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SCHOOL OF CIVIL AND ENVIROMENTAL ENGINEERING

WATER SUPPLY AND ENVIROMENTAL ENGINEERING STREAM

REMOVAL EFFICENCY OF CHROMIUM USING COFFEE HUSK ACTIVATED CARBON IN HAWASSA INDUSTRIAL PARK WASTE WATER TREATMENT

A thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, school of civil and environmental engineering in partial fulfillment of the requirements for the attainment of the Degree of Master of Science in civil Engineering under water supply and Environmental Engineering Stream.

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Abstract

In this study, the potential of activated carbon coffee husk for removal of chromium were examined. The influence of contact time, P^H, adsorbent dosage, initial concentration and adsorption equilibrium were studied at batch experiments at room temperature. The modification process was done by treating the coffee husk with different chemicals and activation. Maximum sorption was found to be at pH 2. The biosorption was rapid for the first 45 minutes of contact, removing more than 75% and equilibrium has attained in 120 minutes. Kinetic studies demonstrate good correlation coefficient (R^2) for a pseudo second order kinetic model. The biosorption capacity was found to increase with higher initial Cr(VI) concentration and lower solution pH. Langmuir model fitted the equilibrium data better.

The calculated biosorption free energies from the D-R isotherm model indicated that the biosorption process proceeds via chemisorptions. Optimization using response surface methodology (RSM) indicated an initial metal ion concentration, solution pH; biosorbent dose and contact time played an important role for the biosorption of Cr (VI).

The study concluded that coffee husk activated carbon could be applied as a low cost alternative biosorbent to remove Cr (VI) from aqueous solution.

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List of abbreviation

Ce	equilibrium concentration in mg/l
Q	biosorption capacity in mg/g
q_{max}	maximum biosorption capacityin mg/g
q_e	equilibrium biosorption capacity in mg/g
q_t	biosorption capacity
K_1	pseudo first order kinetics constant (1/min)
K_2	pseudo second order kinetics constant (g/mg.min)
K_i	intra-particle diffusion constant
B	langmuir constant(l/mg)
K_f	freundlich constant
N	freuindlich constant
ε	Polanyi potential
KDR	activity coefficient related to bio sorption constant
FTIR	fourier transforms infrared spectroscopy
CHAC	coffee husk activated carbon
RSM	response surface methodology
DOE	design of experiments
CCD	central composite design

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1. INTRODUCTION

1.1. Background Information

Industrialization of countries, result in urbanization with ever rising population, the basic amenities of life which are Air, water and land are being polluted continuously. The increase of industrial activities has intensified environmental pollution problems and the worsening of several ecosystems with the accumulation of many pollutants, especially heavy metals. Among them, chromium in the aquatic environment has been categorized as Group “A” of human carcinogens [1].

Nevertheless, the industrial use of chromium has increased, because of the wide-ranging use of chromate and dichromate in electroplating, leather tanning, metal finishing, nuclear power plants, and textile industries [2]. ; Different Literatures reported that more than 1,700,000 tons of Chromium wastes are being discharged to the environment annually as a result of industrial manufacturing activities [3]. Due to its high oxidation potential it can easily go through biological membranes and cause health hazards [3, 4].

Chromium in waste water exists in two oxidation states namely, Chromium (III) which normally exist in the form of $Cr\ (OH)^{2+}$, $Cr\ (OH)_4$ - and Chromium (VI) which exist in the form Cr_2O_{72} and CrO_{42}- depending on the pH of the solutions [5, 6]. Cr (VI) is considered to be highly toxic compared to Cr (III). Each of these oxidation states has different biocides, medicinal and toxicological properties [5, 7]. At high concentrations, all the compounds of Chromium are harmful to the health. Chromium (VI) is hazardous to health when its level in potable water exceeds 0.05mg/l [8, 9]. The target organ for acute systemic toxicity is the Kidney resulting in acute tubular necrosis of the kidney and subsequent death. Chromium compounds are also reported to produce allergic reaction and dermatitis in some individuals [9, 10]. Therefore, the reduction of Cr (VI) is imperative to meet the discharge levels, and recycling and reuse are promoted. Consequently, the removal of Cr (VI) from industrial wastewater has attracted much research interest.

Various treatment technologies have been developed for the decontamination of water and wastewater contaminated with heavy metals. The most commonly used methods for the removal of Cr (VI) ions from industrial effluents include: chemical precipitation, Chemical reduction, 1dialysis/electro dialysis, membrane filtration, ion-exchange, etc. Most of these methods suffer from drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries [11].There is a need to develop new bio sorbent which are readily available at low cost to remove metal contaminants in aqueous system. Low cost agricultural wastes without or with little processing are considered promising bio sorbent for heavy metals due to their high surface areas, micro porous characters and surface chemical natures. Conversion of this waste to a useful bio sorbent contributes not only for the treatment of heavy metals contaminated environment but also to minimizing the solid wastes.

1.2. Statement of problem

In our country, the rate of industrial growth coupled with lack of technology for low cost and efficient effluent treatment and unimplemented or/and lack of effluent discharge standards or policies leads to serious consequences for water bodies receiving industrial effluents containing heavy metals such as chrome which is considered to be group "A" carcinogenic material for humans and Hawassa industrial park is one of the huge newly developed industrial park which is estimated to have high amount of chrome in its waste water effluent. If appropriate and efficient removal is not taken place it will have huge negative impact on Hawassa Lake which already has many problems including sedimentation and others.

Various technologies are employed for the removal of heavy metals from water including chemical precipitation , ion exchange, reeverse osmosis, membrane filtration, and adsorption. Adsorption is the most efficient and extensively used removal method.activated carbon is one of the most effective adsorbents due to its simplicity, high capacity and ability to remove low concentrations of chromium.

Although several adsorbents have been utilized for the removal of heavy metal ions from waste water, no single adsorbent was found to be effective for different types of water pollutants.

Low cost adsorbents are strongly recommended in industries for waste water treatment applications due to their local obtainablity, technical viability, and engineering applicability.

The spent coffee grounds produced by instant coffee industry as a waste can be economically reused for the adsorption of toxic metal ions.

Therefore it is a great necessity for developing inexpensive and efficient bio sorbent material that is easily available in large quantity and economically feasible for removal of chrome from industrial effluents.

1.3. Objectives

1.3.1. General objective

- To investigate and examine the adsorption performance and potential of the as-prepared activated carbon coffee husk using chromium as a model adsorbate in aqueous solution.

1.3.2. Specific objectives

- To determine the amount of chromium found in the waste water effluent before and after adsorption takes place.
- To determine the efficiency of coffee husk activated carbon for removal of chromium.
- To determine the effect of contact time, P^H, adsorbent dosage, initial concentration and adsorption equilibrium.
- To determine the industrial adsorption application of the proposed coffee husk activated carbon.
- To determine the effect of contact time, P^H, adsorbent dosage, initial concentration and adsorption equilibrium using a modeling software.

1.4 Research Question

The aim of this research work is therefore to prepare activated carbon coffee husk and to carry out biosorption kinetics and biosorption equilibrium studies of chromium on the activated carbon coffee husk carbon sample.

Research questions

1. To overcome the challenges in developing economical and commonly available biosorbent for chromium removal.
2. How effective coffee husk is in removing chromium ffrom waste waters.
3. To redefine the growing concern for detoxification of industrial effluents.

4. To check whether coffee husk has a high biosorption capacity or not.

1.5 Basic hypothesis

Heightened awareness of chromium toxicity and lack of regulatory changes has prompted considerable research effort towards developing methods for chromium removal from industrial waste water.A waste water which is treated with coffee husk activated carbon will have a lower rate of chromium amount than a waste water which is treated with other conventional adsorption process.

2. LITERATURE REVIEW

2.1. Chromium

2.1.1. Occurrence of Chromium in the Environment

Chromium is a naturally occurring element found in rocks, animals, plants, and soil. The name of the element is derived from the Greek word "chrōma" meaning color, because many of its compounds are intensely colored. It was discovered by Louis Nicolas Vauquelin in the mineral crocoites (lead chromate) in 1797. Crocoites were used as a pigment, and after the discovery that the mineral chromites also contain chromium this latter mineral was used to produce pigments as well. Chromium (0) being a member of the transition metals, in group 6, has an electronic configuration of $4s1_3D_5$ due to the lower energy of the high spin configuration. Chromium exhibits a wide range possible oxidation states. The highest oxidation state corresponds to the total of 3D and 4s electrons. The most common oxidation states of chromium are +2, +3, and +6, with +3 being the most stable whereas +1, +4 and +5 are rare. Depending on the form it takes, it can be a liquid, solid, or gas. No taste or odor is associated with chromium compounds. Chromium compounds of oxidation state +6 are powerful oxidants. All (except the chromium hexafluoride) stable chromium compounds of the oxidation state +6 contain oxygen as ligand, for example the chromate (CrO_{42-}) and Chromyl chloride (CrO_2Cl_2) [12].

Chromium exists in several chemical forms displaying oxidation number from 0 to VI. Only two of them, trivalent and hexavalent Chromium, are, however, stable enough to occur in the environment. Cr (IV) and Cr (V) form only unstable intermediates in reactions of trivalent and hexavalent oxidation states with oxidizing and reducing agents, respectively. The Cr (III) oxidation state is the most stable and considerable energy would be required to convert it to lower or higher states.

2.1.2 Uses of Chromium

Chromium is a strategic metal of the twentieth century but it is also used in dozens of industrial processes creating thousands of consumer products. Cr is used in the manufacturing of stainless steel, numerous alloys, chrome plating, pigments, catalysts, dye, tanning, wood impregnation, refractory bricks, magnetic tapes, and more. Until the early 1900s, $FeCr_2O_4$ was used mainly in the manufacturing of chemicals. In the early 1900s, $FeCr_2O_4$ became widely used in the manufacturing of metallurgical and refractory products, notably in stainless steels and basic refractory bricks [13].

Refractory bricks and shapes formed of Cr are useful owing to the high melting temperature of Cr, moderate thermal expansion, and the general stability of the Cr crystalline structure. Chrome steels have no substitute when combined high-temperature rigidity and resistance to tarnish and abrasion are required as in the case of roller bearings or in the aerospace and machine tool industries [13].

Chromium compounds are used in paint pigments. Chromates of barium (Ba), lead (Pb), and zinc(Zn) gives the pigments of lemon chrome, chrome yellow, chrome red, chrome orange, zinc yellow, and zinc green. Chrome green is used in the making of green glass. Cr chemicals enhance the colors of fabrics and are used to achieve the brightly colored Cr-based paints for automobiles and buildings [14].

One of the major consumers of chromium metal are stainless steel production plants. As an alloy, Cr has been referred to as the "guardian metal." With as little as 10% Cr, an alloy made with steel or Fe protects these materials from corrosion, yielding the stainless steel and rust less Fe which are common household items, such as stainless steel knives, ball bearings, watch cases, and chrome front and rear vehicle bumpers [13]. Chromium containing compounds are also used for furnace linings. Chrome plating has replaced Ni-plating owing to Cr's superior hardness and resistance to chemical action. Heat-resistant Cr oxides are used for high temperature applications, such as the bricks used in lining furnaces [13].

Chromium containing compounds such as chrome alum and chromic acid are used in the tanning and dyeing processes [13]. Chromium is also used in the photographic industries. When $K_2Cr_2O_7$ is mixed with water and the solution is dried and exposed to light, it becomes solid again. This property is applied to the manufacture of waterproof glues and in photography and photo engravings [13].

2.1.3. Toxicity of Chromium

Water insoluble Cr (III) compounds and chromium metal are not considered a health hazard, while the toxicity and carcinogenic properties of Cr (VI) have been known for a long time. Because of the specific transport mechanisms and bigger size, only limited amounts of Cr (III) enter into the cells. Several in vitro studies indicated that high concentrations of Cr (III) in the cell can lead to DNA damage. The human body contains approximately 0.03 ppm of chromium. Daily intake strongly depends upon feed levels, and is usually approximately 15-200 µg, but may be as high as 1 mg. The placenta is the organ with the highest chromium amounts. Cr (III) is an essential trace element for humans. Chromium deficits may enhance diabetes symptoms. Chromium can also be found in RNA. Cr (III) toxicity is unlikely, at least when it is taken up through food and drinking water. It may even improve health, and cure neuropathy and encephalopathy. Cr (VI) is known for its negative health and environmental impact, and its extreme toxicity. It causes allergic and asthmatic reactions, is carcinogenic and is 1000 times as toxic as Cr (III). Health effects related to Cr (VI) exposure include diarrhea, stomach and intestinal bleedings, cramps, paralysis and liver and kidney damage. Toxic effects may be passed on to children through the placenta. Cr (VI) oxide is a strong oxidant. Upon dissolution chromium acid is formed which corrodes the organs.

People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous Cr (IV), Cr (VI). For most people eating food that contains Cr (III) is the main route of chromium uptake, as Cr (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food. When food is stores in steel tanks or cans chromium concentrations may rise. Cr (III) is an essential nutrient for humans and shortage may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much Cr (III) can cause health effects as well, for instance skin rashes. Cr (VI) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium. Cr (VI) is known to cause various health effects. The various health effects of Cr (VI) are Respiratory effects, Skin effects, Carcinogenic effects, renal effects, and Hepatic effects, Hematological Effects, Hem toxic and Mutagenic Effects [13-16].

2.2 Coffee and Coffee Husk Production in Ethiopia

Coffee is one of the most important beverages (popular drink) in the world and its yearly production is about seven million tons in more than 60 countries. The coffee plant is an evergreen shrub with a straight trunk which can survive for about 70 years. Coffee classify as a member of the Rubiaceae family. Among different species of coffee plant, two alone dominate world trade - the Coffee Arabica and Robusta. Coffee is a tropical plant which grows between the latitudes of 250 North and 250 south. Ideal average temperatures range between 15 – 24 0C for Arabica coffee and 24 - 30 0C for Robusta. In general, coffee needs an annual rainfall of 1500 to 3000 mm, Arabica needing less than other species [17-18].

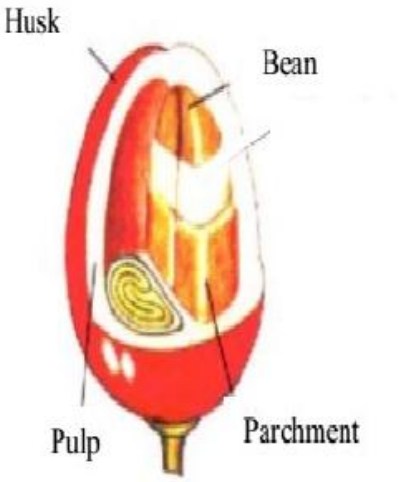


Figure 2:1 parts of coffee bean

Coffee is the most important cash or export crop in Ethiopia. Ethiopia is the seventh largest coffee producer worldwide and ranked ninth in coffee export. In fact the word "coffee" comes from the name of a region of Ethiopia where coffee was first discovered – ‘Kaffa’. Ethiopia is the home of biodiversity of Arabica coffee [19]. In Ethiopia, coffee is produced in four production systems, namely: forest, semi-forest, garden and plantation coffee in the Western, Southern, and Southwestern parts of the country. Coffee production is mainly in South West, South and East of the country, around 90% based on smallholders. An estimated 1.2 million smallholder farmers are engaged in coffee production. Ethiopia and Brazil are the only coffee producing countries that consume a significant portion of their production; around 50% of the production for Ethiopia [18].

Coffee is Ethiopia's number one source of foreign exchange. Annual coffee export from Ethiopia is around 200,000 tons valued at around US$ 500 million. The quality of Arabica from Ethiopia is generally good. Some regions (Sidamo, Yirgacheffe and Haraar) receive very high prices [20]. Coffee berries are processed through wet and dry processing. During the wet processing coffee pulp and parchment produced while the dry process resulting in coffee husk. The dry processing is natural, simplest and cheapest method of obtaining coffee bean.

2.2.1 Processing of Coffee Cherries Using Dry Method

The dry method (also called the natural method) is the oldest, simplest and requires little machinery. The method involves drying the whole cherry. There are variations on how the process may be carried out, depending on the size of the plantation, the facilities available and the final quality desired. The three basic steps, cleaning, drying and hulling, are described below [21]. Firstly, the harvested cherries are usually sorted and cleaned, to separate the unripe, overripe and damaged cherries and to remove dirt, soil and leaves. This can be done by winnowing, which is commonly done by hand, using a large sieve. Any unwanted cherries or other material not winnowed away can be picked out from the top of the sieve. The ripe cherries can also be separated by flotation in washing channels close to the drying areas. The coffee cherries are then spread out in the sun, either on large concrete or on matting raised to waist height wire mesh tables to dry. As the cherries dry, they are raked or turned by hand to ensure even drying. It may take up to 4 weeks before the cherries are dried to the optimum 11.5% moisture content, depending on the weather conditions. On larger plantations, machine drying is sometimes used to speed up the process after the coffee has been pre-dried in the sun for a few days [18]. The drying operation is the most important stage of the process, since it affects the final quality of the green coffee. A coffee that has been over dried will become brittle and produce too many broken beans during hulling (broken beans are considered defective beans). Coffee that has not been dried sufficiently will be too moist and prone to rapid deterioration caused by the attack of fungi and bacteria [22]

The dried cherries are stored in bulk in special silos or in bags until they are sent to the mill where hulling, sorting, grading and bagging take place. All the outer layers of the dried cherry are removed in one step by the hulling machine [23]. The dry method is used for about 95% of the Arabica coffee produced in Brazil; most of the coffee's produced in Ethiopia, Haiti and Paraguay, as well as for some Arabica produced in India and Ecuador. Almost all Robusta are processed by this method. It is not practical in very rainy regions, where the humidity of the atmosphere is too high or where it rains frequently during harvesting. Coffee husks, which are produced through these methods, are the major solid residues from the handling and processing of coffee. For the year 2010/2011 G.C., 3,704,730.63 quintals of coffee was produced in Ethiopia, which implies more than 3 million quintal of coffee husk is produced [24]. Therefore the large amount of coffee husk is available to be cheaply to be used as a biosorbent for removal of heavy metals at large scale.

2.2.2 Chemical Composition of Coffee Husk

Coffee husks are the major solid residues from the handling and processing of coffee. Coffee husk consists of different chemicals such as cellulose, lignin, carbohydrate, pectin and proteins [25]. This chemical components contained different surface functional groups such as the carboxylic, hydroxyl and the amine groups with are mainly responsible for the biosorption of heavy metals [25].

Table 2:2 Chemical composition of coffee husk (% dry basis)

Components	**Percentage (%)**
Carbohydrate	58-85
Protein	8-11
Fibers	-
Fats	0.5-3
Caffeine	1.3
Tannin	4.5-5.4
Lignin	20
Cellulose	19-26
Pectin	12.4-13

2.2. Conventional Technologies for Chromium Removal

Chromium contamination is common all over the world. For water resources, the impact of this contamination is severe. Consequently, it is desirable to remove chromium from the contaminated water. Many treatment processes have been developed to remove chromium from wastewater as have been mentioned in the introduction chapter of this thesis. A brief description of common treatment technologies is found below [26].

2.2.1. Chemical Precipitation

Chemical precipitation is the method, in which dissolved and suspended metal ions are transformed to the insoluble solid through a chemical reaction. Usually a precipitating agent accelerates this conversion from metal ions into insoluble solid. The commonly used precipitation agents are lime and magnesia. This technique has been proven as an effective way to remediate heavy metals including chromium from wastewater. This technique has some advantages. It is a simple, inexpensive, convenient, and safe method. However, this technique requires large amounts of chemicals, and excessive toxic sludge is produced. Sludge filtration and disposal increase the overall cost of the process. Sometimes metal precipitation is slow, and aggregation of metal precipitates take place [26, 27].

2.2.2. Chemical Reduction

Reduction is a treatment process in which the higher valance state of metal ion is converted or reduced to the lower valance state. In case of chromium removal, a step involves to convert hexavalent chromium ion into the trivalent ion. Reduction process alone does not remove total chromium from solution except the reduction from hexavalent to trivalent. Thus in case of chromium removal reduction process must be coupled to a removal process such as coagulation, sorption, or ion exchange. Reduction treatment method can be done in various ways such as through chemical reduction, electrochemical reduction, and electro-catalytic reduction. Chemical reduction involves a reduction reaction that takes place to transform Cr (VI) to Cr(III) with the assistance of reducing agents. There are several reducing agents that are widely used to reduce Cr (VI), including iron, hydrogen peroxide, and hydrogen sulfide. Most of these reducing agents have drawbacks. An alternative to the chemical reduction technique of Cr (VI) could be electrochemical reduction. An electric current is applied to assist chemical reduction; that is why this technique is called electrochemical reduction. This technique offers several advantages such as recovery of metals from contaminated wastewaters; recycle of treated water and short treatment times. However, the disadvantages include additional chemicals requirement, and hazardous sludge formation. It is also, quite expensive, and it often requires new infrastructure to be constructed [27].

2.2.3. Ion Exchange

Ion-exchange resins have recently found a niche in the market of water and waste-water treatment. Also, they are an effective means of removing heavy metals from wastewater. When the resins are saturated, they must be regenerated with an acid or alkaline medium to remove the metal ions from the resin bed. Due to the fact that ion exchange is efficient in removal of dissolved solids from normally dilute spent rinse waters, it is well suited for use in water purification and recycles. Ion exchange may be capable of treating for high purity heavy metal solution and sequential operation.

However, it requires pretreatment process to reduce suspended solid concentration in solution to prevent fouling or channeling. However, apart from their cost, which can be prohibitive especially to smaller processing plants, resins are vulnerable to oxidation by chemicals, are affected by the presence of magnesium or calcium ions in solution, and are prone to fouling by precipitates and organics [26-28].

2.2.4. Membrane Technology

The use of membrane technology for valuable metal removal is gaining considerable attention in many industries. The ultra-filtration can be used to remove water from wastewater containing emulsified oil, and exclude the metal particles. However, ultra-filtration membranes need to be cleaned and back flushed regularly to operate efficiently and replaced periodically.

Reverse osmosis (RO) may be applied in plating processes removing sodium chloride. RO system requires high-quality feed for efficient operation, thus wastewater must be treated to remove solids prior to RO treatment. Application of membrane technology to metal-bearing waste streams has several major drawbacks. Apart from the expense, membranes are also unable to resist certain types of chemicals and P^H values and are prone to deterioration in the presence of microorganisms. Membrane fouling, compaction, scaling, limited life of membranes, dissolution of the membrane by oxidized agents, solvents and other organic compounds, and applicability only to feed streams with low concentrations of metal ions are major limitations associated with the use of membrane technologies [26].

2.2.5. Flocculation and Coagulation

The coagulation–flocculation processes facilitate the removal of suspended solids, colloidal particles. It is used in the final stage of solids–liquids separation. Coagulation is the destabilization of colloidal particles brought about by the addition of a chemical reagent called coagulant.

Flocculation is the agglomeration of destabilized particles into microfloc and after into bulky floccules that can be settled called floc. The addition of another reagent called flocculent or flocculent aid may promote the formation of the floc. Flocculation is the slow stirring or gentle agitation to aggregate the destabilized particles and form a rapid settling floc. This technique has been known to be capable of removing heavy metals from solution. The use of lime softening and coagulation (using ferric sulfate or alum) for removal of heavy metals as Pb^{2+}, Cd^{2+}, Cr^{3+}, Cr^{6+}, etc.are reported [26-29].

Short coming of coagulation–flocculation process:

- Requirement of High capital for operational and regular maintenance cost.
- In some cases, considerable quantities of coagulant and flocculants are needed to achieve the required result.
- The accuracy, with which chemicals must be dosed, makes it a complex process.
- Qualified personnel required for design (e.g.: construction of chambers and dosage of chemicals) and system maintenance.
- Transfer of toxic compounds into solid phase and formation of sludge that has to be treated subsequently.
- Relatively time consuming process.

2.2.6. Electro dialysis

Electrolytic metal recovery is one of a number of technologies capable of removing metals from wastewater. In this process, the Cr (VI) is separated through the use of ion selective semi-permeable membranes. The application of an electrical potential between the two electrodes causes the migration of cationic or anionic metal ions towards respective electrodes. The major limitation of electro dialysis is that it leads to the formation of metal hydroxides which in turn clogs the membrane and moderately high capital cost, increase in the number of possible exposures with regard to the handling of hazardous waste [28].

2.3. Bio sorption Process

Biosorption can be defined as the removal of metals from solution by the certain types of biomass which has an ability to bind and concentrate metals as much as at lower concentrations. The bio sorption process involves interaction between the bio sorbent (solid phase) and a solvent (liquid phase) containing the dissolved species to be sorbed.

2.3.1. Advantages of Bio sorption Technique over Other Methods

The conventional heavy metal removal processes have several disadvantages such as less effective removal of metal ion, high reagent requirements, high costs, the generation of toxic sludge, and the problem of the safe disposal of the materials [26]. Compared with conventional methods for removal of toxic heavy metals, biosorption process offers the advantages of low cost, minimization of the volume of chemical and/or biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents, and high metal selectivity. These advantages have served as the primary incentives for developing biosorption processes to treat waste water contaminated by toxic heavy metals. Also the increasing demand for eco-friendly and economical technologies has led to the search of low-cost alternatives for heavy metal treatment. In this light, biological materials have emerged as an eco-friendly and economic option.

The advantages of biosorption are summarized as follows:

Cost effective. The cost for biosorbent is low since often they are made from abundant natural source or waste biomass from industry.

Metal selective. The metal sorption capacity of different types of biomass can be more or less selective on different metals. This depends on various factors, such as type of biomass, mixture in the solution, type of biomass preparation, and physico-chemical environment.

Regenerative. Biosorbent can be reused after the metal is recycled. Some types of biomass are immobilized in a synthetic polymer matrix to obtain the required mechanical propertied for repeated reuse.

Minimization of sludge generation. No secondary problems with sludge occur with biosorption, as is the case with many other techniques such as precipitation.

Metal recovery possible. Metal can be recovered after being sorbed from the solution by desorbing solutions such as acid and chelate agents.

Competitive performance. Biosorption is capable of a performance comparable to the most similar technique, ion exchange treatment.

2.3.2 Factors that Affect the Biosorption Process

Biosorption can be carried out under a wide range of conditions. However, the efficiency of biosorption is affected by the parameters discussed as below.

Effect of contact time: Contact time is one of the most important parameters affecting the amount of metal ions adsorbed on the biomass. Metal removed is relatively rapid in the initial stage of the biosorption process and the uptake of heavy metals slowdown in the later stage because large numbers of available sites are occupied by the metal ions.

Effect of metal ion concentration: One of the most important factors influencing metal uptake is the concentration of the metal ion. With a fixed biomass concentration, an increase in the concentration of the metal ions will result in an increase in the specific metal uptake. Further increase will reach saturation where all the available binding sites are fully bound. Conversely, at a low equilibrium metal ion concentration, not all the binding sites on the biomass are fully bound.

Effect of biomass concentration: The biomass dosage influences the specific uptake (q) as well as the removal efficiency in the biosorption system. In general, specific uptake decreases with increasing biomass, while the removal efficiency increases. Higher biomass loading results in a higher ratio of binding sites to the available metal ions; more metal ions are thus adsorbed and higher removal percentage can be achieved. As the specific uptake is a measure of amount of metal ions bound by unit weight of biomass, its magnitude decrease with the increasing biomass loading.

Effect of solution P^H: Most research studies reported in the literature have evaluated the influence of P^H on the adsorption capacity. These results have showed that the removal of metal ions is highly dependent on pH [30-31]. This can be explained since the solution pH affects both the surface charge of the adsorbent (i.e. the degree of ionization of surface functional groups) and the speciation of metals in solutions. In aqueous solutions above pH 6, Cr(VI) will chromate ion CrO4-2 , while between pH 2&6,HCrO4- and Cr2O7-2 are in equilibrium while of pH<1 the main species is H2CrO4. For solution pH less than that of point of zero charge (pH pzc), the adsorbent surface charge is predominantly positive and therefore could adsorb negatively-charged species (metal anions such as Cr (VI) or OH-). When increasing the solution pH above the P^H pzc, the metal adsorption capacity decrease because fewer ionized groups (e.g. Protonated carboxyl) are available to adsorb an ionic metal species as a result the adsorption potential will decrease.

Effect of Temperature: Temperature appears to be a less important factor in biosorption studies and has no significant influence to the biosorption efficiency over the range 20-35 OC. higher temperature will increase the kinetic energy of metal ions, which facilitates attachment of metal ions on the surface [32]. However, very high temperature may cause distortion of some sites of the cell surface available. Hence, biosorption processes are normally operated at temperature range from 5 to 40 C.

Previous Studies

Saw dust

Saw dust was investigated as a low cost biosorbent for removal of Cr (VI) from synthetically prepared industrial effluent of electroplating and tannery industries [33]. The Experimental results demonstrate that the sawdust adsorbent has a significant capacity for adsorption of Cr (VI) from wastewater streams. The maximum adsorption of Cr (VI) on sawdust was obtained at pH 1. The equilibrium time obtained was 1050 min for Cr (VI) adsorption on sawdust. The equilibrium data for the adsorption of Cr (VI) on sawdust was tested with various adsorption isotherm models such as Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan, Tempkin, Dubinin- Radushkevich and Generalized equation. The Langmuir isotherm model was found to be most suitable for the Cr (VI) adsorption using sawdust. The maximum adsorption capacity obtained using the Langmuir isotherm model was 41.5 mg g-1 at pH 1. The dimensionless equilibrium parameter, RL, signifies a favorable adsorption of Cr (VI) on sawdust adsorbent and was found to be between 0.00453 and 0.0435 (0 < RL <1). Various kinetic models such as pseudo first-order, second order and Elovich model were used to evaluate the mechanism of adsorption of Cr (VI) on sawdust. The adsorption process follows second order kinetics and the corresponding rate constants, for initial Cr (VI) concentration ranging from 100 was found to be 3.39 × 10-3 g mg-1 min-1.

Papaya seed

Papaya fruit seed powder was used for removal of Cr (VI) synthetic waste water [34]. It was found that the maximum Cr (VI) removal of 90.58% was obtained at solution pH of 2. Above the pH 2 the percentage removal decreases to around 70% at pH 4. All the Cr (VI) was removed with absorbent concentration of 200 mg/L for 10 mg/L of initial Cr (VI) concentration. The Experimental data fitted well to Langmuirs isotherm with q_{max}=8.86 mg/g. The biosorption kinetics on papaya seed powder obeyed the Langergren equation.

Wheat shell

The use of Wheat shell was examined as a potential biosorbent for Cr (VI) removal from aqueous solutions [35]. The experimental results showed that the biosorption process is pH dependent and have maximum removal at pH less than 3 at 350C. They also reported that the experimental data fitted best to both Langmuir's isotherm (R2=0.9998) and Freundlich isotherm (R2=0.9998) with qmax=0.1574 mg/g and K_f=1.9288 mg/g respectively at initial metal concentration of 5 g/L, adsorbent concentration 20 g/L and temperature of 350C.

Orange peel

Orange peel modified with 10 % NaOH solution was evaluated as a cheap biosorbent for biosorption of Cr (VI) and Cd (II) from aqueous solution [36]. It was discovered that the optimum pH for maximum removal 95% of both metals at pH 4. The sorption equilibrium followed the Langmuir's and Freundlich models. The R^2 with respect to Langmuir model was 0.935 for Cr (VI) removal which while for Freundlich model R^2 was 0.965 for Cr (VI) removal. The qmax of Cr (VI) was found to be 8.85 mg/g. Other researchers used orange peel for removal of Cr (VI) and Zn (II) ions from aqueous solutions [37]. The experimental results showed that maximum removal of Cr (VI) 95.4% was obtained at 300C. It was also found that the maximum removal of (90.2, 80, and 1%) both ions were obtained at pH 3. The kinetics study showed that equilibrium was reached within 30 minutes of contact time. The experimental data on the adsorption isotherm fitted well with Langmuir model yielding qmax=8.068 mg/g and 1.078 mg/g for Cr (VI) and Zn (II) respectively.

Avocado shell

The potential of avocado shell was evaluated for removal of hexavalent chromium and total chromium from aqueous solution [38]. The experimental results showed that avocado shell removed Cr (VI) by two mechanisms; by chromium biosorption and bioreduction of Cr (VI) to Cr (III). The maximum Cr (VI) and total chromium removal of 101.81 mg/gm and 61.67 mg/g 28 respectively, was occurred at pH 2±0.1 and temperature of 28 ^{o}C after 2 hours. The pH of aqueous solution shifted from 1.95 to 2.23 as the contact time increased from 0 to 2 hours. The analysis on the experimental data suggested that the kinetics for adsorption of chromium ions on the avocado shell followed pseudo-second order model (R^2=0.9998) indicating that the rate limiting step in the biosorption process was chemisorptions involving valance forces through the shelling or exchange of electrons between sorbent and sorbet ,complexation, coordination and/or chelating. They concluded that avocado shell can be used as efficient and environmental friendly biomaterial for the removal of Cr (VI) and total chromium from aqueous solutions.

Fungal biomass

Fungal biomass Pacecilomayces Sp. was examined as a potential biosorbent for removal of Cr (VI) from aqueous solution [39]. It found that with 100 mg/lit initial Cr (VI) concentration and 1g/lit of dead fungal biomass, Cr (VI) removal of 100% and 72 % were obtained at pH 1 and pH 2 respectively. They also reported that the increase in temperature resulted in increase in Cr (VI) uptake. The experimental results also showed that the increase in Cr (VI) concentration from 100 mg/L to 1000 mg/L at constant temperature of 60 ^{o}C resulted in decrease of Cr (VI) uptake from 100% to 80 % at 50 mg/lit of biomass dose and 100 mg/lit of Cr (VI) concentration, 100 % removal was achieved within 70 minutes.

The same researchers also reported that, using living fungal biomass 100 % of Cr (VI) removal Was achieved at pH 4 and equilibrium time of 7 days. The experimental results on the effects of Sell concentration showed that the increase in the cell concentration from 38 mg/L to 114 mg/L resulted in increased Cr (VI) removal from 97.25 % to 99.17%. The potential use of non-living fungal biomass of species Fusarium SP. (filamentous) for removal of Cr (VI) ions was examined [40]. The experimental results showed that at pH 2 and contact time of 2 hours, 4 g/L of biomass dose and 500 mg/lit Cr (VI) initial concentration, the maximum chromium removal obtained was 47.5 mg/L. The experimental results on the adsorption isotherm model fitted well to Langmuir’s isotherm model with q max= 50.25 mg/g and R2 =0.975. Dead fungal biomass of R.Arrhizus and S. cerevisiae were used for reduction of Cr (VI) ions from aqueous solutions [42]. The experimental results showed that maximum Cr (VI) removal of 8.429 mg/g/min was obtained using R. Arrhizus cells and 4.3 mg/g/min using S. cerevisiae between pH1 and 2 for temperature of 35°C and contact time of 60 minutes. The experimental data on the adsorption isotherm well fitted to Freundlinc's isotherm model with K_f= 4.53 mg/g and K_f= 1.59 mg/g for R.Arrhizus and S. cerevisiae respectively.

Algal biomass

Green micro algal isolate, Chlorella Miniata was used for biosorption and bioreduction of Cr (VI) form aqueous solutions [41]. The experimental results showed that, at initial pH of 1.0 and biomass dose of 2 g/L, nearly 100 % Cr (VI) was removed within 58 hours while increasing the pH to 4 resulted in decrease of the removal capacity to 10%.however at pH 2 with 1 g/L, 2 g/L and 5 g/L of biomass dose, the Cr (VI) removal percentages obtained were 60%, 85% and 100% respectively with respective equilibrium time of 240, 215 and 150 hours. The experimental results also showed that the equilibrium time was dependent on initial Cr (VI) concentration. The respective equilibrium time for 100 mg/lit, 60 mg, lit and 200 mg/lit was 105, 72 and 30 hours. The results also showed that Cr (III) appeared gradually in the solution with the removal of Cr (VI) indicating the Cr (VI) adsorbed on the algal biomass was reduced to Cr (III). The experimental results on the adsorption kinetic showed that the data fitted well to the pseudo first order kinetics model with reaction rate constant of 0.0215 h-1, R2 =0.973 for initial metal concentration of 20 mg/L.

Non-living biomass of Sorgassum sea weed (marine algae) was used to remove Cr (VI) from aqueous solution [43]. It was found that at temperature of 22 °C, biomass dose of 2.5 g/L and initial metal concentration of 100 mg/L, maximum Cr (VI) removal of 60 mg/g was obtained within 60 minutes. The experimental data fitted well to the Langmuir isotherm model with q max =114 mg/L with R2 =0.99.

Coffee husk

Coffee husk was investigated for the removal of Cr (VI) metal from aqueous solutions [44]. The experimental results revealed that at pH 2, the percentage Cr (VI) removal was 96%. However, increasing the pH from pH 2 to pH 5 decreased the adsorption capacity. The kinetics study showed that a very fast increase in biosorption rate of Cr (VI) ions occurred at the first 20 minutes and equilibrium was reached after 2 hours. The experimental kinetics data 30 fitted well to pseudo-second order (R^2=0.993) and pseudo-third order (R^2=0.872). The experimental data on the isotherm fitted well to Langmuir's (R^2=0.996) and Freundlich's model (R^2 =0.94) with q_{max}=43.75 mg/g and K_f=12.505mg/g.

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Apparatus and materials

Table 3:1 list of equipments used for the thesis

Instrument or apparatus	Manufacturer and model	use
Cross beater mill	Retsch (Germany)	Size reduction of biosorbent
Analytical sieves with shaker	Retsch, AS200 (Germany)	Sample sieving
Drying Oven	Memmert, 100-800 (Germany)	Sample drying
Analytical balance	Ohaus, EP 214C (Switzerland)	Sample weighing
Vacuum pump	KNF laboport	Vacuum filtration
Spectrophotometer	Jenway 6300 (England)	Cr(VI) analysis
Furnace	Nabertherm LHT 02/16 (Germany)	To convert samples to ash
pH meter with glass electrode	Jenway 3505 (England)	pH measurement
Temperature controlled water bath shaker	Stuart SBS 40 (England)	Shaking samples
Micro pipette (different volume)	Socorex Acura835 (Switzerland)	Volume measurements
Magnetic stirrer		Mixing samples for pH measurement
Low Temperature freezer	Hot point	Preservation of DPC

3.1.2. Chemicals and reagents

- Standard Cr (VI) solution (1000 mg/l): prepared by dissolving 2.829 gram of overnight dried $K_2Cr_2O_7$ (s) in 1000 ml of distilled water.

- Calibration standards: Lower concentration standards were prepared from the stock solution.

- Working Cr (VI) solutions: working solutions at different concentrations was prepared daily from the stock solution.

- pH adjustment: (0.1-1 M) NaOH (RANKEM, India) and (0.1-1 M) HCL (RANKEM, India) was used.

- Biosorbent modifiers: 0.1 M NaOH (RANKEM, India), 0.1 M H_2SO_4 (RANKEM. India) and 97 % (V/V) Ethanol (Balezaf alcohol and liquor, Ethiopia) was used.

- Spectrophotometric analysis: 1, 5-Diphenylcarbzide (Merck, Germany), Acetone 99 % (Sigma Aldrich, USA), 3M H_2SO_4 (RANKEM. India) was used for the Spectrophotometric analysis of Cr (VI) ions.

- Standard Cr(VI) solutions, Calibration standards, Working Cr (VI) solution, P^H adjustment, Biosorbent modifiers, Spectrophotometric analysisand Impregnation solution**.**

3.2. Experimental methodology

3.2.1. Preparation of the adsorbent

A coffee husk waste was used for activated carbon preparation. The coffee husk was gathered from one of the main coffee processing unit found in addis ababa around saris locally named “buna board “. The collected coffee husk was washed with tap water in order to remove dirt and other particulate matter. The washed husk was air dried and grounded to powder with cross beater mill. It was impregnated and soaked with a solution of h_3PO_4 then decantation, drying and activation took place in an oven then the activated carbon coffee husk powder will be carbonized in furnace. After carbonization it will be cooled in tubular furnace then, the produced activated carbon coffee husk was washed with distilled water. Then neutralization took place then after it was dried, grounded and sieved. All The laboratory work has been carried out at addis ababa institute of technology chemical and environmental engineering laboratory.

3.2.2. Treatment of the adsorb ate solution

The stock solution of Cr (VI) containing solution which was collected from Hawassa industrial park effluent was dissolved with de ionized water. The dissolved solution was further dissolved with distilled water to desired concentration of test solution. Then the required P^H of the solution was adjusted by addition 0.1N of NaOH or HCL.

3.2.3 Numerical Optimization

Design expert is a statistical software package . that is specifically dedicated to performing odf design of experts. design expert offers comparative tsts , screening, characterization, optimization, robust parameter design, mixture designs, and combined designs. Design expert provides test matrices for screening up to 50 factors. Statistical significance of theses factors is established with analysis of variance (ANOVA) graphical tools help identify the impact of each factor on the desired outcomes and reveal abnormalities in the data.

Tangible advantages

- A limited and a small number of experiments
- The factor region of interest is covered optimally by the choosen experimental settings
- Using statistical design of experiments also allows for investigating factor interactions (in contrast to the often used “one- factor at at a time” method).
- You do not have to perform the statistical evaluation of your experimental results your self. DOE software tools (e.g the expert system STAVEX) do this automatically for you. STAVEX subsumes in easy understandable , natural language. Therefore it is not necessary to have a deeper preious knowledge in statistics.
- Modern DOE software tools (e.g the expert system STAVEX), make the application of statistical design of experiments easy , even in complex situations. In particular they yield meaningfull result also under real life restrictions, such as insufficient factor independence, presense of mixture factors or alternative factors, or for failed experiments.
- The graphics producd by the DOE software tools allow for a structured and intuitive analysis of the results.

The Design expert 6.0.8 program was used in the regression analysis of variance (ANOVA). The statistical software program was used to generate surface plots, using the fitted equation obtained from the regression analysis, holding one of the independent variables constant.in this study the design expert 6.0.8 program were used for optimization.

3.2.4. Applicability to industrial waste water

The produced activated coffee husk for removal of chromium was applied to the prepared adsorbate solution sample which was collected from Hawassa industrial park wastewater effluent, but the P^H of the adsorbate solution sample was measured before application with the adsorbent.

In order to examine the efficiency of activated coffee husk carbon the effluent was digested with acid then it was filtered. The resulting solution dissolved at different time intervals, at different P^H values including initial P^H value of the waste water and at equilibrium condition of the activated carbon dose, with an adsorbate solution. Finally the solution was subjected to atomic adsorption spectroscopy for extraction of chromium as Cr (VI).

3.2.5 Characterization of coffee husk

A) Determination of % Lignin content [63].

A one-gram, oven-dried sample of extractive-free biosorbent material was placed in a 150 ml beaker. 15 ml of cold sulfuric acid (72 %) was added slowly while stirring and mixed well. The reaction was continued for two hours with frequent stirring in a water bath maintained at 20^0C then after; the specimen was transferred by washing it with 560 ml of distilled water into a 1,000ml flask, diluting the concentration of the sulfuric acid to three percent. An allihn condenser was attached to the flask. The apparatus was placed in a boiling water bath for four hours. Then the flasks were removed from the water bath and the insoluble material was allowed to settle. The contents of the flasks were filtered by vacuum suction into a fritted-glass crucible of known weight. The residue was washed free of acid with 500 ml of hot tap water and then oven-dried at 103±20C. Crucibles were then cooled in a desiccator and weighed until a constant weight was obtained. The following formula was used to calculate the lignin content.

$$\%lingin = \frac{(w_2 - w_3)}{w_1} 10 \qquad \textbf{1}$$

Where:

W_1 = weight of oven dried sample (gram).

W_2= weight of oven-dried residue and crucible (grams).

W_3 = weight of oven-dried crucible (grams).

(B) Determination of % Cellulose content

The method for cellulose purification using nitric acid and acetic acid was based on the method described by Pereira [62]. Oven dried biosorbent (1.0 g) and nitric acid–acetic acid (25 ml) was prepared by diluting nitric acid (90 ml) and acetic acid (732 ml) to 1 L with water was placed in a 50-ml round bottomed flask, and the mixture was refluxed for 25 min. After cooling, the residue was filtered under vacuum into pre weighed sintered porous crucibles and was washed with hot water (500 ml) and the ethanol (25 ml). The yield of cellulose was determined using the following formula.

$$\%cellulose = \frac{(w_2 - w_3)}{w_1} 100 \qquad \mathbf{2}$$

Where:

W_1= weight of oven dried sample (gram).
W_2 = weight of oven dried residue and filter crucible (gram).
W_3 = weight of oven-dried filter crucible (grams).

3.2.5.1 Proximate Analysis on laboratory prepared biosorbent

Determination of % Moisture content

To determine the moisture contents of the laboratory prepared biosorbent material,oven drying method was used . generally oven drying for 2 hours at 105 ºC will be sufficient. But this time may vary depending on the moisture content and grading of the sample. 1 g sample was taken in a clean and dry crucible (W_1) and kept in an oven at 105 ºC for 2 hrs.to dry and verify the sample to a constant weight place the sample back in the oven for 1 hour, then re-weigh. Repeat the drying and weighing at one hour intervals until two consecutive weights remain the same. The sample was then kept in desiccators to cool and weight, again it was kept in an oven until constant weight after drying was obtained (W_2) and % moisture was determined by following the formula:

$$\%moisture = \frac{(w_1 - w_2)}{w_1} 100 \qquad \mathbf{3}$$

Where:

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

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

Determination of % Ash content [64]

An empty crucible and cover was ignited in the muffle at 600°C for 1 hour and cooled in dessicator and weighed to the nearest 0.1 mg. 2 gram sample of air-dried laboratory prepared biosorbent was placed in the crucible, the weight of crucible plus specimen was noted. The crucible and contents was placed in the muffle furnace and ignited until all the carbon was eliminated. The temperature of final ignition was set at to 600 °C; the sample was kept for four hours. After this, the crucible with its contents was removed and placed in a dessiccator to cool to 30 °C. The crucible with its contents was weighed accurately. The following formula was used to obtain the ash content in the biosorbent.

$$\%Ash = \frac{(w_2 - w_3)}{w_1} 100 \qquad \mathbf{4}$$

Where:
W_1=weight of ash (grams).
W_2=weight of oven-dried sample (grams).
W_3 = weight of oven-dried filter crucible (grams).

3.2.5.2 Apparent density measurement [65]

The pycnometer was cleaned using acetone and dried. The mass of the dry pycnometer was determined (W_o). Then the pycnometer was filled with the laboratory prepared biosorbent to 1/3 volume and the weight of the pycnometer plus the sample was measured (W_1). Distilled water was added to the pycnometer with sample, until capillary hole in the stopper is filled with water. The spare water that leaked through the capillary hole was dried with a filter paper and the total weight of the pycnometer, the sample and distilled water was measured (W_2). The particle density was calculated using formula.

$$\rho = \rho_\omega * \frac{(w_1 - w_0)}{(w_2 - w_1)} \qquad \mathbf{5}$$

Where:

ρ_w = Density of water at 20 ° C.

W_o = Mass of dry pycnometer

W_1 = Mass of sample plus pycnometer

W_2 = Total mass of distilled water, sample and pycnometer.

3.2.5.3 Point of zero charge determination

The point of zero charge (pHpzc) of the solid biomass is a function of pH, the pH at which the charge of the solid surface is zero. The point of zero charge (pH pzc) of the biomass was determined by the solid addition method [66]. For this purpose a series of 100 mL of Erlenmeyer flasks 45 mL of standard solution of 0.1 M KNO3 was transferred. The initial pHs of the solution (pHi) were approximately adjusted from 1.0 to 8 by adding either 0.1M HCl or NaOH. The total volume of the solution in each flask was made exactly to 50 ml by adding the 0.1 M KNO3 solution of the same strength. The pHi of the solutions was then accurately noted, and 0.1g of biosorbent was added to each flask, which was securely capped immediately. The suspensions then manually shaken and allowed to equilibrate for 48h with intermittent manual shaking. The final pH values of the supernatant liquid (pHf) were noted. The difference between the initial and final pH (Δ pH) values (Δ pH =pHi−pHf y-axis) was plotted against the initial pHi (x-axis). The point of intersection of the resulting curve with the x axis gave the pHpzc.

3.2.6 Batch biosorption experiments

Batch experiments were carried out at room temperature by shaking 0.5 g of coffee husk activated carbon powder and 100 ml of Cr (VI) solution in a 250 ml conical flask, the samples were agitated at a rate of 200 rpm for 2 hours. After agitation, the powder was removed by filtration using Whatman number 1 filter paper. The concentration of Cr (VI) in the filtrate was determined using Jennway UV-VIS spectrophotometer with 1, 5-diphenyl carbazide in acidic conditions.

The uptake of Cr (VI) was calculated using the equation 6, while the metal uptake q (mg metal ion g^{-1} of biosorbent) was calculated from the mass balance of equation 7:

$$\textbf{\% Cr removal} = \frac{(C_o - C_f)100}{C_o} \qquad \textbf{6}$$

$$\mathbf{q} = \frac{(C_o - C_f)V}{w} \qquad \textbf{7}$$

Where:

C_o and C_f are the initial and equilibrium concentrations of Cr (VI) solution (mg/lit),

V is volume of solution in liter and

W is mass of biosorbent in gram.

3.2.6.1 Effect of solution ph

The biosorption of Cr (VI) was studied for solution pH ranging from 2-5. 0.5g of biosorbent was contacted with 100 ml of 80 mg/l of Cr (VI) solution.0.1 N HCl or NaOH solutions were used to adjust pH values. All pH measurements were taken using a laboratory pH meter. Samples were shaken at 200 rpm for two hours at 20°c.

3.2.6.2 Effect of initial metal concentrations

The initial concentration of Cr (VI) was varied from 80 to 200 mg L^{-1}. 0.5g of biosorbent was contacted with 100 ml of different concentrations of Cr (VI). Samples were shaken at 200 rpm for two hours at 20°c.

3.2.6.3 Effect of adsorbent dose

The concentration of the biosorbent was varied from 2 to 5 g. each sample was contacted with 100 ml of 80 mg/ L of Cr (VI) solution for two hours.

3.2.6.4 Effect of contact time

2.5 g of the biosorbent was contacted with one liter of Cr (VI) (80 mg/ L) for different periods of time. The solution was mixed using a laboratory rotary shaker at rate of 200 rpm. 5 mL of samples was taken in frequent intervals using a micro pipette, and filtered through No. 1 Whatman filter paper. The samples were collected, and analyzed for up to 3 hours. Samples were collected at a 15 minutes interval.

3.2.6.5 Analysis of chromium ions (VI)

The concentration of the residual Cr (VI) ions in the solution was determined spectrophotometrically at 540 nm. A 0.25% w/v solution of diphenyl carbazide was prepared in 100 ml. 5 ml each of the sample solutions, containing various concentrations of Cr (VI) (0.01, 0.1, 0.2, 0.4, 0.6, 0.8 and 1 mg/l) were pipette out into 50 ml standard volumetric flasks. To this 2ml of 3M H_2SO_4 was added followed by 2 ml of diphenyl carbazide and the total volume was made up to 50 ml using distilled water. The solutions were allowed to stand for 10 minutes before analysis.

Chromium concentration estimated by the intensity of the color complex formed was measured using a UV-visible spectrophotometer. The absorbance was measured against a reagent blank at wavelength of 540-nm.A linear plot was obtained indicating adherence to the Beer Lambert's law in the concentration range studied

3.2.7 Biosorption kinetics model

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

3.2.7.1 Pseudo first-order or lagregn kinetic model

It is the first equation for sorption of liquid/solid system based on solid capacity [67-70]. The pseudo-first-order equation is generally expressed as in Eq. (8).

$$dq/dt = k_1(q_e - q_t) \qquad 8$$

Here q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo first- order adsorption (min^{-1}). Integrating Eq. (8) for the boundary conditions $t = 0$ to $t = t$ and $qt = 0$ to $qt = qt$, gives

$$\log(q_e/(q_e - q_t)) = k_1 t/2.303 \qquad 9$$

Eq. (9) can be rearranged to obtain the more useful form Eq. (10).

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \qquad 10$$

The values of log ($q_e - q_t$) will linearly correlated with t. The plot of log (qe −qt) vs. t should give a linear relationship from which k_1 can be determined from the slope. Eq. (10) differs from a true first-order equation in two ways: (i) the parameter k_1 ($q_e - q_t$) does not represent the number of available sites, and (ii) the parameter log qe is an adjustable parameter and often it is found not equal to the intercept of the plot of log ($q_e - q_t$) vs. t, whereas in a true first-order log qe should be equal to the intercept [71].

3.2.7.2 Pseudo-second-order kinetic model

If the sorption rate of system is a pseudo-second-order mechanism, the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or the exchange of electrons between sorbent and sorbate as covalent forces. There are certain assumptions in description of this kinetic model [72].

1. There is a monolayer of metal ion on the surface of sorbent.

2. The energy of sorption for each ion is the same and independent of surface coverage.

3. The sorption occurs only on localized sites and involves no interactions between sorbed ions.

4. The rate of sorption is almost negligible in comparison with the initial rate of sorption.

The pseudo-second-order biosorption kinetic rate equation is expressed in Eq. (11) [73-75]:

$$\mathbf{{}^{dq}/_{dt} = k_2(q_e - q_t)^2} \qquad \mathbf{11}$$

Where K_2 is the rate constant of sorption, (g/mg min), q_{eq} is the amount of metal ion sorbed at equilibrium, (mg/g), q_t is amount of metal ion on the surface of the biosorbent at any time, t, (mg/g).

Separating the variables in Eq. (11) gives:

$$\mathbf{{}^{dq_t}/_{(q_e - q_t)} = k_2 dt} \qquad \mathbf{12}$$

For the boundary conditions $t = 0$ to $t = t$ and $qt = 0$ to $qt = qt$; the integrated form of Eq. (12) becomes:

$$1/(q_e - q_t) = 1/q_e + k_2 t \qquad 13$$

The linear form of equation 13 becomes

$$t/q_t = 1/(K_2 q_e^2) + t/q_e \qquad 14$$

Where, K_2 is the rate constant for the pseudo-second order biosorption process. The rate parameters k and qe can be directly obtained from the intercept and slope of the plot of t/qt vs. t.

3.2.7.3 Intra-particle diffusion model

The adsorption of heavy metals on a porous biosorbent is the combination of four consecutive steps [75]: diffusion in the bulk solution, then diffusion across the thin film surrounding the biosorbent particles, followed by intra-particle diffusion and adsorption within the particles [76]. According to Weber and Morris [77] if the rate limiting step is the intra-particle diffusion, then the amount adsorbed at any time t should be directly proportional to the square root of contact time t and shall pass through the origin which is defined mathematically in Eq. (14).

$$q_t = k_{id} t^{0.5} + C \qquad 14$$

Where q_t is the amount Cr (VI) adsorbed, t is the contact time, k_{id} is the intra-particle diffusion coefficient and c is constant.

A plot of qt against $t^{0.5}$ should give a straight line which pass through the origin for intra-particle diffusion controlled biosorption process. The value of k_{id} can be calculated from slope of such plot. The values of the constant illustrate the effect of boundary layer on the rate of biosorption [78].

3.2.8 Biosorption isotherm model

An biosorption isotherm is used to characterize the interaction of the metal ions with the biosorbent. This provides a relationship between the concentration of metal ions in the solution and the amount of metal ions adsorbed to the solid phase when the two phases are at equilibrium.

Biosorption equilibrium may be expressed in the form of (a) a graphical or tabular record based on measurements, (b) an empirical algebraic expression fitted to the data and usually selected for its generality and simplicity of calculation use, or (c) equations based on the molecular statistics of the underlying process. Any such relationship may apply at only one temperature and is thus known as an equilibrium isotherm.

3.2.8.1 The Langmuir Isotherm

This is proposed by Langmuir [79] for homogeneous adsorption. It assumes a uniform biosorbent surface with energetically identical sorption sites. The Langmuir formula is proposed as follows:

$$q_e = \mathbf{q_{max}\ bC_{eq}} \Big/ \mathbf{1 + bC_{eq}} \qquad \mathbf{15}$$

Where, q_{max} is the maximum metal sorption (mg metal/g of biomass) and b is the Langmuir isotherm constant (l/mg metal). Two derivatives of the Langmuir equation are Eq. (16) and (17):

$$\frac{C_{eq}}{q_e} = \frac{1}{q_{max}\, b} + \frac{C_{eq}}{q_{max}} \qquad \mathbf{16}$$

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}\, b}\,\frac{1}{C_{eq}} \qquad \mathbf{17}$$

The Langmuir isotherm considers sorption as a chemical phenomenon. It was first theoretically examined in the adsorption of gases on solid surfaces. Langmuir constant b is related to the energy of adsorption through the Arrhenius equation. The higher the value of b, the higher is the affinity of the sorbent for the sorbate. A q_{max} can also be interpreted as the total number of binding sites that are available for biosorption and q_{eq} as the number of binding sites that are in fact occupied by the sorbate at the concentration C_{eq}. Although the Langmuir model sheds no light on the mechanistic aspects of sorption, it provides information on uptake capabilities and is capable of reflecting the usual equilibrium sorption process behavior. Langmuir assumed that the forces that are exerted by chemically unsaturated surface atoms (total number of binding sites) do not extend further than the diameter of one sorbed molecule and, therefore, sorption is restricted to a monolayer. In the simplest case the following assumptions were made:

a) Fixed number of adsorption sites: at equilibrium, at any temperature, and gas pressure a fraction of the surface sites θ is occupied by adsorbed molecules and the fraction $1–\theta$ is free.
b) All sorption sites are uniform (i.e., constant heat of adsorption).
c) Only one sorbate.
d) One sorbate molecule reacts with one active site.
e) No interaction between sorbed species.

Assumption of a value for the surface area covered per molecule then could allow computation of the active specific surface area of the sorbent using Avogadro's number. However, the concept of "surface area" cannot be used in gel-like sorbents that most biosorbent may be. As long as its restrictions and limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions for sorption behavior in different sorbate-sorbent systems, or for varied conditions within any given system.

Generally, the Langmuir isotherm does not describe equilibrium behavior accurately, especially with heterogeneous adsorption systems where adsorption continued beyond a monolayer. However, it is of practical importance because it is mathematically convenient and easily integrable.

3.2.8.2 The Freundlich Isotherm

The Freundlich isotherm, first proposed in 1906, is based on multilayer adsorption with interaction between adsorbed molecules [80]. The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. The Freundlich isotherm is the earliest known relationship describing the adsorption equation. The application of the Freundlich equation suggests that adsorption energy exponentially decreases on completion of the adsorptional centers of an biosorbent. For adsorption from solution, the Freundlich isotherm is represented by Eq. (18).

$$\mathbf{q_e = k_f C_{eq}^{1/n}} \qquad \mathbf{18}$$

Where K_f and n are the Freundlich constants. K_f related to the adsorption capacity; the larger its value, the higher the capacity. '***n'*** is the adsorption intensity or the heterogeneity of the sorbent; the more heterogeneous the surface, the larger its value. Equation (18) can be linearized in logarithmic form and the Freundlich constants can be determined.

$$\log q_e = \log k_f + \frac{1}{n} \log C_{eq} \qquad 19$$

This isotherm is widely recommended due to its accuracy. It gives more accurate results than the Langmuir isotherm for a wide variety of heterogeneous adsorption systems. Though accurate and mathematically convenient, one drawback is that Freumdlich isotherm does not converge to Henry's law at low surface coverage and, therefore, fails to describe equilibria as $q \to 0$ and is thermodynamically inconsistent.

3.2.8.3 Dubinin-Radushkevich (D-R) sorption isotherm

Dubinin-Radushkevich (D-R) sorption isotherm model is postulated within the sorption space close to the sorbent space to evaluate the sorption free energy and to help determine the nature of bonding, i.e. physisorption or chemisorptions [81].

The Dubinin-Radushkevich sorption isotherm can be presented as follow:

$$\ln q_m = \ln q_e - K_{DR}\varepsilon^2 \qquad 20$$

Where q_m is the amount of heavy metal adsorbed [mole/g], qe is the maximum adsorption capacity [mole/g], K_{DR} is the activity coefficient constant related to the adsorption free energy of the transfer of the solute from the bulk solution to the solid biosorbent[mol^2/J^2], and Ɛ is the polany potential which is given by the following equation:

$$\varepsilon = RT \ \ln\left(1+\frac{1}{c_e}\right) \qquad 21$$

Where: R is universal gas constant (8.314 $J.mol^{-1}.K^{-1}$), T absolute temperature in Kelvin, C_e is the equilibrium metal concentration [mole/L].

The value of K_{DR} can be determined from the plot of $\mathcal{E}^2$ vrs. ln q_m . The K_{DR} value can be used to determine the mean free energy (E) required to transfer 1 mole of heavy metal from infinity to the surface of the biosorbent from Eq.(22),

$$\mathbf{E = -\frac{1}{\sqrt{2K_{DR}}}} \qquad \mathbf{22}$$

If the value of E is between 8 and 16 KJ/mole, then the adsorption process is supposed to proceed via chemisorptions, while the values of E< 8 KJ/mol the adsorption process is of a physical nature

3.2.9 Statistical analysis of biosorption process by response surface methodology

Design of Experiment (DOE) is a pre-planned approach for finding cause and effect relationships. The purpose of statistically designing an experiment is to collect common relationship between various factors affecting the process towards finding the most suitable conditions. It is essential that an experimental design methodology be economical for extracting the maximum amount of complex information, a significant reduction in experimental time, saving both material and personnel cost [82]. RSM is an empirical statistical technique employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously.

Response Surface Methodology (RSM) consists of a group of mathematical and statistical methods that can be used to define the relationships between the response and the independent variables. Central Composite Design (CCD) [83], Box- Behnken and Doehlert designs (BBD) [] are among the principal response surface methodologies used in experimental design. The CCD has been widely used as the experimental design. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, and also to analyze the interaction between the parameters [84]. The CCD consists of a 2k factorial runs with 2k axial runs and n_0 centre runs. In CCD each variable is investigated at two levels and as the number of factors, k, increases the number of runs for a complete replicate of the design increases rapidly. This kind of design provides equally good predictions at points equally distant from the centre, a very desirable property for RSM. The centre points are used to determine the experimental error and the reproducibility of the data. The independent variables are coded to the $(-\alpha, \alpha)$ interval where the low and high levels are coded as -1 and +1 respectively. Rotatable designs are most efficient and recommended for $k = 4$.

Rotatable designs of second order are efficient in solving research problems when trying to find an optimum [85]. Thus to determine the effect of various operating parameters CCD has been used. The variables studied were pH of the solution (X_1), adsorbent dose (X_2), initial metal concentration (X_3) and time (X_4). For the present study since the number of independent variables is four so for each categorical variable, a 2^4 full factorial CCD, consisting of 16 factorial points, 8 axial points and 6 replicates at the centre points were employed, indicating that altogether 30 experiments were required, as calculated:

4. RESULT AND DISCUSSION

4.1Biosorbent characterization

The physicochemical characterization of coffee husk activated carbon form is presented in table. 4.1 Based on the results, coffee husk activated carbon decreases the cellulose and hemicelluloses content due to decomposition at high temperature. The results confirmed that the availability of surface functional groups such as the hydroxyl and carbonyl groups which are associated with the cellulose and lignin. (45)

Table 4:1 Physio chemical properties of biosorbent prepared from coffee husk.

	Coffee husk activated carbon
Moisture content%	**7.58**
Ash content%	**0.342**
Apparent density g/cm^3	**0.231**
Cellulose content%	**-**
Lignin content%	**-**
Point of zero charge p$_{zc}$	**4.40**

4.2 Point of zero charge determination

Point of zero charge of the solid biomass is afunction of the ph , the ph at which the charge of the solid surface is zero. The initial phi of the solution (phi) were approximately adjusted from 1.0 to 8. By adding either (HCL/NAOH) then, the final ph of the supernatant liquid (phf) were noted . (change in PH is the difference between the initial ph and final ph values.).

The pH$_{pzc}$ of the biosorbent coffee husk activated carbon, was assessed from the graph of The difference between the initial and final pH values (ΔpH = pH$_i$– pH$_f$) was plotted against the initial pH value as displayed in Figure 4.1.

From the graph, it is clear that the biosorbent was positively charged at pH less than 5.0. However, above pH 5.0, there was a charge reversal. The pH pzc of biosorbent was found to be

4.40.

It has been indicated by earlier studies that the pHpzc of a biosorbent decreases with increase in acidic groups on the surface of the biosorbents [46].

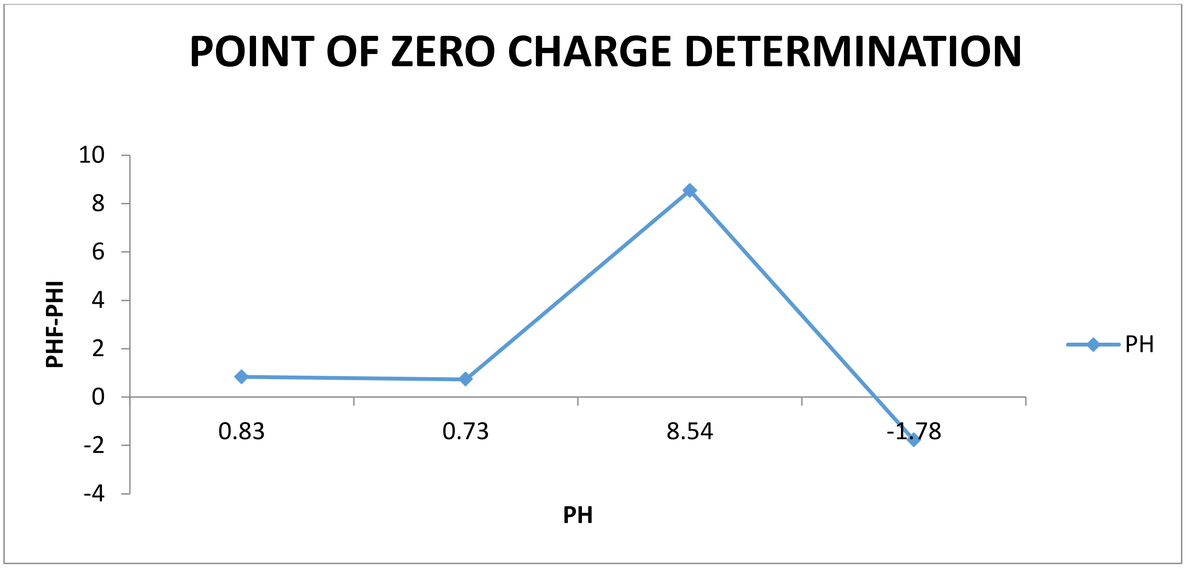


Figure 4:1 Point of zero charge graph of coffee husk activated carbon

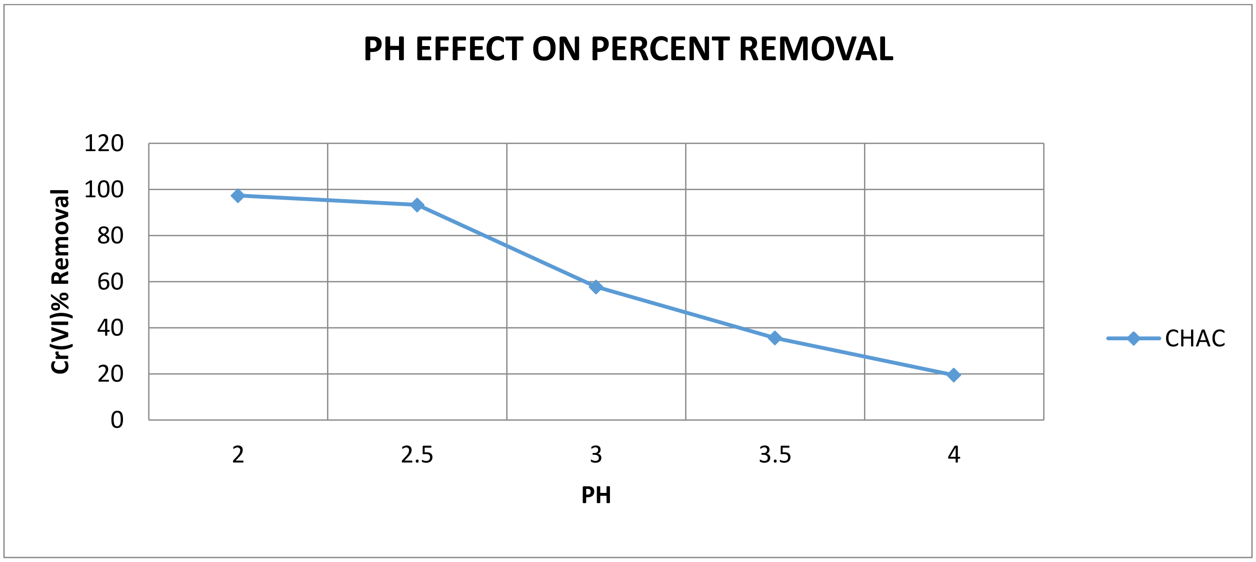
4.3Batch Biosorption Studies

4.3.1Effect of solution pH

This study was carried out to determine the impact that solution pH has on the removal of Cr(VI) by coffee husk activated carbon in order to establish the working pH. The pH was varied from 2to 5. Figure 4.2 showed the Cr (VI) ions removal and biosorption capacity of coffee husk activated carbon at variable solution pH values. From figure 4.2 it is evident that the solution pH affects the biosorption process. The increase in solution pH from pH 2 to 5 resulted decrease in both percentage removal and biosorption capacity. The maximum of 97.3 percent Cr (VI) removal was achieved with biosorption capacity of 15.57 mg/g at solution pH 2. The experimental results undoubtedly showed that, the biosorption of Cr (VI) ions is directly affected by the solution pH.

The results obtained can be explained by the fact that the solution pH was directly related to the large availability of positively charged active sites on the surface of the biosorbent to bind with the metal ions. As solution pH decreased, the surface of the biosorbents exhibits increasing positively charged active sited. Hence the toxic metal to be removed is negatively charged Cr (VI) ions like HCrO4-, Cr2O72-, CrO42-, the biosorption is favored at lower solution pH values. Hence, electrostatic attraction probably plays an important role in biosorption of negatively charged chromium ions at low solution pH.(47) the dominant form of Cr (VI) at pH 2.0 is the acid chromate ion species (HCrO4-) which would shift to other forms, Cr2O72- and CrO42-, with increase in pH. Since there is an increase in sorption of Cr (VI) as pH decreases to 2.0, it may be suggested that HCrO4- is the active form of Cr (VI) which is being biosorbed by coffee husk.

The biosorption of Cr (VI) was studied for solution pH ranging from 2-5. 0.5g of biosorbent was contacted with 100 ml of 80 mg/l of Cr (VI) solution.0.1 N HCl or NaOH solutions were used to adjust pH values. All pH measurements were taken using a laboratory pH meter. Samples were shaken at 200 rpm for two hours at 20°c.



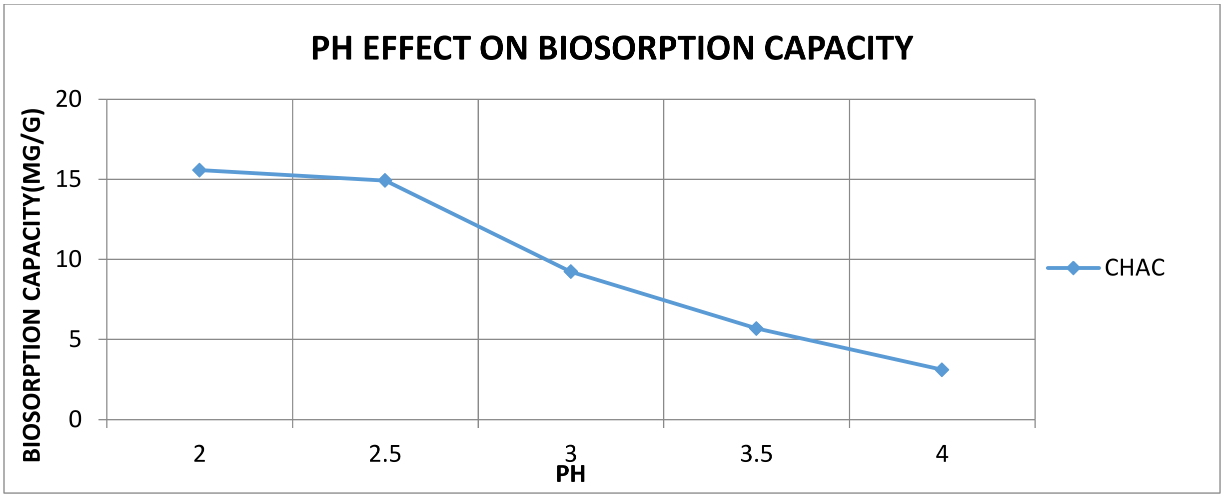


Figure 4:2 Effect of solution pH on biosorption percent removal and biosorption capacity of Cr (VI) ions of coffee husk activated carbon.

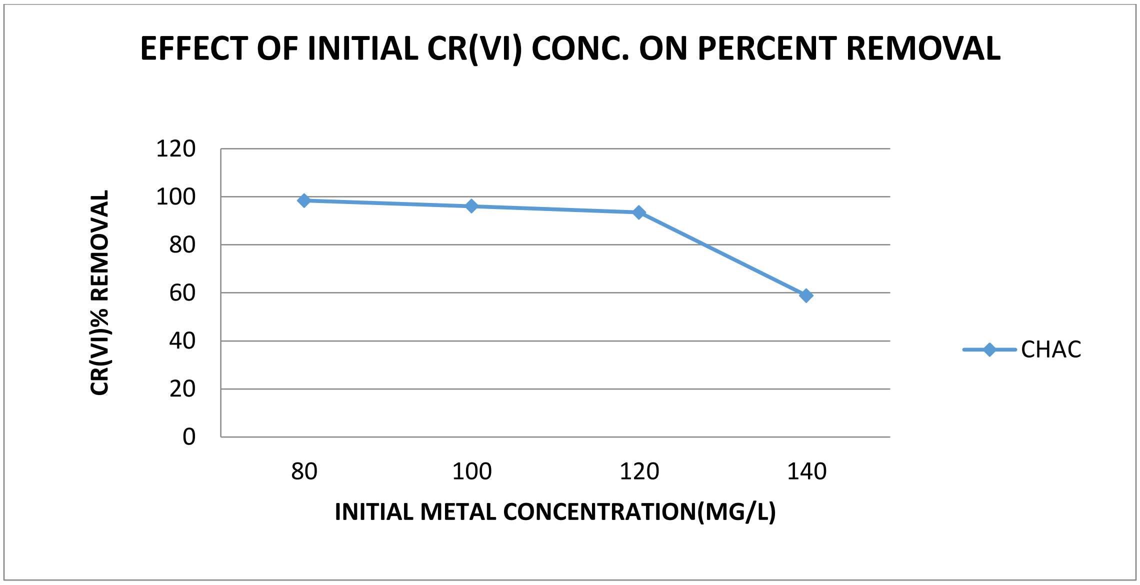
4.3.2Effect of Initial Metal Concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of chromium (VI) ions between the aqueous and solid phases. The biosorption of Cr(VI) ions was carried out at different initial metal concentration ranging from 80-200 mg/L at pH 2. Under given experimental conditions, the relationship between initial Cr (VI) ion concentrations, the Cr (VI) percentage removal and the biosorption capacity have been investigated. The results obtained from the study are given below:

The initial concentration of Cr (VI) was varied from 80 to 200 mg L^{-1}. 0.5g of biosorbent was contacted with 100 ml of different concentrations of Cr (VI). Samples were shaken at 200 rpm for two hours at 20°c.

The biosorption capacity (mg/g) and percent removal of coffee husk activated carbon at different initial concentration of Cr (VI) are shown in Figure 4.3. The percentage removal showed negative slop while the biosorption capacity showed positive slop with increase in Cr (VI) concentration.

The maximum Cr (VI) removal of 97.2 % and maximum biosorption capacity of 33.40 mg/g were achieved at Cr (VI) concentration of 80 mg/L and 200 mg/L.It is evident from the above results that percentage removal of Cr (VI) ions and the biosorption capacity are directly affected by the variation in the initial Cr (VI) ions concentration. The results obtained can be attributed to the fact that the biosorbent dose being constant (5 g/L) the number of available binding site at the surface remains the same while the number of chromium ions increased with increase in the metal concentration. This in turn results in the increase of ratio of metal ions to that of the available binding sites resulting in the decrease in the Cr (VI) ions removed. However, the increase in the biosorption capacity with increase in the initial Cr (VI) concentration may be explained as, at fixed biosorbent dose and increasing the metal concentration, all the available active sites of the biosorbent will be fully exposed to get occupied by the Cr (VI) ions that are in excess saturating and yielding a higher biosorption capacity [48]. Similar pattern in the biosorption capacity and percentage removal were reported by different researchers [49,50 and 51].



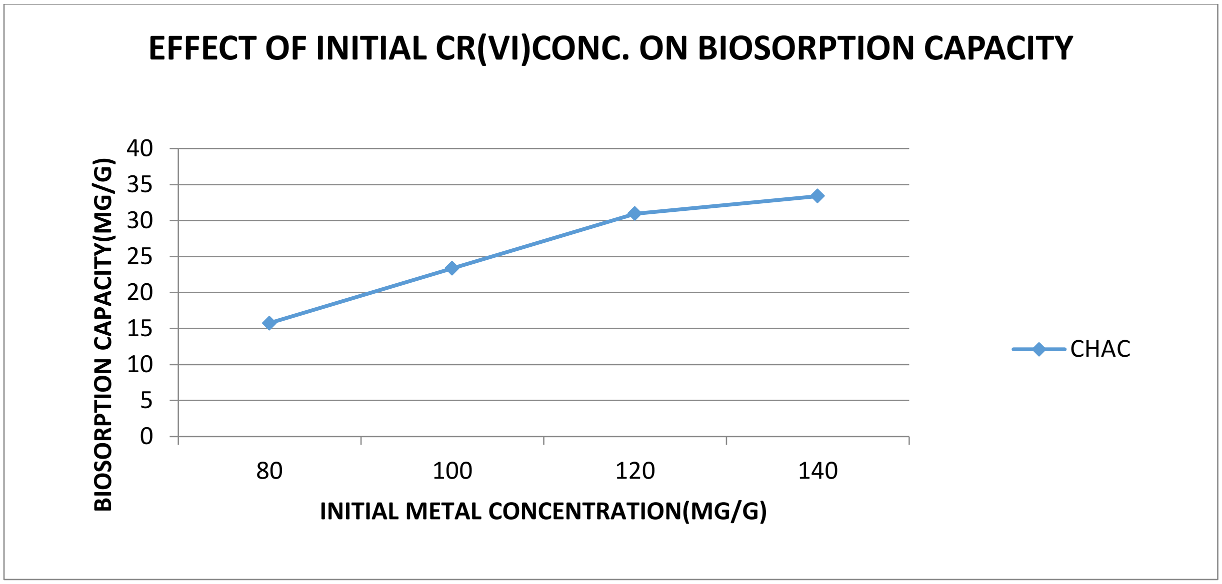
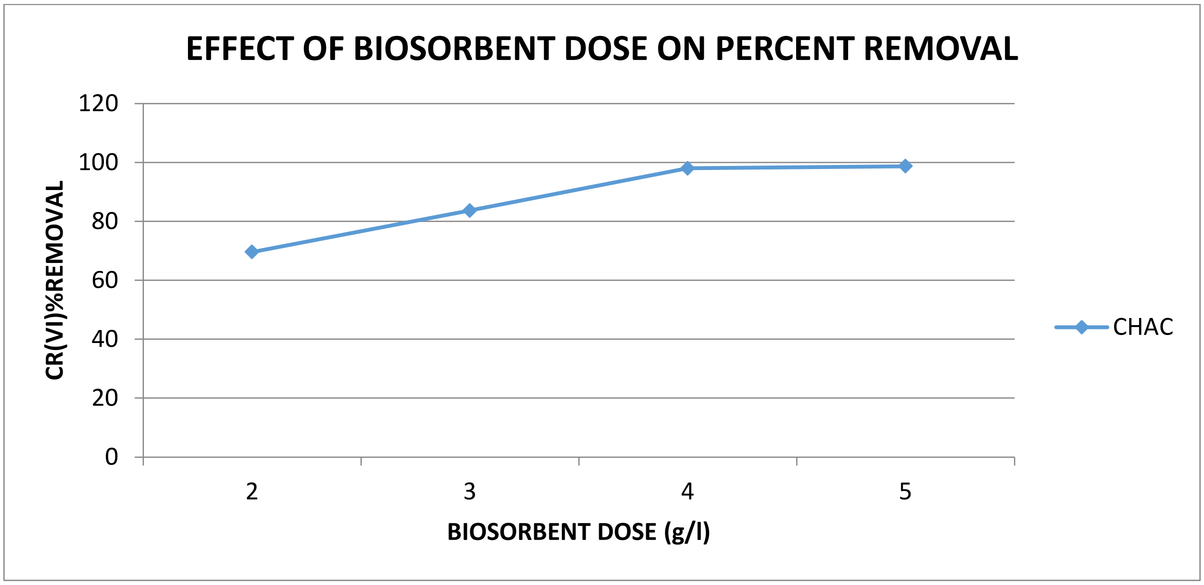


Figure 4:3 Effect of initial Cr (VI) concentration on biosorption percent removal and biosorption capacity of coffee husk activated carbon

4.3.3Effect of adsorbent dose

The adsorbent dose strongly affects the extent of biosorption. It determines the sorbate – sorbent equilibrium of the system [52]. The biosorption of Cr (VI) ions from the test solutions were analyzed in terms of percentage removal and biosorption capacity of the coffee husk activated carbon. The data obtained is discussed as follows.

The concentration of the adsorbent was varied from 2 to 5 g. each sample was contacted with 100 ml of 80 mg/ L of Cr (VI) solution for two hours. A higher adsorbent dose may cause aggregation which decreases the total surface area of the adsorbent leading to a a decrease in adsorption. The percentage removal and the biosorption capacity of CHAC with variation in biosorbent dose are presented in Figure 4.4. The respective results obtained for the Cr (VI) percentage removal was 98.72 % at biosorbent dose of 5 g/L and 69.59 % at biosorbent dose of 2 gm/L. The maximum biosorbent dose of 2.78 mg/gm was obtained at biosorbent dose of 2 gm/L. It is clear from the experimental results obtained that, the increase in the biosorbent dose increased the percentage removal with decreasing the biosorption capacity. These results can be justified by the fact that the total metal removed depends on the number of the available binding sites, whereas the specific metal uptake was the ratio of the amount of the metal ion removed per unit weight of the biosorbent.



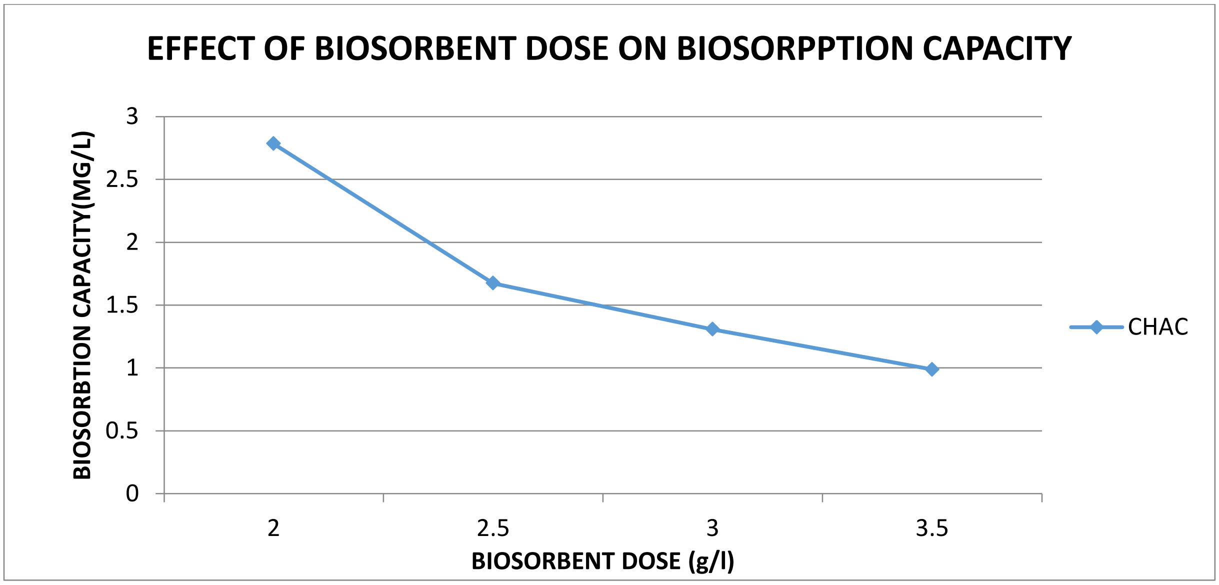


Figure 4:4 Effect of biosorbent dose on biosorption percent removal and biosorption capacity of Cr (VI) Ions of coffee husk activated carbon

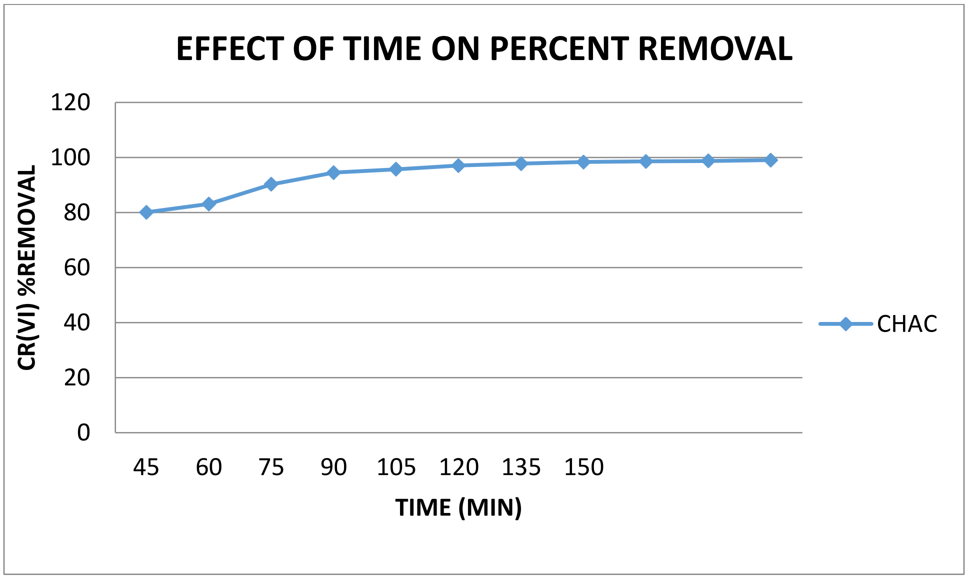
An increase in the biosorbent dose generally increases the metal ion removed due to the increase Surface area of the biosorbent which in turn increase the number of binding sites available for the biosorption process. On the other hand, the quantity of biosorbed metal ion per unit weight of the biosorbent decreases with increase in the biosorbent dose which may be due to the complex interaction of several factors. One important factor at high biosorbent concentration is that the available metal to be sorbed is insufficient to completely cover the available exchangeable sites which in turn results in low biosorption capacity [53]

4.3.4Effect of contact time

The biosorption capacity and the removal efficiency of metal ions by biosorbents will increase with increase in contact time. However, in practice it is necessary to optimize the contact time, considering the biosorption process. The effect of contact time on the biosorption of Cr (VI) ions using biosorbents prepared from coffee husk was investigated over time intervals of 45to 120 minutes. The results obtained are summarized as follows.

2.5 g of the biosorbent was contacted with one liter of Cr (VI) (80 mg/ L) for different periods of time. The solution was mixed using a laboratory rotary shaker at rate of 200 rpm. 5 mL of samples was taken in frequent intervals using a micro pipette, and filtered through No. 1 Whatman filter paper. The samples were collected, and analyzed for up to 3 hours. Samples were collected at a 15 minutes interval.

It should be noted that there are several parameters which affect the equilibrium biosorption time.Some of these parameters are the stirring rate, the physicochemical properties of the biosorbents (e.g. surface charge density, protein and carbohydrate composition of the biosorbents, surface area, etc...), biosorbent dose, initial metal concentration, presence of the competitive ions and the properties of the metal under study.



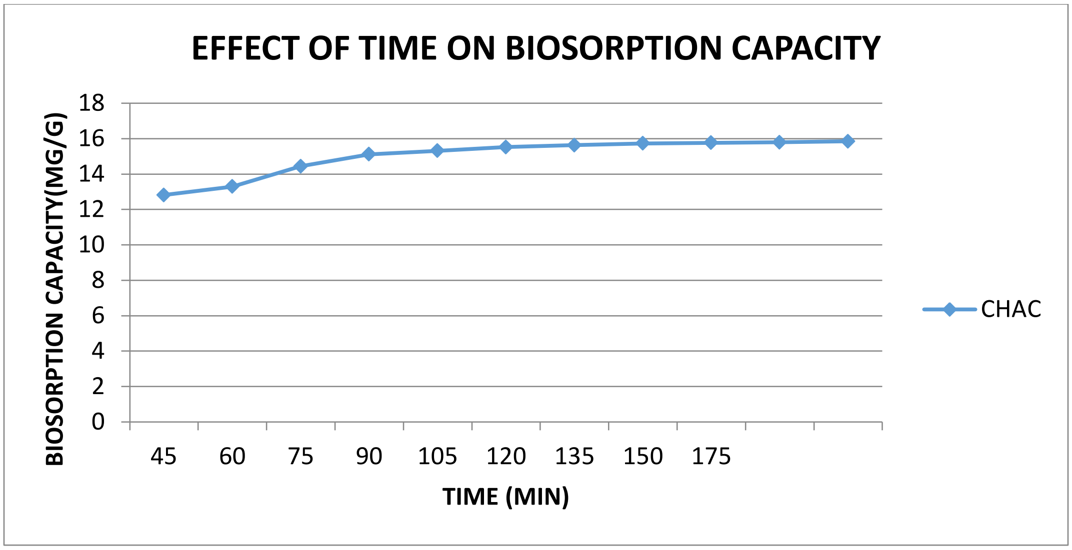


Figure 4:5 Effect of time on biosorption percent removal and biosorption capacity of Cr (VI) ions of coffee husk activated carbon.

The variation of Cr (VI) percentage removal and the biosorption capacity of coffee husk activated carbon with respect to contact time is presented in figure 4:5. Both the Cr (VI) removal and the biosorption capacity showed a rapid increment up to 75 minutes then proceeds slow increase until both reached the maximum at 120 minutes with 99 % removal of Cr (VI) ions and 15.84 mg/g biosorption capacity. After 120 minutes there were no change in the biosorption capacity and the percentage removal.

As time progress, the number of available binding sites decreased thus decreasing the rate of biosorption. This phenomenon indicates biosorption of Cr (VI) took place in two stages, the first one the rapid surface biosorption followed by the slow pore diffusion to the internal binding sites [54].

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

4.4Biosorption kinetics model

Kinetic models can be helpful in better understanding of the mechanisms of heavy metal biosorption and in evaluating the performance of the biosorbents for heavy metal removal [55]. The kinetics also describes the solute uptake, which in turn controls the residence time of the sorbate at the solid solution interface.

In order to examine the controlling mechanism of the biosorption process, various kinetics models were used to test the experimental data. In order to obtain the rate constants and the order of sorption reactions, pseudo first order, pseudo second order kinetic models and intra-particle diffusion model were applied to the kinetic data obtained at solution pH 2, initial metal concentration of 80 mg/L and biosorbent dose of 5 g/L.

4.4.1 Pseudo first order kinetics model

Kinetic model applied in the present study was Lagergren first-order model which is based on the assumption that sorption of the metal ions on to the biosorbent is a reversible process [55]. Lagergren equation for rate kinetics was used for the determination of biosorption rate constant through its kinetic plot that is plot of Log (q_{eq}–q_t) versus t. The kinetic plots for corresponding biosorbent are presented in figure 4.6.

The pseudo first order graphs showed that the values of Log (q_{eq} –q_t) versus time decreased with time giving the metal ions more opportunity to be taken up by the biosorbent. However, within 45 to 60 minutes majority of Cr (VI) ions have been removed from the aqueous solution The regression correlation coefficients for the pseudo first order model is found to be 0.952. The values of regression correlation coefficient obtained from the graph seemed to be good showing the applicability of the pseudo first order model for removal of Cr (VI) ions using coffee husk activated carbon. However, the value of the biosorption capacity (q_{eq}) calculated from the pseudo first order kinetic model is not in agreement with the true biosorption capacity (qep) obtained from the experimental result. The result conformed the biosorption process using was not a strict surface adsorption. The values of the pseudo first order rate constant K_1 (min-1), calculated

q_{eq}(mg/g) and the regression correlation coefficient calculated from the slope and intercept of the corresponding plot is clumped in the table 4.2.

4.4.2 Pseudo second order kinetic model

Pseudo second order model for rate kinetics was used for the determination of biosorption rate kinetics. The pseudo second order rate constant (K_2), the equilibrium biosorption capacity (q_{eq}), and initial rate of uptake (h) were calculated from the slope and intercept of the linear plot of t/q versus t. Figure 4.7 showed the linear plot of pseudo second order kinetic model for coffee husk activated carbon. The calculated values of K_2 , q_{eq}, and R^2 for the biosorbent is summarized in table 4.2.

From table 4.2, it is evident that, there is a very good agreement between the experimental q_{eq} and the calculated q_{eq} values as compared to the pseudo first order kinetic model. Data obtained from the biosorption of kinetics, when modeled with pseudo second order equation showed excellent fitting having regression correlation coefficient values greater than 0.999 for the biosorbent. The experimental results obtained suggested that the Cr (VI) biosorption followed a pseudo second order kinetics.

4.4.3 Intra particle diffusion model

The possibility of intra-particle diffusion on the biosorption of Cr (VI) by using CHAC was explored by intra-particle diffusion model. According to Weber and Morris (1963) [56], a plot of qt versus $t^{0.5}$ should be a linear line which pass through origin with a slope of K_{id} and intercept C when the biosorption mechanism follows the intra-particle diffusion model.

The plot of q_t versus $t^{0.5}$ for the corresponding biosorbent is given in figure 4.8. The calculated values of K_{id} with the regression correlation coefficient are summarized in table 4.2. From the figures it is clear that the graphs linear within certain range, but the trend of the data did not pass through the origin. The calculated values of K_{id} and C was 9.94 mg/min . The value of the intercept gives idea about the thickness of boundary layer i.e. the larger the intercept the larger the boundary layer effect [57]. The deviation of the straight line from the origin may be due to the difference in the rate of mass transfer in the initial and final stage of the biosorption process. Furthermore such deviation of the straight line from the origin indicates that pore diffusion is not the sole rate controlling step [56].

Over all analysis of the pseudo first order, pseudo second order and the intra-particle diffusion model data revealed that, the kinetics of Cr (VI) biosorption by using coffee husk activated carbon can be best described by assumption of the pseudo second order kinetics model indicting the biosorption rate was proportional to the number of the unoccupied sites. The high values of the regression correlations coefficient of the graph and the high proximity of calculated and experimental equilibrium biosorption capacity (q_{eq}, mg/g) supports the present study. Moreover, the successful application of the pseudo second order model to describe the actual biosorption process comes as an indication that the rate limiting step in biosorption of Cr (VI) by using CHAC is chemical sorption (chemisorption) involving the valence forces through the sharing or exchange of electrons between the Cr (VI) ions and the biosorbent, complexation, coordination and/or chelation [58].Applicability of pseudo second order kinetic model was also favored for biosorption of Cr (VI) using wide range of biosorbents.[49 and 51]

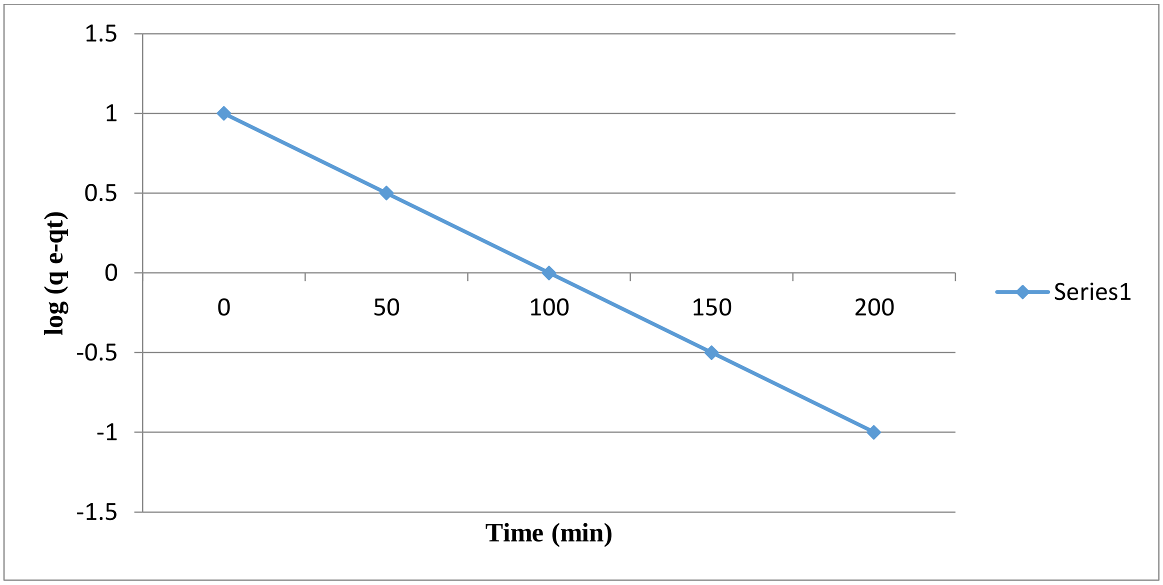


Figure 4.6 pseudo first order plot for coffee husk activated carbon

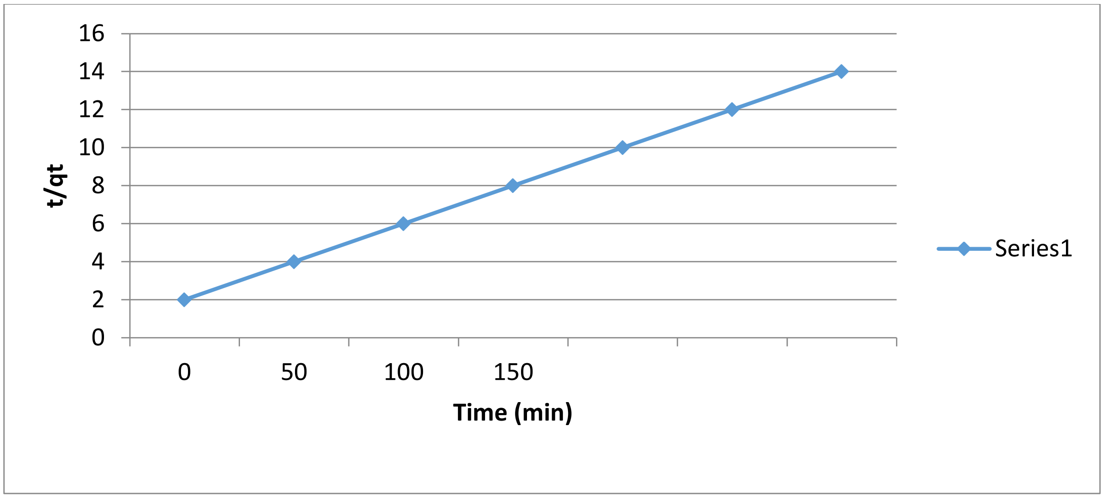


Figure 4.7 pseudo second order plot for coffee husk activated carbon

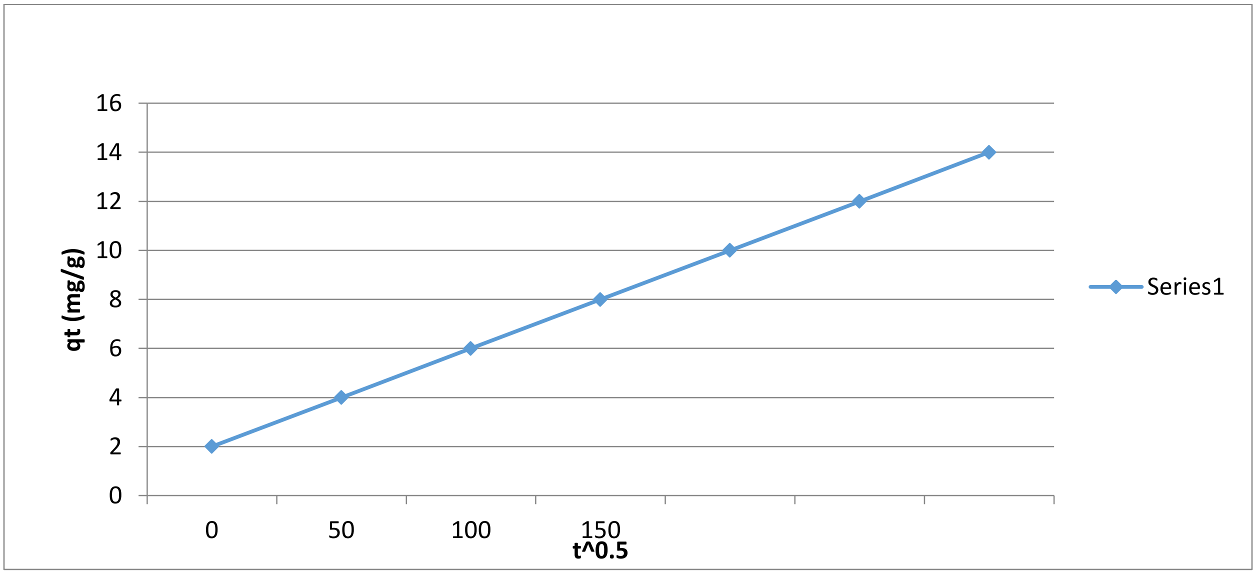


Figure 4.8 Intra-particle diffusion model plot for coffee husk activated carbon

Table 4.2 Biosorption kinetics constants for coffee husk activated carbon

	q_{Exp} [mg/g]	***Pseudo first order kinetic model***			***Pseudo second order kinetic model***			***Intra-particle diffusion***	
		q_{cal} [mg/g]	K_1 [min-1]	R^2	q_{cal} [mg/g]	K_2 [g/mg.min]	R^2	K_{id} [mg/g. min]	R^2
CHAC	15.812	9.531	0.021	0.952	16.949	0.086	0.998	0.478	0.788

4.5 Biosorption Equilibrium Isotherm Models

The equilibrium established between the adsorbed metal ion on the biosorbent surface and un ad sorbed metal ion in the solution can be represented by biosorption isotherm models. Biosorption isotherms are mathematical models that describe the distribution of the biosorbate species among the liquid and the solid (biosorbents) based on a set of assumptions that are mainly related to the heterogeneity or homogeneity of biosorbent, the type of coverage and the possibility of interactions between the biosorbate species [59]. The sorption data collected in this study were fitted in to three well known biosorption isotherm models, namely Langmuir, Freudlich and Dubnin- Radushkevich isotherm models.

4.5.1 Langmuir Isotherm Model

The Langmuir isotherm is valid for monolayer sorption onto the biosorbent surface with a finite number of identical sites, which are homogeneously distributed over the sorbent surface. To determine the Langmuir constants, experiments were conducted by varying the initial metal concentration from 80-200 mg/L at temperature of 20 °C, biosorbent concentration of 2 g/100ml Of metal solution, pH 2 and agitation speed of 200 rpm. The results obtained were plotted as 1/qe vs. 1/Ce and the values of Langmuir's constants q_{max} (mg/g) and b (L/mg) were determined from the plots presented from figure 4.9 for the corresponding biosorbent form. The Langmuir constant calculated for the biosorbent is presented in table 4.3. With respective regression correlation coefficient (R^2).

The coffee husk activated carbon biosorbent showed biosorption capacity of 33.41 mg/g and showed regression coefficient of R^2=0.8732 indicating the sorption can be described by the Langmuir model.

Direct comparison of coffee husk with other biosorbent materials is difficult, owing to the different applied experimental conditions. In the present study, coffee husk activated carbon has been compared with other biosorbents based on their maximum biosorption capacity for Cr (VI) and shown in Table 4.3. It can be observed that coffee husk activated carbon compares well with the other biosorbents listed in Table 4.3, Neem sawdust and sawdust are biosorbents that exhibited higher adsorption capacity. Hence, coffee husk in chemical treated form or in untreated form can be considered to be viable biosorbent for the removal of Cr (VI) from aqueous solutions

4.5.2 Fruendlich Biosorption Isotherm

The empirical Freundlich equation which is based on sorption on a heterogeneous surface was used to determine the Freundlich constants (1/n and K_f) which are given in the table K_f (L/mg) and n are Freundlich's constants, which indicate the extent of the biosorption and the degree of Linearity between the solution concentration and the biosorbent.

The Fruendlich isotherm constants (K_f and n) were determined for coffee husk activated carbon from the plot of Log qe versus Log Ce. Figure 4.4 shows the Freundlich plot for the biosorbent.

From the Freundlich's plot the calculated values of K_f and n were 16.018 L/mg and 4.209. The regression correlation coefficient was 0.8732.

Accordingly to traybal (59) an adsorbent with the n value in between 1 and 10 is considered as good biosorbent. Accordingly coffee husk activated carbon has n value greater than 1 indicating effective biosorption.

When the regression correlation coefficients are compared between Langmuir's and Fruendlich's isotherm models, the Fruendlich's isotherm model showed lower regression correlation coefficients. Freundlich isotherm model is widely used isotherm model. But it does not provide any information on the monolayer biosorption capacity. The results obtained indicated that the equilibrium data are not fitted well with Freundlich isotherm model.

4.5.3 Dubnin- Radushkevich (D-R) Isotherm Model

The biosorption equilibrium data were further subjected to D-R isotherm model to identify the biosorption mechanism. The linear plots of ln qe versus ε^2 were used to determine D-R isotherm constants K_{DR} ($mole^2/KJ^2$) and biosorption free energy E (KJ/mole). The results are reported in

Table. Figure 4.11 shows the plot of D-R isotherm model for CHAC. From the D-R plot, it is clear that the regression correlation coefficient obtained for the D-R isotherm model were lower than that of the Langmuir isotherm model. However, the calculated biosorption free energy was found to be 14.434 KJ/mol coffee husk activated carbon. This result indicated that the biosorption process proceeds via chemisorptions. This phenomenon was also justified by [60].

The researchers stated that the Cr (VI) biosorption followed two steps, the first step the biosorption of negatively charged Cr (VI) ions due to positively charged surface functional groups. The second step involved the reduction of Cr (VI) to Cr (III) by adjacent electron donor groups on surface of biosorbents. Other conformation of biosorption by chemisorptions is obtained from the biosorption kinetics in which the successful application of the pseudo second order kinetic model to represent the actual biosorption process.

	Biosorbent	Maximum biosorption capacity qmax (mg/g)	Optimum pH	Reference
1	Neem sawdust	58.2	2	41
2	Mango sawdust	37.3	2	41
3	Orange peel	8.068	2	41
4	Saw dust	41.52	1	33
5	Papaya seed	8.86	2	35
6	Compost	6.25	2	38
7	Wheat shell	0.1574	2	44
8	Coffee husk activated carbon	33.29	2	Present study

Table 4:3 Comparison of biosorption capacities of coffee husk activated carbon for Cr (VI) with other biosorbents.

Biosorbent	***Langmuir***			**Freundlich**			**Dubnin- Radushkevich**		
	q_{max}	***b***	R^2	K_f	***n***	R^2	K_{DR}	***E***	R^2
Coffee husk activated carbon	37.037	0.600	0.8732	16.018	4.209	0.6824	0.0024	14.434	0.7161

Table 4.4 Biosorption isotherm constants

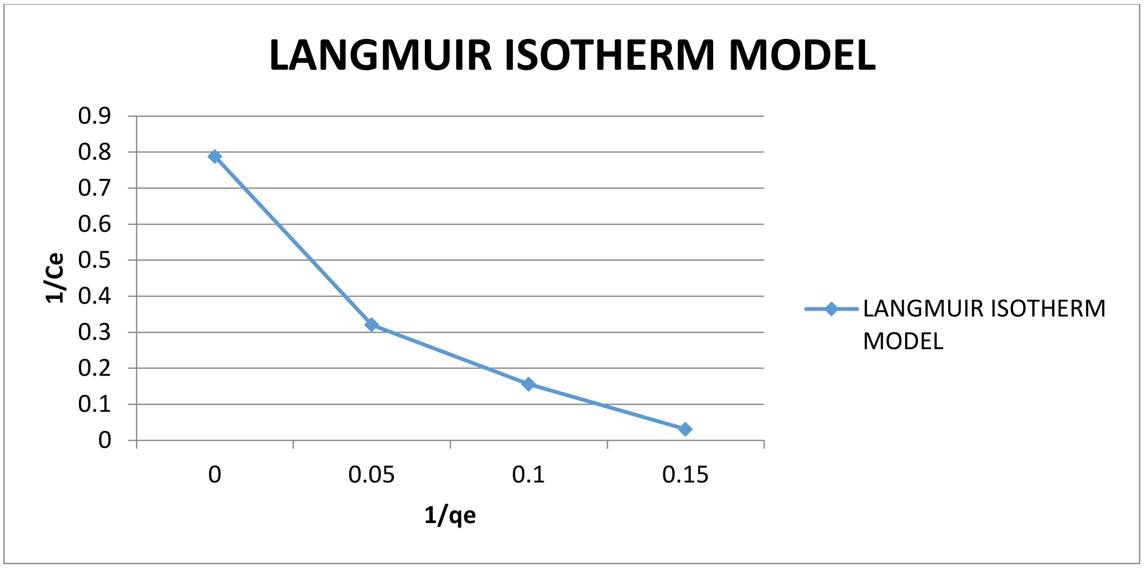


Figure 4:9 Langmuir Isotherm Model for coffee husk activated carbon

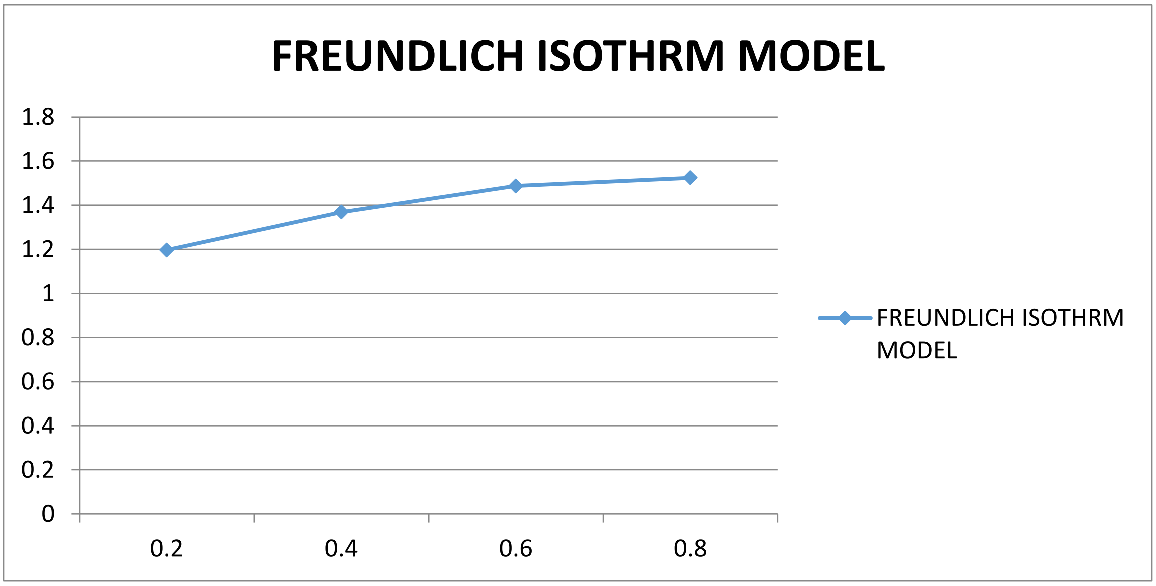


Figure 4.10 Freundlich Isotherm Model for coffee husk activated carbon.

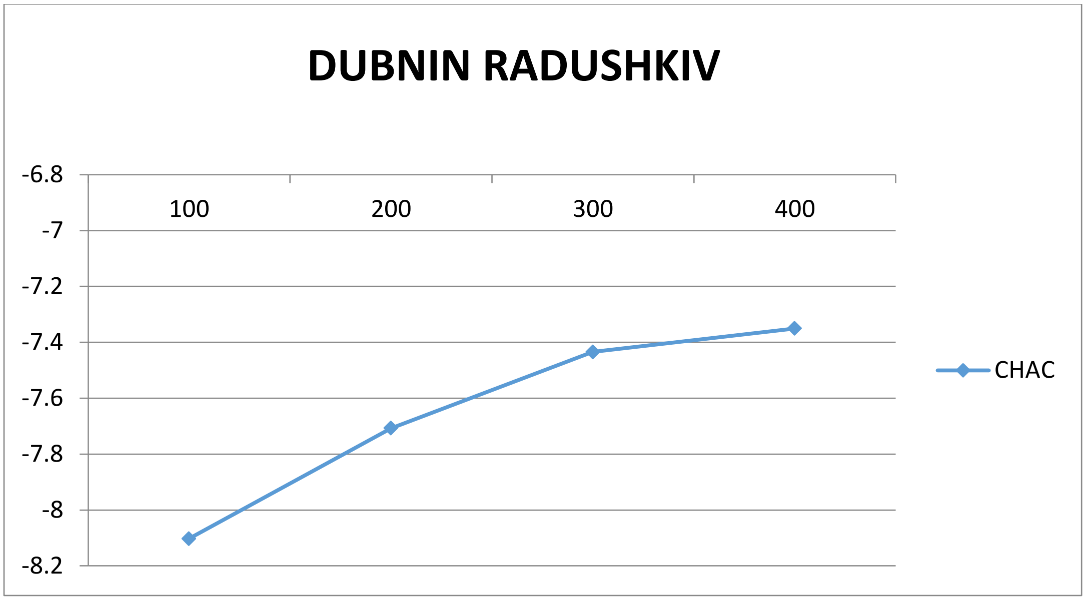


Figure 4.11 Dubnin Radushkevich isotherm plot for coffee husk activated carbon

4.6 Experimental Optimization of Chromium (VI) Adsorption

Optimization of process parameters of Cr (VI) biosorption experiments conducted using CHAC by response surface methodology (RSM). The percentage removal of Cr (VI) were entered as a response in the design lay out given in table. The major statistical analyses of the biosorption process (i.e. model generation, model fitness test and ANOVA analysis) are summarized below.

Table 4.5 design summary

			Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Response 1**
Std	**Run**	**Block**	**A:pH**	**B:Initial metal**	**C:Adsorbent**	**D:Time**	**Cr(VI)**
				mg/l	***g/100ml***	***min***	***%***
7	1	Block 1	2	200	5	45	68.52
29	2	Block 1	3.5	140	3.5	82.5	68.52
21	3	Block 1	3.5	140	0.5	82.5	58.54
23	4	Block 1	3.5	140	3.5	7.5	33.84
4	5	Block 1	5	200	2	45	10.24
24	6	Block 1	3.5	140	3.5	157.5	66.64
19	7	Block 1	3.5	20	3.5	82.5	61.21
3	8	Block 1	2	200	2	45	50.54
6	9	Block 1	5	80	5	45	56.34
16	10	Block 1	5	200	5	120	48.52
22	11	Block 1	3.5	140	6.5	82.5	97.63
5	12	Block 1	2	80	5	45	90.98
25	13	Block 1	3.5	140	3.5	82.5	66.85
26	14	Block 1	3.5	140	3.5	82.5	69.85
2	15	Block 1	5	80	2	45	39.84
28	16	Block 1	3.5	140	3.5	82.5	68.98
18	17	Block 1	6.5	140	3.5	82.5	19.98
20	18	Block 1	3.5	260	3.5	82.5	25.01
27	19	Block 1	3.5	140	3.5	82.5	69.42
30	20	Block 1	3.5	140	3.5	82.5	70.24
13	21	Block 1	2	80	5	120	96.64
11	22	Block 1	2	200	2	120	61.51
8	23	Block 1	5	200	5	45	19.85
14	24	Block 1	5	80	5	120	76.89
12	25	Block 1	5	200	2	120	37.84
9	26	Block 1	2	80	2	120	64.38

4.6.1 Optimization of Chromium (VI) biosorption modeling and model analysis

Biosorption experiments were carried out using CHAC according to the Central composite design procedure (CCD) of the response surface methodology. The results (% Cr (VI) removal) from the interaction of the four process factors (pH, biosorbent dose, and initial Cr (VI) concentration and biosorption time) were used for the model generation. A second order quadratic regression was performed to estimate the response function as a second order polynomial after the examination of the model fit summery revealed that a quadratic model was statistically significant for the response (% Cr (VI) removal).

The resulting biosorption model equation which express the relationship between the interactions of the biosorption factors and the response (% Cr (VI) removal) are given in table in terms of coded values and equation in terms of actual factors.

The significance of the model equation to represent the biosorption process was indicated by the model F value of 150.16. The Fisher F- test with the very low probability value (P model> F=0.0001) demonstrates a very high significance for the regression model equation. The fitness of the model was checked by the determination coefficient (R^2). The value of the determination coefficient (R^2) for model was calculated to be 0.8989. This implies that more than 89.89 % of the experimental data were compatible with the data predicted by the model and only less than 1.11 % of the total variations data were not explained by the model. R^2 value is always between 0 and 1, and R^2 value greater than 0.75 indicates the aptness of the model [60].

For good statistical model, R^2value should be close to 1.0. The adjusted R^2 value corrects the model R^2 value for the sample size and number of terms in the model [60]. For the quadratic model, the Adj. R^2 (0.8045) was also high to advocate a high significance of the model. The predicted determination coefficient, Pred. R^2 of 0.7377 was also in the reasonable agreement with the Adj. R^2.

ANOVA analysis was performed in order to determine the significance of each coefficient in the model using the student’s “t- test” and “P” values which are given in table . In general, the larger the magnitude of “t” and the smaller the value of “P”, the more the significance is the corresponding coefficient term [JHJ]. The value of “prob. > F” less than 0.0500 indicated the model terms are significant. For the biosorption of Cr (VI) using CHAC, the model terms solution pH (A), initial Cr (VI) concentration (B), biosorbent dose (C), biosorption time (D), interaction between solution PH and initial Cr(VI) concentration (AB), interaction between solution PH and adsorbent dose (AC), interaction between solution PH and time (AD), interaction between initial Cr(VI) concentration and biosorbent dose (BC), interaction between initial Cr (VI) concentration and time (BD), , and the interaction between effect of square of Solution pH (A^2), the interaction effect of square of initial Cr (VI) concentration (B2), the interaction effect of square of biosorbent dose(C^2) and the interaction effect of square of biosorption time (D^2) were significant model terms. The value of “prob. > F” greater than 0.1indicates that the model term is not significant. Therefore, the interaction between time and Bio sorbent dose (AC) and solution PH and time (AC) was not a significant model term.

Additionally, from the ANOVA analysis the lower value of coefficient of variation (C.V. =3.17) indicates the better precession and reliability of the experiments carried out. The C.V. as a ratio of the standard error of estimate to the mean value of the observed response (as % Cr (VI) removal) is the measure of reproducibility of the model and as general rule a model can be considered reasonably reproducible, if the model C.V. value is not greater than 10% [61].

4.6.2 Optimization of Chromium (VI) Removal by CHAC

Biosorption experiments were carried out using CHAC according to the Central composite design procedure (CCD) of the response surface methodology. The results (% Cr (VI) removal) from the interaction of the four process factors (pH, initial Cr (VI) concentration, biosorbent dose and biosorption time) were used for the model generation. A second order quadratic regression was performed to estimate the response function as a second order polynomial after the examination of the model fit summery revealed that a quadratic model was statistically significant for the response (% Cr (VI) removal). The resulting biosorption model equation which express the relationship between the interactions of the biosorption factors and the response (% Cr (VI) removal) are shown below in terms of coded values and in terms of actual factors.

Table 4.6: Model equations in terms of coded and actual values

Final Equation in Terms of Coded Factors:

Cr(VI) removal =

+64.19	
-13.09	* A
-10.51	* B
+8.63	* C
+4.33	* D
-3.40	* A2
-5.00	* B2
+3.75	* C2
-1.03	* D2
-3.93	* A * B
-6.06	* A * C
+1.02	* A * D
-0.22	* B * C
+3.81	* B * D
+3.98	* C * D

Final Equation in Terms of Actual Factors:

Cr(VI) removal =

+48.97628	
+15.88623	* PH
+0.23509	* Initial metal concentration
-1.96388	* adsorbant dose
-0.31263	* time
-1.51011	* PH2
-1.38826E-003	* Initial metal concentration2
+1.66489	* adsorbant dose2
-7.29587E-004	* time2
-0.043646	* PH * Initial metal concentration
-2.69361	* PH * adsorbant dose
+0.018122	* PH * time
-2.46528E-003	* Initial metal concentration * adsorbant dose
+1.69472E-003	* Initial metal concentration * time
+0.070767	* adsorbant dose * time

4.6.2.1 Effect of interaction of biosorption parameters on percentage removal of Cr (VI)

The results obtained from 30 experimental runs conducted to observe the effect of the four biosorption factors (solution pH, initial Cr (VI) concentration, biosorbent dose and time) using biosorbent which is presented in table 4.5. In this section the interaction effects of the four factors on the biosorption (% removal) of Cr (VI) ions are discussed in detail. The analyses are supported by the 3D and contour plots of the interaction effects of the four factors on the percentage removal of Cr (VI) ions.

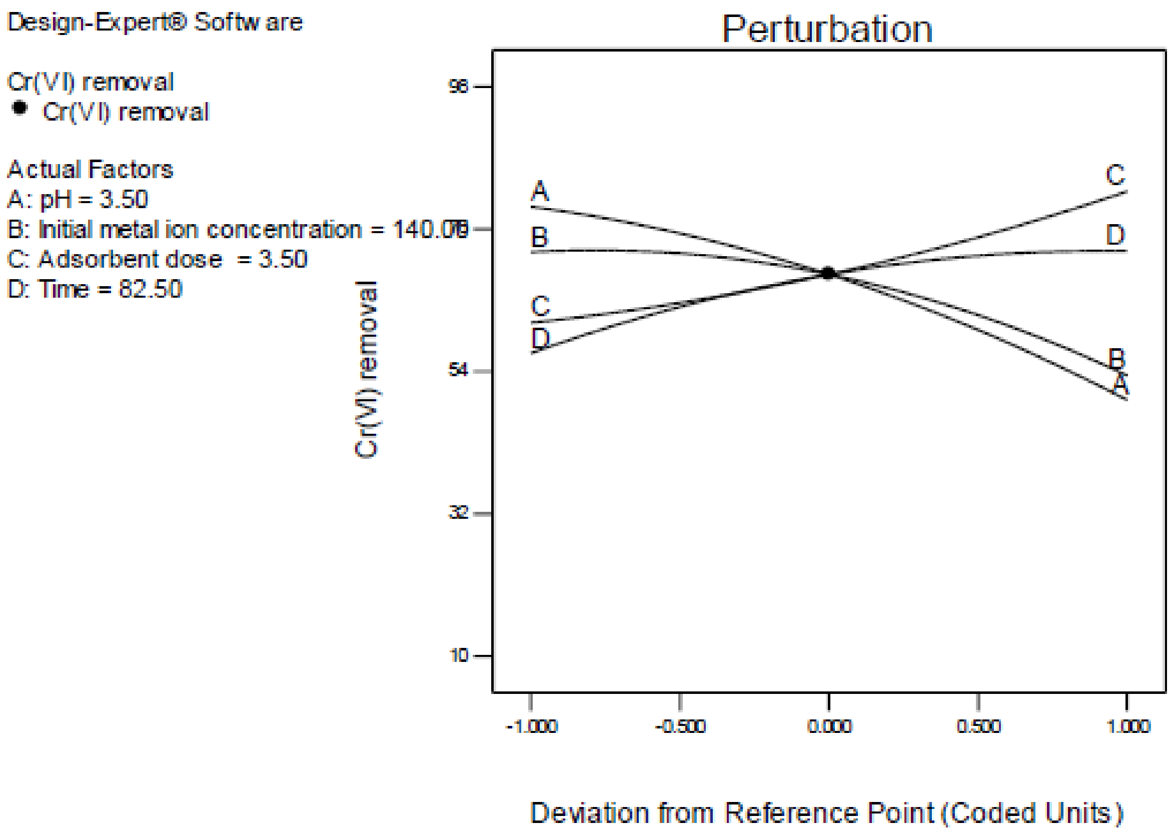


Figure 4:12 Perturbation of all factors

4.6.2.2 The interaction effect of solution pH and initial Cr (VI) concentration

Generally, as the solution pH decreases the percentage removal of Cr (VI) ions increased. While the increase in the initial Cr (VI) concentration will result in reduction in the percentage removal. As briefly discussed , the percentage removal increase with decrease in solution pH is due to the protonation of surface functional groups which are responsible for biosorption process at lower solution pH. Additionally, the presence of these positively charged functional groups also increases the percentage removal due to the attraction of the negatively charged Cr (VI) ions by the positively charged surface functional groups. While the decrease in the percentage removal with increase in initial Cr (VI) concentration is due to the presence of large amount of Cr (VI) ions to the fixed amount of surface functional groups present on the biosorbent surface to interact with the Cr (VI) ions.

Table 4:7 Analysis of ANOVA for quadratic second order model

ANOVA for Response Surface Quadratic Model						
Analysis of variance table [Partial sum of squares]						
	Sum of		Mean	F		
Source	Squares	DF	Square	Value	Prob > F	
Model	11830.91	14	845.0653	9.522951	< 0.0001	significant
A	4113.14	1	4113.14	46.35053	< 0.0001	
B	2652.094	1	2652.094	29.88616	< 0.0001	
C	1788.999	1	1788.999	20.16004	0.0004	
D	321.5452	1	321.5452	3.623458	0.0763	
A2	321.1221	1	321.1221	3.61869	0.0765	
B2	694.7632	1	694.7632	7.829212	0.0135	
C2	390.3241	1	390.3241	4.398521	0.0533	
D2	17.13012	1	17.13012	0.193037	0.6667	
AB	246.8827	1	246.8827	2.782094	0.1161	
AC	587.6988	1	587.6988	6.622715	0.0212	
AD	16.62601	1	16.62601	0.187357	0.6713	
BC	0.787656	1	0.787656	0.008876	0.9262	
BD	232.6388	1	232.6388	2.621581	0.1262	
CD	253.526	1	253.526	2.856958	0.1116	
Residual	1331.098	15	88.73986			
Lack of Fit	1324.055	10	132.4055	94.00151	< 0.0001	significant
Pure Error	7.042733	5	1.408547			
Cor Total	13162.01	29				

Figure 4:13, represents the effects of solution pH and initial Cr (VI) concentration on the percentage removal of Cr (VI) ions. From figure 4:13, it can be seen that at low solution pH value (pH < 3), more than 72 % of initial Cr (VI) present in the solution was removed irrespective of the initial concentration of Cr (VI) ions. While the increase in the solution pH (pH

> 3) with increase in the initial Cr (VI) concentration resulted in significance reduction in the percentage removal. This is due to the reduction of the protonated surface functional groups with increase in solution pH. These result showed the significance of the solution pH on the biosorption of Cr (VI) ions.

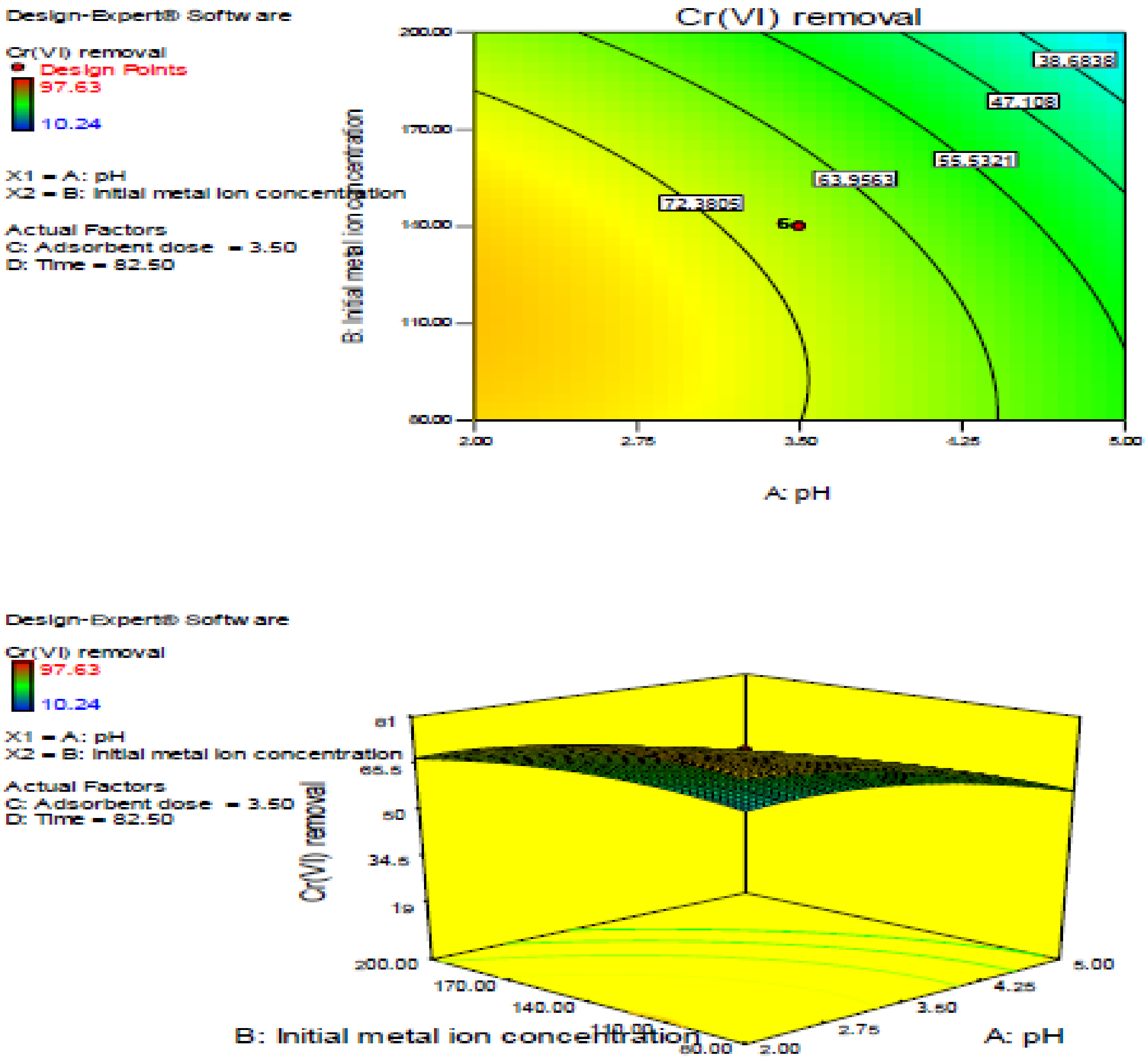
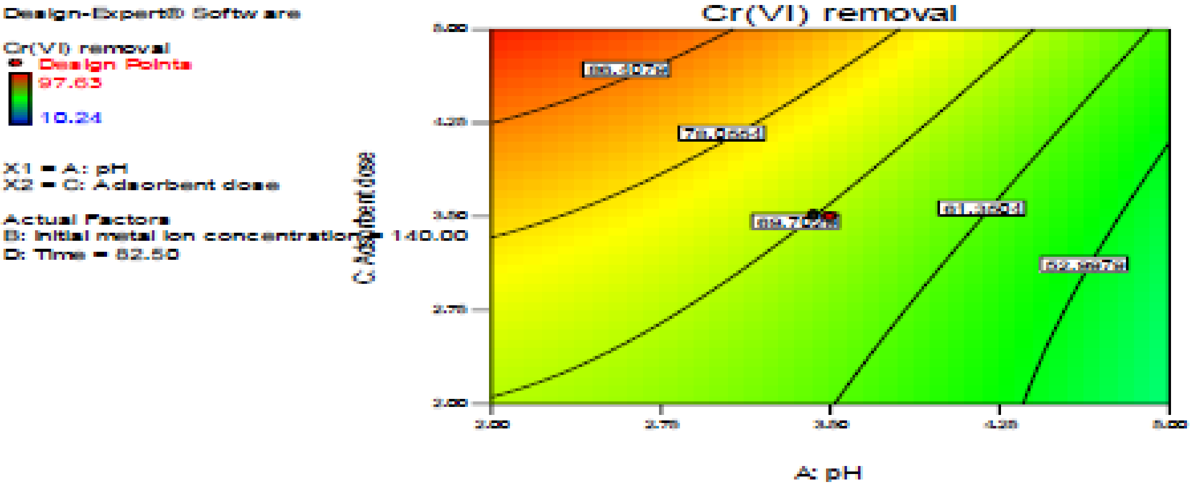


Figure 4:13 the interaction effect of solution pH and initial metal concentration on biosorption of Cr (VI) ions. contour plot and 3D plot respectively.

4.6.2.3 The interaction effect of solution ph and biosorbent dose

The effect of solution pH and biosorbent dose on the Cr (VI) percentage removal is shown in the form of 3D and contour plots in figure . As it can be seen in figure , increase in solution pH resulted in the reduction of Cr (VI) percentage removal while for the biosorbent dose resulted in the increasing of Cr (VI) percentage removal. However, at lower solution pH (pH < 2.75) more than 78 % of the Cr (VI) was removed irrespective of the change in the biosorbent dose the result showed the significance of solution pH on the biosorption process of Cr (VI) ions. The maximum percentage removal of 97.63 % was predicted at solution pH of 2 and biosorbent dose of 5 gram. These results can be justified by the presence of large quantity of positively charged surface. Functional groups at lower solution pH and large amount of biosorbent dose.



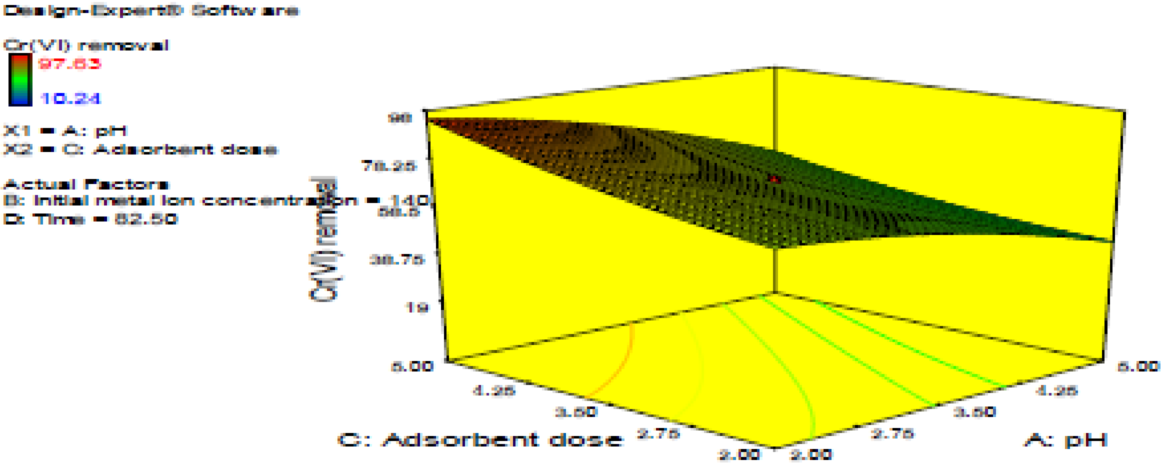
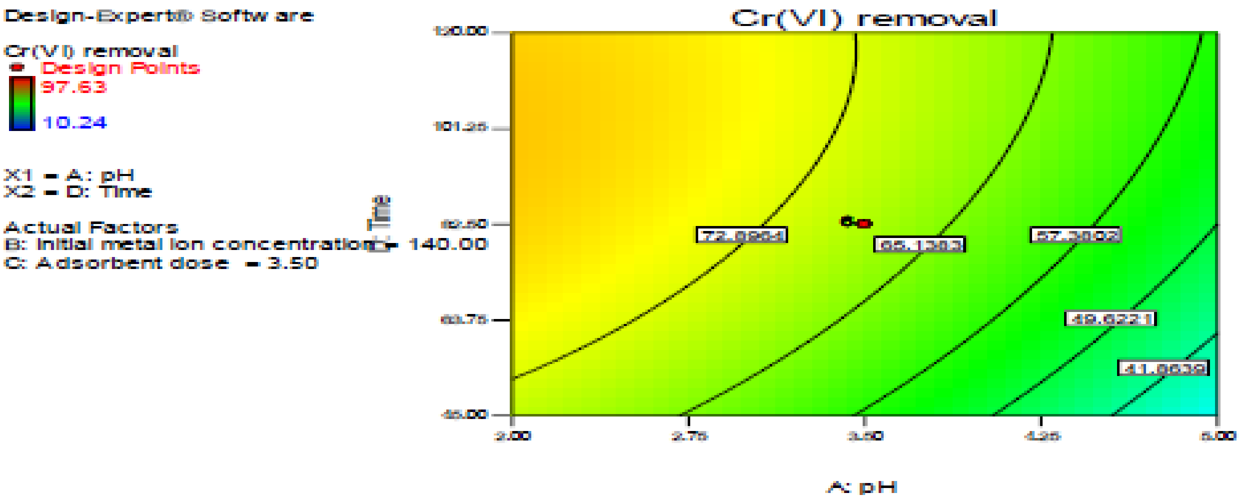


Figure 4:14 the interaction effect of solution pH and biosorbent dose on the percentage removal of Cr (VI).Contour plot and 3D plot respectively.

4.6.2.4 The interaction effect of solution pH and contact time

Figure 4.15 showed the effect of solution pH and biosorption contact time on the percentage removal of Cr (VI) ions by CHAC. From the contour plot it can be seen that, with increase in contact time and decrease in solution pH, the % removal of Cr (VI) increased significantly. This result indicates that both biosorption factors have significant effect on the %removal of Cr (VI). The ANOVA analysis also showed the interactions effect of solution pH and contact time have “Prob.>F” value of 0.0001, which indicates the significance of the factors on the % removal of Cr (VI).



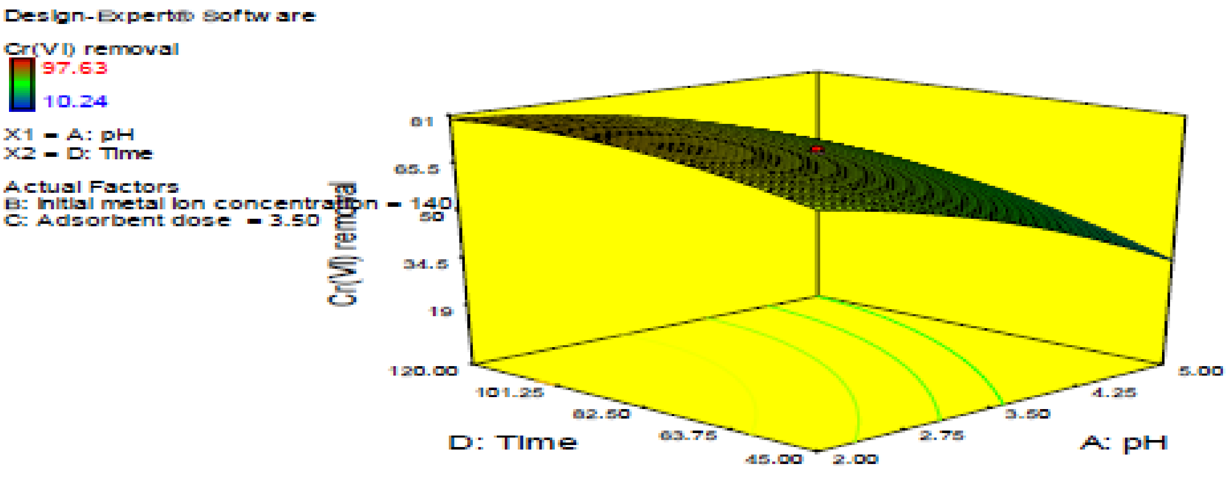


Figure 4:15the interaction effect solution pH and contact time on the percentage removal of Cr (VI). Contour plot and 3D plot respectively.

4.6.2.5 The interaction effect of biosorbent concentration and contact time

Figure 4.16 presented the interaction effect of biosorbent dose and contact time on the % removal of Cr (VI). From the plots it can be seen that, increasing in both biosorbent concentration and contact time resulted in increased % removal of Cr (VI). The results also indicated that as lower solution pH (pH=2), both terms have significant effect on the % removal of Cr (VI).

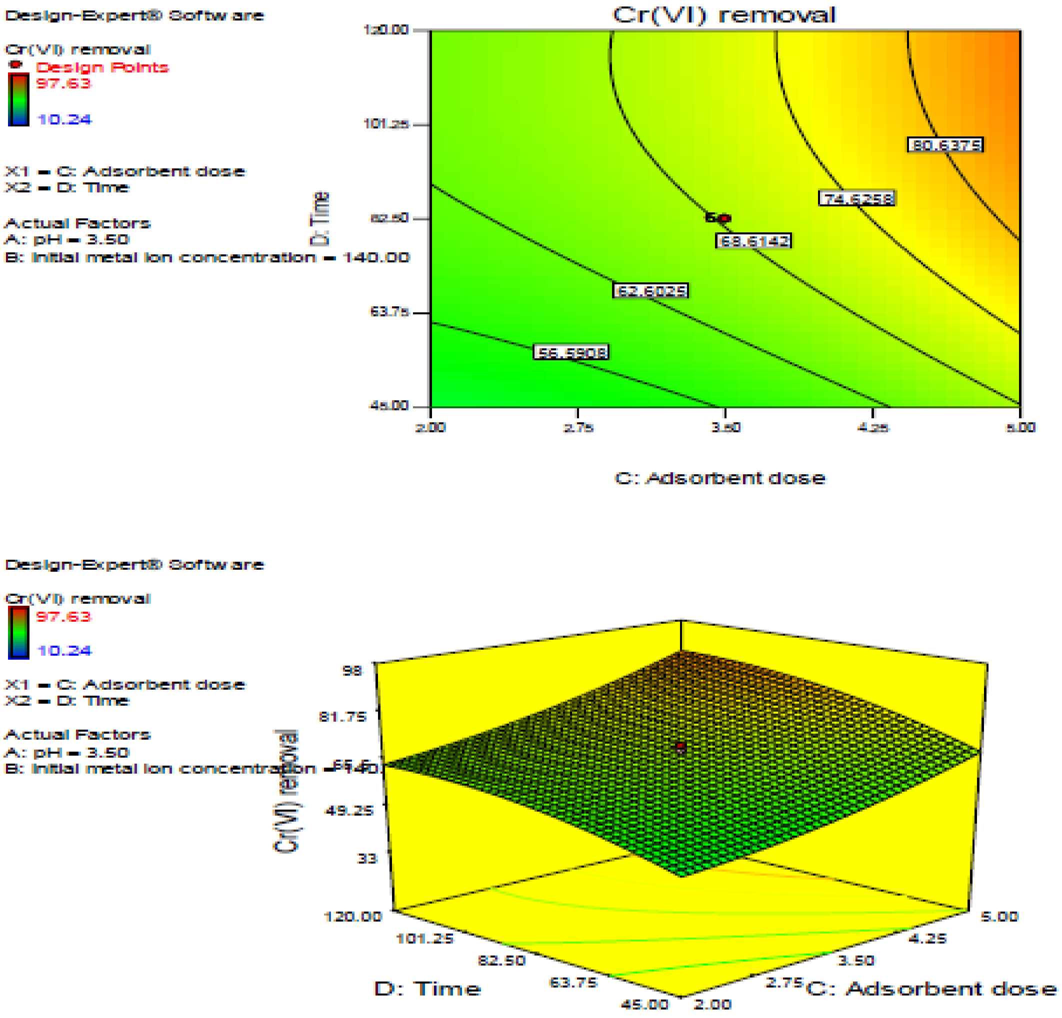


Figure 4:17 the interaction effect of biosorbent dose and contact time on the percentage removal of Cr (VI). Contour plot and 3D plot respectively.

4.6.2.6 The interaction effect of initial Cr (VI) concentration and contact time

The interaction effect of initial Cr (VI) concentration and contact time on the percentage removal of Cr (VI) is shown in figure. From the plots it can be seen that, the increase in initial Cr (VI) concentration resulted in reduction in % removal of Cr (VI), while the increase in contact time increased the % removal of Cr (VI). The plots also showed that at lower solution pH value, the variation in contact time has more effect on the % removal of Cr (VI) than the initial metal concentration.

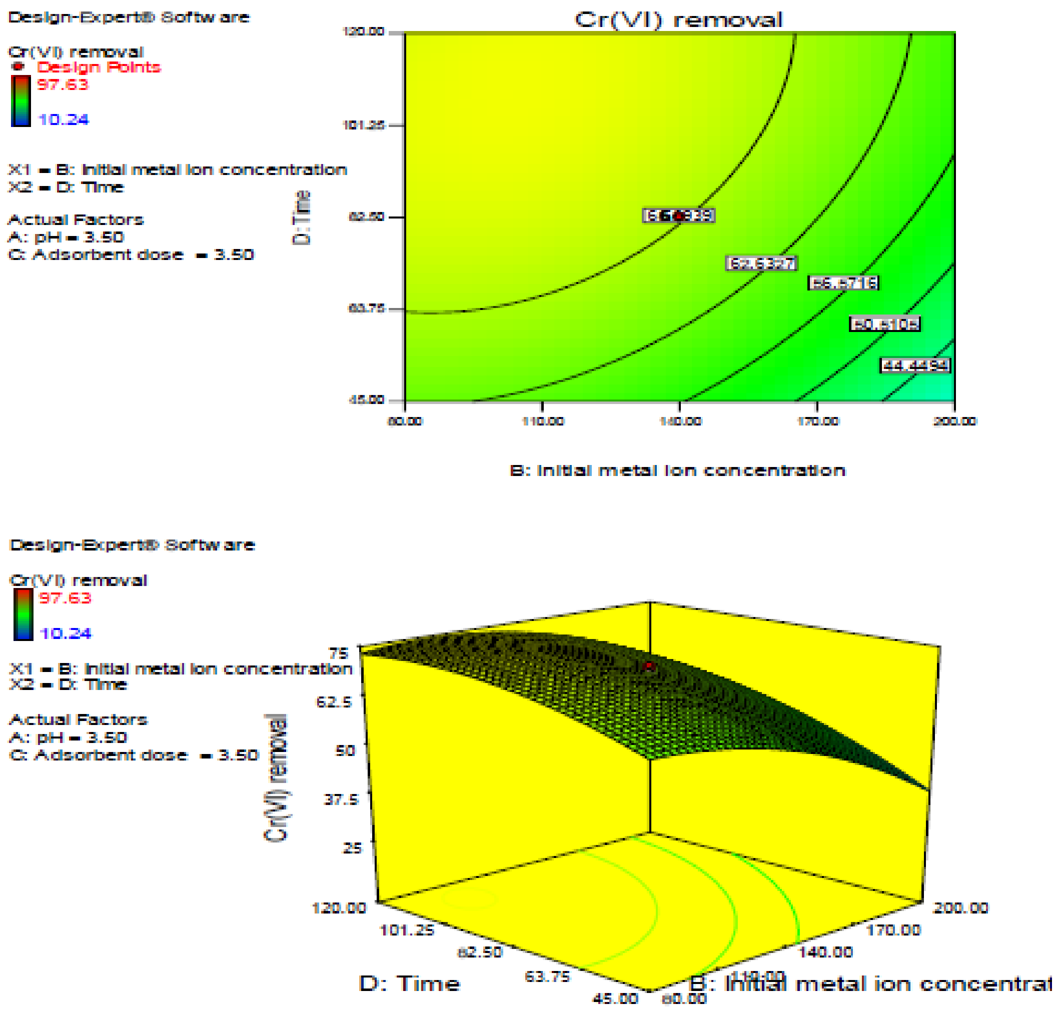


Figure 4:17 the interaction effect of initial Cr (VI) concentration and contact time on the percentage removal of Cr (VI). Contour plot and 3D plot respectively.

4.6.3 Numerical optimization

The optimum conditions for four factors were determined using the numerical optimization feature of the Design expert software. The software searched for a combination of factors that simultaneously satisfied the requirements placed on the response and each of the factors. Table 4.8 shows the optimum working conditions (ultimate goals, high and low limits) of the response (% removal of Cr (VI)) and factors (solution pH, biosorbent dose, and initial Cr (VI) concentration and contact time) employed during the optimization analysis. In view of the increasingly stringent effluent discharge limits, the targeted criterion was maximized for % removal of Cr (VI) while the values of solution pH, biosorbent concentration, initial Cr (VI) concentration and contact time were set in the ranges studied. The optimum conditions obtained were then evaluated by the composite desirability, which has a value from 0 to 1, to determine the degree of satisfactory of the optimum conditions for the ultimate goal of response. Table presents the optimum conditions in uncoded values.

Top alternatives for Design -Expert softwares

- **Sigma XL :** a powerfull but easy to use Excel Add-in , that will enable you to measure, analyze, improve and control your processes.
- **Statgraphics centurion :** acess and utilize a wide range of statistical procedures from summary statistics to design of experiments in an intuitive interface.
- **Intellectus statistics :** provide statistcs software where students understood their analysis and it was easy to use.
- **Tableau :** helps people see and understand data. It delivers fast analytics, visualization and business intelligence.
- **JMP statistical software :** JMP, data analysis software for scientists and engineers , links dynamic data visualization with powerfull statistics , on the desktop.

Table 4.8 optimization condition of all factors

Constraints						
		Lower	Upper	Lower	Upper	
Name	Goal	Limit	Limit	Weight	Weight	Importance
PH	is in range	2	5	1	1	3
Initial metal concentration	is in range	80	200	1	1	3
adsorbent dose	is in range	2	5	1	1	3
Time	is in range	45	120	1	1	3
Cr(VI) removal	maximize	19	99	1	1	3

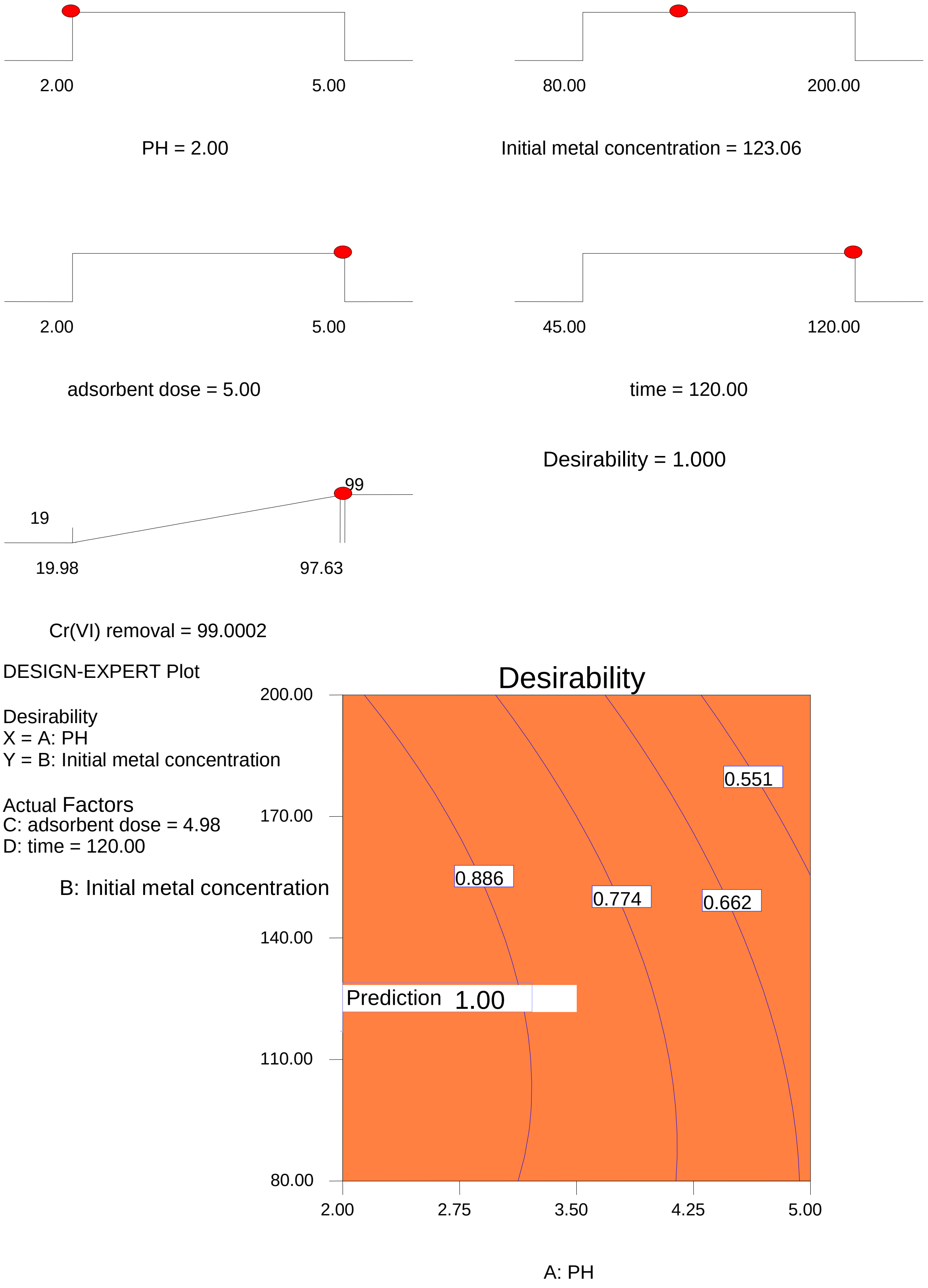


Figure 1:18 **optimization Result with Desirablity 2D plot and 3d plot respectively**

4.6.4 Validation of Experimental optimization

In order to verify the optimization results, an experiment was performed under predicted conditions by the developed model. Which give the highest composite desirability (1.00) from the Design expert software. The predicted (99.036 %) at pH –2.0, concentration – 123.06 mg/L, adsorbent dose – 5.0 g/L and time 120 min and the experimental result of (97.63 %) removal of Cr (VI) under the optimum conditions are presented with small deviation, i.e., 1.046%, between the predicted and experimental values of % removal of Cr (VI) indicates that the model equation is suitable and sufficient to predict the Cr (VI) biosorption process using the acid treated coffee husk in the range of variables studied.

Response	Prediction	SE Mean	99% CI low	99% CI high	SE Pred	99% PI low	99% PI high
Cr(VI) removal	99.036	5.84	81.82	116.25	11.08	66.37	131.7

4.7 Applicability to Industrial waste water

Biosorption process coupled with the produced activated coffee husk for removal of chromium undertaken with an actual effluent containing Chrome collected from Hawassa industrial park. Chrome tanning effluent had a P^H of 4.25 and 1502.5 mg/lt chromium concentration which was measured before application.

In order to observe the efficiency of coffee husk activated carbon, the effluent was digested with sulfuric acid then it was filtered through whatmann no. 41 filter paper. The solution was dissolved at the optimized contact time-120 min, at optimized PH value – 2 including initial P^H value of the waste water which is 4.25g/l and at equilibrium condition of the activated carbon dose-5,and with actual adsorb ate solution. Finally the solution was subjected to atomic adsorption spectroscopy for extraction of chromium as Cr (VI).

Figure 4:19 shows the percentage adsorption of chromium on coffee husk activated carbon increasing in time with the optimized parameters in aqueous solution. The biosorption capacity showed a rapid increase up to 90 minutes then proceeds slow increase until reached the maximum at 120 minutes with 93.40 % removal of Cr (VI).

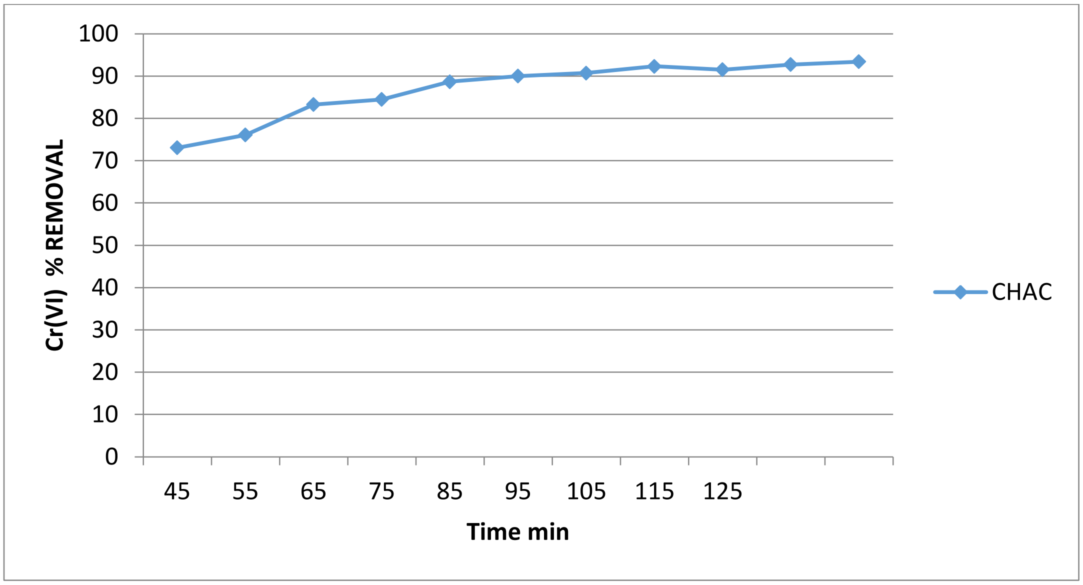


Figure 4:19 effect of contact time on cr(VI) conc. From actual effluent on optimum condition of pH- 2 and adsorbent dosage of 5g/l

From the figure above the biosorption of chromium (VI) after reaching the optimum time and the result obtained from the aqueous solution is almost similar only with a little bit difference.

4.7.1 Industrial adsorption separation processes

4.7.1.1 Types of adsorption separation processes

Industrial adsorption processes may be classified in three different ways, as regards to:

- Sorbate concentrations,
- modes of operation,
- Adsorbent regeneration methods

It must be emphasized at this point that these classifications are established only to help the understanding of the several aspects involved in any adsorption process, giving only qualitative references to guide the comprehension of the important differences in industrial adsorption processes.

Sorbate Concentrations

Adsorption separation processes may be classified in purification processes (if the process only removes trace contaminants from a process stream), and bulk separation processes (if more than one component is to be recovered selectively from a mixture in high concentrations). Table presents some processes of each type.

Table 4.9: Adsorption Industrial applications

Adsorption industrial applications

Bulk separation processes	Purification processes
Normal Paraffin, isoparaffins, aromatics	Organics/vent streams
N_2/O_2	Water/natural gas, air, syn gas
CO, CH_4, CO_2, N_2	Sulfur compounds/natural gas, hydrogen, LPG
Acetone/vent streams	Solvents/air
Ethylene/vent streams	Odors/air
Water/Ethanol	Nox/N_2
p-xylene, o-xylene, m-xylene	SO_2/vent streams
p-diethylbenzene/isomers mixture	Water/organics, oxygenated organics, chlorinated organics
fructose, glucose	Odor, taste bodies/drinking water
detergent range oleffins/paraffins	Sulfur compounds/organics
	Decolorizing petroleum fractions, sugar syrups, vegetable oils, etc.

Modes of Operation

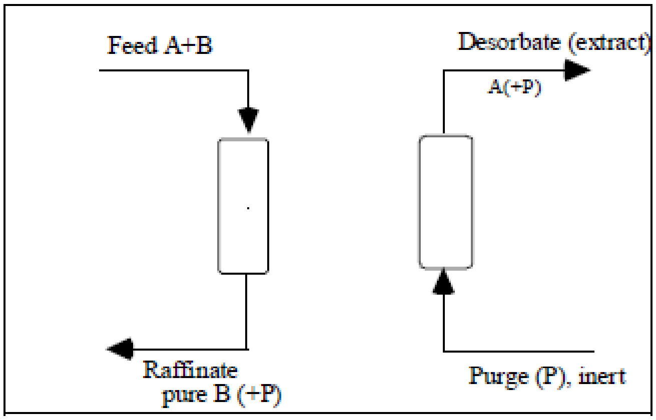
Adsorption processes may also be classified as

- Cyclic batch,
- Continuous counter-current, and
- Chromatographic.

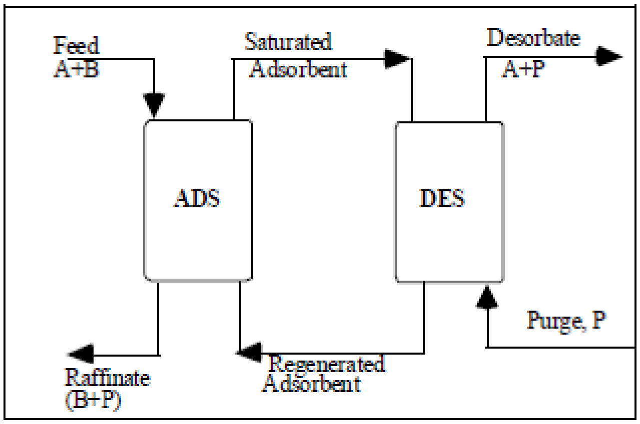
The batch process is the intuitive way of using adsorption phenomena in a process. The feed stream is percolated through a fixed bed containing the adsorbent until saturation with the most adsorbed compound after saturation; the adsorbed compound is purged using temperature, pressure or inert displacement.

In order to maximize mass transfer within the system and reduce cycle turn-over lost time, a continuous counter-current process may be devised adsorbent around the two beds, it may be submitted continuously to the adsorption and desorption steps at the same time. This was first proposed in the Hyper sorption process (86) some decades ago, but was discontinued due to problems with the solids circulation.

A convenient way to avoid the solids circulation is by simulating counter-current fluxes in a fixed bed of adsorbent (simulated moving bed). This can be done by changing the injection and withdrawing points throughout the system at given time intervals (87). The time intervals can be made as short as possible thus providing a good approach to the real continuous counter-current process. Figure shows a scheme for the simulated moving bed concept.

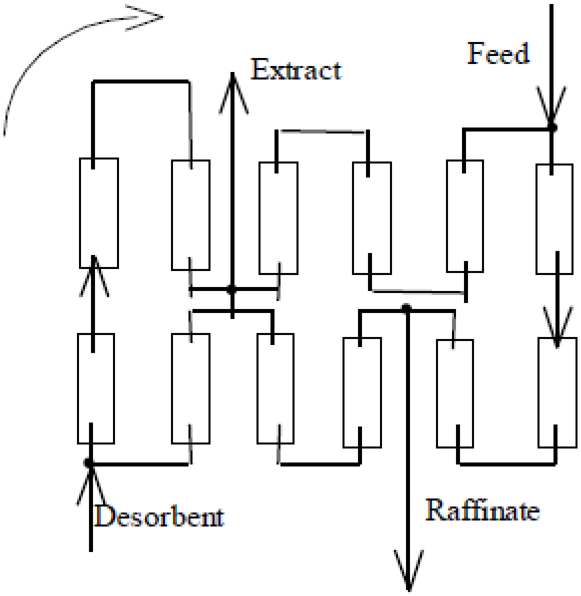


Cyclic batch processes



Continous counter current processes

A third operation mode is that in which the feed stream is introduced as a pulse in a purge stream, similarly to gas or liquid phase chromatography. Chromatographic processes try to reproduce, in commercial scale, the component separations that are observed in laboratory chromatography. This method has been proposed for xylenes separation (86) and was operated in pilot scale. The method has been applied for small scale production (up to 1 ton/day) of fine chemicals (88). Large scale operation of the chromatographic mode suffers, of course, limitations due to severe undesirable effects of axial dispersion as feed throughput increases.



Simulated moving bed

Adsorbent regeneration methods

The use of physical adsorption becomes more attractive (being essentially a reversible process), because it may be possible to regenerate the adsorbent with the usage of an agent (physical or chemical) that change the equilibrium conditions. Regeneration methods more commonly employed are

- Temperature swing adsorption (TSA);
- Pressure swing adsorption (PSA);
- Desorbent displacement;
- Purge with inert

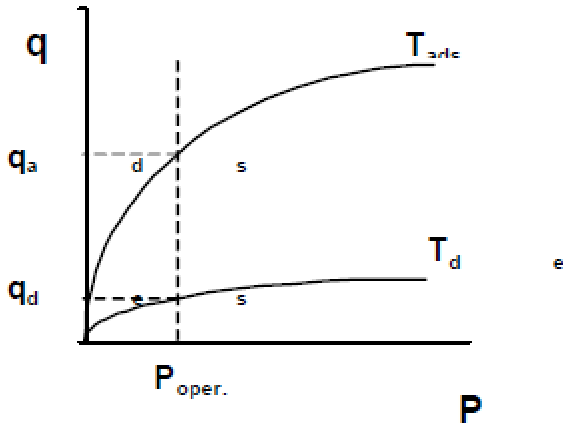
Table summarizes the main advantages and disadvantages of each method. TSA processes normally operate in cyclic batch mode and their operating principle is shown in Figure 4. They usually consist of at least two adsorbent beds, one adsorbing while the other one is regenerating. It is typically used for removal of strongly adsorbed species, normally along with other regeneration method such as inert purge or low pressures. Main applications are refinery gases drying, solvent recovery and natural gas sweetening.(89) points out concisely design conditions of adsorbent beds for gas drying, as regards to equilibrium isotherms, purge flow rates and concentration and temperature fronts within the adsorbers.

PSA processes are also typically cyclic batch processes and their operating principle is shown in Figure 5. For the same temperature, the amount adsorbed decreases with decreasing partial pressure of the sorbate in the fluid phase. Unsuitable for rapid cycling so adsorbent cannot be used with maximum efficiency

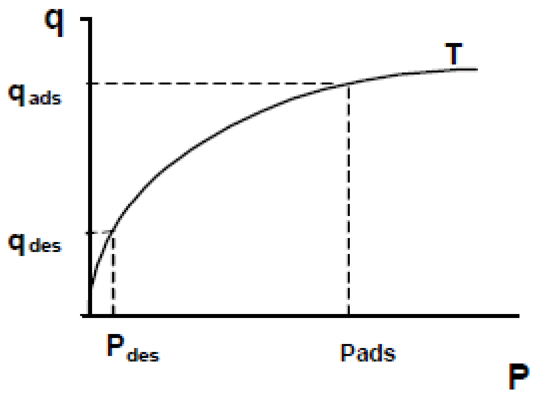
Table 4.10: adsorbent regeneration methods

Methods	Advantages	Disadvantages
TSA	Good for strongly adsorbed species; small change in T gives large change in q Desorbate may be recovered at high Concentration Gases and liquids	Thermal aging of adsorbent Heat loss means inefficiency in energy usage Unsuitable for rapid cycling so adsorbent cannot be used with maximum efficiency In liquid streams high latent heat of intersticial liquid must be added
PSA	Good where weakly adsorbed species is required in high purity Rapid cycling efficient use of adsorbent	Very low P may be required Mechanical energy more expensive than heat Desorbate recovered at low purity
INERT PURGE	Operation at constant T and P	Large purge volume required
Desorbent displacement	Good for strongly held species Avoids risk of cracking reactions during regeneration Avoids risk of cracking reactions during regeneration Avoids thermal aging of adsorbent.	Product separation and recovery needed (choice of desorbent is crucial)

As pressure can be changed much faster than temperature, PSA processes can be used in much faster cycles than TSA processes thus enabling higher throughputs for the same volume of adsorbent. Their main limitation is for strongly adsorbed species which would require very low pressures for desorption (high vacuum) and increasing unit operating costs. PSA main applications are listed in Table. A full review of PSA processes and their modeling has been presented by (86).



TSA principle of operation



PSA principle of operations

PSA main applications

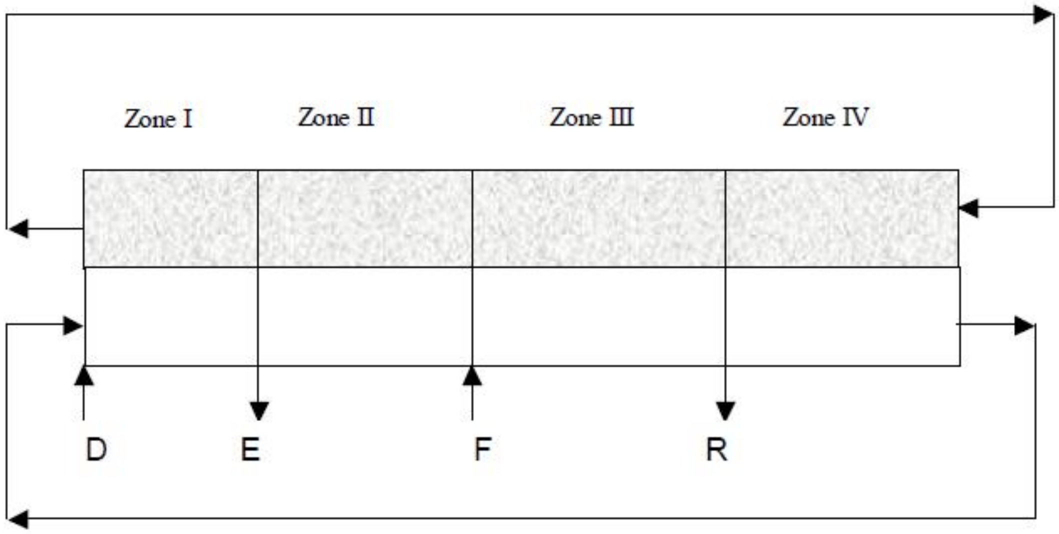
Process	product	aadsorbent
H2 recovery from fuel gas	ultrapure H2	Activated carbon or zeolite
Heatless drier	Dry air (for instruments)	Activated alumina
Air separation	O2 (+Ar)	5A Zeolite
Isosiv	N2 (+Ar)	Carbon Molecular Sieve
Air separation	Linear/Branched Hydrocarbons	5A Zeolite
Landfill gas separation	CO2 and CH4	Carbon Molecular Sieve

Another way of regenerating the adsorbent is by sorbate displacement with a third compound (desorbent) that may also be preferentially adsorbed. To be effectively used, it is imperative that the desorbent have similar affinity to the adsorbent as the adsorbed compound of the feed. It has the advantage of avoiding the need of high temperatures or very low pressures for desorption, but requires further separation of the sorbate and desorbent, normally by distillation. For instance, in p-xylene separation from a mixture of aromatics C8, toluene or p-diethylbenzene may be used as p-xylene desorbent and easily separated by distillation.

Moving Bed Adsorption Processes

Moving Bed processes are typically continuous countercurrent processes and may be schematically represented as in Figure. In this sketch the fluid phase flows clockwise while the solid phase flows in the other direction. Feed F (containing species A and B) is introduced at the center of the sketch. In zone III, the most strongly adsorbed species B is adsorbed onto the solids from the feed mixture of A and B, so A is withdrawn at the end of zone III (raffinate stream R). In zone I, B must then be displaced from the solid phase coming from Zone II by desorbent D which is injected at the beginning of zone I. So the extract stream E is taken out at the end of Zone I rich in species B. Zones II and IV act as buffer zones to avoid contamination of the extract stream by A (zone II) or of the raffinate stream by B (zone IV). However, since actual solids circulation can be a cumbersome task, commercial processes normally operate using Simulated Moving Bed schemes, such as shown in Figure. UOP (Universal Oil Products) has developed in the last 30 years several successful commercial SMB processes, to separate products such as: n-paraffin/iso-paraffin mixtures UOP’s Molex®), glucose/ fructose (UOP’s Sarex®), paraffin/olefin, mostly propane and propylene (UOP’s Olex®) and xylene mixtures, mostly p-xylene/m-xylene (UOP’s Sorbex®), with at least 115 licensed units around the world (90). More recently, small scale applications have been developed in biotechnology, pharmaceuticals and fine chemistry (91-96), for products such as proteins, antibodiesand chiral compounds (e.g. thalidomide, epoxides, and naphtols).

Solids circulations



Liquids circulations

Sketch of moving bed process with 4 zones

Modeling of moving bed adsorption process

The modeling of moving bed processes may follow two approaches: the TMB (true moving bed) model and the SMB (Simulated Moving Bed) model. The TMB model is the limiting case for the SMB model for the case of infinite stages. Both models will be presented and results will be compared for xylenes in adsorption on Y zeolite.

True Moving Bed Model

TMB model, although not rigorously equivalent to the real SMB unit, may be useful for quick estimates or for initial data for the more rigorous SMB model. The column balance is shown in Equation 1:

$$\varepsilon\frac{\partial \mathrm{C_i}}{\partial_{\mathrm{t}}} + (1-\varepsilon)\frac{\partial C_p}{\partial_t} = \varepsilon D_L\frac{\partial^2 C_i}{\partial z^2} - \varepsilon v\frac{\partial C_i}{\partial z} + (1-\varepsilon)u\frac{\partial C_p}{\partial z} \qquad \mathbf{23}$$

where v are u are fluid and solid velocity, respectively, Cl and Cp are fluid phase and solid phase concentrations, respectively,Ɛ is bed porosity and DL is axial dispersion

mass balance in the solid particle may be written as

$$u\frac{\partial C_{pij}}{\partial z} + k(q_{ij} - C_{pij}) = \frac{\partial \mathrm{C}_{pij}}{\partial t} \qquad \mathbf{24}$$

In which q is the average solid pase concentration in the solid phase particle.

The initial and boundary conditions are :

$$C_{ij}(z,0) = C_{oi}(z), at\ t = 0$$

$$v.c_{lij}^{F} = v.C_{lij} - \varepsilon . D_{AX} \frac{\partial C_{lij}}{\partial z}, at\ z = 0$$

$$\frac{\partial C_{lij}}{\partial z} = 0\,, \qquad at\ z = L_j$$

$$C_{pi}^{j} = C_{pi}^{j+1}$$

Mass balance at the nodes :

Eluent: $C_{li}^{(1,0)} = \frac{Q_4 . C_{li}^{(4,L)} + Q_E . C_{li}^{E}}{Q_4 + Q_E}$ **25**

Extract: $C_{li}^{(2,0)} = C_{li}^{(1,L)}$ **26**

Feed: $C_{li}^{(2,0)} = \frac{Q_2 . C_{li}^{(2,L)} + Q_F . C_{li}^{F}}{Q_2 + Q_F}$ **27**

Raffinate: $C_{li}^{(4,0)} = C_{li}^{(3,L)}$ **28**

Q is the flow rate at each zone or at inlet and outlet of the column. Almeida (1998) used the orthogonal collocation method in finite elements with algebraic-differential approach to solve this model, using Butt’s correlation (1980) for axial dispersion (Eqs. 5a and 5b), Gluekauf’s approximation (1955) for internal particle mass transfer coefficient (Eq. 6) and Wilson and Geankoplis’ correlation (1966) for external film mass transfer coefficient (Eq. 7).

$\varepsilon . Pe = 0,2 + 0,011 . R^{0.48}$ **29**

Pe $Pe = \frac{v . d_p}{\varepsilon . D_{AX}}$ **30**

$K_i = \frac{5.D_m/\tau}{R_p}$ **31**

$sh = \frac{k_e\, d_p}{D_m} = \frac{1,09}{\varepsilon} Re^{0,33} . sc^{0,33}$, **32**

Full details of parameter investigation regarding switch time (or fluid/solid relative velocity, feed flow rate , extract flow rate and number of columns per zone may be found in Almeida (1998), in which results are compared for a system of chiral bi-naphtol reported by (91). A general comment is that best operating conditions are very narrow, requesting therefore good operating controls for ideal operation of the industrial unit. This model was also recently used for evaluation of the xylenes separation in Y zeolite, using data obtained previously in our laboratory (97), obtaining p-xylene recoveries of 97.5%wt with 99.6%wt purity (98), quite close to values observed in industrial units.

Simulated Moving Bed Model

The Simulated Moving Bed model (SMB) uses the same mass balance equations as for a single fixed bed Desorbent node: column (Eqs. 8–10), only periodically modifying the boundary conditions (inlet and outlet of feed, desorbent, extract and raffinate), to simulate the solids motion throughout n fixed beds in series. A FORTRAN computer code was implemented in (Azevêdo et al., 1997) with inputs of equilibrium, kinetics and physicochemical data. Other inputs are relative positions of feed, desorbent, extract and raffinate streams. At given time intervals, each stream moves one bed forward at the same direction of the liquid flow in the system. Further details may be found in Azevêdo et Raffinate: Almeida (1998) used the orthogonal collocation method in finite elements with algebraic-differential al. (1997).

$$-K_{L,j}\left(C_{e,j} - C_{i,j}\right)\frac{3}{r_p}(1-\varepsilon_e) \qquad \textbf{33}$$

$$\varepsilon_i \frac{\partial C_{i,j}}{\partial t} = K_{L,j}\frac{3}{r_p}\left(C_{e,j} - C_{i,j}\right) - \rho_s(1-\varepsilon_i)\frac{dq_i}{dt} \qquad \textbf{34}$$

$$\frac{\partial q_j}{\partial t} = \sum \frac{\partial f_{eq}\,(C_{i.l})}{\partial C_{i,l}}\frac{\partial C_{i,l}}{\partial t} \qquad \textbf{35}$$

Equilibrium was represented by the multi component langmuir equation

$$f_{eq}(C_{i,j}) = \frac{q_{mj}K_jC_{i,j}}{1+\sum K_iC_{i,l}} \qquad \textbf{36}$$

Initial and boundary conditions at each fixed bed are:

$$uC^F_{e,j} = uC_{e,j} - \varepsilon_e D_L \frac{\partial C_{e,j}}{\partial z}|o,\ z = 0, t > 0 \qquad \textbf{37}$$

$$\frac{\partial C_{e,j}}{\partial z}|\,L = 0 \quad z = L, \qquad t > 0 \qquad \textbf{38}$$

$C_{e,j}(z,0) = C^0_{e,j}(z)$ $\qquad$ t = 0. $z > 0$

$C_{i,j}(z,0) = C^0_{ii,j}(z)$ $\qquad$ t = 0, $z > 0$

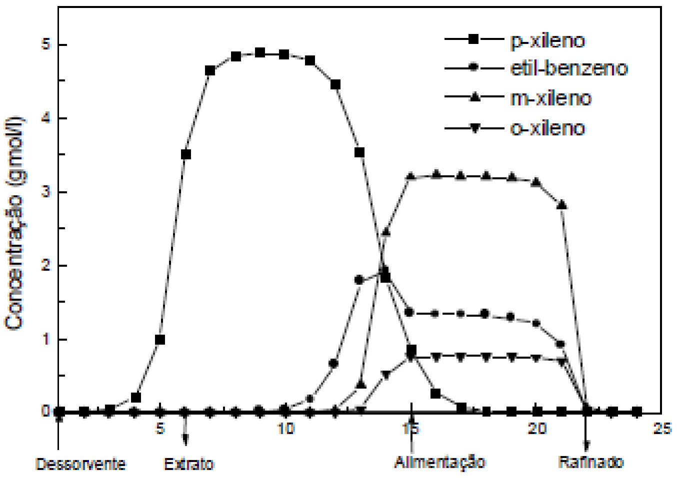
$q_j(z,0) = q^0_j(z)$ $\qquad$ t = 0, z > 0

This set of equations describes the process at each of the n beds used in the system. So, given the initial concentration profiles throughout all the beds of the SMB, one may simulate the adsorption dynamics within all the system. For each bed, the inlet fluid concentration, CFe,j, is exactly the same as the fluid concentration at the outlet of the previous bed, except in the nodes of feed and desorbent. For these nodes, the balance is given by:

Feed: $C_{e,j1}^{I} = C_{e,j,n}^{IV} + C_{e,j}^{eluente}$ **39**

Desorbent node: $C_{e,j,1}^{I} + C_{e,j}^{eluente}$ **40**

This model was used to simulate the xylenes separation by adsorption in SMB. Again, correlations given by Eqs. 5-7 were used to estimate axial dispersion, external film mass transfer coefficient and internal mass transfer coefficient. Again, experimental data obtained previously in our laboratory (Lima et al. 1996; Cavalcante Jr. et al., 1997; Guimarães, 1997) were used. The concentrations profile inside the column at steady-state is shown in Figure 7. This steady-state situation was achieved after 25 complete cycles around the column, starting with pure desorbent full inventory of the system. The obtained profile is comparable to what has been reported for pilot plant operations with a similar system (Rossett et al., 1978). Purities as high as 99%wt in the extract stream and 97%wt in the raffinate stream were observed (Azevêdo et al., 1997).



Concentrations profile inside the SMB system for xylenes with Y zeolite (Azevêdo et al., 1997)

5. CONCLUSION AND RECOMMENDATION

5.1 conclusions

This study mainly focused on developing a low cost and effective biosorbent for Cr (VI) removal from aqueous solution. Among many biosorbents, coffee husk was selected and treated with easily available chemicals and physical activation (size reduction and activated carbon). To observe the variation in percentage removal of Cr (VI) was subjected to different experimental conditions like PH, biosorbent dose, contact time and initial metal ion concentration. Furthermore chemical composition, surface charge (point of zero charge) and activation of biosorbent was investigated. The correlation between experimental data for different parameters was assessed using biosorption isotherm models and biosorption kinetics models.biosorption model generation and analysis of interaction of biosorption process parameters on percentage removal of Cr (VI) using Design expert software. Finally, application to industrial waste water

- Chemical composition analysis indicated that the biosorbents contain cellulose and lignin.

- Results from batch biosorption experiments indicated solution pH, biosorbent dose, initial Cr (VI) concentration, contact time and the chemical activation affected biosorption of Cr(VI) ions. The percentage removal of Cr (VI) ions increased with increasing contact time and biosorbent concentration and decreasing solution pH and Cr (VI) concentration.

- The results showed that the removal increased, as decreasing pH and increasing the adsorbent dose and contact time.

- The kinetic results obtained from this study fitted well with the pseudo second order kinetic model and the equilibrium biosorption capacity (q_{eq}) calculated based on the pseudo second order kinetic model showed good agreement with the biosorption capacity obtained from experimental results.

- The biosorption equilibrium isotherm data conformed well to the Langmuir isotherm model for coffee husk activated carbon ($R^2 = 0.8732$) indicating the biosorption of Cr (VI) ions by CHAC followed a monolayer pattern.

- The rate limiting step was the biosorption of Cr(VI) by the binding sites within the pores.
- The results from the statistical analysis of the biosorption process using the response surface methodology revealed that the biosorption process using CHAC can be represented by a quadratic regression model based on the determination coefficient of $R^2=0.9989$ and adequate precision ratio of 123.04.

- The ANOVA analysis showed that the removal of Cr (VI) ions is highly affected by the solution pH, the biosorbent concentration, the initial Cr (VI) concentration, contact time and the interaction between the solution pH with initial Cr (VI) concentration, the biosorbent dose with contact time, initial Cr (VI) concentration with contact time and initial Cr (VI) concentration with biosorbent dose.

Thus this research has demonstrated that coffee husk activated carbon yields a better Cr (VI) removal efficiency from aqueous solution. And biosorption experiments can be effectively modeled using response surface methodology.

5.2 Recommendations

For a low-cost waste material, Biosorbent prepared from coffee husk has shown good potential in removing Cr (VI) ions from aqueous solution. Thus in order to further investigate its effectiveness the following studies could be carried out

- Investigation on the application of the biosorbent to remove other heavy metal ions from synthetic and actual waste water in a single metal and multiple metal systems.

- Investigate on the desorption kinetics and the reusability of the biosorbent.

- Analyze the BOD and COD of the effluent after treatment.

- Conduct column studies and explore the possibilities of developing a pilot or even an industrial process unit for the effective removal of heavy metals from aqueous solutions using coffee husk.

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