For example, phenol adsorption on macropores was reported to be less significant than that on meso- and micropores.

In the case of mesopores, the adsorbent surface area has a distinct physical meaning. Mono- and multilayer adsorptions takes place successively on the surface of mesopores, and adsorptions proceeds according to the mechanism of capillary adsorbate condensations. Specific surface area,

pore volume, and pore size distributions are basic parameters characterizing mesopores. Mesopores and macropores play an essential role in the transport of adsorbate molecules through the micropores.

The sizes of micropores are usually comparable to those of adsorbate molecules. All atoms or molecules of the adsorbent can interact with the adsorbate species. This is the fundamental difference between adsorptions in micropores and larger pores like meso- and macropores. Consequently, adsorption in micropore is essentially a pore-filling process. Therefore, volume is the main controlling parameter for adsorptions in micropores. Considering also that most of the total surface area is found in the micropores and the contributions of macropores to the total surface area is very low, the contributions of micropores to adsorptions would be expected to be higher. Also, the higher adsorption energy in micropores makes them more available adsorptions sites for relatively low-molecular-weight organics.(Cecen & Aktas, 2011)

2.9.3.5 Chemical surface characteristics

The adsorptions performance is dependent on chemical surface characteristics of the adsorbent. Heterogeneity of the activated carbon surface significantly contributes to adsorptions capacity. Heterogeneity of the carbon surface arises particularly due to surface oxygen groups which, although present in relatively small amounts, affect surface properties such as surface acidity, polarity or hydrophobicity, and surface charge. The presence of heterogeneous oxygen groups on the carbon surface is known to reduce the adsorptions capacity due to adsorptions of water onto these groups via hydrogen bonding. It has been stated that increasing the number of oxygen-containing surface functional groups increases the polarity of carbon surfaces. Therefore, the selectivity of carbon surface for water increases, and thus adsorbed water clusters may block carbon pores.

Such water clusters can prevent pollutant access to hydrophobic regions on the carbon surface, reduce interactions energy between the pollutant and carbon surface, and block pollutant access to micropores. The negative influence of surface oxides has also been attributed to the depletions of the electronic-band of graphite-like layers resulting in consequent lowering of van der Waals forces of interactions and reduced oxidative polymerizations of phenols. On the other hand,

surface oxides consisting of carbonyl groups enhance adsorptions of aromatic solutes such as phenol and naphthalene.

Chemically activated carbons have a pore surface which is less hydrophobic and more negatively charged. Chemical treatment of activated carbon increases the quantity of acidic surface functional groups, whereas thermal treatment results in a decrease in the number of acidic surface functional groups. Adsorptions capacities of thermally activated carbons have been found to be relatively higher than those of chemically activated carbons. This is certainly caused by the activations method, which sometimes results in different surface characteristics.

Oxygenating the carbon surface decreases its affinity for simple aromatic compounds in the case of chemical activations. Extensive oxidation of carbon surfaces leads to a large decrease in the adsorbed amounts of phenol, nitrobenzene, benzene, and benzene sulfonate. The formation of functional groups is dependent on activations temperature. For example, phenolic and lactone functional groups appear at activations temperatures up to 4001C.(Cecen & Aktas, 2011)

2.9.4 Kinetics of Adsorptions

In an adsorptions system, equilibrium is established between the adsorbent and the adsorbate in the bulk phase. The definitions of adsorptions kinetics is the rate of approach to equilibrium. Adsorptions equilibrium does not appear instantaneously because the rate of adsorptions is usually limited by the following mass transport mechanisms and depends both on the properties of the adsorbent and the adsorbate(Çeçen & Aktaş, 2011b).

2.9.5 Adsorptions Equilibrium and Isotherms

Adsorption is usually investigated in stirred batch reactors, where the fluid concentration is uniform and there is no feed or exit streams. In the case of a reversible adsorptions, molecules continue to accumulate on the surface until the rate of the forward reactions (adsorptions) equals the rate of the reverse reactions (desorption). When these two rates are equal to each other, equilibrium has been reached and no further accumulations will occur. Thus, in batch adsorptions, after a sufficiently long time, the adsorbent and the surrounding fluid reach a dynamic equilibrium. At the positions of equilibrium, there is a defined distribution of adsorbate

between the adsorbent and fluid. The partitions ratio (wp) indicates the amount of adsorbate mass adsorbed per amount of initial total mass in solutions and is defined as follows:

$$w_p = {}^{qM_c}/_{C_0V_0} = {}^{(C_0 - C_e)}/_{C_0} \qquad (2.1)$$

where :

- ✓ q: equilibrium expressed in solid phase in mass of adsorbate per mass of the adsorbent (Ms/Mc),
- ✓ M_c: mass of the adsorbent (Mc),
- ✓ C_o: initial adsorbate concentrations in the fluid phase (Ms/L^3),
- ✓ C_e: equilibrium adsorbate concentrations (Ms/L^3),
- ✓ V_o: volume of the liquid phase (L^3).

In this equation the subscripts ‘s’ and ‘c’ denote the ‘adsorbate’ and ‘activated carbon,’ respectively. The adsorption isotherm represents the distribution of the adsorbed material between the adsorbed phase and the solution phase at equilibrium. An isotherm is characteristic of a specific system at a particular temperature. The adsorption isotherm is the primary source of information on the adsorption process. The relations between amount adsorbed, q, and the equilibrium concentration in the liquid phase, C_e, at temperature, T, is called the adsorption isotherm at T[Eq. (2.2].

$$q = q(C_e) at\ temperature\ T \qquad (2.2)$$

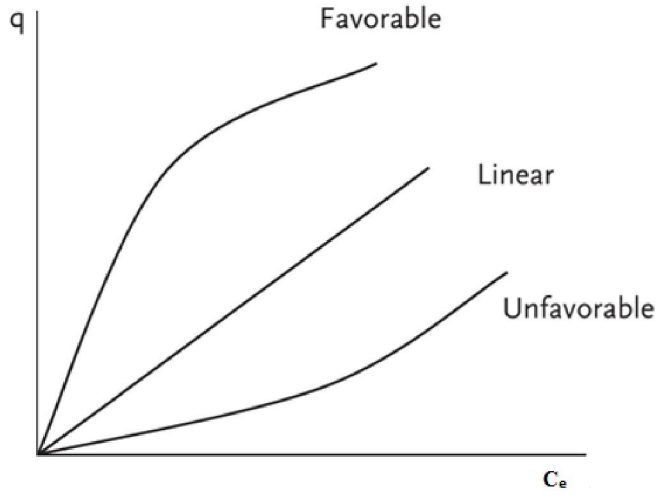


Figure 2: Adsorptions isotherm curves.(Cecen & Aktas, 2011)

The amount of adsorbed material per unit weight of adsorbent increases with increasing concentration, but not in direct proportion. Generally, an isotherm is favorable if its shape is convex upward, and unfavorable if it is concave upward (Figure 2). Any point on an isotherm curve gives the amount of adsorbed contaminant per unit weight of carbon, in other words the adsorptions capacity at a particular concentration.

For practical purposes, isotherms can be used to select the appropriate activated carbon type, to estimate the carbon service life, and to test the remaining adsorptions capacity of a carbon adsorber in continuous-flow operations. Due to structural and energetic heterogeneity of solid surfaces, adsorptions isotherms are characterized by complex analytical equations. This heterogenous characteristic is valid for most of the adsorbents used in practice, including activated carbons.

Adsorptions isotherms are described in many mathematical forms, some of which are based on a simplified physical picture of adsorptions, while others are purely empirical and intended to correlate the experimental data in simple equations. The most widely used mathematical expressions of adsorptions equilibrium are the Freundlich, Langmuir, and BET (Brunauer, Emmett, and Teller) isotherms. The Freundlich isotherm can be used to determine the adsorptions capacity of activated carbon over a wide range of concentrations. Adsorbents that follow the Freundlich isotherm equations are assumed to have a heterogeneous surface consisting

of sites with different adsorptions potentials, and each site is assumed to adsorb molecules. The Freundlich equation as shown below is very widely used for activated carbon applications.

$$q = K_F C_e^{\,1/n} \qquad (2.3)$$

- ✓ q: adsorptions capacity (mg adsorbate adsorbed per g adsorbent),(Ms/Mc)
- ✓ C_e: equilibrium adsorbate concentrations, (Ms/L^3)
- ✓ K_F: Freundlich exponent
- ✓ 1/n: Freundlich slope

The K_F value is an indicator of adsorptions capacity. The adsorptions intensity, 1/n, is shown by the slope of the adsorptions isotherm curve. An increase in activated carbon dose is more effective at low 1/n values than in the case of steeper isotherm curves with high 1/n values.

The theoretical Langmuir equation, defined as in Eq. (2.4), is also very widely used for the adsorptions isotherm. The Langmuir equation often does not describe adsorption data as accurately as the Freundlich equation. However, the Langmuir expressions introduced a clear concept of the monomolecular adsorptions on energetically homogeneous surfaces. Adsorbents that exhibit the Langmuir isotherm behavior are supposed to contain fixed individual sites, each of which equally adsorbs only one molecule, forming thus a monolayer, namely, a layer with the thickness of a molecule. The constants in the Langmuir equations have a strictly defined physical meaning in contrast to the ones in the empirical Freundlich equations.

$$q = \frac{q_{max} b C_e}{(1 + bC_e)} \qquad (2.4)$$

- ✓ q_{max}: solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface, (Ms/Mc)
- ✓ b: a constant related to the energy of adsorptions.

The linear form of the Langmuir equations is given in Eq. (2.5). From the slope and intercept, band q_{max} can be calculated.

$$\frac{1}{q} = \frac{1}{q_{max}} + \left(\frac{1}{bq_{max}}\right)\left(\frac{1}{C_e}\right) \quad (2.5)$$

The essential characteristics of the Langmuir equations can be expressed in terms of a dimensionsless separations factor R_L, which is defined by the following equations:

$$R_L = {}^{1}/_{(1 + q_{max} * b * C_0)} \quad (2.6)$$

where C_o is the initial solute concentrations in Ms/L^3.

The value of R_L indicates the shape of the isotherm to be either unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1) or irreversible (R_L=0). By using the dimensionsless separations factor R_L from the Langmuir equations, adsorptions isotherms can be successfully used to have an idea on the reversibility of adsorptions.

The Freundlich equations is a special case of heterogeneous surface energies in which the energy term (b) in the Langmuir equations Eq. (2.4) varies as a functions of surface coverage (q), strictly due to variations in the heat of adsorptions. The Freundlich equations cannot apply to all equilibrium concentrations. It agrees quite well with the Langmuir equations at moderate concentrations ranges. However, unlike the Langmuir equations, it does not reduce to a linear adsorptions expressions at very low concentrations and does not agree well with the Langmuir equations at very high concentrations. As seen in Eq. (2.4), in the Langmuir equations as C_e increases q increases until the adsorbent approaches saturations. At saturations, q is a constant, independent of further increases in Ce , and the Freundlich equations no longer applies. Also, the Freundlich equations may not apply to concentrations less than the saturations concentrations.

2.10 Sesame (*Sesamum indicum*) husks

Sesame is a flowering plant in the genus *Sesamum*. Numerous wild relatives occur in Africa and a smaller number in India. It is widely naturalized in tropical regions around the world and is cultivated for its edible seeds, which grow in pods. Ethiopia is the world's second largest exporter of sesame – exports are currently U.S. $300 millions per year and expected to increase to $500 millions in the next two years. Ethiopian sesame farms employ over 500,000 workers

during the peak season. Among the oil crops of Ethiopia, sesame seed commands a leading position because it is highly adapted to arid & semiarid lowland environment and yields well. Whitish Humera Type has good demand in the world market & known for its top quality. Also used as a reference for grading in the internationsal market and Wellega type which is mixed/brownish. After the extractions of oil, alarge amount of husk is left behind.

3 Experimental methods and materials

3.1 Chemical reagents

All chemical reagents in this study were analytical grade. Potassium dichromate ($K_2Cr_2O_7$) was used as the source for chromium stock solutions. All the required solutions are prepared with analytical reagents and double-distilled water. The chromium (VI) stock solution (1000mg/L) was made by dissolved 2.835g of 99% $K_2Cr_2O_7$ in 1.0L distilled water. Synthetic samples of different concentrations of chromium (VI) are prepared from this stock solution by appropriate dilutions. The chromium stock solutions (100mg/L) was prepared by diluting 100mL of 1000mg/L chromium stock solutions with distilled water in 1000mL volumetric flask up to the mark. Similarly solutions with different metal concentrations such as (10, 20, and 30 mg/L) are prepared and stored in an amber bottle.

3.2 Optimization of process parameters in preparation of SHAC

3.2.1 Experimental design for AC preparations

The effect of activating agent concentrations, impregnations ratio (weight of activating agent to weight of sesame husk), carbonizations temperature and holding time were analyzed as main factor variable using RSM method based on Box-Behnken design. Adsorption % of Cr(VI) was used as response (dependent) variable. Independent process variables involved in activations/carbonizations process and their experimental levels were presented in Table 5 below. In RSM for response adsorptions %, a model was defined that can predict the individual and interactions effect of different parameters. The coded values of independent variables were found from equations:

$$x_i = \frac{X_i - X_0}{\Delta X}, \qquad i = 1, 2, 3, \dots, k \qquad (3.1)$$

Where x_i is the dimensionless value of an independent variable; X_i is the real value of an independent variable; X_0 is the value of X_i at the center point; and ΔX is the step change. General form of a quadratic model for four variables as presented below was used.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} {x_i}^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \varepsilon \qquad (3.2)$$

Where Y = predicted response, β_0= constant coefficient, β_i = linear effect coefficients, β_{ii}= quadratic effect coefficients, β_{ij} =interactions effect coefficients, x_i= independent variables

Table 5: Independent variable ranges and levels

Variable		Unit	Range and Level		
			-1	0	+1
Holding Time	A	min	30	60	90
Carbonization Temperature	B	^{0}C	500	600	700
Concentration of activating agent (H_2SO_4)	C	M (mole)	1	3	5
Impregnation Ratio	D	w/w	1	2	3

3.2.2 Activated Carbon Preparations

A nine-step procedure adopted for the modifications of the Sesame Husk by Sulfuric Acid includes.

1. Separating the sesame husk from the agro byproduct of sesame.
2. Repeated washing the SH using distilled water to remove the impurities.
3. Drying the SH using dry oven at 105^{o}C for 24hr. to remove the impurities and color
4. Crushing or powdering the SH by size reductions machine using 750µm sieve size to reduce the consumptions of activating agent.
5. Soaking 100g powdered SH using modifying agent or activating agent by sulfuric acid (concentrations of sulfuric acid =1M, 3M and 5M) in three different impregnation ratios (IR =1, 2 and 3) for 24hr to improve the adsorptions % or adsorption capacity.
6. Repeated washing the modified SH using distilled water to remove the free sulfuric acid until the pH of supernatant remained neutral by comparing the pH of the distilled water with the supernatant.
7. Drying the modified SH at 105^{0}C for 24hr.

8. Carbonizing at different carbonizations temperature (500^0C, 600^0C, 700^0C) and holding time (30, 60, 90min) in a horizontal cylindrical furnace with continuous Nitrogen flow of 10mL/min and heating rate of 10^oC/min.
9. Crushing and sieving to desired mesh size 300µm to eliminate the effect of sieve size in the study and storing in glass bottles.

3.2.3 Adsorption study

For each product batch adsorption study was conducted to determine the response variable % adsorption. Batch adsorptions is conducted by taking 200mL of 100mg/L Cr(VI) solutions and adjusting the pH at 2 using dilute NaOH and H_2SO_4. Then the 0.5g of the prepared SHAC was added and the solutions were agitated at 200rpm in thermostat shaker at 25^oC for 6 hours. After contact time solutions was decanted, filtered with 0.45µm pore size glass filter and final Cr(VI) concentrations was determined by 1-5 diphenylcarbazide method. Batch adsorptions studied at constant pH, contact time, initial chromium concentration and temperature to optimize process parameters in preparation of SHAC. % adsorption of which is response variable in the optimization study was determined as follows:

$$\%\ Adsorption = \frac{C_o - C_f}{C_o} x\ 100 \qquad (3.3)$$

where: C_o and C_f are initial and final concentrations of Cr(VI).

All the experimental sequences received by the Design Expert software (Versions 9.0.6, Stat Ease, Inc., Minneapolis, USA) were performed in triplicate. Average % adsorption value was fed to the software by which regressions analysis and predictions model development undertaken. The optimum values of the factors were obtained by solving the regressions equations, analyzing the surface of the three-dimensional response surface plot, and also by the setting up of constraints for the levels of the variables. The goal fixed for the degradations was to employ the adsorption process for a minimum holding time, carbonizations temperature, impregnations ratio and concentrations of activating agent, so as to maximize the adsorption percentage to be cost effective. Based on the predicted optimum point SHAC was prepared.

3.3 Characterization of sesame husk based activated carbon

3.3.1 Proximate analysis

Proximate analysis was conducted to determine moisture content, Volatile content, % ash and fixed carbon.

Moisture content; Moisture content was determined according to ASTM 2867-99 method. Each AC sample (2g) was weighed and dried in a furnace continuously. The drying sample was constantly reweighed at a 10min interval until a constant weight (W_p) was obtained. The crucible and its content was retrieved and cooled in desiccators. The difference in weight (∂W) was recorded and the moisture content (MC) calculated from Eq. (3.4) as loss in weight on drying divided by initial weight of carbon multiplied by 100.

$$MC = \frac{W_o - W_p}{W_o} * 100\% \qquad (3.4)$$

where W_p= weight of Carbon retrieved from the furnace and W_o= initial dry weight of the AC sample.

Volatile content and Ash content: The volatile ash content of activated carbon is the noncombustible residue left after burning samples at 750-800°c for 0.5 hr. in muffle furnace. Ash content determination was done according to the ASTM D2866-94 method. Dry AC sample (1.0g) was placed in to a porcelain crucible and transferred into a preheated muffle furnace set at a temperature of 1000^{o}C. The furnace was left on for one hour after which the crucible and its content was transferred to desiccators and allowed to cool. The crucible and content was reweighed and the weight lost was recorded as the ash content of the AC sample (W_{ash}). Then the % ash content (dry basis) was calculated from the equations;

$$Ash\ cont. = \frac{W_{ash}}{W_o} * 100\% \qquad (3.5)$$

$$Volatile\ Content(\%) = \frac{W_o - W_{ash}}{W_o} * 100\% \qquad (3.6)$$

where: W_o is the dry weight of carbon sample before ashing

Fixed Carbon: Fixed Carbon was determined by assuming that the sulphur content was negligible in all cases the fixed carbon content (FC) was given as:

$$FC = 100\% - MC - VC \quad (3.7)$$

where; FC= Fixed Carbon(%), MC= Moisture Content (%), VC=Volatile Content (%), Ash= ash content (%)

3.3.2 pH and Conductivity

The pH and conductivity were determined according to the method of ASTM D3838-80 with slight modifications as follows; 1.0g of carbon activated carbon sample was weighed and transferred into a 250mL beaker and 100mL of distilled water was added and stirred for 1 hour. Samples were allowed to stabilize and then pH measured using an electronic pH/Conductivity meter, Jenway 430 Model. The same samples were further used for electrical conductivity (EC) of the ACs and results read off in mS.

3.3.3 Pore (Void) Volume

The sample (1g) was collected and transferred completely into a 10ml measuring cylinder in order to get the total volume of the sample. The sample was then poured into a beaker containing 20ml of deionized water and boiled for 15 min. the content in the beaker was then filtered, superficially dried, and weighed. The pore volume was calculated as increase in weight (∂w) divided by the density (ℓ) of water at 20^{o}C using equations

$$Pore\ Volume = \frac{\partial w}{\iota_{t20}} \quad (3.8)$$

3.3.4 Bulk Density and Porosity

A cylinder and an aluminum plate were each weighed. A sample of activated carbon was placed into the cylinder, reweighed and transferred into the aluminum plate and then oven dried to a constant weight at a temperature of 105^{0}C for 60min. The weight of dry sample was recorded

after drying. A cleaned, dried well-cooked density bottle was weighed. A small quantity of sample of activated carbon was taken and ground to powder; sieved using 110μm mesh size, and gradually put into the density bottle with a little amount of water added and weighed. The volume of void (Vv) was obtained by first determining the total volume of the cylinder used for the experiment and also determining the volume of the AC used:

The volume of void (Vv) was obtained as;

$$V_v = V_{cylinder} - V_{activated\ carbon\ used} \tag{3.9}$$

The bulk density and porosity were calculated as;

$$Bulk\ density = \frac{mass\ of\ carbon\ sample}{volume} \tag{3.10}$$

$$porosity(\eta) = \frac{volume\ of\ void}{total\ volume} \tag{3.11}$$

3.4 Batch adsorption study using SHAC prepared at optimum point

Batch adsorptions of Cr(VI) on to SHAC was conducted to describe the parameter effect of pH, contact time, Initial concentrations of Cr(VI) and adsorptions temperature. All batch experiments were carried out with adsorbent samples in 250mL Erlenmeyer flasks with 200mL Cr (VI) aqueous solutions on a thermostat shaker at 200 r min^{-1}. The concentration of Cr (VI) ions was determined spectrophotometrically at 540nm using diphenylcarbazide as the complexing agent. All the sesame husk activated carbons used in adsorption study are the activated carbons which were prepared at optimum preparation conditions.

3.4.1 Effect of pH

The effect of pH on the Cr(VI) adsorptions onto sesame husk activated carbon was studied at pH range of 1.0 to 9.0. For this study 200mL of Cr(VI) solutions with initial concentration of 100mg/L, was taken in 250mL Erlenmeyer flasks and pH was adjusted to pH of 1.0 – 9.0 using

required quantity of 1 N HCl (or) 1 N NaOH before mixing the adsorbent. Then 0.5g of sesame husk activated carbon was added to the solutions and agitated at 200rpm in a thermostat water bath shaker at 20^{o}C of temperature using a contact time of 360 min.

3.4.2 Effect of contact time and initial concentrations

To examine effect of contact time and initial Cr(VI) concentrations, 200ml of Cr(VI) solutions with different initial Cr(VI) concentrations, (100, 200, and 300mg/L) was taken in 250mL conical flask and pH was adjusted to 2. Then 0.5g of sesame husk activated carbon was added and the solution was agitated at rate of 200rpm in thermostatic shaker set at 20^{0}C. Cr(VI) was determined from the sample taken from the solutions at time interval of 1, 2, 3, 4, 5, and 6 hours.

3.4.3 Effect of contact time and temperature

To examine the effect of contact time and temperature, 200ml of Cr(VI) solutions with initial concentrations of 100mg/L was taken in 250mL conical flask at different temperature, (20, 30, 40 and 50 ^{0}C) and pH was adjusted to 2. Then 0.5g of sesame husk activated carbon was added and the solution was agitated at rate of 200rpm in thermostatic shaker. Cr(VI) was determined from the sample taken from the solutions at time interval of 1, 2, 3, 4, 5, and 6 hours.

3.4.4 Isotherm study/equilibrium study

Equilibrium isotherms were studied by taking 200mL of Cr(VI) solutions at different initial concentrations (50 - 400mg/L) in 250mL Erlenmeyer flasks and solutions pH was adjusted to 2. The 0.5g of SHAC was added to the solutions and agitated at 200rpm for 6 hr. (equilibrium time) in thermostat shaker at temperature of 30, 40, 50^{o}C. To establish the adsorptions capacity of SHAC experimental data was fitted against isotherm equations of Langmuir, and Freundlich.

3.4.5 Kinetic study

Kinetic study was conducted by taking 200mL of Cr(VI) solutions with initial concentrations of 100mg/L in 250mL Erlenmeyer flasks and adjusting the pH to 2. Then 0.5g of sesame husk activated carbon was added and the solution was agitated at 200rpm in thermostat shaker at 30, 40 and 50^{o}C. Solutions was sampled at time interval of (1, 2, 3, 4, 5, and 6 hr.) and the filtrate

was analyzed for the remaining Cr(VI) concentration. A spectrophotometer was employed at a wavelength of 540 nm with 1,5-diphenylcarbazide reagent to determine the remaining concentrations of Cr(VI) in each sample after adsorption at the desired time intervals. Experimental data were analyzed against kinetic models, which explain the mechanism of the adsorptions processes. The kinetics of Cr(VI) adsorptions on SHAC were analyzed using pseudo first-order (Lagergren S., 1898), and pseudo second-order (Ho YS, McKay G., Wase DaJ., & Foster CF., 2000) kinetic models.

3.2.6 Analysis of Cr(VI) and statistics

After predetermined contact time adsorbent was decanted and separated from the solutions using filter paper (using 0.45mm membrane filter) and the filtrate analyzed. For this purpose a 0.25% (w/v) solutions of 1,5-diphenylcarbazide was prepared in acetone. Each sample solutions (15mL) containing various concentrations of Cr(VI) were pipette out into 25mL standard flasks. To this 2mL of 3 M H_2SO_4 (to lower the pH) was added followed by 1 mL of 1-5 diphenylcarbazide and total volume was made up to 25mL using distilled water. Cr(VI) concentrations estimated by the intensity of the brownish-red color complex formed, was measured using UV -spectrophotometer (Perkin-Elmer lambda 950 UV/VIS Spectrometer) at 540nm (APHA, AWWA, & WPCF, 1998).

The amount of Cr(VI) adsorbed on the carbon surface was determined by mass balance equations.

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{3.12}$$

Percentage adsorption was calculated according to the expressions:

$$\%\, Adsoption\ = \frac{(C_0 - C_t)}{C_0} \tag{3.13}$$

where q_t (mg/g) is the amount of chromium adsorbed per unit mass of adsorbent; C_t and C_0(mgL^{-1}) are the liquid phase and initial concentrations of concentrations of metal ions respectively. V the volume of solutions (L), m is the mass of the carbon material (g).

In isotherm, and kinetic studies, the conformity between experimental data and the model predicted values was expressed by the correlation coefficients (r^2).

4 Result and discussions

Result and discussion is presented in three consecutive parts based on the stated specific objectives as follows;

First, it was found to be important to prepare AC with good adsorptive property. However adsorptive property depends on level and combination of operational parameters involved in production of activated carbon. Thus the first objective of this research addresses this issue by identifying process parameters which result optimum adsorptive capacity which is indicated by adsorption % of prepared activated carbon. This is carried out by application of Surface Response Methodology to modeling and optimization of process parameters involved in preparation of sesame husk activated carbon by chemical activation using H_2SO_4.

Second, it is important to characterize activated carbon prepared. Activated carbon characteristics, adsorption % which is used in optimization study are not enough to fully understand the activated carbon produced. The standard method of characterization of surface area and pore volume are important. Thus second objective of this research is intended to fully characterize activated carbon produced at optimized operational conditions.

Third, as engineering (applied) research, this study address application of produced activated carbon for adsorptive removal model environmental pollutant. Cr (VI) is selected as model environmental pollutant. Thus objective three is intended to address potential application of produced activated carbon for adsorptive treatment of Cr (VI) through batch adsorption isotherm study.

4.1 Modeling and Optimization

The effect of concentration of H_2SO_4, impregnation ratio, carbonization temperature and holding time on adsorption % of sesame husk activated carbon was analyzed. RSM was applied to model and optimize different process parameters in the preparation of sesame husk activated carbon. Operational parameters with optimum adsorption % were predicted using developed model. Accordingly, first model development and evaluation was discussed. Second the effect of

independent variables on response variables was examined. Then finally using the model optimum points of operational parameters were predicted.

4.1.1 Development and evolution of adsorption percentage model prediction

Twenty five unique experimental conditions and five central replicate, total of twenty nine experimental runs were carried out. Each of experimental runs was conducted according to procedure described above in methodology part. For each of thus experimental runs adsorption % was determined using the methodology described. Experimental results of adsorption % were fed to design expert soft ware for multiple regression fitting. Linear model was fitted with backward elimination regression with alpha to exit = 0.10.

Table 6: Sequential Model Sum of Squares (Type I)

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	210631.4569	1	210631.4569			
Linear vs Mean	2154.25	4	538.5625	239.1702026	5.86439E-19	Suggested
2FI vs Linear	18.25	6	3.041666667	1.529624277	0.224876236	
Quadratic vs 2FI	13.95977011	4	3.489942529	2.237825744	0.117209855	
Cubic vs Quadratic	19.5	8	2.4375	6.267857143	0.01902877	Aliased
Residual	2.333333333	6	0.388888889			
Total	212839.75	29	7339.301724			

The sequential model sum of squares is presented in Table 6. Model summary statistics is presented in Table 7. The Box-Behnken experimental matrix, experimental and predicted values of adsorption % obtained under different experimental conditions are presented in Table 8. Analysis of variance is presented in Table 9. Residual plots presented in Fig 3-5.

Sequential model sum of square (Type I) selected the highest order polynomial where the additional terms are significant and the model is not aliased. From sequential model sum of squares (Table 6) it was found that linear vs mean model was the most suitable model to describe effect of selected process condition in preparation of sesame husk activated carbon on adsorption % of produced sesame husk activated carbon. The final obtained equation for prediction of response variable based on coded factors was as follows;

$$Y_R = 85.67647059 + 2.583333333A + 11.58333333B + 3.333333333C + 5.25D - 1.093137255B^2 - 1.5AB \quad (4.1)$$

Y_R is the predicted response variable for adsorption percentage in terms of coded factors. The regressions coefficient and the determination coefficient (R^2) for the quadratic regressions model for Cr(VI) adsorption are presented in Table 9.

Table 7: Model Summary Statistics

Source	Std. dev.	R-Squared	Adj. R squared	pred. R squared	PRESS	
Linear	1.500599	0.975527	0.971448	0.961736	84.49744	Suggested
2FI	1.410144	0.983792	0.974787	0.946581	117.9655	
Quadratic	1.248809	0.990113	0.980226	0.943051	125.76	
Cubic	0.62361	0.998943	0.995069	0.847846	336	Aliased

Table 8: Box-Behnken design matrix in a coded terms and actual terms with experimental and predicted values for adsorption % of Cr(VI) adsorptions by SHAC

Std. order	Actual factors				Coded factors				Adsorption %	
	HT(Min)	CT(0C)	CA(M)	IR(w/w)	A	B	C	D	Expt.	Pred.
1	30	500	3	2	-1	-1	0	0	65.5	68.916
2	90	500	3	2	1	-1	0	0	75.5	77.083
3	30	700	3	2	-1	1	0	0	94.5	95.083
4	90	700	3	2	1	1	0	0	98.5	97.25
5	60	600	1	1	0	0	-1	-1	77.5	77.093
6	60	600	5	1	0	0	1	-1	83.5	83.759
7	60	600	1	3	0	0	-1	1	87.5	87.593
8	60	600	5	3	0	0	1	1	95.5	94.259
9	30	600	3	1	-1	0	0	-1	78.5	77.843
10	90	600	3	1	1	0	0	-1	82.5	83.009
11	30	600	3	3	-1	0	0	1	88.5	88.343
12	90	600	3	3	1	0	0	1	93.5	93.509
13	60	500	1	2	0	-1	-1	0	69.5	69.666
14	60	700	1	2	0	1	-1	0	94	92.833
15	60	500	5	2	0	-1	1	0	78.5	76.333
16	60	700	5	2	0	1	1	0	99	99.5
17	30	600	1	2	-1	0	-1	0	80.5	79.759
18	90	600	1	2	1	0	-1	0	84.5	84.926
19	30	600	5	2	-1	0	1	0	86.5	86.426
20	90	600	5	2	1	0	1	0	90.5	91.593
21	60	500	3	1	0	-1	0	-1	68.5	67.75
22	60	700	3	1	0	1	0	-1	91.5	90.916
23	60	500	3	3	0	-1	0	1	80.5	78.25
24	60	700	3	3	0	1	0	1	99.5	101.416
25	60	600	3	2	0	0	0	0	85.5	85.676

To assess the adequacy of a model, the coefficient of determination (R^2) and the lack of fit test were commonly used. Coefficient of determination (R^2) refers to the changes described by the model to the overall changes. Therefore, whatever R^2 is closer to 1, the power of fitted model is greater to describe the response changes as a function of the independent variables.

From the Model Summary Statistics (Table 7) it can be seen that the regression coefficient of the linear model developed for adsorption % is 0.9755 which shows that the model adequately

explains 97.55% of the variation and also the R^2 adj. of 0.9714 is in reasonable agreement with the pred. R^2 of 0.9617 for the linear model.

The statistical significance of the model was investigated by analysis of variance (ANOVA). The significance of the model and model terms are determined by applying the F-test and p-test. The F and p-values denote the significance of the model and model terms. They are important in understanding the pattern of mutual interactions between the variables. The larger the magnitude of F-test and smaller the p value, the more significant is the corresponding model and model terms.

The ANOVA result (Table 9) shows that the model F-value of 217.34 for adsorption % implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

The associated p value is used to estimate whether F is large enough to indicate statistical significance. The values of p > F, less than 0.05 indicates that the model is considered to be statistically significant whereas values greater than 0.10 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the predicted model.

Regarding this, the model is statistically significant at level of p-value <0.0001. The ANOVA result also presented p- values of individual model terms. According to the result all four linear terms, interaction of holding time and impregnation ratio and second order terms of carbonization temperature (A, B, C, D, AB, B^2) are significant model terms in adsorption % medel.

Table 9: ANOVA for Response Surface Reduction Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	*2171.66*	*6*	*361.94*	*217.34*	*< 0.0001*	*Significant*
A-A:Holding Time	*80.08*	*1*	*80.08*	*48.09*	*< 0.0001*	
B-B:Carbinization Temperature	*1610.08*	*1*	*1610.08*	*966.83*	*< 0.0001*	
C-C:Concentration of Activating Agent	*133.33*	*1*	*133.33*	*80.06*	*< 0.0001*	
D-D:Impregnation Ratio	*330.75*	*1*	*330.75*	*198.61*	*< 0.0001*	
AB	*9.00*	*1*	*9.00*	*5.40*	*0.0297*	
B^2	*8.41*	*1*	*8.41*	*5.05*	*0.0350*	
Residual	*36.64*	*22*	*1.67*			
Lack of Fit	*36.64*	*18*	*2.04*			
Pure Error	*0.000*	*4*	*0.000*			
Cor Total	*2208.29*	*28*				

Std. Dev =1.290476566, Mean=85.22413793, C.V. %=1.514214866, PRESS=100.2824811, R-Squared=0.983409243, Adj R-Squared=0.978884491, Pred R-Squared=0.954588238, Adeq Precision=53.10066689

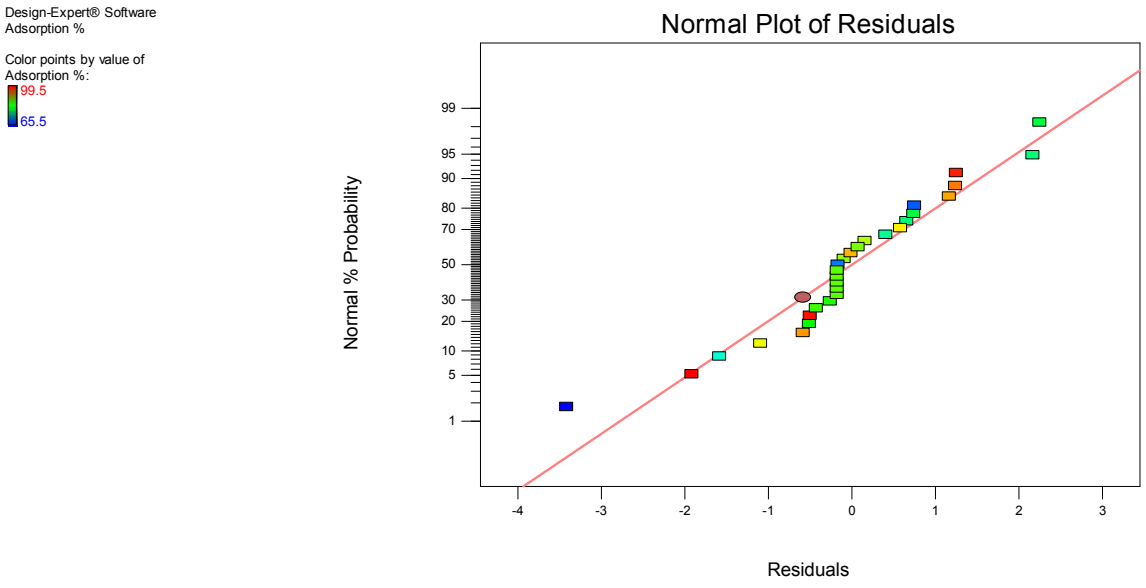
The "Pred R-Squared" of 0.9546 is in reasonable agreement with the "Adj R-Squared" of 0.9789; i.e. the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. As can be seen from analysis of variance (Table 9), this ratio is 53.101 for adsorption % model indicating an adequacy of signal. This in turn asserts that the model can be used to navigate the design space.

Model diagnostic plots are graphical summaries for case statistics. The plots of residuals show that how well the model satisfies the residual assumptions of the analysis of variance. Externally studentized residuals are the default for randomized designs with internally studentized and raw residuals as options. Split-plot designs default to internally studentized residuals. The raw residuals can potentially belong to different normal populations (one for each different standard error) and should not be used for checking the regression assumptions. Studentizing the residuals maps all the different normal distributions to a standard normal distribution. Externally

studentized residuals appearing outside the red lines indicate the observed value is an outlier. Different model diagnostic plotes were ploted.

Diagnostics are:

- ✓ Normal Probability: The normal probability plot compares the distribution of the residuals to a normal distribution (the straight line). Expect some scatter even with normal data. Look only for definite patterns like an "S-shaped" curve, which indicates that a transformation of the response may provide a better analysis.
- ✓ Residuals vs. Predicted: This plot checks for constant variance across the range of predictions. Non-constant variance is indicated by a pattern in the plot (megaphone, upward or downward curves, etc.). If the plot appears randomly scattered between the red lines then the assumption of constant variance is confirmed.
- ✓ Predicted vs. Actual: A graph of the predicted response values versus the actual response values. It primarily used to detect a value, or group of values, that are not predicted well by the model.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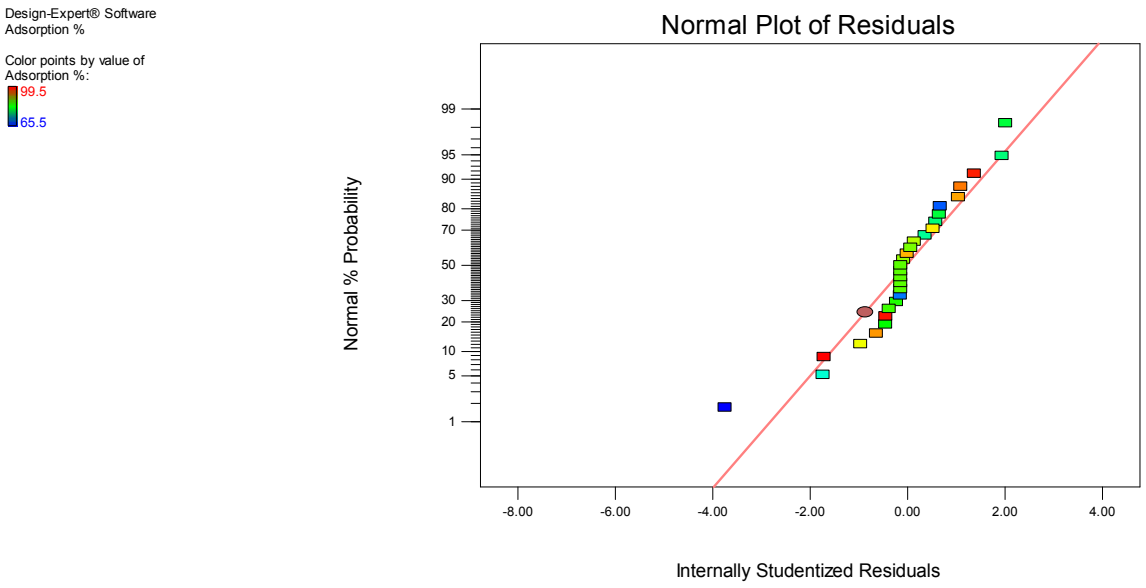
Adsorption %
Color points by value of
Adsorption %:
99.5
65.5
Normal Plot of Residuals
Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-4
-3
-2
-1
0
1
2
3
Residuals

(a)


Design-Expert® Software
Adsorption %
Color points by value of
Adsorption %:
99.5
65.5
Normal Plot of Residuals
Normal % Probability
99
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80
70
50
30
20
10
5
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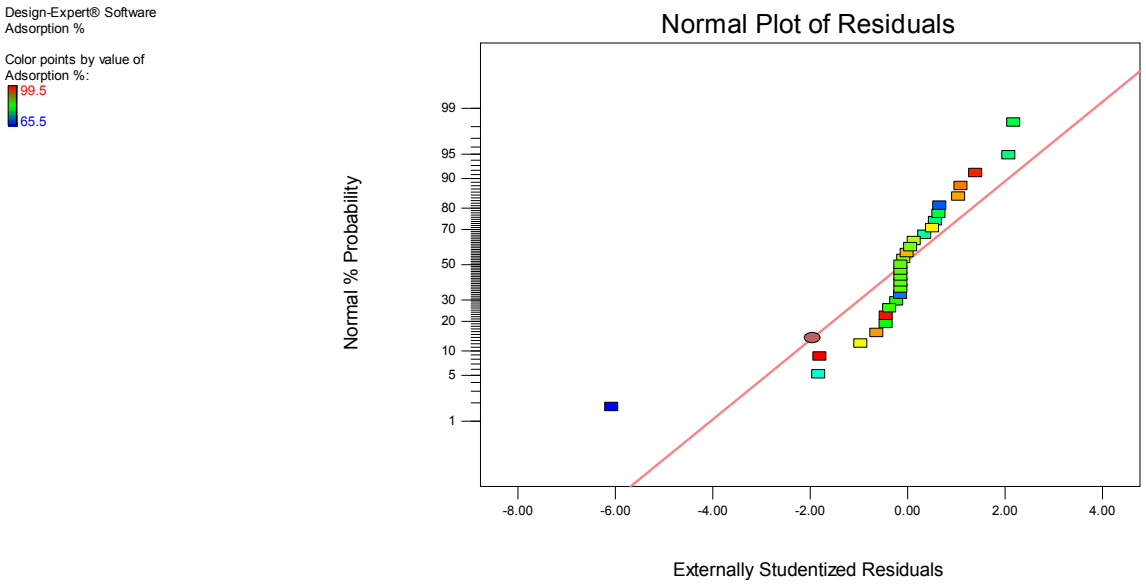
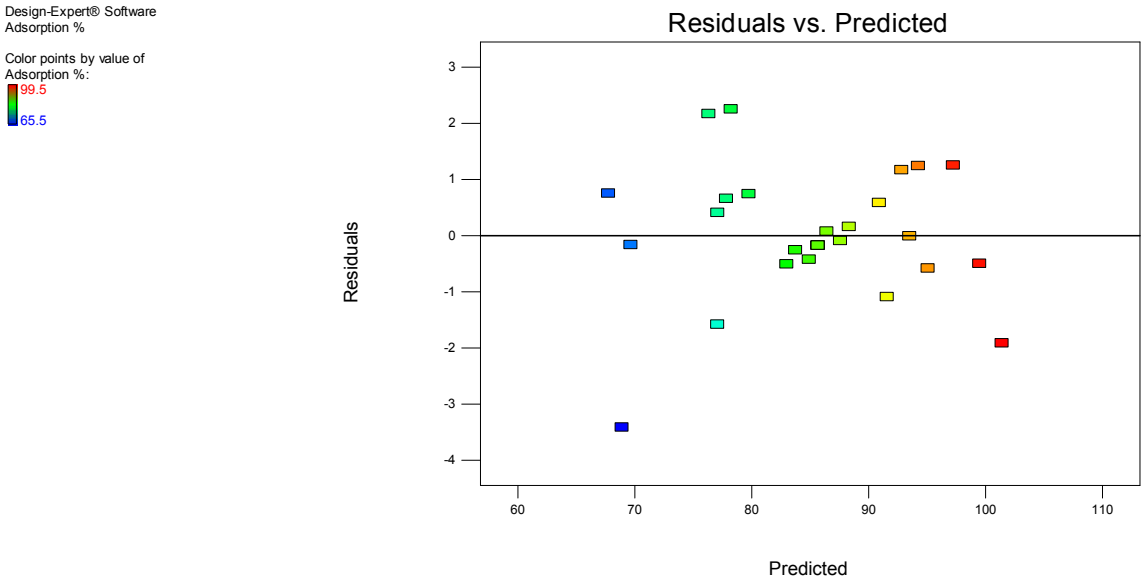
-6.00
-4.00
-2.00
0.00
2.00
4.00
Internally Studentized Residuals

(b)

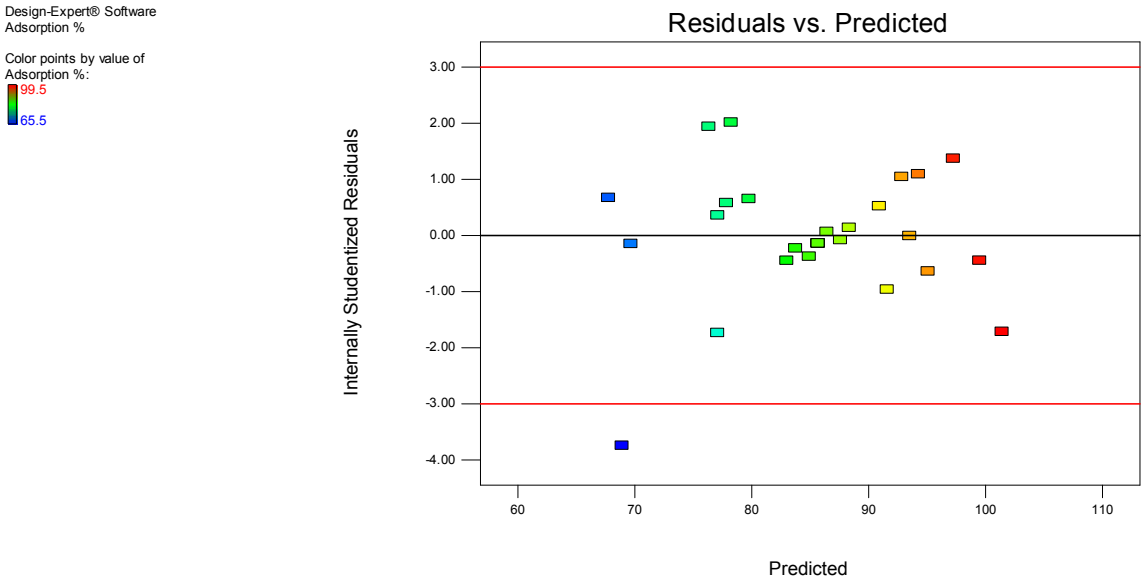


(c)

Figure 3: Normal probability plot, (a) residuals, (b) internally studentized residuals, (c) externally syudentized residuals, indicating meeting of normality assumption


Design-Expert® Software
Adsorption %
Color points by value of
Adsorption %:
99.5
65.5
Residuals vs. Predicted
Residuals
Predicted
3
2
1
0
-1
-2
-3
-4
60
70
80
90
100
110

(a)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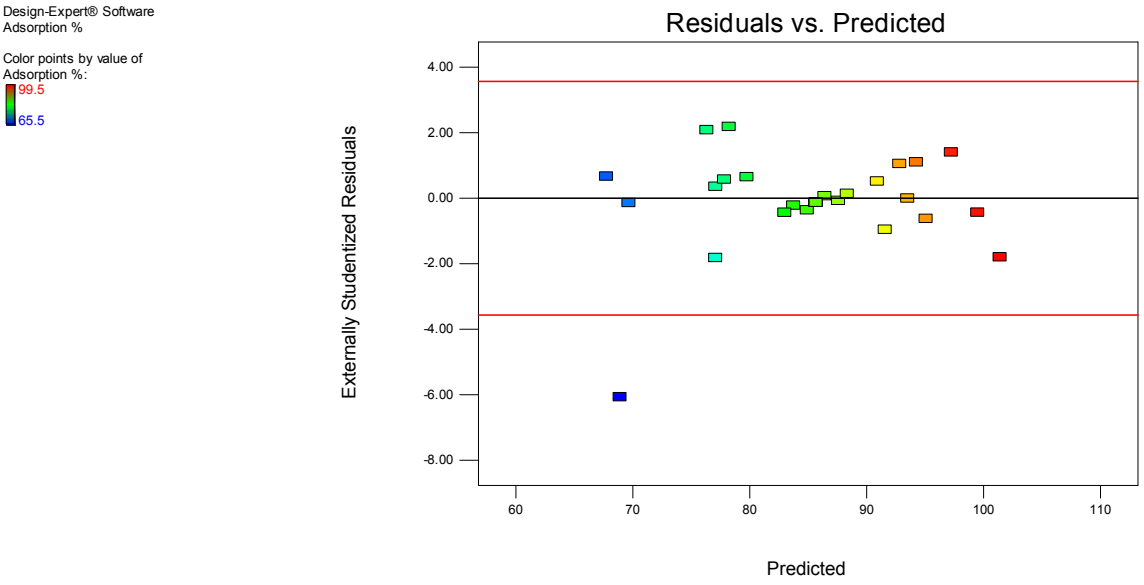
Adsorption %
Color points by value of
Adsorption %:
99.5
65.5
Residuals vs. Predicted
Internally Studentized Residuals
Predicted
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
-4.00
60
70
80
90
100
110

(b)



(c)

Figure 4: Residuals vs Predicted plot (a) residuals, (b) internally studentized residuals, (c) externally syudentized residuals

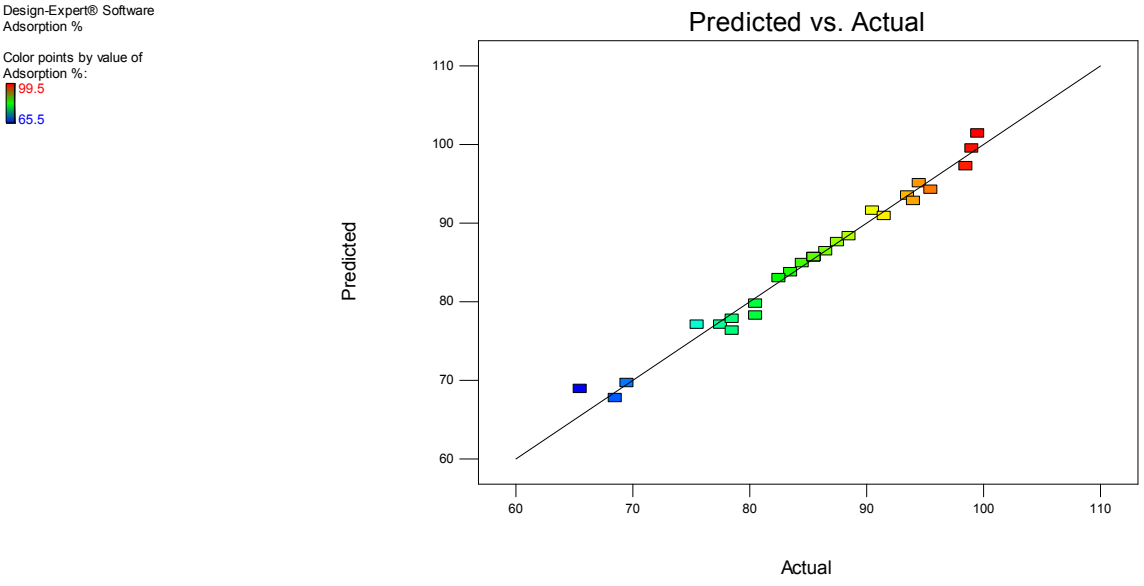


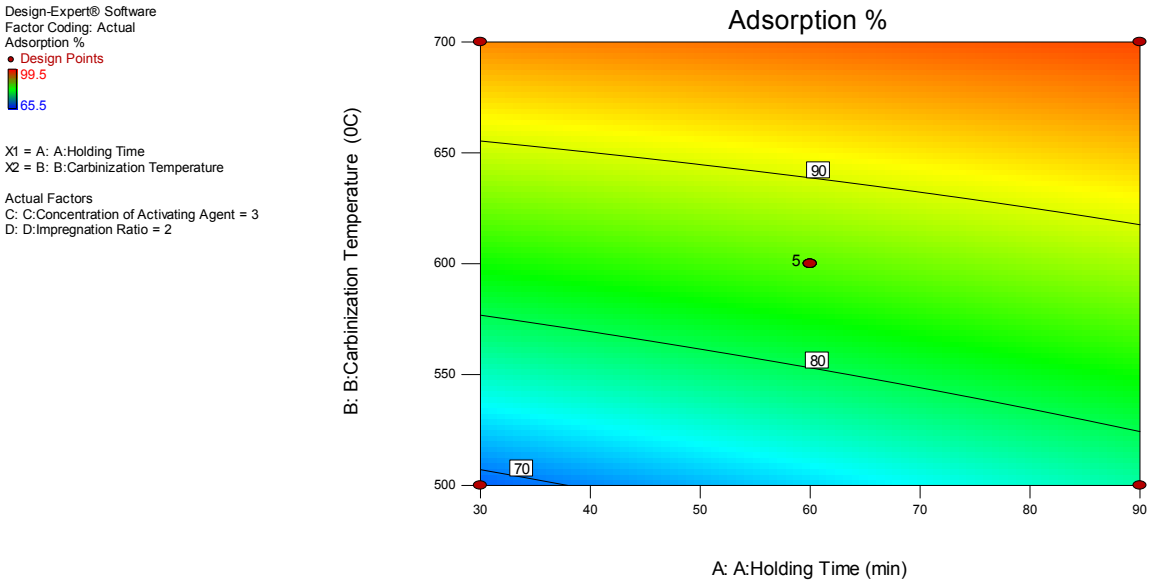
Figure 5: predicted vs actual plot

Normal probability plot of the studentized residuals are used to check for normality of residuals. Studentized residuals versus predicted values plots are used to check for constant error. Externally Studentized Residuals are used to look for outliers, i.e., influential values. As shown in the above all the model statistics and diagnostic plots are OK. So we can proceed to finish up with the Model Graphs icon.

The response surface graphs and contour plots are the graphical representations of the regression equations. The response surface, the primary graphs were the contour and 3D surface. Both of these show how any two factors affect the response and focus on the effects of the significant terms. i.e. the three-dimensional response surface and their corresponding contour plots for Cr(VI) adsorption percentages against any two independent variables by keeping the other independent variables at zero levels(i.e. holding time 60 min, carbonization temperature 600^0C, impregnation ratio 2 and concentration of activating agent 3M) are presented in Figs. (6) - (7). A total of 12 response surfaces were obtained by considering all the possible combinations for the three-dimensional response surface and their corresponding contour plots for Cr(VI) adsorption %. These plots show the type of interactions between the tested variables. The linear contour plot indicates the enhancing effect of the test variables on the response. Each contour curve represents an infinite number of combinations of the two tested variables, with the other two maintained at zero levels.

Second-degree effects of carbonization temprature is also significant. Factor interaction terms of carbonization temprature with holding is also significant. Effect of factor interactions on adsorption % is presented by three-dimensional and contoure response surface plots.

The contour plot is a two-dimensional (2D) representation of the response across the factors displayed on an axis. When there are more than two factors, the 2D graph displays a slice through the factor space. The 3D Surface plot is a projection of the contour plot giving shape in addition to the color and contour.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Factor Coding: Actual
Adsorption %
Design Points
99.5
65.5
X1 = A: A:Holding Time
X2 = B: B:Carbinization Temperature
Actual Factors
C: C:Concentration of Activating Agent = 3
D: D:Impregnation Ratio = 2
Adsorption %
B: B:Carbinization Temperature (0C)
A: A:Holding Time (min)
90
80
70
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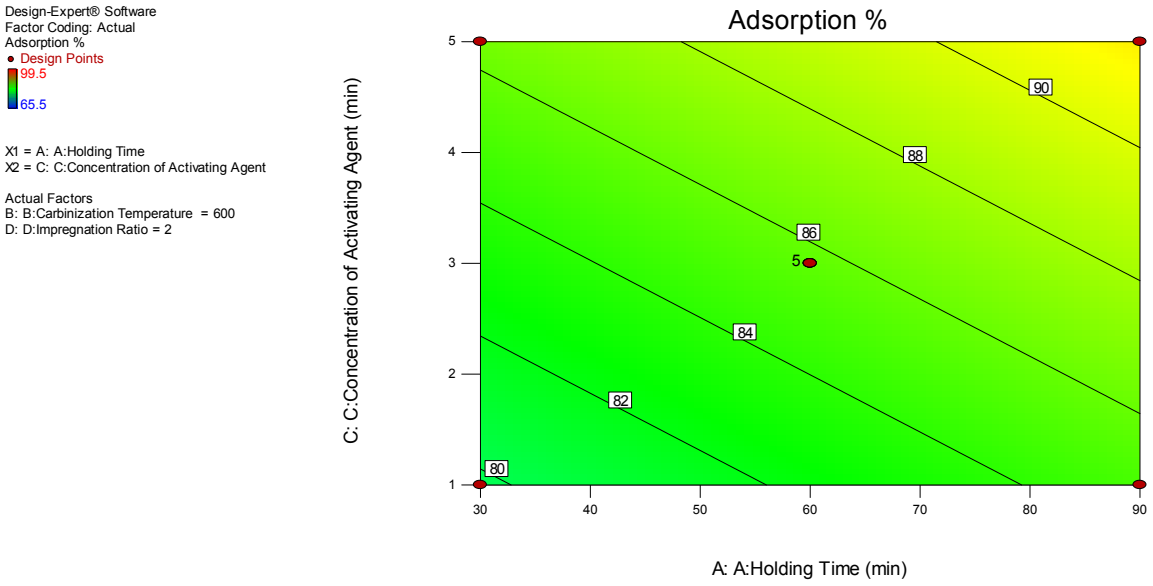
700
650
600
550
500
30
40
50
60
70
80
90

(a)


Design-Expert® Software
Factor Coding: Actual
Adsorption %
Design Points
99.5
65.5
X1 = A: A:Holding Time
X2 = C: C:Concentration of Activating Agent
Actual Factors
B: B:Carbinization Temperature = 600
D: D:Impregnation Ratio = 2
Adsorption %
C: C:Concentration of Activating Agent (min)
A: A:Holding Time (min)
90
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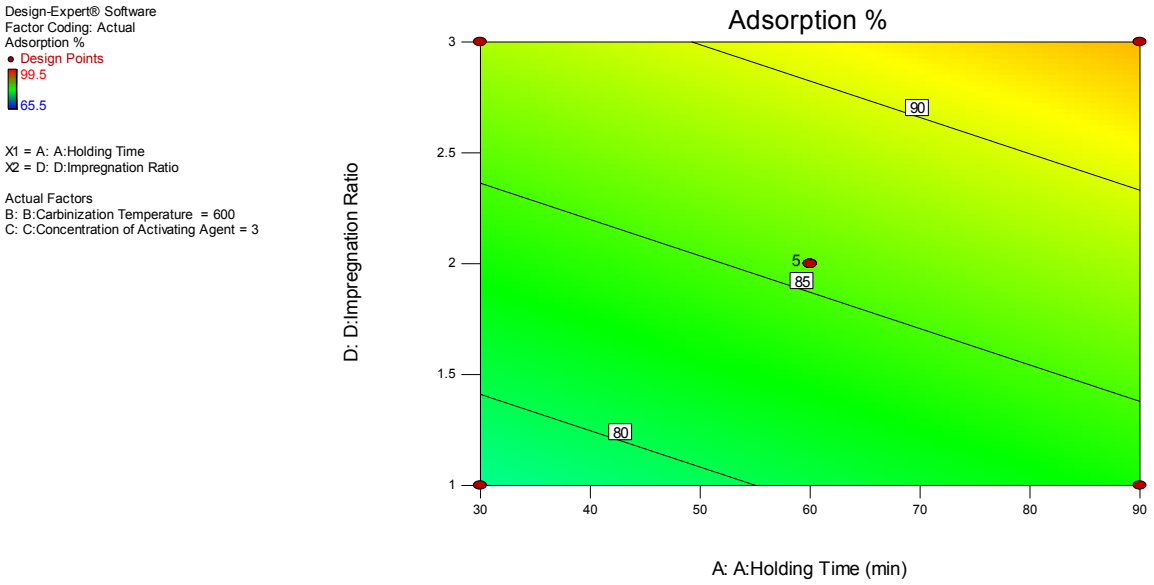
1
30
40
50
60
70
80
90

(b)


Design-Expert® Software
Factor Coding: Actual
Adsorption %
Design Points
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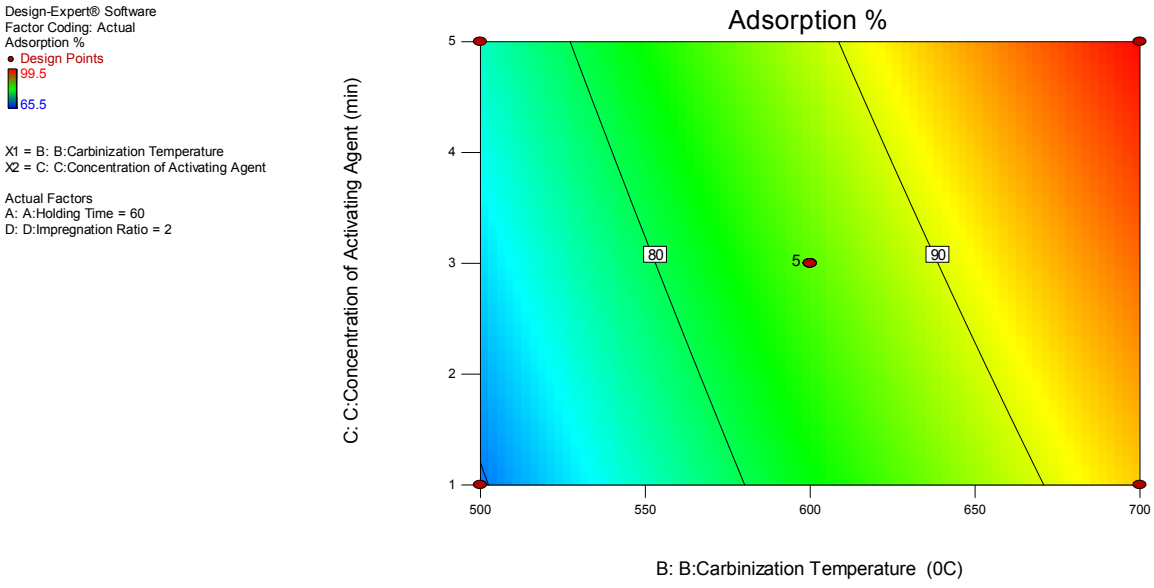
65.5
X1 = A: A:Holding Time
X2 = D: D:Impregnation Ratio
Actual Factors
B: B:Carbinization Temperature = 600
C: C:Concentration of Activating Agent = 3
Adsorption %
D: D:Impregnation Ratio
A: A:Holding Time (min)
90
85
80
5
3
2.5
2
1.5
1
30
40
50
60
70
80
90

(c)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Factor Coding: Actual
Adsorption %
Design Points
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65.5
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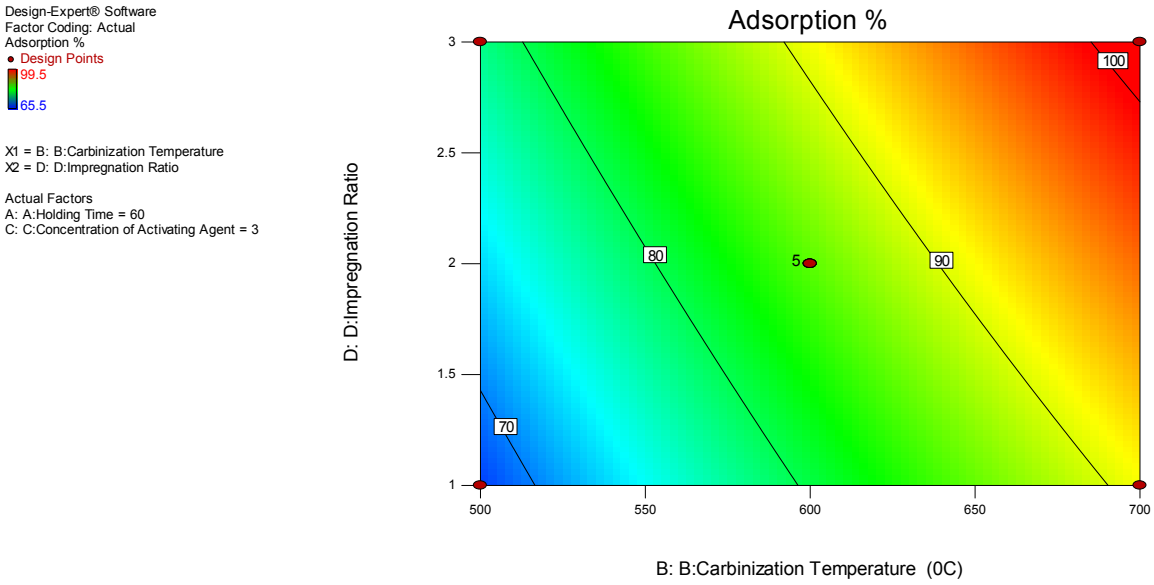
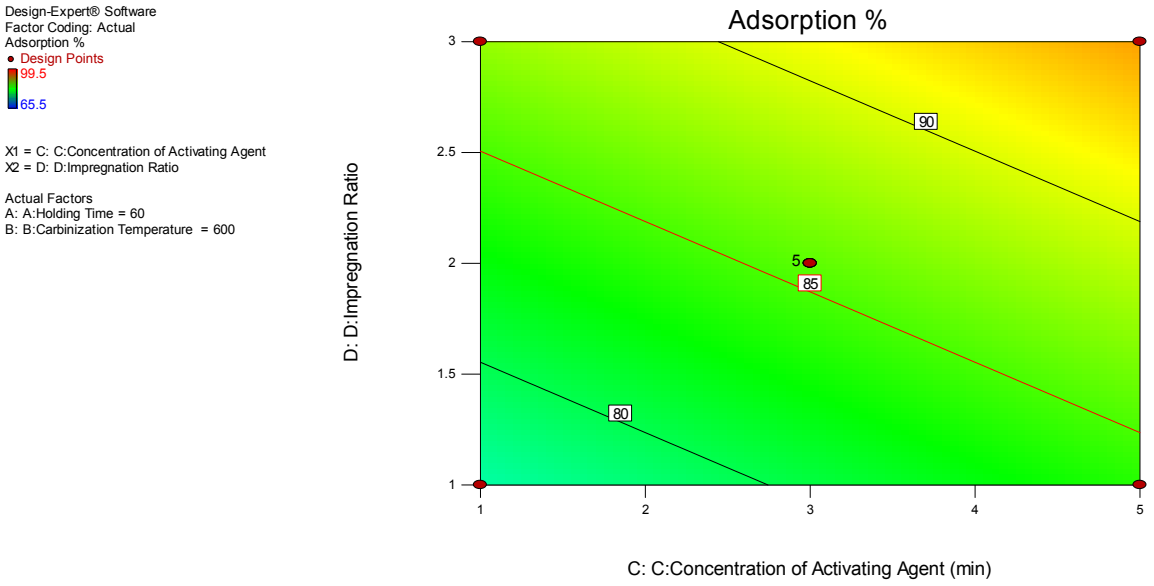
X2 = C: C:Concentration of Activating Agent
Actual Factors
A: A:Holding Time = 60
D: D:Impregnation Ratio = 2
Adsorption %
C: C:Concentration of Activating Agent (min)
B: B:Carbinization Temperature (0C)
80
90
5
5
4
3
2
1
500
550
600
650
700

(d)

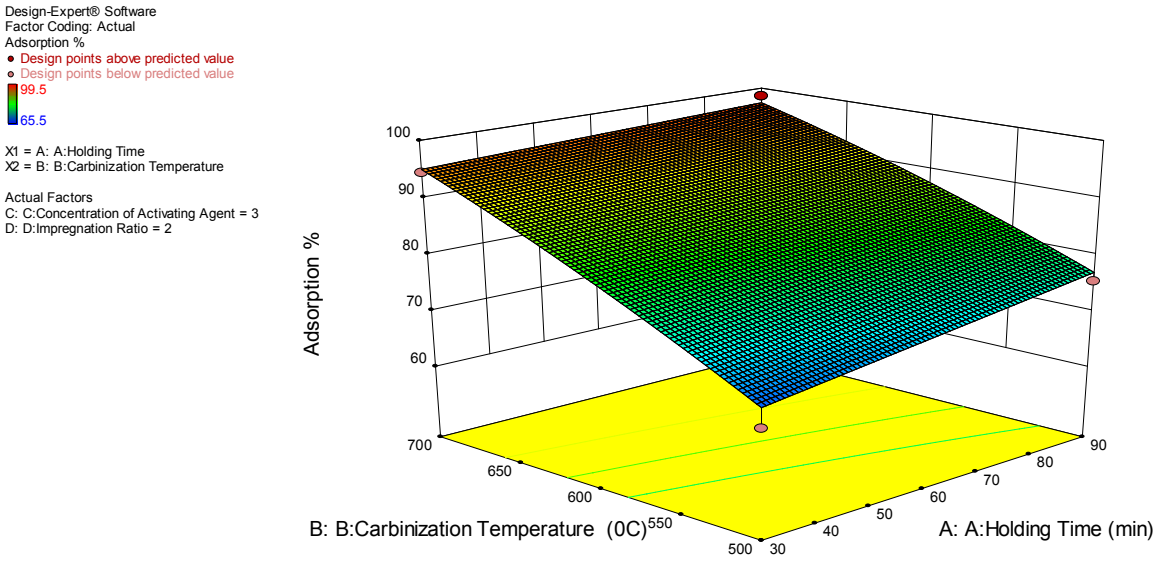


(e)

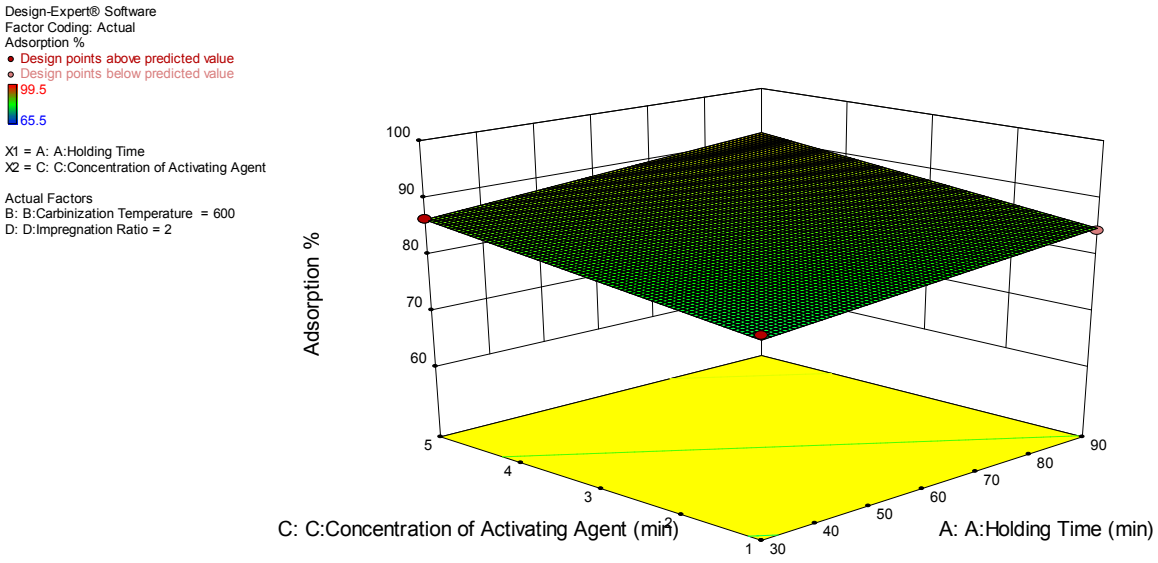


(f)

Figure 6: contour plots for adsorption %, (a) HT vs CT, (b) HT vs CA, (c) HT vs IR, (d) CT vs CA, (e) CT vs IR, (f) CA vs IR


Design-Expert® Software
Factor Coding: Actual
Adsorption %
Design points above predicted value
Design points below predicted value
99.5
65.5
X1 = A: A:Holding Time
X2 = B: B:Carbinization Temperature
Actual Factors
C: C:Concentration of Activating Agent = 3
D: D:Impregnation Ratio = 2
Adsorption %
100
90
80
70
60
700
650
600
550
500
B: B:Carbinization Temperature (0C)
30
40
50
60
70
80
90
A: A:Holding Time (min)

(a)


Design-Expert® Software
Factor Coding: Actual
Adsorption %
Design points above predicted value
Design points below predicted value
99.5
65.5
X1 = A: A:Holding Time
X2 = C: C:Concentration of Activating Agent
Actual Factors
B: B:Carbinization Temperature = 600
D: D:Impregnation Ratio = 2
Adsorption %
100
90
80
70
60
5
4
3
2
1
C: C:Concentration of Activating Agent (min)
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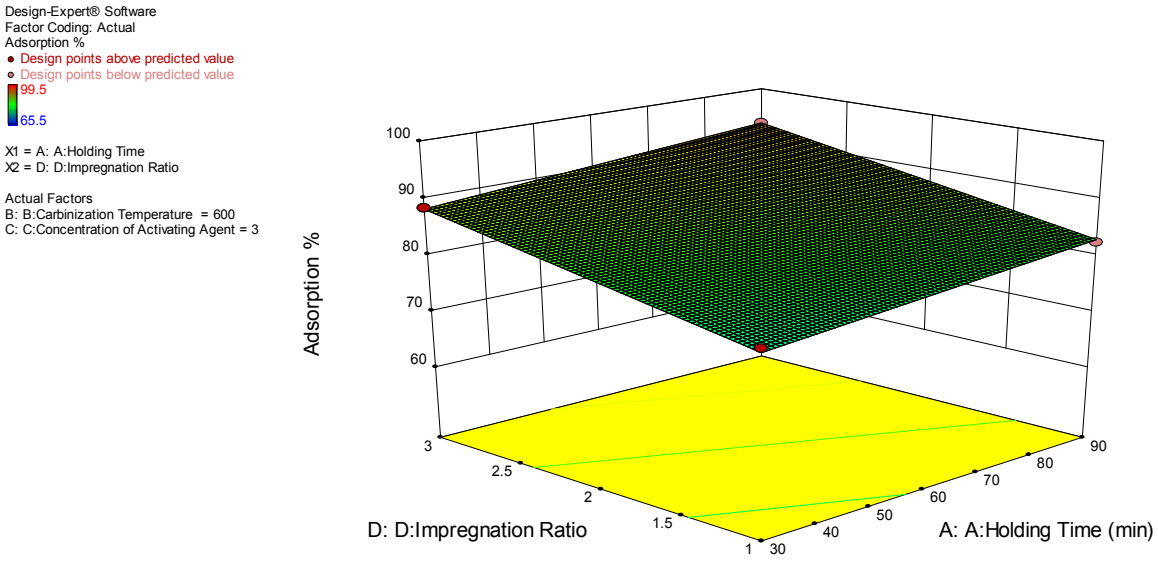
50
60
70
80
90
A: A:Holding Time (min)

(b)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Adsorption %
Design points above predicted value
Design points below predicted value
99.5
65.5
X1 = A: A:Holding Time
X2 = D: D:Impregnation Ratio
Actual Factors
B: B:Carbinization Temperature = 600
C: C:Concentration of Activating Agent = 3
Adsorption %
100
90
80
70
60
3
2.5
2
1.5
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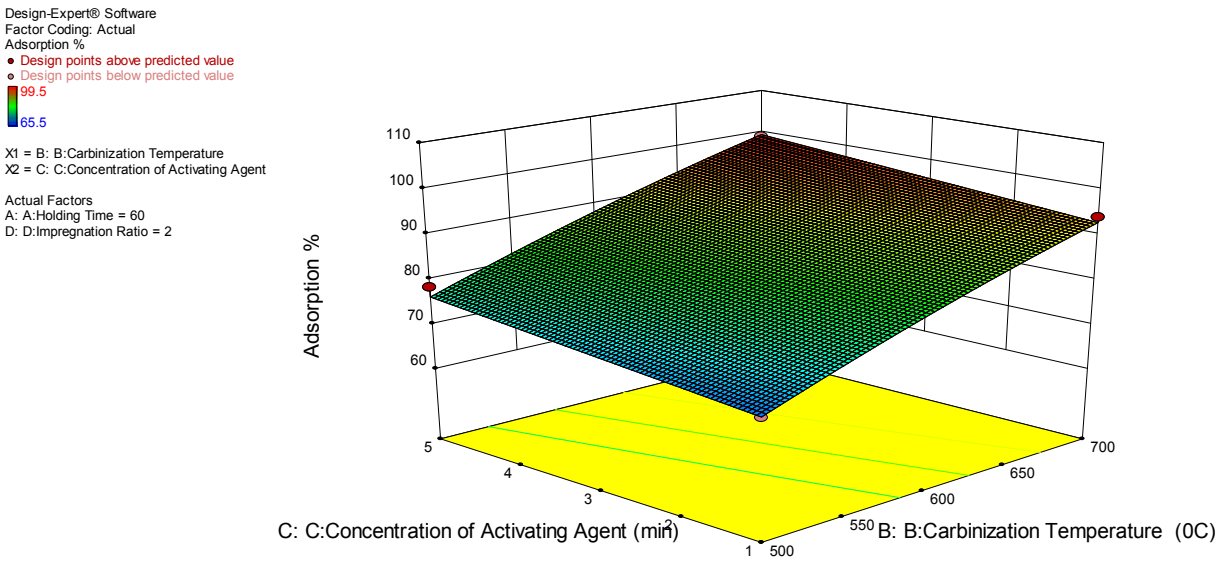
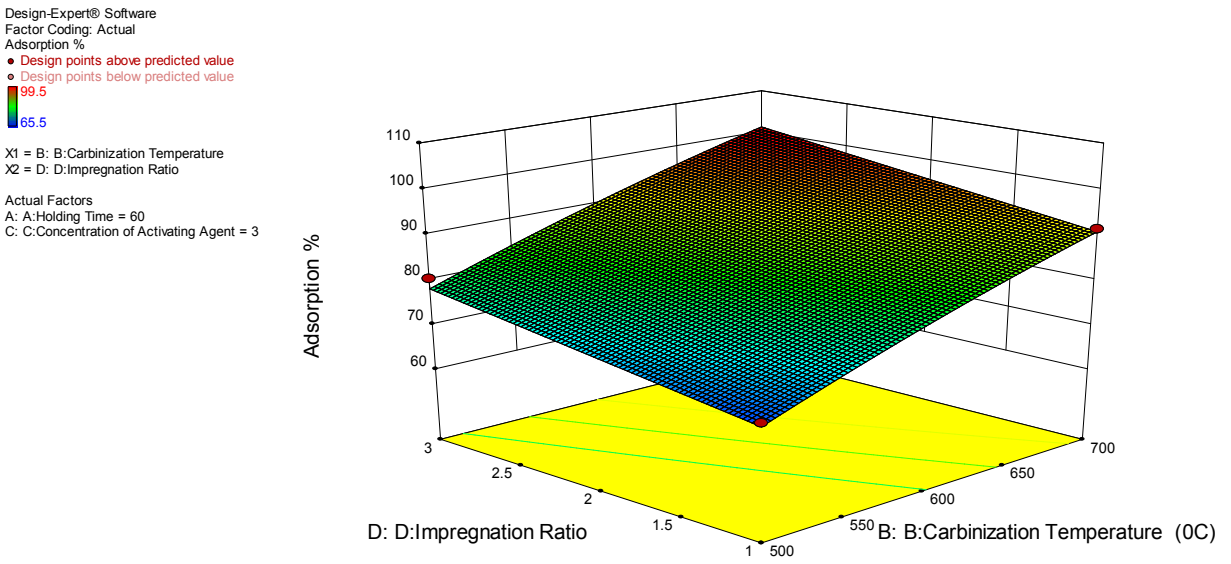
D: D:Impregnation Ratio
30
40
50
60
70
80
90
A: A:Holding Time (min)

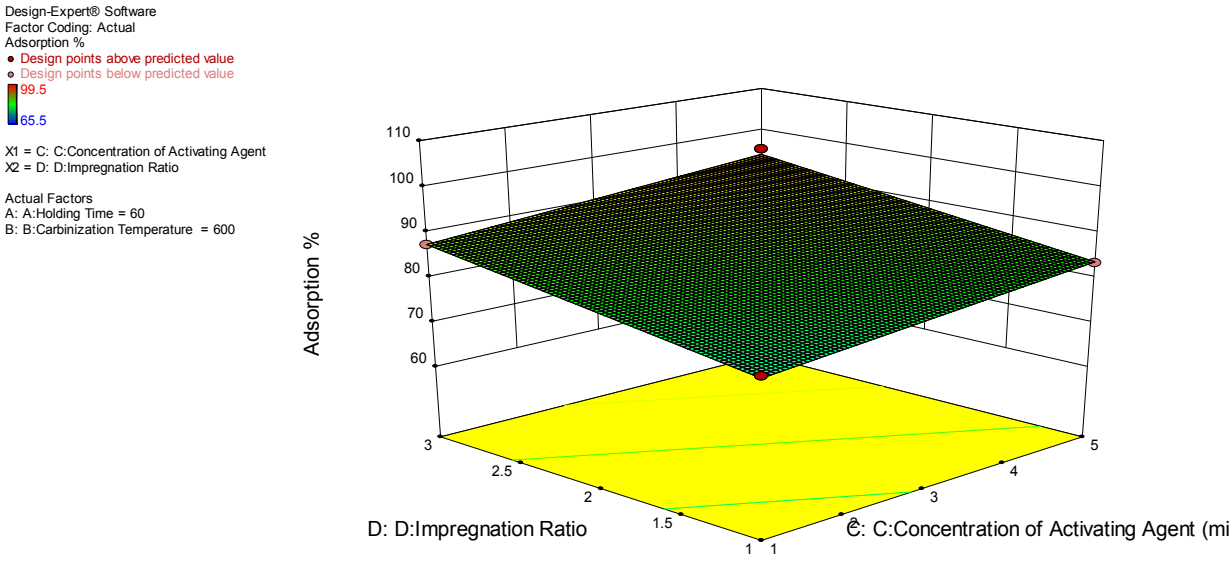
(c)


Design-Expert® Software
Factor Coding: Actual
Adsorption %
Design points above predicted value
Design points below predicted value
99.5
65.5
X1 = B: B:Carbinization Temperature
X2 = C: C:Concentration of Activating Agent
Actual Factors
A: A:Holding Time = 60
D: D:Impregnation Ratio = 2
Adsorption %
110
100
90
80
70
60
5
4
3
2
1
C: C:Concentration of Activating Agent (min)
500
550
600
650
700
B: B:Carbinization Temperature (0C)

(d)



(e)



(f)

Figure 7: Response surface 3D plots for adsorption %, (a) HT vs CT, (b) HT vs CA, (c) HT vs IR, (d) CT vs CA, (e) CT vs IR, (f) CA vs IR

Interactions between the holding time and carbonization temperature, holding time and concentration of activating agent, holding time and impregnation ratio, carbonization temperature and concentration of activating agent, carbonization temperature and impregnation ratio, concentration of activating agent and impregnation ratio are shown in figs. 6 and 7 for adsorption %.

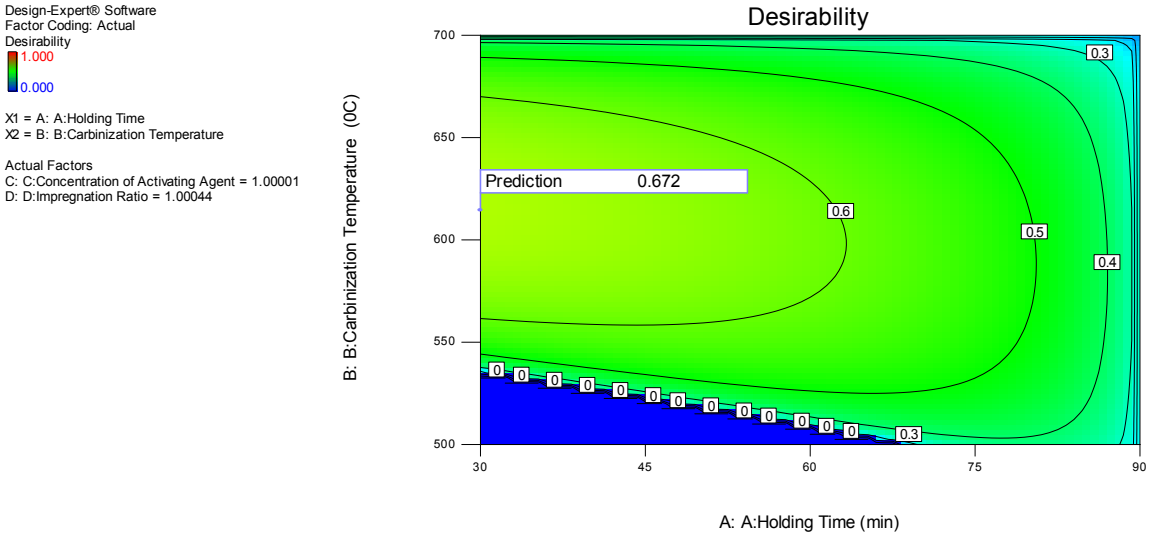


Figure 8: Desirability for CT vs HT

Desirability is an objective function that ranges from 0 outside of the limit to 1 at the goal. Numerical optimization finds a point that maximizes the desirability function. Desirability plot is shown in Fig 8. Myers and Montgomery (*Response Surface Methodology*, p. 244) describe a multiple response method called desirability. The method makes use of an objective function, D(X), called the desirability function. It reflects the desirable ranges for each response (d_i). The desirable ranges are from zero to one (least to most desirable, respectively). The simultaneous objective function is a geometric mean of all transformed responses. The result of graphical optimization is the overlay plot shown in Fig 9. It displays the area of feasible response values in the factor space. The most acceptable area showing prediction for response is represented by a flag planted at the most suitable location in space.

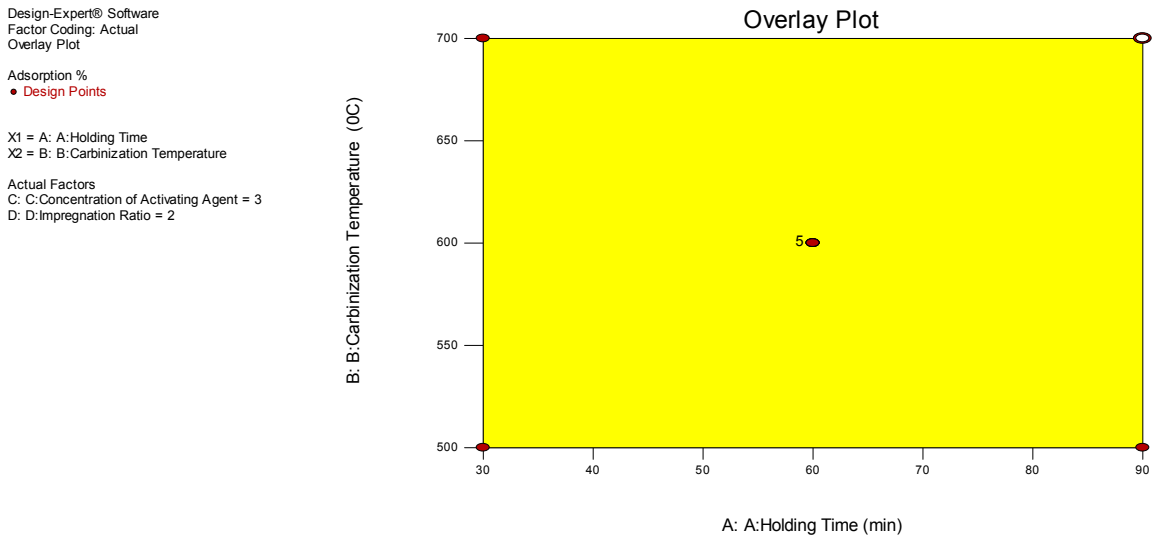


Figure 9: Overlay Plot for CT vs HT

4.1.2 Effect of Independent Variables on adsorption %

According to Table 7, the linear effects of all four independent variables are significant (P< 0.0001). Thus, each variable in turn can effect the quality of sesame husk activated carbon. In the investigated expermental region adsorption % increase with increase in all of the variables i.e all four indipendent variables have positive effect on adsorption % of the sesame husk activated carbon.

Preturbation plot in Figure 10 is an important diagramatic representation to compare all effects of all factor at particular point in design space. The response is plotted by changing only one factor over its range while holding all the other factors constant. A steep slope or curvature in a factor shows that the response is sensitive to that factor. A relatively flat line shows insensitivity to change in that particular factor. There are four factors in this study, the perturbation plot could be used to find those factors that most affect the response i.e. B, D, C and A.

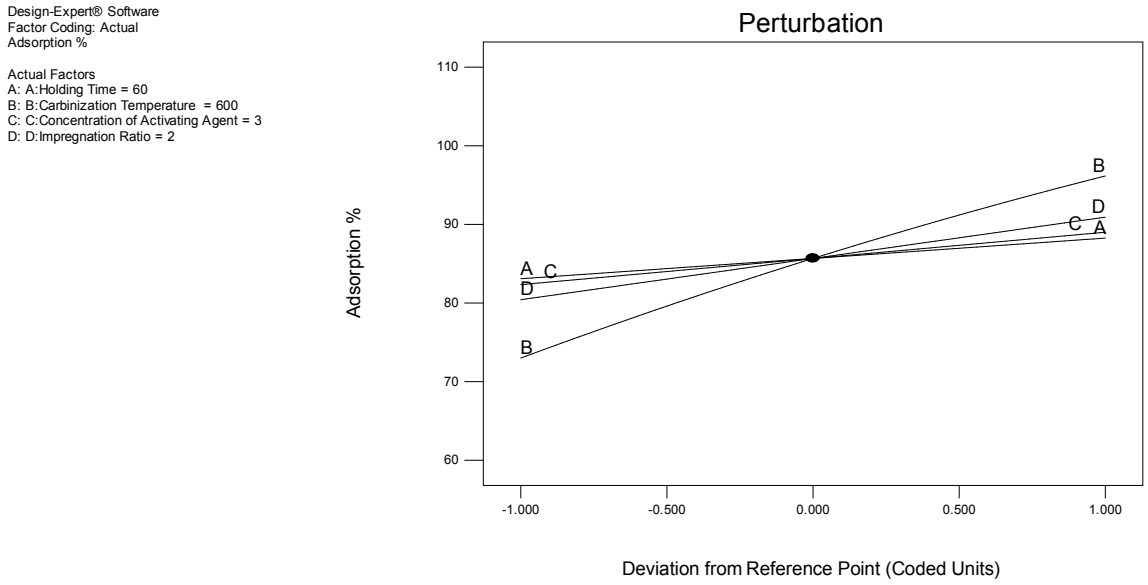


Figure 10: perturbation plot depicting the effect of operational parameters for preparation of activated carbon on adsorption % of sesame husk activated carbon

The plot in Figure 10 depicted that all factores have positive effect on dsorption %. it can be also seen that respons variable is most sensetive to carbonization temprature followed by imprignation ratio. This can be also evidenced by ANOVA result. According to ANOVA result, the effect of imprignation ratio (F= 198.61, P-value < 0.0001) and carbonization temprature (F=966.83, P-value < 0.0001) is much more influatial than that of concentration of activating agent (F= 80.06) and holding time (F=48.09).

4.1.3 Process optimization and evaluation

One of the main objectives of RSM is the determination of the optimum settings of the control variables that result in a maximum (or a minimum) response over a certain region of interest $\Re$ (Andr´ e I. Khuri & Siuli Mukhopadhyay, 2010).

Process parameters were optimized to adsorption % while minimizing consumption of activating agent which is attained at minimum concentration of the acid and impregnation ratio and power consumption for thermal treatment attained at minimum carbonization temperature and holding time. Predicted optimum values of process variables and optimized response variable were

presented in Table 10. Accordingly, Adsorption % of 76.41 % was determined at the optimum conditions of independent variables.

Table 10: Predicted Optimum Conditions

Variable	Optimum value
A:Holding Time (min)	30.00
B:Carbinization Temperature (^{0}C)	614.7
C:Concentration of Activating Agent(M)	1.00
D:Impregnation Ratio	1.00
Y: Adsorption %	76.41
Desirability	0.672

To validate the model five confirmation experiments were conducted at optimum point and varying one factor at time as shown in Table 11. Verifications of the calculated optimum conditions for Cr(VI) was done by carrying out the experiments in shake flasks using SHAC as adsorbent that prepared under the conditions predicted by the model. Under these conditions, pretreated SHAC removed 76.1 % Cr(VI), which is in agreement with the predicted value (76.41 %) suggested by the model.

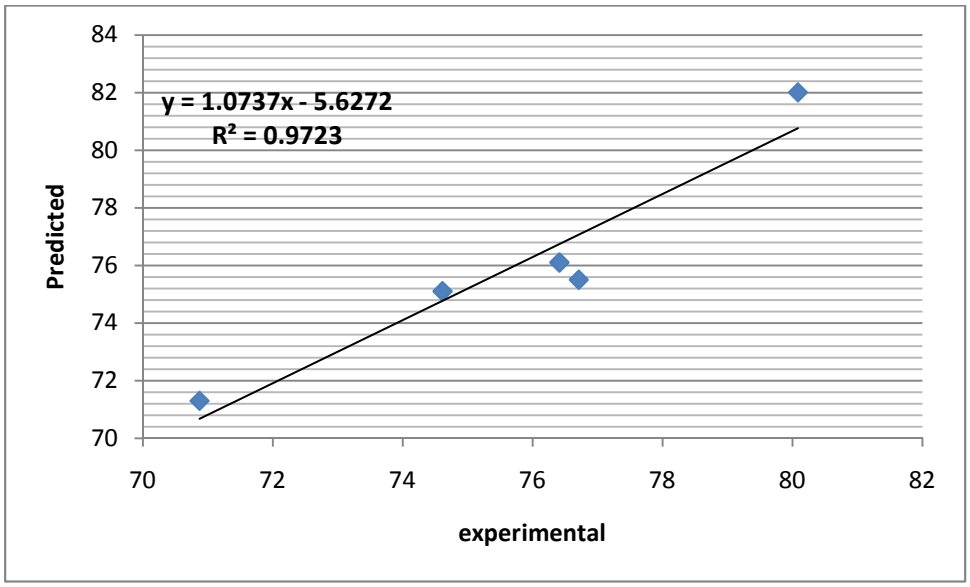


Figure 11: Predicted versus Experimental values for Model Validations

As shown in plots there was a good agreement between the predicted and experimental result adsorptions % (R^2=0.9723). The experimental values were found to be close to the predicted values and hence, the model was successfully validated.

Table 11: Confirmations experimental set up and results

	Factor				Adsorption %	
	A	B	C	D	Predicted	Experimental
1	25	614.7	1	1	74.6111	75.1
2	30	575	1	1	70.8716	71.3
3	30	614.4	2	1	76.7083	75.5
4	30	614.7	1	2	80.0816	82
5	30	614.7	1	1	76.41	76.1

Concluding remark on modeling and optimization: To conclude on this section; the section has presented Box-Behnken experimental design for modeling and process optimization, involving a study of a given system by set of variables over specific region of interest by identifying influence of individual variable. By using this method, four main effect variables including concentration of H_2SO_4, impregnation ratio, carbonization temperature and holding time were examined. A linear model was developed using multiple quadratic regression analysis. Statistical test (ANOVA) indicated a good agreement between experimental data and the built model for prediction of adsorption % of sesame husk activated carbon. The optimal operating conditions were determined using numerical optimization techniques by desirability approach. The adsorption % of sesame husk activated carbon was optimized while minimizing consumption of activation agent and minimizing power consumption. Accordingly H_2SO_4 concentration of 1M, impregnation ratio of 1w/w, carbonization temperature of 614.7^oC and holding time 30 minutes were best conditions for sesame husk activated carbon production which optimize adsorption % of sesame husk activated carbon. Under these conditions, adsorption % of 76.41 was predicted. Confirmation experiment conducted showed agreement between experimental value and predicted value with R^2 of 0.9723. This study demonstrated that AC with good adsorption % can

be prepared from sesame husk at reasonable adsorption capacity and RSM is important tool to model and optimize process parameters in production of sesame husk activated carbon.

4.2 Characteristics of SHAC prepared at optimum point

This section of the work is presented to address specific objective to which is intended to describe physico- chemical and surface characteristics of sesame husk activated carbon produced at previously predicted optimum production parameters.

Some physico-chemical properties of SHAC were presented in table below;

Table 12: Experimental data on the Characterization of SHAC prepared at optimum point

Characteristics	Value at optimum point	Reference value
Moisture Content	6.3 %	5-6
Volatile Content	13.3%	25-40
%Ash	8.4%	2 – 10 %
Fixed Carbon	73.4%	55-70
PH	5.0	5.1(0.2)
Conductivity	0.48ms/cm	
Porosity	54.5%	
Pore volume	0.89 cm^3/g	0.3 – 1.8
Bulk density	0.65g/mL	

According to (Hernández-Montoya et al., 2012), some reference values were reported and these can be used for comparison with the experimental data on the characterization of SHAC prepared at optimum point. I.e. for MC, VC and FC table 2 and 13 can be also used as reference value.

4.2.1 Proximate analysis

Proximate analysis is one of the thermal analysis techniques. These are analytical techniques in which a physical property is measured with a temperature-programmed variation. In this case, the property measured is the weight. Proximate analysis provides an approach to estimate the content of: moisture, volatile matter, fixed carbon, and ash. Moisture measurements refer to the matter volatilized until near 373K, mostly water. Volatile matter is determined by the same procedure but in a temperature range of 373 to 1223K. Fixed carbon is the material burned in air

at 1223K in a third step and is made of the more stable organic structures. Lastly, the non-combustible matter is the ash. Generally, the composition of ash, fixed carbon, and volatile matter are given on a dry basis. The representation of weight versus temperature (or time) also gives information about the thermal stability of the activated carbon. The proximate analyses as presented in Table 13 showed a low amount of moisture, ash and volatile matter, and high value of fixed carbon indicating that high graphitization grade. This intern shows that the activated carbon can be an excellent raw material for adsorbents to be used in column or fixed-bed reactors. Ash content can also affect activated carbon i.e. it reduces the overall activity of activated carbon. It also reduces the efficiency of reactivation, the lower the ash value therefore the better the activated.

Table 13: proximate values of comparative low-cost activated carbon

Activated carbon	MC %	VC %	Ash %	FC %	Ref
Coffee husk	6.03	24.62	2.01	67.34	(Mohd Azmier Ahmad & Nazira Khabibor Rahman, 2011)
durian shell	5.53	69.59	2.52	22.36	(Chandra, Mirna, Sunarso, Sudaryanto, & Ismadji, 2009)
Fluted steam activation	19.50	40.15	22.38	-	(Ekpete O.A. & Horsfall M.JNR, 2011)
Fluted seed shell	4.2	-	16	64.0	(Verla, Horsfall, Verla, Spiff, & Ekpete, 2012)

Volatile content in AC is mainly due to the presence of non carbonaceous matters. The elimination of non-carbonaceous matters is controlled by activating agent and temperature. The acid attacks non-carbonaceous matters present in the feed and detaches them from their native sites. The deep penetration of acid detaches more non-carbonaceous matters. The application of temperature aids in moving these matters from the surface during activation.

Finally, Characterization result using table 2, 12 and 13 as reference shows that SH can be used as row material for production of activated carbon with comparable property with other reported Activated carbons.

4.3 Batch Adsorptions Study of Cr(VI) onto Sesame Husks Activated Carbon

4.3.1 Effect of pH

The result presented in Figure-12 asserted that solution pH is one of the parameters having considerable influence on the adsorption of metal ions. This may be attributed to the surface charge density of the adsorbent and the metallic species which depend on the pH. The behaviour for better adsorption at low pH by activated carbon may be attributed to the large number of H^+ ions present at low pH values which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of chromate ions (B. Veena Devi, A.A. Jahagirdar, & Ahmed, 2012). From figure-12, it is evident that at pH 2 the adsorption is maximum. The adsorption increases from 0.2mg/g (6.1% removal) to 46.95mg/g (99.6% removal) because of the decrease of pH from 9 to 2. This indicates that the Cr(VI) adsorption capacity of the adsorbent is dependent upon pH. The influence of pH on the removal of Cr(VI) by adsorption on sulfuric acid-treated sesame husks was studied by varying the pH values (1.0 - 9.0) and using a contact time of 360 min at each pH value at 20^0C.

Table 14: Experimental data on the effect of pH on adsorption %

Ph	Cr (IV) removal, %	Ce(mg/L)*10^2
1	97.8	0.002
1.5	98.8	0.006
2	99.6	0.011
2.5	84.8	0.076
3	77.8	0.111
3.5	17.8	0.411
4	11.8	0.441
4.5	12.4	0.438
5	9.8	0.451
5.5	9.6	0.452
6	9.3	0.4535
6.5	9	0.455
7	8.6	0.457
7.5	7	0.465
8	7.2	0.464

8.5	6.3	0.4685
9	6.1	0.4695

The results are shown in Fig.12. The pH affected the adsorption by the SHAC significantly, as evidenced by the drastic changes in the adsorption percentage depending on the pH of the solutions. The pH affected the adsorption process through the dissociation of functional groups on the active sites on the surface of the adsorbent. The optimum pH value for the adsorption was determined to be 2, at which the adsorption % was determined to be approximately 99.6%.

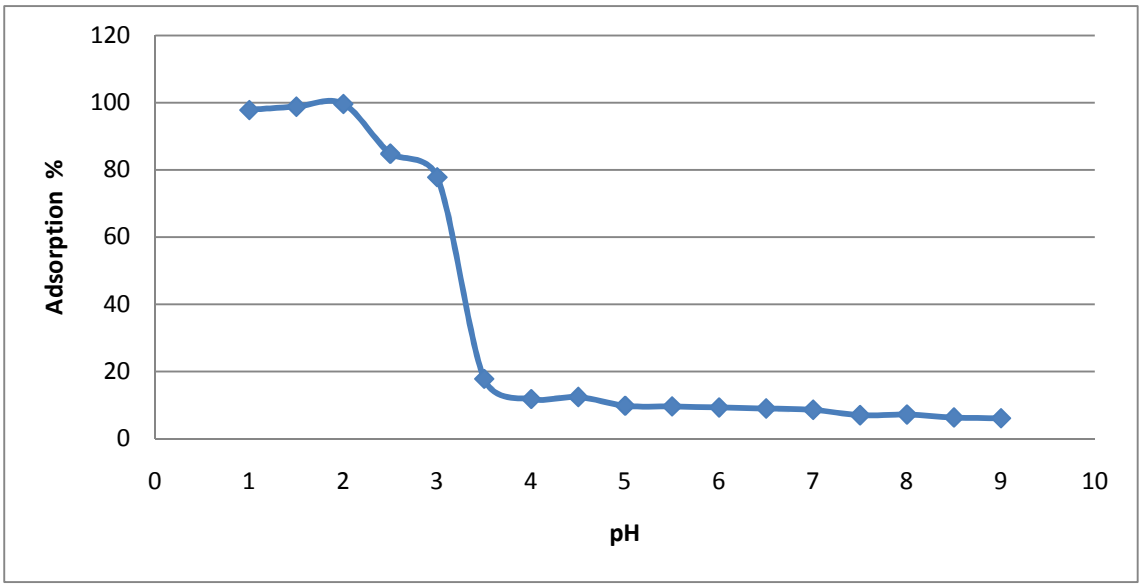


Figure 12: Effect of pH on Cr(VI) adsorption onto sesame husk activated carbon, adsorption condition; Volume of solution 200mL, Cr(CI) concentration 100mg/L, amount of sesame husk activated carbon 0.5g, temperature 20^{o}C, pH(1.0-9.0), agitation speed 200rpm, and contact time 6Hrs.

The adsorption levels of decreased sharply as the pH increased from 2 to 3.8, and thereafter, the effect of further increases in pH on the removal yield were negligible. Similar results have been reported by many studies for adsorption by different lignocellulose-based materials. The species may be represented in various forms, such as H_2CrO_4, $HCrO^{-4}$, CrO_2^{-4}, and $Cr_2O_2^{-7}$ in the solution phase as a function of pH. Speciation is affected by the pH of the solutions pH the following equilibrium relationships:

$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+ \qquad pKa = 4.1 \qquad (4.2)$$

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+ \qquad pKa = 5.9 \qquad (4.3)$$

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \qquad pKa = 2.2 \qquad (4.4)$$

It is known that $HCrO^{-4}$ and $Cr_2O_2^{-7}$ ions are predominant species of in a very acidic medium. At very low pH values, the surface of the adsorbent also would be surrounded by hydronium ions, which enhance the interactions of with the binding sites of the adsorbent due to their greater attractive forces. As the pH was increased, the overall charge on the surface of the adsorbent became negative, and the adsorptions of the oxyanions of decreased.

4.3.2 Effect of Contact Time and Initial Cr(VI) Concentrations

The result were shown in figure 13 the adsorptions % of Cr(VI) was found 96, 98, and 99 for initial Cr(VI) concentrations of 100, 200, and 300mg/L respectively. The extent of adsorptions increased rapidly in the initial stages but became slow in the later stages till the attainment of equilibrium. Equilibrium time for the adsorptions of Cr(VI) on sesame husk activated carbon at various Cr(VI) concentrations was found to be 6 Hrs, which showed that equilibrium time was independent of initial Cr(VI) concentrations. The curves are single smooth and continuous suggesting the formations of monolayer of adsorbate on the surface of the adsorbent.

Table 15: Experimental data on the effect of Contact Time and Initial Cr(VI) Concentrations on adsorption %

	adsorption %		
contact time	100 mg/L	200mg/L	300mg/L
60	41	43	45
120	70	72	74
180	85	87	89
240	90	92	94
300	95	97	98.5
360	96	98	99
420	96	98	99
480	96	98	99

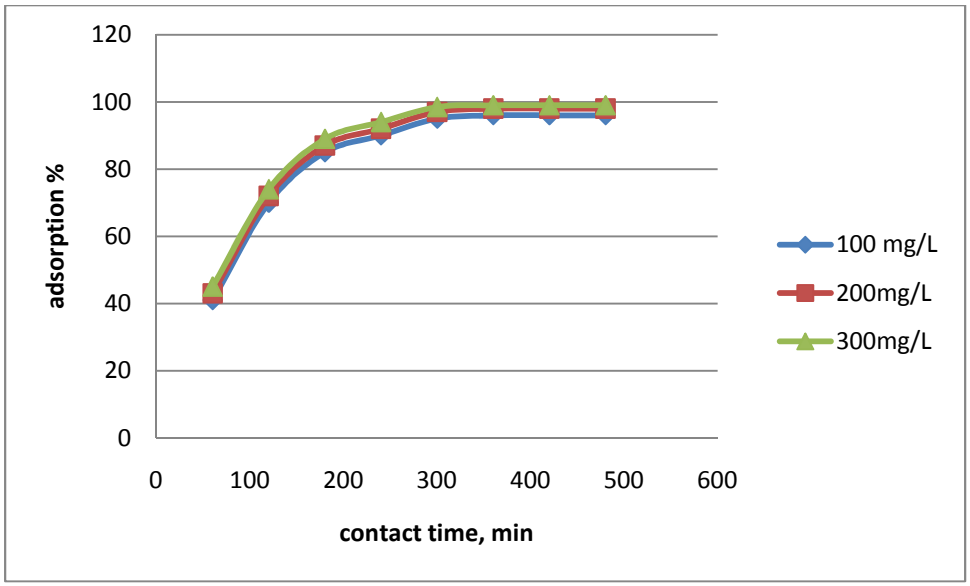


Figure 13: Effect of Cr(VI) concentration and contact time on Cr(VI) adsorption onto sesame husks activated carbon. Adsorption conditions; Volume of solution 200mL, pH 2, amount of sesame husks activated carbon 0.5g temperature 20^{o}C.

4.3.3 Effect of Contact Time and Temperature

The uptake of chromium from solutions by SHAC increased with contact time and attained equilibrium at 360min for all of the temperatures studied. Time-dependent adsorptions experiments were conducted at 20, 30, 40 and 50^{0}C to investigate the effect of temperature. The results of these experiments are shown in Fig.14. It is evident in the figure that the adsorptions percentage of chromium increased as temperature increased and reached its maximum value at 50^{0}C, indicating that the adsorption of Cr (VI) ions on SHAC was an endothermic process. It was observed that the adsorptions percentage of chromium increased from approximately 45–96 % when the temperature of the solutions was increased from 20 to 50^{0}C. Chemical interactions between the surface groups of the adsorbent and the adsorbate ions have an important effect on the adsorptions capacity, and the effect depends significantly on the temperature of the solutions. The increase in adsorptions percentage as temperature increased may be due to the increase in the intraparticle diffusions rate of adsorbate ions in the pores at higher temperatures, since

diffusions is an endothermic process. Similar trends were also observed by other researchers for aqueous phase adsorptions.

Table 16: Experimental data on the effect of Contact Time and Temperature on adsorption %

	Cr (IV) removal %			
Contact Time, min	20^0C	30^0C	40^0C	50^0C
60	45.5	46.5	47.5	48.5
120	74.5	75.5	76.5	77.5
180	78.3	80.3	82.3	84.3
240	78.6	80.6	82.6	84.6
300	78.7	80.7	82.7	84.7
360	78.8	80.8	82.8	84.8
420	78.9	80.9	82.9	84.9
480	79.5	81.5	83.5	85.5

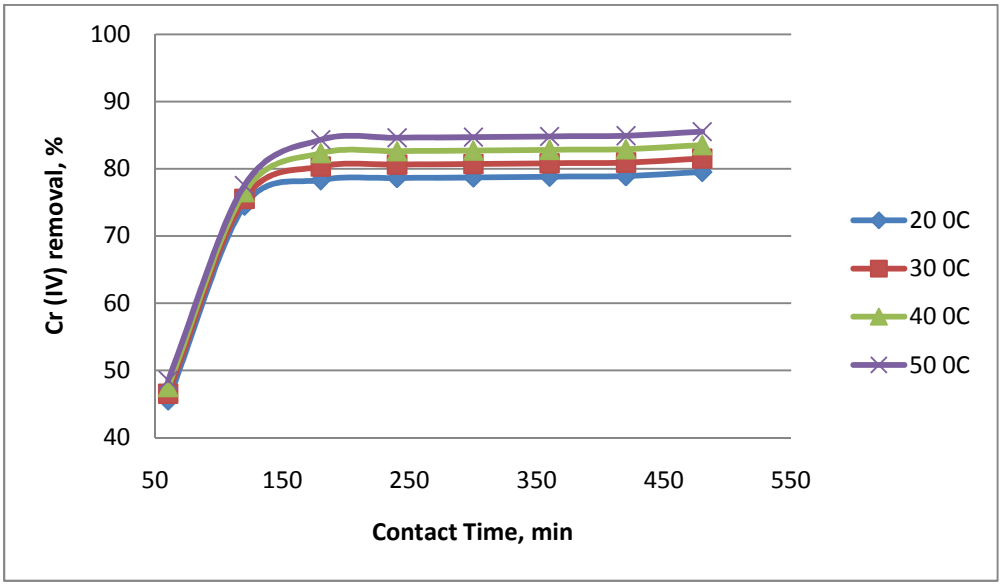


Figure 14: Effect of temperatures and contact time on the adsorptions of chromium by SHAC (conditions: 0.5g SHAC, 200mL 100mg/L solutions, initial pH: 2)

4.3.4 Equilibrium Study

Equilibrium relationships between the adsorbate concentration in the liquid phase and that on the adsorbent's surface at a given condition, generally known as adsorption isotherms, describe how

pollutants interact with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems (Demiral et al., 2008; K. Y. Foo & B. H. Hameed, 2010). Thus an accurate mathematical description of equilibrium adsorption capacity is indispensable for reliable prediction of adsorption parameters and quantitative comparison of adsorption behaviour for different adsorption system or for varied conditions within any given systems. There are many equations for analyzing experimental adsorption equilibrium data. In this study the experimental data was analyzed against two parameter isotherm equations, namely Langmuir and Freundlich isotherm equations.

This work aims to find the models that can describe with precisions the experimental results of adsorptions isotherms, specify the parameters that can be determined, compare the Cr(VI) adsorptions behavior, and determine the theoretical adsorptions isotherms. Several mathematical models can be used to describe experimental data of adsorptions isotherms. The equilibrium data were modeled with the Langmuir, and Freundlich models.

The Langmuir isotherm model estimates the maximum adsorption capacity produced from complete monolayer coverage on the adsorbent surface. The Langmuir model assumes uniform energies of adsorptions onto the surface and no transmigrations of adsorbate in the plane of the surface. The non-linear equation of Langmuir isotherm model can be expressed in the following non-linear form:

$$qe = \frac{q_m b C_e}{1 + bC_e} \qquad (4.5)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg g−1), C_e the equilibrium concentrations of the solute in the bulk solutions (mg L−1), q_m the maximum adsorptions capacity (mg g−1), and b is the constant related to the free energy of adsorptions (L mg−1).

The above equation 4.5 can be linearized to different and one of these linier forms is

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e \qquad (4.6)$$

A plot of $\frac{C_e}{q_e}$ Vs. C_e (Figure 15) should yield a straight line if the Langmuir equation is obeyed by the adsorptions equilibrium. The slope and the intercept of this line then give the values of q_m and b. A further analysis of the Langmuir equations can be made on the basis of a dimensionless equilibrium parameter, R_L, also known as the separations factor, given by;

$$R_L = \frac{1}{1 + bC_o} \qquad (4.7)$$

If the average of the R_L values for each of the different initial concentrations used is between 0 and 1, it indicates favorable adsorptions.

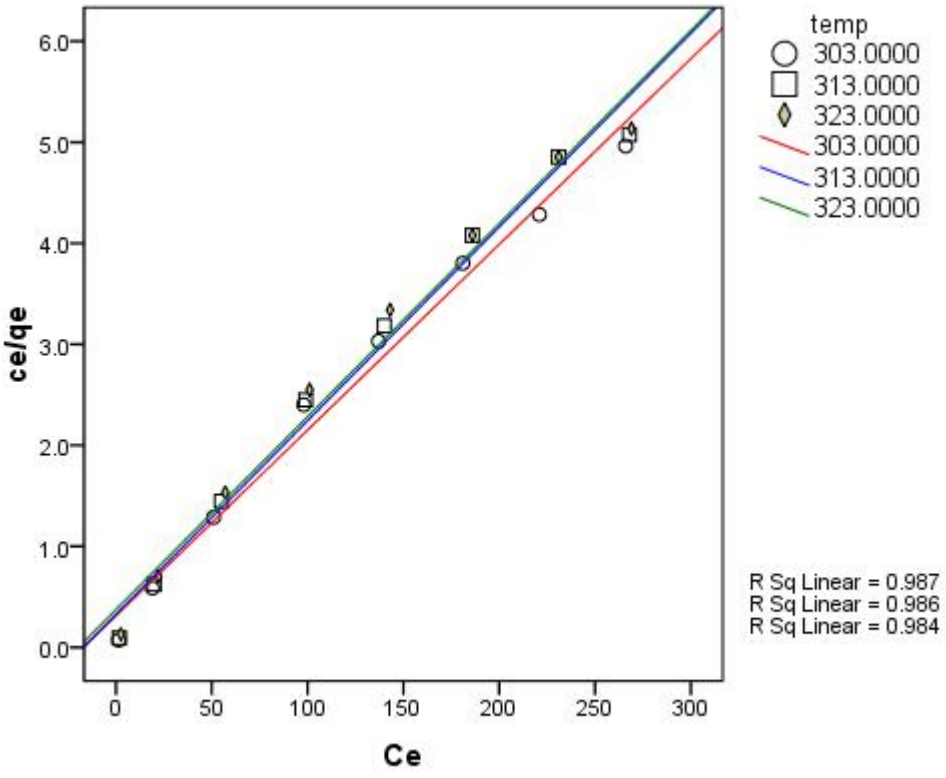


Figure 15: Equilibrium Study using Langmuir models

Table 17: Experimental data on Equilibrium Study

Temp. (K)	C_o	C_e	q_e	ce/q_e	$LogC_e$	$Logq_e$
303	50	1.4	19.44	0.072016	0.146128	1.288696
303	100	19	32.4	0.58642	1.278754	1.510545
303	150	51	39.6	1.287879	1.70757	1.597695
303	200	98	40.8	2.401961	1.991226	1.61066
303	250	137	45.2	3.030973	2.136721	1.655138
303	300	181	47.6	3.802521	2.257679	1.677607
303	350	221	51.6	4.282946	2.344392	1.71265
303	400	266	53.6	4.962687	2.424882	1.729165
313	50	1.80	19.28	0.093361	0.255273	1.285107
313	100	20.00	32	0.625	1.30103	1.50515
313	150	55.00	38	1.447368	1.740363	1.579784
313	200	99.00	40.4	2.450495	1.995635	1.606381
313	250	140.00	44	3.181818	2.146128	1.643453
313	300	186.00	45.6	4.078947	2.269513	1.658965
313	350	231.00	47.6	4.852941	2.363612	1.677607
313	400	268.00	52.8	5.075758	2.428135	1.722634
323	50	2.5	19	0.131579	0.39794	1.278754
323	100	22	31.2	0.705128	1.342423	1.494155
323	150	57	37.2	1.532258	1.755875	1.570543
323	200	101	39.6	2.550505	2.004321	1.597695
323	250	143	42.8	3.341121	2.155336	1.631444
323	300	186	45.6	4.078947	2.269513	1.658965
323	350	231	47.6	4.852941	2.363612	1.677607
323	400	269	52.4	5.133588	2.429752	1.719331

Freundlich isotherm is an empirical equation. This equation is one among the most widely used isotherms for the descriptions of adsorptions equilibrium. Adsorbents that follow the Freundlich isotherm equations are assumed to have a heterogeneous surface consisting of sites with different adsorptions potentials, and each site is assumed to adsorb molecules. Freundlich isotherm is capable of describing the adsorptions of organic and inorganic compounds on a wide variety of adsorbents including biosorbent. This equations has the following form

$$q_e = K + C^{1/n} \qquad (4.8)$$

Can also be expressed in the linearized logarithmic form

$$\log q_e = \log K + \frac{1}{n}\log C_e \qquad (4.9)$$

The plot of log(qe)Vs. log(Ce) shown in figure 16 has a slope with the value of 1/n and an intercept magnitude of log(K_f).

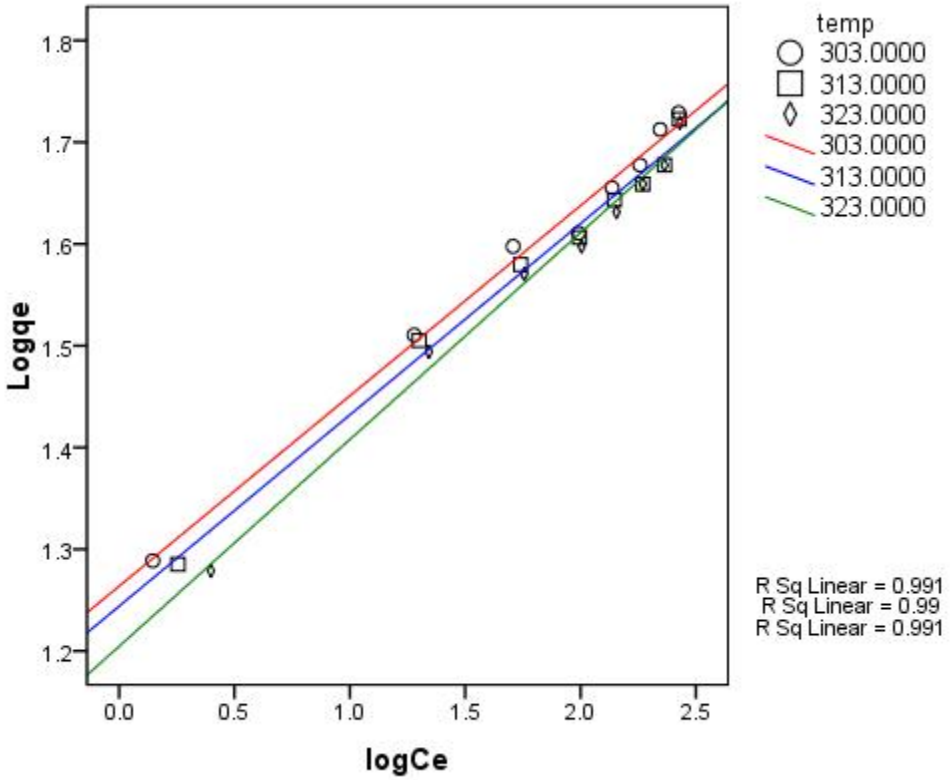


Figure 16: Equilibrium Study using Freundlich models

Model parameters for Langmuir and Freundlich isotherm models were presented in table 18. Coefficient of determinations identified that Freundlich isotherm model better fit with the experimental data with r^2 >0.99 for all three temperatures.

Table 18: Isotherm models, value of respective parameters at different temperature and correlations coefficient

	Isotherm & parameters	Value of parameter at three temperatures		
		30^0C	40^0C	50^0C
1	Langmuir			
	Regressions eq. of $\frac{C_e}{q_e}$ Vs. C_e	y = 0.0184x + 0.3158	y = 0.0192x + 0.3272	y = 0.0191x + 0.3755
	q_m(mg/g)	54.34	52.08	52.63
	b(L/mg)	0.058	0.058	0.050
	r^2	0.9868	0.9857	0.9845
2	Freundlich			
	Regressions eq. of $\log q_e$ Vs. $\log C_e$	y = 0.1871x + 1.2636	y = 0.1881x + 1.244	y = 0.2033x + 1.2045
	K_f(mg/g)	18.34	17.54	16.01
	N	5.34	5.32	4.92
	r^2	0.9908	0.9901	0.9906

The isotherm constants were calculated from the slope and intercept of Figure 15 and 16 presented in Table 18.

Value of K_f, which is defined as the maximum capacity of adsorbent, was calculated from the Freundlich plots. The maximum capacity of sesame husk activated carbon for Cr(VI) removal was calculated in the range of 16.01–18.34mg/g at different temperatures that indicated the good adsorbing capacity of the sesame husk activated carbon. The equilibrium parameter R_L is in the range of $0< R_L <1$ which reflects the favorable adsorption process. This indicated to the fact that the adsorption process was very favorable and the adsorbent employed exhibited a good potential.

4.3.5 Kinetic Study

Predicting the rate of adsorptions for a given system is among the most important factors in adsorptions system design, as the system's kinetics determines adsorbate residence time and the reactor dimensions. As previously noted, although various factors govern the adsorptions capacity, initial heavy metals concentrations, temperature, pH of solutions, sorbent particle size, heavy metals nature, a kinetic model is only concerned with the effect of observable parameters on the overall rate.

Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the adsorbate in the solid–solution interface (Febrianto et al., 2009). In practice, kinetic studies were carried out in batch reactions using various initial adsorbate concentrations, sorbent doses, particle sizes, agitations speeds, pH values and temperatures along with different sorbent and adsorbate types. Then, linear regression was used to determine the best-fitting kinetic rate equations. Adsorption kinetics is of great significance to evaluate the performance of a given adsorbent and gain insight into the underlying mechanisms. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established. Also, one can know the scale of an adsorption apparatus based on the kinetic information (Ho & McKay, 1999; Qiu et al., 2009). Several adsorptions kinetic models have been established to understand the adsorptions kinetics and rate-limiting step. The pseudo-first and pseudo-second-order kinetic models are the most well liked model to study the adsorptions kinetics of heavy metals and quantify the extent of uptake in adsorptions kinetics.

In the present study, kinetic data were analyzed against two kinetic models explain the mechanism of the adsorption processes. The two models were adsorption reaction models, viz., pseudo first-order (Lagergren S., 1898) and pseudo second-order (Ho YS et al., 2000), analyzed to identify rate limiting step.

Pseudo first-order: The pseudo first-order equation (Lagergren S., 1898), is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (4.10)$$

where: q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g), k_1 is the rate constant of pseudo first-order adsorption (l/min). After integration and applying boundary conditions t= 0 to t= t and qt= 0 to qt= qt, the integrated form becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \qquad (4.11)$$

The values of $\log(q_e - q_t)$ were linearly correlated with t. The plot of $\log(q_e - q_t)$ vs. t (Figure 17) gives a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

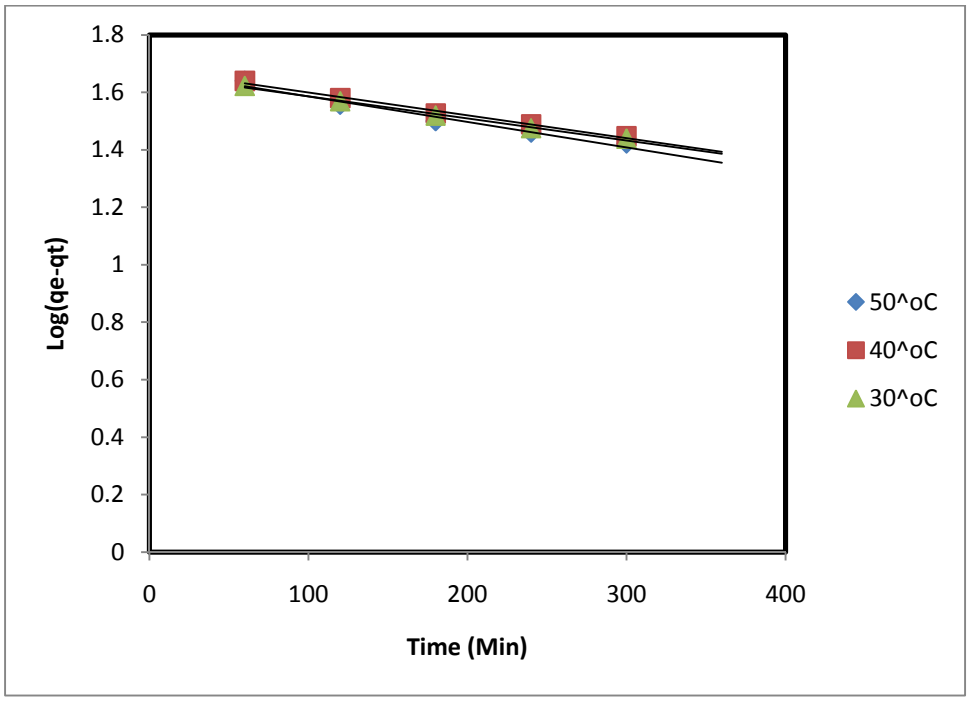


Figure 17: Pseudo-First Order Kinetic Model Fitting

Table 19: Experimental data on kinetic study

	C_t			q_t			$Log(q_e-q_t)$			q/t		
time	30	40	50	30	40	50	30	40	50	30	40	50
60	54	49	43	11.5	12.75	14.25	1.703	1.709	1.70	5.21	4.705	4.210
120	35	35	31	16.25	16.25	17.25	1.660	1.678	1.67	7.38	7.384	6.956
180	24	24	21	19	19	19.75	1.633	1.653	1.65	9.47	9.473	9.113
240	17	17	13	20.75	20.75	21.75	1.615	1.635	1.63	11.56	11.56	11.034
300	11	10	7	22.25	22.5	23.25	1.599	1.618	1.61	13.48	13.33	12.903
360	5	3	2	23.75	24.25	24.5				15.15	14.84	14.693

Pseudo second-order: The pseudo second-order adsorption kinetic rate equation(Ho YS et al., 2000) is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (4.12)$$

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

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (4.13)$$

which is the integrated rate law for a pseudo second-order reaction. This equation can be rearranged to obtain a linear form which is:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e}(t) \qquad (4.14)$$

if the initial adsorption rate, h (mg/g/min) is given by :

$$h = k_2 {q_e}^2 \qquad (4.15)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}(t) \qquad (4.16)$$

The plot of (t/qt) and t (Figure 18) of Eq. (4.16) should give a linear relationship from which qe and k_2 can be determined from the slope and intercept of the plot, respectively.

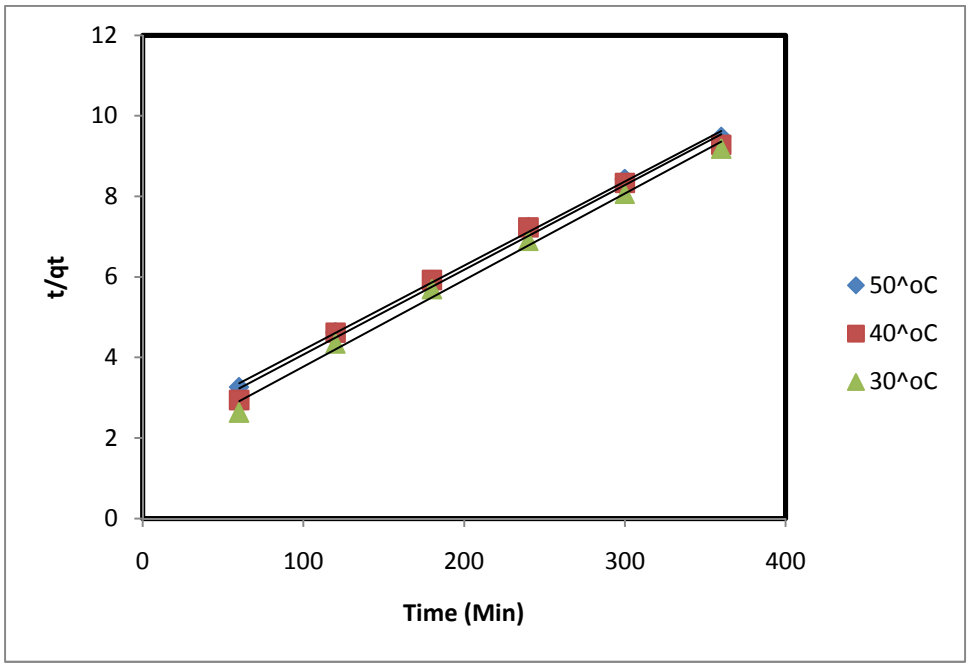


Figure 18: Pseudo-Second Order Kinetic Model Fitting

The model parameters for both pseudo-first order and pseudo-second order parameters were presented in table 20. According to value of r^2 pseudo-second order better fitted the experimental data.

Table 20: Constant parameters and correlations coefficients calculated for different adsorptions models

Kinetic Constants		Value		
		30°C	40°C	50°C
1	pseudo first-order			
	qe (exp.) (mg/g)	24.5	24.25	23.75
	$q_{e,m}$.(mg/g)	52.52	53.34	52.26
	$k1$ (min-1)x 10^{-4}	1.73	1.73	1.73
	r^2	0.989	0.983	0.955
	Regressions equations	y = -0.0004x + 1.7182	y = -0.0004x + 1.7271	y = -0.0004x + 1.7203
2	Pseudo-second-order			
	qe (exp.) (mg/g)	24.5	24.25	23.75
	$q_{e,m}$.(mg/g)	29.06	29.76	29.94
	$k2$(mg/g/hr) x 10^{-4}	4.552	3.579	3.308
	r^2	0.993	0.991	0.998
	Regressions equations	y = 0.0344x + 2.601	y = 0.0336x + 3.1546	y = 0.0334x + 3.3714

4.3.6 Concluding remark on Cr(VI) adsorption

The study shows that chemically modified sesame husk, can be used as an adsorbent for removal of Cr(VI) from aqueous solutions. The adsorption characteristics were shown to be influenced by several factors. The adsorption process was highly pH dependent and the optimum pH for maximum adsorption was found to be at pH 2. The isotherms exhibited the Freundlich behaviour at all temperatures, which indicates Adsorbents that follow the Freundlich isotherm equations are assumed to have a heterogeneous surface consisting of sites with different adsorptions potentials, and each site is assumed to adsorb molecules. The adsorption data showed good agreement with the pseudo-second-order kinetic model for different adsorbent concentration. The rate constant decreased with increase in temperature indicating endothermic nature of adsorption.

5 Conclusions

Response Surface Method (SRM) using Box-Behnken design technique was applied to optimize process parameters involved in preparation of activated carbon from sesame husk by chemical activation using H_2SO_4. The effect of concentration of H_2SO_4, impregnation ratio, carbonization temperature and holding time on adsorption % of sesame husk activated carbon is better described by linear model adequately. Analysis of variance (ANOVA) revealed a good agreement between experimental and predicted value. Confirmation experiment conducted showed agreement between experimental value and predicted value.

The result of the characterization showed that the sesame husk activated carbon has good properties and compared favourably with other reference activated carbons.

The parametric effects of pH, initial concentration of Cr(VI), and contact time on Cr(VI) removal using sesame husk activated carbon system were investigated. The system was found to be pH dependent and maximum adsorption % was obtained at lower pH. The adsorption kinetics of Pseudo-first order and Pseudo-second order kinetic models were examined and showed that pseudo-second order rate expression better fitted for all temperature. Equilibrium isotherms were measured experimentally at all temperature and results were analyzed by the Langmuir and Freundlich equations using linearized correlation coefficient identified that Freundlich isotherm model better fitted for all temperatures.

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7 Annex

7.1 Row experimental date on adsorptions study

Effect of pH on adsorptions

Adsorptions conditions; Volume of solutions 200mL, Cr(VI) concentrations 100mg/L, amount of sesame husk activated carbon 0.5g, temperature 20^oC, and contact time 6Hrs

Ph	Cr (IV) removal, %	Ce(mg/L)*10^2
1	97.8	0.002
1.5	98.8	0.006
2	99.6	0.011
2.5	84.8	0.076
3	77.8	0.111
3.5	17.8	0.411
4	11.8	0.441
4.5	12.4	0.438
5	9.8	0.451
5.5	9.6	0.452
6	9.3	0.4535
6.5	9	0.455
7	8.6	0.457
7.5	7	0.465
8	7.2	0.464
8.5	6.3	0.4685
9	6.1	0.4695

Effect of contact time and temperature on the adsorption of Cr(VI)

Adsorption condition: Volume of solution 200mL, Cr(CI) concentration 100mg/L, amount of sesame husk activated carbon 0.5g, temperature 20, 30, 40, 50^oC, and contact time 1-6hrs and equilibrium attained at contact time 6Hrs

	Cr (IV) removal, %			
Contact Time, min	20^0C	30^0C	40^0C	50^0C
60	45.5	46.5	47.5	48.5
120	74.5	75.5	76.5	77.5
180	78.3	80.3	82.3	84.3
240	78.6	80.6	82.6	84.6
300	78.7	80.7	82.7	84.7
360	78.8	80.8	82.8	84.8
420	78.9	80.9	82.9	84.9
480	79.5	81.5	83.5	85.5

Effect of contact time and initial concentrations on the adsorption of Cr(VI) ions

Adsorptions conditions; Volume of solutions 200mL,initial concentrations 100, 200 and 300mg/L pH 2, amount of sesame husk activated carbon 0.5g temperature 20^oC, contact time 1-24hrs

	adsorption %		
contact time	100 mg/L	200mg/L	300mg/L
60	41	43	45
120	70	72	74
180	85	87	89
240	90	92	94
300	95	97	98.5
360	96	98	99
420	96	98	99
480	96	98	99

7.2 Data on Equilibrium study at three temperatures

Adsorption condition: volume of solution = 200mL, Cr(VI) concentration= 50-500mg/L, pH=2, amount of sesame husk activated carbon = 0.5g, contact time = 6hrs at temperature of 30, 40, and 50^0C.

Temp. (K)	Co	Ce	qe	ce/qe	Logce	Logqe
303	50	1.4	19.44	0.072016	0.146128	1.288696
303	100	19	32.4	0.58642	1.278754	1.510545
303	150	51	39.6	1.287879	1.70757	1.597695
303	200	98	40.8	2.401961	1.991226	1.61066
303	250	137	45.2	3.030973	2.136721	1.655138
303	300	181	47.6	3.802521	2.257679	1.677607
303	350	221	51.6	4.282946	2.344392	1.71265
303	400	266	53.6	4.962687	2.424882	1.729165
313	50	1.80	19.28	0.093361	0.255273	1.285107
313	100	20.00	32	0.625	1.30103	1.50515
313	150	55.00	38	1.447368	1.740363	1.579784
313	200	99.00	40.4	2.450495	1.995635	1.606381
313	250	140.00	44	3.181818	2.146128	1.643453
313	300	186.00	45.6	4.078947	2.269513	1.658965
313	350	231.00	47.6	4.852941	2.363612	1.677607
313	400	268.00	52.8	5.075758	2.428135	1.722634
323	50	2.5	19	0.131579	0.39794	1.278754
323	100	22	31.2	0.705128	1.342423	1.494155
323	150	57	37.2	1.532258	1.755875	1.570543
323	200	101	39.6	2.550505	2.004321	1.597695
323	250	143	42.8	3.341121	2.155336	1.631444
323	300	186	45.6	4.078947	2.269513	1.658965
323	350	231	47.6	4.852941	2.363612	1.677607
323	400	269	52.4	5.133588	2.429752	1.719331

7.3 Data on kinetic study at three temperatures

Adsorptions Conditions: volume of solution = 200mL, initial Cr(VI) concentration= 100mg/L, pH=2, amount of sesame husk activated carbon = 0.5g, contact time =1- 6hrs at temperature of 30, 40, and 50^0C.

	C_t			q_t			$Log(q_e-q_t)$			q/t		
time	30	40	50	30	40	50	30	40	50	30	40	50
60	54	49	43	11.5	12.75	14.25	1.703	1.709	1.70	5.21	4.705	4.210
120	35	35	31	16.25	16.25	17.25	1.660	1.678	1.67	7.38	7.384	6.956
180	24	24	21	19	19	19.75	1.633	1.653	1.65	9.47	9.473	9.113
240	17	17	13	20.75	20.75	21.75	1.615	1.635	1.63	11.56	11.56	11.034
300	11	10	7	22.25	22.5	23.25	1.599	1.618	1.61	13.48	13.33	12.903
360	5	3	2	23.75	24.25	24.5				15.15	14.84	14.693