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INVESTIGATION OF THE ADSORPTION PERFORMANCE OF ACID TREATED LIGNITE COAL FOR Cr(VI) REMOVAL FROM AQUEOUS SOLUTION

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Declaration

I the undersigned declare that this Thesis is my original work and has not been presented for any degree in any university and all the resource of materials used for the Thesis have been duly acknowledged.

Regassa Beksissa _____

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List of Acronyms

AC	Activated Carbon
ALC	Acid treated Lignite Coal
CEC	Cation Exchangeable Capacity
DOE	Design Of Expert software
DPC	Diphenylcarbazide
EPA	Environmental Protection Authority
FTIR	Fourier Transform Infrared Spectrophotometer
GFFD	General Full Factorial design
LC	Lignite Coal
RPM	Rotation Per Minutes of agitation speed
RSM	Response surface methodology
UV-vis	Ultra violate visible spectrophotometer
WHO	World Health Organization

Abstract

The presence of heavy metals in aqueous streams arising from the discharge of industrial effluents into water bodies is one of the most important environmental issues because of their toxic nature and its removal is highly essential. This paper deals with the adsorption studies for the removal of hexavalent chromium ions from aqueous solutions using acid treated lignite coal as adsorbent. The collected samples were stage crushed and sieved to a wide particle size range of (250-500µm) and washed using hydrochloric acidic solution to remove any inorganic ash material for production of adsorbent. Preliminary investigation of proximate analyses for raw lignite coal and acid treated was done. The adsorption study was evaluated as the function of initial chromium(VI) concentration, adsorbent dosage and pH. Batch experiments were conducted using artificial wastewater containing Cr(VI). The effects of independent variables on various initial Cr(VI) concentrations between 20 mg/l and 100 mg/l were evaluated. A Cr(VI) removal efficiency of 98 % was achieved at pH 1 with 3.5 g of acid treated lignite in 200mL of solution at 4 hours contact time using initial Cr(VI) concentration of 20 mg/l. Adsorption of Cr(VI) ions was highly pH-dependent and the results showed that the optimum pH for the removal was found to be pH 1. The equilibrium adsorption isotherm (Langmuir and Frendlich) and adsorption kinetic models (first and second order) were evaluated using experimental data. Frendlich isotherm model and second order kinetic model were better for the description of acid treated lignite coal for the adsorption of Cr(VI).

Keywords: *Cr(VI) Adsorption, Acid treated Lignite Coal, Equilibrium Isotherms, Kinetics.*

1. Introduction

1.1 Background

From different environmental issues, pollution by heavy metals of surface water, ground water and soil in urban areas are the major environmental problems. Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products. The presence of heavy metal ions is of major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, paint, radiator manufacturing, smelting, alloy industries and storage batteries industries. The most common and harmful heavy metals are mercury, lead, copper, nickel, chromium and zinc. They are stable elements that cannot be metabolized by the body and get passed up in the food chain to human beings. When waste is disposed into the environment, a further long- term hazard is encountered (Ibrahim Olaniyi,2011).

Chromium (Cr) is considered an essential nutrient and a health hazard. How is this possible? The answer is that Cr exists in more than one oxidation state. Specifically, Cr in oxidation state +6, written as Cr(VI), is considered harmful even in small intake quantity (dose) whereas Cr in oxidation state +3, written as Cr(III), is considered essential for good health in moderate intake (Jacques Guertin, 2004). Chromium(VI),is one of many well-known heavy metals that are known to be toxic and poisonous even at low concentrations. Since chromium(VI), does not decay, degrade, and cannot be destroyed, remediation of its contamination is the only option. Toxicity and carcinogenicity are the two significant phenomena that chromium(VI),has as a heavy metal. Chromium(VI),toxicity depends on various factors, but mainly depends on pH (Hyder, A. H. M. G., 2013).

In the environment, the level of chromium concentration has increased as a consequence of different human activities. Chromium contamination in the environment has been detected for several years from its primary industrial applications. In recent years, major chromium contamination has been found in many developed and developing countrieswhereits industrialapplication is common. The worst chromium poisoninghas been noted in

areaswhereelectroplating,tannery, automobile,pigments,paper andpulp, fertilizer, textile, steel, and metalfinishing industries are frequentlylocated (Ibrahim Olaniyi, 2011).The increasing awareness of the environmental consequences arising from heavy metal contamination of the aquatic environment has led to the demand for the treatment of industrial wastewater before discharge into the aquatic environment (Ibrahim Olaniyi,2011).

Thus, treatment of this polluted liquid is recognized as one of the most burning issues. Many processes for the removal of heavy metals from water and wastewaters have been proposed. Amongst these removal methods, chemical precipitation, coagulation, physical treatment such as ion exchange, membraneseparation, and activated carbon adsorption are some of the processes that have been reported to be the most effective (Huang; Wu. M.H.,1975).

Therefore, there is currently a need for new, innovative and cost effective methods for their removal of toxic substances from wastewaters. Lignite coal usedas anadsorbent isan effective andversatilemeans and can be easily adopted in low cost to remove Cr(VI), metals from wastewaters.

1.2 Statement of problems

Chromium discharges from industries effluent in Ethiopia are above the permissible standards and it is one of the most toxic metals to plants, animals and microorganisms (Ethiopia EPA, 2001). Even in low concentrations, it has a toxic effect upon aquatic biota such as fish, thus disturbing the food chain for fish life, cause soil salinity in irrigated farm land and possibly inhibiting photosynthesis in aquatic organisms in river (Tadesse Alemu,2010). However, treatment of tannery chromium-rich effluents by primary treatment systems such as; biological, oxidation or physico-chemical processes still leaves chromium levels in the treated wastewater above the legal discharge limit for surface waters (Alves *et al.*, 1993; Assaye Ketema, 2009).

In view of the above circumstances, the development of suitable treatment systems for hexavalent chromium removal from industrial wastewater appears to be the most promising option. The treatment options should be effective, reliable, and affordable for chromium removal from wastewater. In Ethiopian due to the indiscriminate discharge of waste waters containing heavy metal ions by small, medium and large scale industries have posed a serious challenge.

These industries lack the financial muscle to engage the use of conventional methods of treatments such as ion-exchange resins, precipitation, chemical coagulation, sedimentation and conventional biological treatment (activated sludge) which are quite effective but unattainable for small and medium scale industries because of the prohibitive cost (Huang; Wu.M.H, 1975). However, most of the above mentioned treatment technologies have limitations which include (Hyder**A.** H. M. Golam, 2013):

Generation of toxic sludge,

Increased over all cost of the process due to treatment, handling, and disposal of sludge,

High operational and maintenance expenditure,

Negative impact on water quality parameters,

Requirement of additional chemical.

Thus, the most important measure needed to prevent further environmental pollution of chromium by developing effective treatment methods to remove chromium before discharged to the environment or contaminated water and soils (Hyder, A. H. M. G., 2013).

Hence, it is expedient to seek alternative methods of removing heavy metal ions from wastewaters by using locally available cheap raw material like lignite coal. wide variety of material for activated carbon have been studied for adsorption of removing Cr(VI) from wastewater. Most of the researches on adsorbent as activated carbon development were on agricultural waste, and with few on industrial waste, petroleum residue and coals. However, as a locally available and low cost natural carbonaceous raw material adsorbent, Ethiopian lignite has rarely been investigated. In this present study, acid treated lignite coal produced from Yayo lignite coal was used as adsorbent to evaluate its performances for Cr(VI) removal from aqueous solution.

1.3 Objectives

1.3.1 General objective

The main objective of this study is to evaluate the performance of locally available, low-cost, acid treated lignite coal adsorbent for Cr(VI) removal from aqueous solution.

1.3.2 Specific objective

- ✓ To analyze and compare the proximate composition of the raw Ethiopian lignite coal and acid treated lignite coal adsorbent,
- ✓ To study the adsorption capacity of acid treated lignite coal for Cr(VI) metal ions from aqueous solution,
- ✓ To investigate the effect of selected process variables (pH, initial Cr(VI) ions concentration, and adsorbent dosages) on the adsorption performance of acid treated lignite coal,
- ✓ To determine the optimum adsorption behavior of adsorbents using response surface methodology,
- ✓ To investigate the surface functional groups of acid treated fresh lignite and used adsorbent using FTIR, and
- ✓ To investigate Cr(VI) ions adsorption isotherm (Langmuir and Freundulich Model) and kinetic (Pseudo first order, second order) study on acid treated lignite sample.

1.4 Significance of the study

There are large numbers of method for treatment of effluent with regard to heavy metals. Recently, new technologies involving the removal of toxic metals from wastewaters have directed attention to adsorption, based on metal-binding capacities of various materials. All except locally available raw material activated carbon have been found to be expensive and may not be suitable for developing countries like Ethiopia (Olayinka, *et al*.,2007). The main reasons to give much attention to this method is the major advantages of adsorption cost, the materials are cheap and widely available, minimization of chemical and/or biological sludge, no additional nutrient requirement, simple process, no daily dosage of chemicals, activated carbon has large specific surface area, pore size distribution and the presence of different functional groups on its surface. and the possibility of metal recovery and recycling of adsorbet

metals from adsorbent (Ibrahim Olaniyi, 2011). Therefore, it is necessary to investigate and develop adsorbent as activated carbon from lignite coal that is inexpensive and highly capable of removing Cr(VI) metal ions by adsorption.

2. Literature review

2.1 General description of chromium in environment

Chromium(Cr) is a naturally occurring element present in the earth's crust, with variable oxidation states. The most common oxidation states of chromium are 0, +2, +3 and +6 with +3 being the most stable. But only three oxidation states are found in nature; these are: Cr(0) which occur in metallic form, Cr(III) in chromic compounds and Cr(VI) occurs as soluble chromate(CrO_4^{2-})and dichromate ($Cr_2O_7^{2}$) compounds (Jacobs JA**.;** Testa SM.,2005). Chromium compounds are stable in the trivalent [Cr(III)] form and occur in nature in this state in ores, such as ferrochromite. The hexavalent [Cr(VI)] form is the second-most stable state next to lead (Baig*et al*.,2003). Elemental chromium [Cr(0)] does not occur naturally. Chromium enters into various environmental matrices (air, water, and soil) from a wide variety of natural and anthropogenic sources with the largest release coming from industrial establishments. Industries with the largest contribution to chromium release include metal processing, tannery facilities, chromate production, stainless steel welding, and ferrochrome and chrome pigment production. The increase in the environmental concentrations of chromium has been linked to air and wastewater release of chromium, mainly from metallurgical, refractory, and chemical industries. Chromium released into the environment from anthropogenic activity occurs mainly in the hexavalent form [Cr(VI)] (U.S. Department of Health and Public Health Service,1992). Hexavalent chromium [Cr(VI)] is a toxic industrial pollutant that is classified as human carcinogen by several regulatory and non-regulatory agencies (International Agency for Research Center, 1990). The health hazard associated with exposure to chromium depends on its oxidation state, ranging from the low toxicity of the metal form to the high toxicity of the hexavalent form. All Cr(VI)-containing compounds were once thought to be man-made, with only Cr(III) naturally ubiquitous in air, water, soil and biological materials. Recently, however, naturally occurring Cr(VI) has been found in ground and surface waters at values exceeding the World Health Organization limit for drinking water of 50 µg of Cr(VI) per liter (Velma V. *et al*., 2009). Chromium is widely used in numerous industrial processes and as a result, is a contaminant of many environmental systems. Commercially chromium compounds are used in industrial welding, chrome plating, dyes and pigments, leather tanning and wood preservation. Chromium is also used as anticorrosive in cooking systems and boilers (Velma V. *et al*., 2009).

The formation of the different Cr(VI) species depends on the pH and the chromium concentration. The pH effect is shown Figure (1). Hexavalent chromium compounds such as chromate and dichromate behave as strong oxidants at low pH. Cr(VI) has complicated hydrolysis and it can form only neutral and anionic species. According to Figure (1),Cr(VI) exists primarily as salts of chromic acid (H_2CrO_4), hydrogen chromate ion ($HCrO_4^-$), and chromate ion (CrO_4^{2-}) (Hyder,A.H.M.G.,2013). In the pH range from 1 to 6.5 and chromium concentrations above 1g/L, dichromate ions ($Cr_2O_7^{2-}$) predominate. H_2CrO_4 predominates at pH below 1.0, $HCrO_4^-$ at pH between 1.0 and 6.0, and CrO_4^{2-} at pH above 6.0.

2.2 Chemical and physical properties of chromium(VI) compounds

Chromium (VI), also known as hexavalent chromium, is the second most stable oxidation state of chromium. Rarely occurring naturally, most chromium (VI) compounds are manufactured (products or by-products). Chromium (VI) can be reduced to the more stable chromium (III) in the presence of reducing agents (e.g. iron) or oxidizable organic matter (OSHA, 2006). Chromium (VI) compounds are customarily classed as soluble or insoluble in water. Examples of water-soluble chromium (VI) compounds are sodium chromate (873 g/L at 30°C) and potassium chromate (629 g/L at 20°C). Water insoluble chromium (VI) compounds include barium chromate(2.6 mg/L at 20°C), and lead chromate (0.17 mg/L at 20°C) (Lide, 2008). Compounds with solubilities in the middle of this range are not easily classified, and technical-grade compounds, such as the various zinc chromates, can have a wide range of solubilities (International Agency for Research Center, 1990). In the United States of America, the department of Occupational Safety and Health Administration (OSHA) has divided chromium (VI) compounds and mixtures into the following three categories: water-insoluble (solubility < 0.01 g/L), slightly soluble (solubility 0.01 g/L–500 g/L), and, highly water-soluble (solubility = 500 g/L) (OSHA, 2006).

Chromium (VI) compounds are mostly lemon-yellow to orange to dark red in colour. They are typically solid (i.e. crystalline, granular, or powdery) although one compound (chromyl chloride) is a dark red liquid that decomposes into chromate ion and hydrochloric acid in water (OSHA, 2006).

2.3 Anthropogenic sources of chromium compounds

Anthropogenic sources involve the man-made activities that are taken in to consideration in the formation of chromium compounds. The level of chromium concentration in anthropogenic sources is much higher compared to natural sources. Thus chromium contamination in the environment is mainly due to anthropogenic sources. Chromium levels in soil vary according to area and the degree of contamination from anthropogenic chromium sources. Tests on soils have shown chromium concentrations ranging from 1 to 1000 mg/kg, with an average concentration ranging from 14 to about 70 mg/kg (United States Environmental Protection Agency, 1984). Chromium(VI) in soil can be rapidly reduced to chromium(III) by organic matter. As chromium is almost ubiquitous in nature, chromium in the air may originate from wind erosion of shales, clay and many other kinds of soil. In countries where chromite is mined, production processes may constitute a major source of airborne chromium. In Europe, endpoint production of chromium compounds is probably the most important source of chromium in air (WHO, 2000).

Cr(VI) is found in industrial effluents such as metallurgical refractory, chemical, and pigment industry where as tannery, textile, and plating industry effluent exhibits Cr(III) affluence in wastewater. Some other prominent sources of chromium include the chromite-ore processing industry, automobile, paper and pulp, fertilizer, textile, steel, metal finishing, magnetic tapes, leather tanning, wood protection, petroleum refining, brass, electrical and electronic equipment etc.(Hyder**A.** H. M. Golam, 2013). They generate huge quantities of chromium containing effluents which can end up contaminating surface and ground water resources. Other significant man-made sources of chromium include municipal wastes, and sludge generated from the municipal waste. Sewage treatment plants from industrial and residential sources also discharge substantial amounts of chromium in waste stream.

2.4 Advantages of chromium compounds

Since its discovery chromium has become a very important industrial metal because of its many application in ferrous and non-ferrous alloy metal fabrication, and in the chemical industry. Chromium compounds are used in a wide variety of industrial and manufacturing applications including steel alloy fabrications, where they enhance corrosion and heat resistance and in plated product fabrication where they are used for metal decoration or increased wear resistance. They

are also used in nonferrous alloy metal fabrication to impart special qualities to the alloys; in production and processing of insoluble salts, as chemical intermediates; in the textile industry for dyeing, silk treating, in the leather industry for tanning to obtain leather of desirable quality; in the manufacture of green varnishes inks, paints and glazes; as catalyst for halogenations, alkylation and catalytic cracking of hydrocarbons; as fuel and propellant additives; and in ceramics (Sumathi *et al.*,2004).

Table 1: Uses and color of different forms of chromium.

Form	Appearance (colour)	Uses
Cr(0)	Metallic grey / silvery	Stainless steel production, Alloy production, etc.
Cr(III)	Green	Alloy manufacturing, brick lining, chrome plating, tanning, and textiles, copying machine toner.
Cr(VI)	Red, orange or yellow	Chrome plating, Leather tanning, textiles and machine toner.

Source:(Agaje Bedemo, 2007)

2.5 Toxicity and health effect of chromium compounds

The presence of heavy metals in the environment is a major concern because of their toxicity to many life forms. Heavy metals like mercury, lead, cadmium copper, chromium and nickel are toxic even in extremely minute quantities (Selvaraj *et al*.,2003). Since the majority of heavy metals do not degrade in to harmless end products, their concentrations must be reduced to acceptable levels prior to discharge of industrial effluents. Otherwise, they could pose threats to public health and affect the aesthetic quality of potable water.

According to the WHO, the metals of most immediate concern are aluminum, chromium manganese, iron, cobalt, nickel, copper, zinc, cadmium, and mercury and lead (Baig *et al.*, 2003). Chromium contamination of soil and ground water is one of the significant environmental problems today. Chromium is believed to be the second common inorganic contaminant after lead. The toxicity of chromium does not reside solely with the elemental form but varies greatly among a wide variety of chromium compounds. Oxidation state and solubility are crucial factors in this regard (Hyder **A.** H. M. Golam, 2013). Chromium occurs in the environment primarily in

two valence states, the oxidized hexavalent chromium, Cr(VI), and the less oxidized trivalent chromium, Cr(III). Under common environmental conditions of pH, Cr(III) compounds are slightly soluble in water, where as Cr(VI) compounds are quite soluble. Chromium(III) is considered to be essential to mammals for glucose, lipid, and protein metabolism and hence is an essential dietary element. On the other hand, Cr(VI) is much more toxic and mobile in ground water than the relatively immobile Cr(III) and possesses mutagenic and carcinogenic activity (Nomanbhay; Palanisamy, 2005).

In humans, Cr(VI) exposure causes marked irritation of the respiratory track and ulceration and perforation of the nasal septum in workers in the chromate producing and using industries (Ageje Bedemo,2007). Ingestion of 1.0 to 5.0g of Cr(VI) as chromate results in severe acute gastrointestinal disorders, hemorrhagic diathesis, convulsions and death may occur following cardiovascular shock. The maximum levels in drinking water are 5 mg/L for trivalent and 0.05 mg/L for hexavalent chromium. But, there is still uncertainty regarding what daily dose of Cr(VI) is considered toxic and what ingestion concentration of Cr(VI) is acceptable (Acar; Malkoc,2004).

2.6 Overview of chromium removal technologies

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. The most important of these technologies include; chemical precipitation, filtration, ion-exchange, electrolysis, lime coagulation, solvent extraction, reverse osmosis and electro-coagulation. However, all these technologies have their inherent advantages and limitations in application. Most of the methods suffer from some drawbacks such as incomplete metal removal, low selectivity, high reagent and energy requirement, high capital and operational cost and generation of toxic sludge or other waste product that require careful disposal has made it imperative for a cost effective treatment method.

2.6.1 Chemical precipitation

Chemical precipitation is the method, in which dissolved and suspended Cr(VI) ions are transformed to the insoluble solid through a chemical reaction. Usually a precipitating agent accelerates this conversion from Cr(VI) ions into insoluble solid. The commonly used precipitation agents are lime and magnesia. This technique has been proven as an effective way to remediate chromium from wastewater. 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 Cr(VI) precipitation is slow, and aggregation of metal precipitates take place (HyderA. H. M. Golam, 2013).

2.6.2 Electro-coagulation

Electro-coagulation is an efficient method where the flocculating agent is generated by electro-oxidation of a sacrificial anode, generally made of iron or aluminum. In this process, treatment is done without adding any chemical coagulant or flocculants, thus reducing the amount of sludge, which must be disposed. A great deal of work performed in the last decades has proved that electro-coagulation is an effective technology for the treatment of heavy metal containing solutions.

2.6.3 Reduction

Reduction is a treatment process in which the higher valance state of Cr(VI) ion is converted or reduced to the lower valance state using reducing agents. This technique offers several advantages such as recovery of Cr(VI) 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 (Hyder**A.** H. M. Golam, 2013).

2.6.4 Ion exchange

Ion exchange is a suitable technique to remove heavy metals from the wastewater and this technique has also been applied as a remediation measure for Cr(VI). Various ion exchange resins are commercially available which can effectively remove Cr(VI) below the standard limit of Cr(VI) (0.1 mg/L) in wastewater. This process reduces the amount of waste for disposal and

the cost of operation is generally lower. However, limitation of this method is that efficiency dependent on the pH of water (Rengaraj Joo.,*et al.*, 2003).

2.6.5 Adsorption

Adsorption is a process in which substances dissolved in fluid phase are accumulated onto the surface of a solid through the chemical or physical forces. Generally, Vander Waals forces between molecules are responsible for the accumulation. The adsorption technique has several benefits and drawbacks (Mohan *et al*.,2008). It is effective and economical. It can remove the contaminating metals as well as recovery and recycle of adsorbet metals from adsorbent. It has evolved as the suitable alternative for those metal ions that cannot be removed easily by other techniques. The removal efficiency is excellent for this process. However, the removal efficiency depends on pH, influent concentration, and adsorbent dosages. The solid material onto which accumulation of the pollutant or contaminant takes place is called the adsorbent. Depending on the adsorbent materials, the adsorption efficiency varies. All adsorbents tend to have the following properties:

A large internal surface areas (250–1500m^2/g)

A large pore volume (0.1–1.0cm^3/g)

A low bed density(0.3–0.6 g/cm^3)

A adsorptioncapacityupto0.2g of adsorbate per gram of adsorbent

There are various types of adsorbent available onto which chromium can be adsorbed. The common adsorbents include (Hyder**A.** H. M. Golam, 2013):

Synthetic polymeric adsorbents such as resins.

Natural and synthetic zeolites such as porous alumino silicates.

Fiber and Lignite.

Industrial waste/by-products such as fly ash, waste sludge.

Agricultural by-products such as straw, husk, wheat bran, rice bran and hulls.

Bio-adsorbents such as algae, fungi, bacteria.

Activated carbon such as coconut shells, wood char, lignin, bone char, and bio-char.

Clay minerals and oxides such as kaolinite, and bauxite.

2.7 Principles and conditions influencing adsorption in batch systems

According to (Vernon*etal.*, 1967) several factors have been determined that could affect the outcome of the results in batch adsorption experiments, as described the following principles and conditions:

2.7.1 Nature of the adsorbent

The adsorption process is mainly a surface phenomenon in which adsorption depends on the portion of the total surface area available to the adsorption process. The adsorption capacity is directly proportional to the specific surface area (Weber,1972). The physicochemical nature of the surface of carbon is an important factor in the adsorption process, and should be considered in selection or preparation of carbons for specific applications (Vernon*etal.*,1967).

2.7.2 Nature of the adsorbate

The adsorption process is mainly affected by the nature of the adsorbate in the sense of its solubility in the solute. The adsorption capacity is inversely proportional to the solubility of an adsorbate in the solute, and this is the Lundelius rule, one of two rules used to predict the effect of a solute's chemical character on its uptake (Weber,1972). The greater the solubility, the stronger the solute-solvent bond is and therefore the smaller the extent of adsorption. The molecular size of the adsorbate is of significance too. The molecular size relates to the rate of uptake of solutes from aqueous solution by porous adsorbents so that the smaller the molecular size, the faster the reaction is. However, it must be kept in mind that the adsorption process dependence on molecular size can be generalized only within a particular chemical class. For example, large molecular size of a certain type of a chemical series may be adsorbed more rapidly than smaller ones of another class. Moreover, the rate of uptake dependence on the molecular size is expected only for rapidly agitated batch reactors which are of limited interest in water and wastewater systems. In contrast to the molecular size effects, the variations in the geometry and structure of the molecules have smaller effects on the equilibrium conditions (Faust,1998).

Ionization also plays a role in the uptake capacity, where many components of water and wastewater exist as ionic species. For example, fatty acids, amines, and pesticides have the

property of being ionized under appropriate conditions of pH. The ionization of some chemical components and classes is believed to be of significance for the carbon adsorption process due to the fact that activated carbon commonly exists with a net negative charge in water. It has also been observed that as long as the compounds are structurally simple, the uptake capacity decreases for the charged species and increases for the neutral ones. As compounds become more complex, the effect of ionization becomes less important. Thus, the adsorption capacity was on the decrease by the increasing of ionization for many different types of simple organic acids. To conclude, it has been observed that a polar solute will tend to be strongly adsorbed by a polar adsorbent in anon polar solvent (Stafiej *etal.*, 2007).

2.7.3 Solution pH

The uptake capacity of adsorbates from the aqueous solution is affected by the value of the pH of the solution. This is due mainly to the fact that hydrogen and hydroxide ions are being adsorbed strongly by activated carbon, so the adsorption of other ions is influenced by the pH of the solution. Furthermore, since the ionization has an effect on the uptake capacity of the adsorbates from the solvent, pH affects the adsorption as well in that it governs the degree of ionization of acidic or basic compounds. The adsorption of heavy metals is affected by the carbon type, pH, and surface loading. The pH impacts the extent of metal removal in the senses of ionization where the free metal ions, M^{2+}, and their hydroxo specie $M(OH)_2$all participate in the adsorption reaction. The pH-adsorption values increase depending on the cationic metal ion for every metal (Hyder A. H. M. Golam, 2013).

2.8 Activated carbon as adsorbent

AC is widely known as an effective and inexpensive adsorbent in removing heavy metals such as chromium from wastewater (Acharya*etal.*,2009). The carbonaceous material that are commonly used to produce activated carbon include coal, palm kernel, wood, petroleum coke, coconut shell, lignite, peat, etc. (Khezami; Capart,2005) observed that more than 90% removal was achieved on wastewater containing 200mg/L of Cr(VI) with dosage of 400mg/L of activated carbon. They also examined that the removal of Cr(VI) was found to increase with the increase of temperature. Because the diffusion rate of the adsorbate molecules across the external boundary layer and within the pores of the adsorbent is increased at an elevated temperature.

2.9 Lignite as adsorbent

This century coal is the heart in energy field. Global coal consumption grew by 7.6% in 2010 which is the fastest global energy rate since 2003 (Liang X.*et.al.*, 2013). Coal represent at present about 70 % of world's proven fossil fuel resources. Moreover coal is also a more delocalized resource; it has lower cost among the different fossil fuel (Franco A.; Diaz A.R**.,** 2009). The physical and chemical properties of coals depend upon a number of factors, including the origin and the type of coal. Coal is derived from peat and as geological processes apply pressure to peat over time, it is transformed from law rank into high rank of the coal types based on their organic maturity. Coal is classified mainly (a) Anthracite (b) Bituminous (c) Lignite (brown coal). Among them Bituminous and Lignite has high ash content.

Table 2: Bulk chemical composition of coal ash

Composition (%)	Bituminous	Lignite
SiO_2	20-60	15-45
Al_2O_3	5-35	10-25
Fe_2O_3	10-40	4-15
CaO	1-12	15-40
MgO	0-5	3-10

Source:(Ahmaruzzaman, M., 2010).

Ethiopian coal has high ash content and is to be fallen into Bituminous and lignite category, so it is very poor in quality compared to other countries as shown in Table 2.

Table 3: The Typical Average of Coal Ash Composition (%Wt) of different countries

Compound (%)	India	Australia	Canada	South Africa	Ethiopia
SiO_2	57	59	53	49	62.71
Al_2O_3	27	28.5	30.5	30.1	17.4
Fe_2O_3	10	3.6	4.8	6.9	6.87
CaO	1.7	1.35	3.9	5.5	1.8
MgO	0.63	0.75	0.4	1.3	3.65
Na_2O	0.35	0.65	0.9	0.8	1.55
SO_3	0.56	0.9	2.5	3.6	1.23

Source: (Chinese Academy of science 2002; Wolela Ahmed, 2008).

Generally, coal is used for various environmental applications that include: Phosphorus retention, Heavy metal immobilization, acid mine drainage mitigation, and mine site reclamation, and carbon sequestration. The primary aim of this research was to determine the adsorption properties of the low-cost natural carbonaceous materials for adsorption of heavy metals from aqueous solutions. Lignite exhibited a better capability to remove metals than all plant materials. Using lignite as adsorbent of metals from waters is advanced mainly for silver and copper at lower initial concentrations (lower than 200 mg/l). (Allen S. J.; Brown P.A.,1995) have stated that brown coal could be used for removing a range of metals from solutions. Lignite was characterized by a high content of oxygen-rich functional groups and its CEC was equal to 15.7 meq/100 g.

2.10 Adsorption mechanism of acid treated lignite coal

One of the main problems with the use of low rank coal for combustion purposes lies in its inherently high oxygen content. The high oxygen content results in increased coal reactivity and degradation during mining and storage as well as serving to decrease the overall calorific value of the coal. The high oxygen contents of selected low rank coals can, however, be of great value in certain situations, especially with respect to high oxygen containing functional groups containing an exchangeable hydrogen ion. The ability of low rank coals to form stable complexes with several heavy metal ions has long been recognized. This property has been successfully utilized to estimate the concentration of acidic oxygen functional groups present in low rank coals (Allen S. J.; Brown P.A.,1995). The relatively high ion exchange capacity of several low rank coals studied, coupled with the low overall cost of the bulk material, indicates great potential for the utilization of low rank coals as a means to remove a range of metals from aqueous waste streams. All of the North American lignites investigated showed relatively high adsorptive capacities for the heavy metals investigated. Using multi-stage treatments of heavy metal solutions with these lignite, it should therefore be possible to meet EPA discharge limits much more cheaply than using conventional heavy metal treatment processes (Lafferty;VerheyenI, 1990).

The adsorption of metal from solution is not necessarily a simple process involving a single species(Sing.S*et. a l*.,2001). In most cases, more than one species is being absorbed into more

than one type of surface site during the adsorption process. The mechanism of adsorption of heavy metals often involves the chemical reaction between the functional groups on the adsorbent and the metal ions, or cation- exchange reaction due to the high cation-exchange capacity (CEC) of the adsorbent (Chantawong v.; Bashkin, 2003). Some other mechanisms may also be involved such as transport in the bulk of liquid phase, diffusion across the liquid film surrounding the solid particles and diffusion in macro pores or micro pores. The chemical reaction for the adsorption of metal onto a solid substance is described by (WilliamD., 2007)

$$M+S \longrightarrow MS \qquad (1)$$

Where M is the metal, adsorbate, S is the solid, adsorbent and MS is the metal-solid adsorbent complex. On the surface of the adsorbent primarily the adsorption follows two mechanisms, chemical adsorption and physical adsorption. The amount of adsorbate that adsorbent can accumulate is a key parameter for process engineering design. This capacity is determined by generating an equilibrium adsorption isotherm. (Sing.S.*et. al.*,2001), concluded that in addition to chromium metal-adsorbent formation several other possible mechanisms may have contributed simultaneously to heavy metals removed by adsorbent, including surface complexation, ion-exchange, diffusion and precipitation of metal ions adsorbent.

3. Materials and methods

Laboratory experiments presented in this chapter were carried out in order to evaluate the adsorption efficiency of the acid treated lignite coal. A series of experiments were conducted to determine the removal efficiency of heavy metals; namely, Cr(VI) using lignite coal. The experiments utilized with acid treated lignite coal on adsorption processes. In addition to the adsorption experiments, a material physical characteristics experiments were carried out in order to know the surface characteristics of the lignite coal and acid treated lignite coal used in these experiments.

Therefore, the purpose of this section is to mention the chemicals, material, and instruments used and methodology followed to achieve the objectives of the study.

3.1 Materials

3.1.1 Chemicals, apparatus and equipment used

All chemicals used in this study were analytical reagent grade and were used without further purification. Analytical grade of potassium dichromate ($K_2Cr_2O_7$) salt was dissolved in distilled water for stock solution preparation tostimulate the industrial wastewater, concentrated Hydrochloric acid (4M HCI) was used for lignite soaking to remove some impurities and oxides of metals, 0.1MNaOH and 0.1MHCl were used to adjust the solution pH of the experiments.

In this experiment the apparatus and equipment were required to set up the batch tests and to analyze the samples. Beaker, volumetric flasks, graduated cylinder, funnel, tube, pipettes, plastic and glass bottles, glass stirrer, and magnetic stirrer are some of the apparatus were used during batch tests. Acid treated sample was dried in hot air oven at 105^oC for 12hrs, and electrical furnace was used to determined ash content and volatile content of the samples. Fourier transform infrared (FTIR) spectra were recorded using (Perkin Elmer, Spectrum 65FT-IR spectrophotometer) to analyze the functional groups present in the adsorbent. Solution pH was adjusted using pH meter. The orbital shaker for mixing of sample in the solution and computerized atomic concentration analyzer UV-spectrophotometer (Perkin Elmer lambda 950 UV/visible Spectrometer) were used to evaluate the final Cr(VI) ions concentration.

3.2 Methods

3.2.1 Collection of lignite coal

The raw lignite was collected from Yayo Basin area, Oromia Region, South Western part of Ethiopia. The Yayo Basin is situated 8° 22' 00" - 8° 24' 00" N and 35° 36' 21"-36° 01' 12" E latitude and longitude, respectively. Yayo is 564 km from Addis Ababa along Jimma-Bedle Gambella road or 500 km along Nekemte-Bedle-Gambella road. The basin is found between 1300 and 1700 m above sea level (Wolela Ahmed, 2008).

Chemically, 90–99 % of coal ash comprises Si, Al, Fe, Ca, Mg, Na, and K, with Si and Al being the major components. The mineralogical, physical, and chemical properties of coal ash depend on the nature of the parent coal (Adriano D.C., 1980; Carlson C.L.; Adriano D.C., 1993). Therefore, the material collected has to be modified by removing ashes and some impurities using hydrochloric acid for Cr(VI) adsorption process.

3.2.2 Preparation of adsorbent (lignite coal) via acid treatment

The samples received were stage crushed and sieved to a wide particle size range (more than 250µm and less than 500 µm), washed using a acidic solution to clean an adsorbent from any inorganic material. The lignite coal powdered particle was treated with 4MHCl in 1000ml beaker and then kept in magnetic stir at60°C for an hour. After the solution was allowed to settle for 12 hours, then filtered with filter paper and washing with warm water and distilled water continues until the pH of the filter solution was neutral. The solid was then filtered and dried in the oven at 105^{o}C for 12 hours. The dried acid treated Lignite Coal (ALC) surface characterization was carried out to understand the performance of Lignite Coal (LC) for further adsorption studies. Figure (1) summarizes this process, which will be referred to as the acidic treatment raw lignite activated carbon synthesis process in this study.

3.3 Adsorbent proximate analysis and surface characterization studies

In order to evaluate the adsorption properties of adsorbent produced from LC, the physical characteristics study was carried out on both the LC and ALC used as adsorbent and to compare the surface character or proximate analysis of the lignite sample which have been named as :Bulk density, moisture content, dry matter, total ash content, volatile content, and fixed carbon.

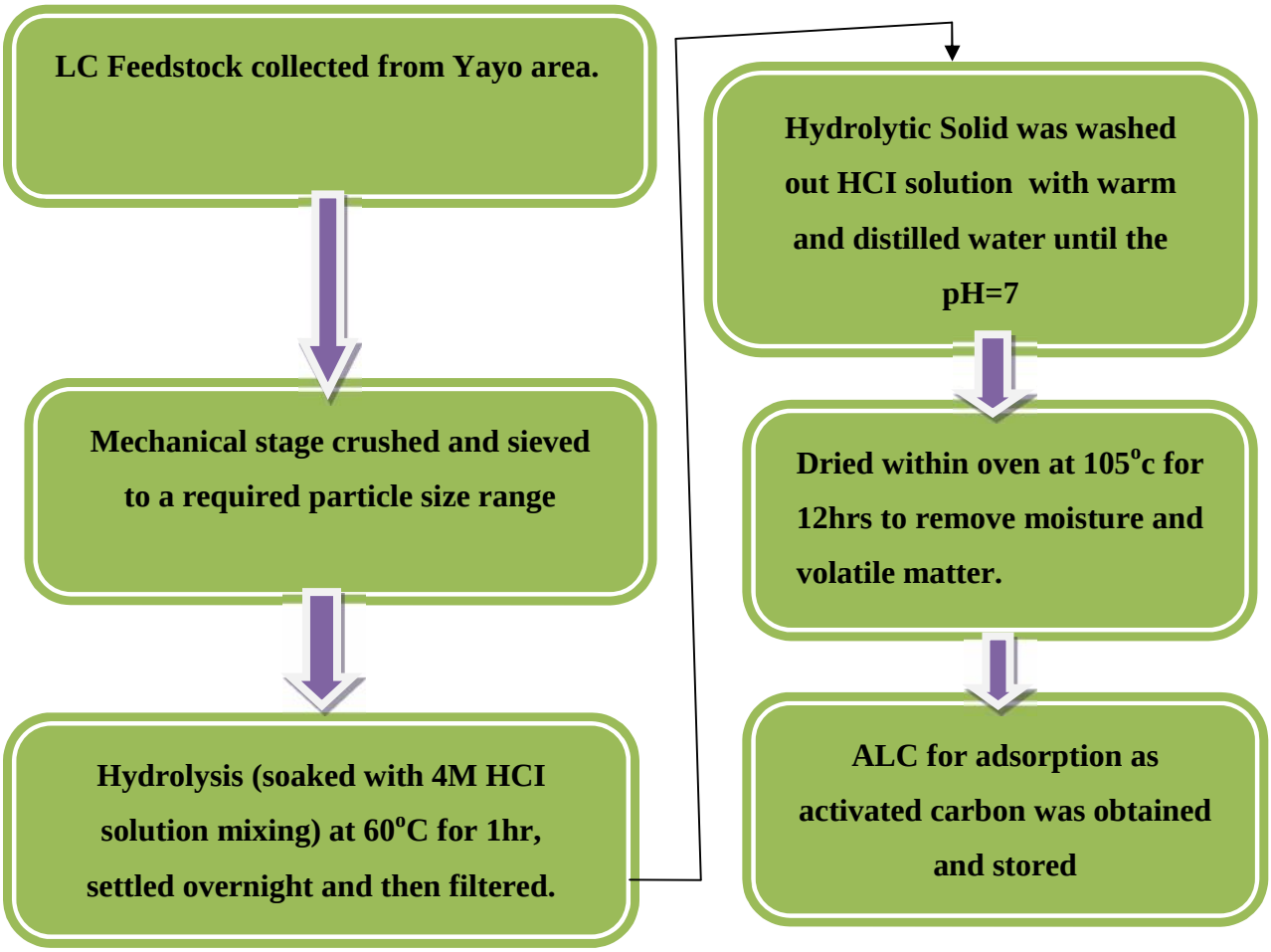


Figure 1: Summary of Acid Treated Processes of LC for Adsorption.

3.3.1 Bulk density determination

This was determined by measuring the volume of water displaced when a known weight (2.00 g) of sample of lignite carbon were dropped into a graduated measuring cylinder with tapping until the carbon occupied a initial volume (Bhatia,2006).

A 100 cm^3 calibrated measuring cylinders was washed and dried. 50 cm^3 of the water was added to the measuring cylinder and was noted. 2 grams of the sample was transferred into the measuring cylinder and volume of the increased water level was recorded. Care was taken to ensure there were no air bubbles before taking volume measurements.

Volume of water displaced (cm^3) = Final volume – Initial volume

$$\text{Bulk density (g/cm}^3\text{)} = \frac{\text{Mass of samples (g)}}{\text{Volume of water displaced (cm}^{3)}} \quad (2)$$

3.3.2 Moisture content and dry matter determination

Moisture is an important property of coal, as all coals are mined wet. Groundwater and other extraneous moisture is known as adventitious moisture and is readily evaporated. Moisture held within the coal itself is known as inherent moisture and is analyzed quantitatively. Total moisture was analyzed by loss of mass between an untreated sample and the sample once analyzed. This can be achieved by drying in air at 100 to 105°C and relative loss of mass determined (Ercin*et.al.*, 2001).Therefore, 2g of the lignite (adsorbent) sample was weighed out in a pre-weighedcrusible.Thesamplewasplacedinthethermostaticovenforone night at a temperature of 105^{O}C. After which the sample was cooled in adessicator. The oven dried sample wasreweighed and the moisture content was determined. Thus, the percentage moisture content of lignite were calculated from the formula in the Eq. (3).

$$\text{Moisture content (Mc\%)} = \frac{W_O - W_1\,(g)}{W_O\,(g)} \text{ x100} \quad (3)$$

Where, W_o is initial sample weight of dry adsorbent (g) and W_1 is loss in weight on drying in oven after cooling (g)

$$\text{Dry matter (\%)} = \frac{\text{Oven dry weight (g)}}{\text{Initial sample weight (g)}} \text{ x100} \quad (4)$$

3.3.3 Ash content determination

Ash comprises the non combustible mineral content of the lignite and predominantly consists of oxides of alkali and alkaline earth metals, such as potassium, calcium and magnesium. Ash content of coal is the non-combustible residue left after coal is burnt. It represents the bulk mineral matter after carbon, oxygen, sulfur and water (including from clays) has been driven off during combustion. Analysis is fairly straight forward, with the coal thoroughly burnt and the ash material expressed as a percentage of the original weight (Khan A.A.*et al.*,2009).

2 g of the adsorbent was placed in a pre-weighed porcelain crucible and transferred into a preheated muffle furnace at a temperature of 600^{O}C for 2hours,subsequently; the crucible and its

content were cooled in a dessicator. The crucible and its content were reweighed and the new weight was noted. The percentage ash content was calculated from the formula in Eq. (5).

$$\text{Ash Content } (A_C\%) = \frac{W_a}{W_o} \times 100 \quad (5)$$

Where, W_a is weight of ash after cooling (g) and W_o is original weight of dry adsorbent (g)

3.3.4 Volatile content determination

Volatile matter in coal refers to the components of coal, except for moisture, which are liberated at high temperature in the absence of air. This is usually a mixture of short and long chain hydrocarbons, aromatic hydrocarbons and some sulfur (Khan A.A.*et al.*,2009).

2g of the sample was heated under a temperature of 850^{O}C for 10 minutes in a partially closed porcelain crucible placed in a muffle furnace. The crucible and its content were retrieved and cooled in adessicator. The difference in weight was recorded and the volatile content determined thus. The percentage volatile content was calculated from the formula in Eq.(6).

$$V_C\ (\%) = \frac{W_O - W_a}{W_O} \times 100 \quad (6)$$

Where, V_C is volatile content in percentage, W_O is the original weight of dry adsorbent (g) and $W_a$is the weight of matter from furnace after cooling (g).

3.3.5 Fixed carbon determination

The fixed carbon content of the coal is the carbon found in the material which is left after volatile materials are driven off. This differs from the ultimate carbon content of the coal because some carbon is lost in hydrocarbons with the volatiles. Fixed carbon is used as an estimate of the amount of coke that will be yielded from a sample of coal. Fixed carbon was determined by removing the mass of volatiles determined by the volatility test, ash test, and moisture test above, from the original mass of the coal sample (Bai*et al.*,2006).The fixed carbon content was determined using the formula in the Eq. (7).

$$F_c\ (\%) = 100 - V_c - A_c - M_c \quad (7)$$

Where, Fc is fixed carbon, V_C is volatile content, A_C is ash content and M_C is moisture content

3.4 Determination of adsorbent surface functional group by FTIR method

It helps to study the effect of acid attack and the change that have taken place in the structure of lignite and determination of surface oxygen-containing functional group. Functional groups in ALC (unabsorbed) and chromium absorbed ALC were examined by using the Fourier Transform Infrared (FTIR) method of analysis. The FTIR spectrophotometer was based on changes in dipole moment resulting from bond vibration upon absorption of IR radiation. It was carried out at room temperature using Spectrum 65FT-IR (Perkin Elmer) in the range 4000-400 cm^{-1} using KBr pellets. The discs were prepared by first mixing 1mg of dried sample with 500mg of KBr (Merck, for spectroscopy) in an agate mortar and then pressing the resulting mixture at 10 tons cm^{-2} for 15 min under vacuum. The spectra were recorded from 4000 to 400 cm^{-1} by 128 interferograms at a resolution of 4 cm^{-1}. The wave numbers associated to signals in the FTIR spectra from chemical functional groups were determined.

3.5 Batch Adsorption studies

3.5.1 Preparation and dilution of Cr(VI) stock solution

The Cr(VI) ion stock solution of 1000 mg/l was prepared by dissolving 2.83 g of 99 % potassium dichromate, ($K_2Cr_2O_7$) salt in distilled water (Appendix II). Potassium dichromate was mixed properly with distilled water in a volumetric flask just after 2-3 minutes of shaking by hand. The solution color turned yellow is hand the volume was made to the mark in a 1000mL volumetric flask using distilled water. Synthetic wastewater sample of Cr(VI) ions solution of varying concentrations were prepared using a serial dilution from the standard stock solution of metal ions is shown in Figure (2).

Figure 2: Stock solution

3.5.2 Batch adsorption experimental set up

In this study, batch adsorption process with ALC was employed to find out the effects and the optimum experimental parameters for each experimental run of 200mLglass flask of known initial Cr(VI) concentration of aqueous solution produced from stock solution and the desired pH was adjusted by adding 0.1M HCI or 0.1MNaOH. After that known amount of adsorbent dosage was added in a 250ml glass flask. The flasks were shaken at room temperature, at a constant rate, and allowing sufficient time for adsorption equilibrium.

The glass flasks containing adsorption solution were collected at the end of time required for adsorptions. The supernatant liquid was filtered using filter paper (What man No-1), stored and the final concentrations of Cr(VI) ions were determined. The amount of Cr(VI) adsorbed onto ALC from solution was evaluated and the optimum parameters were then used to analyze the appropriate equilibrium isotherm, and adsorption reaction kinetic rates. The detailed description of experimental procedure of batch tests is shown in the Figure (3):

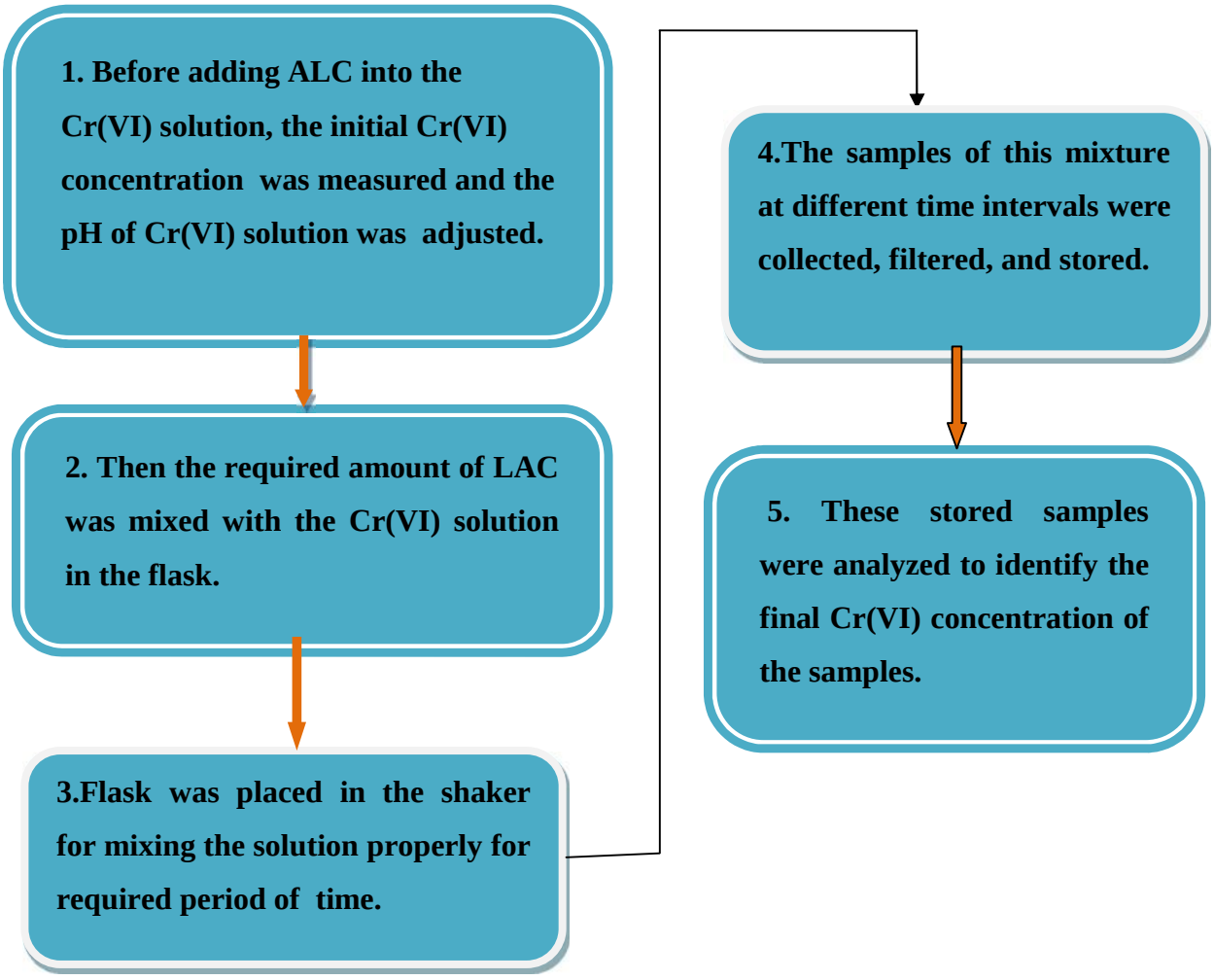


Figure 3: Experimental procedure of batch test

3.5.3 Cr(VI) analysis using UV-visible spectrophotometer

The samples were analyzed to measure the concentrations of Cr(VI) by using 1,5Diphenylcarbazide (DPC). 250 mg (1,5 DPC) was dissolved in 50 mL acetone solution. 15mL sample was taken and 2mL of 3M H_2SO_4 and 1mL of DPC was added. Chromium (VI) concentrations was estimated by the intensity of the red brownish color complex formed and it was measured using UV spectrophotometer (Perkin Elmer lambda 950 UV-vis Spectrometer) at 540nm, following the 1,5 DPC method (APHA*et al.*, 1998).

An absorbance calibration curve was developed using series dilutions of Cr(VI) concentration as shown in Table (4) from 5 to 40 mg/l, against blanked solution mixture of distilled water and

DPC solution. Each standard solution was prepared in identically the same fashion, the only difference between them being their concentrations. The absorbance of diluted Cr(VI) concentration standards was measured at 540nm, where absorbance by chromium is the highest (APHA *et al*.,1998). The calibration curve (Appendix V) was constructed by plotting absorbance against known Cr(VI) concentration. Sample absorbance was also blanked against mixture of distilled water and DPC solution. Samples with absorbance over 1.0 were diluted as the chromium-absorbance relationship became non-linear. Because calibration curves were used in reading off the unknown concentrations, their accuracy was of absolute importance. Therefore, make the standard solutions as accurately as possible and measure their absorbance's carefully. The absorbance of samples was converted to a Cr(VI) concentration using the calibration curve equation developed in the equation of (y = mx + b) the value you see for the intercept (b), slope(m), absorbance (y), and concentration (x). slope of the best straight line through the data points in the calibration plot passing through the origin, and y-intercept (b) zero is given by:

$$\text{Slope}(m) = \frac{y\ (\text{Adsorbance})}{x\ (\text{Concentration})} \qquad (8)$$

Table 4: Standard solutions and measured absorbance for calibration carve.

S/N	Cr(VI) Concentration (mg/l)	Absorbance units
1	0	0.00
2	5	0.008
3	10	0.038
4	20	0.079
5	30	0.361
6	40	0.731

3.6 Determination of the percentage removal and adsorption capacity

3.6.1 Determination of the percentage removal of Cr(VI) ions using ALC

Adsorption studies were carried out by determining the controlled variables (conditions) such as room temperature, the equilibrium time and agitation speed for a known concentration of the metal ion solution. Batch adsorption studies were also conducted to investigate the effect of initial metal ion concentration, adsorbent dosage and pH at optimum adsorption time and agitation speed in a rotary shaker. The supernatant liquid was filtered and the concentrations of Cr(VI) ions were determined using UV/Visible spectrophotometer at a wave length of 540 nm. To estimate the percentage removal of chromium (VI), the following Eq.(9) was used.

$$\% \text{ Removal} = \left(\frac{Co-Ct}{Co}\right) * 100 \qquad (9)$$

Where, Co and Ct are the concentrations of Cr(VI) at the beginning and at the end of the adsorption process at time (t), respectively.

3.6.2 Determination of the adsorption capacity of Cr(VI) ions using ALC

In this study two types of adsorption capacities were determined: (1) adsorption capacity of adsorbent at a particular time (q_t), and (2) equilibrium adsorption capacity of adsorbent (q_e). The (q_t) values were used to draw the plot of Cr(VI) adsorption kinetic model onto the adsorbents, and the (q_e) values were applied to draw the plot of Cr(VI) adsorption isotherms onto the adsorbents. The optimum adsorbent dosage, volume of solution, and concentration change of Cr(VI), were used to find out the adsorption capacity of adsorbent at a particular time (q_t) in mg/g was calculated using Eq. (10).

$$qt = \left(\frac{Co-Ct}{m}\right) * V \qquad (10)$$

The equilibrium adsorption capacity of the adsorbent (q_e) in mg/g was also determined by using the optimum adsorbent dosage, volume of solution, and Cr(VI) concentration change according to Eq. (11). The equilibrium adsorption capacity of adsorbent (q_e) was found in another way by using the values of adsorption capacity of adsorbent at a particular time (q_t) for different initial Cr(VI) concentrations. When q_t value became constant after a certain period of time, which constant value of q_t was termed as equilibrium sorption capacity (q_e).

$$qe = \left(\frac{Co-Ce}{m}\right) * V \qquad (11)$$

where C_o and C_e are the initial concentration of Cr(VI) ion and final concentration of Cr(VI) ion at any instant in mg/l, Vis the volume of the solution (L), W is the mass of adsorbent (g).

3.7 Experimental design for adsorption.

Batch experiment study was conducted to show the statistical significance of or influence of the study variables (initial Cr(VI) concentration, adsorbent dosage, and pH) on percentage Cr(VI) removal from aqueous solution. Response surface study type with initial of General Factorial design was applied to generate full factor combinations effect and easily to obtain the optimum adsorption of metal ions using Design of Expert (DOE) software version 7.0.0.

Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions. RSM is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by several variables (Montgomery; Wiley, 2001).

3.7.1 Description of experimental for factors and response variables

A standard RSM design called General Full Factorial design (GFFD) was applied in this work to study the variables for adsorption of chromium in a batch process. Number of observations =27 (a complete 3^3 factorial design experiments). The purpose was to determine the effect of all factors on percentage Cr(VI) removal. The analysis of GFFD for three variable factors, each with three level was carried out according to the design showed in Table (5).

Table 5: Variables and levels considered for the adsorption of Cr(VI) using GFFD.

Independent Variables	Factors	Range and Level		
		Low Level	Medium Level	High Level
1. Initial Cr(VI) concentration (ppm)	(A)	20	60	100
2. Adsorbent dosage (g)	(B)	0.5	2	3.5
3. pH	(C)	1	3	5

The Percentage removal of Cr(VI), (Y) was taken as the response variable of the system as in the Eq. (12).

Response Variable Y = (over 2 replication) of Percentage removal of Cr (VI) ions on ALC

$$Y = f(A,B, C) \qquad (12)$$

3.8 Determination of adsorption isotherm model (Langmuir and Freundlich)

Adsorption of a solute from a solution can be determined basically by the use of two equations described by (Sundstrom *et al.*, 1976), i.e. the Langmuir (1) and Freundlich (2) equations:

3.8.1 Langmuir equilibrium adsorption isotherm

In 1916,Irving Langmuir published an isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses:

1) The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
2) Adsorbed molecules do not interact.
3) All adsorption occurs through the same mechanism
4) At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other already adsorbed molecules of adsorbate, only on the free surface of the adsorbent. The Langmuir sorption isotherm (Langmuir, 1916) has been successfully applied to many pollutants adsorption processes and has been the most widely used adsorption isotherm for the adsorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogenous sites within the sorbent. It is then assumed that once a metal ion occupies a site, no further adsorption can take place at that site.

In this study, physically the Langmuir model represents that adsorption of monolayer Cr(VI) take place on the homogeneous surface of adsorbents (ALC), and Cr(VI) species do not interact with each other during the adsorption process. The Langmuir model is expressed linearly in Eq. (12) as follow.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (13)$$

Equation (13) yields Equation (14) as follows;

$$\frac{1}{qe} = \frac{1}{q_m K_L} * \frac{1}{C_e} + \frac{1}{q_m} \quad (14)$$

To effectively evaluate the Langmuir isotherm, the values of $1/q_e$ were plotted against $1/C_e$. Using this $1/q_e$ versus 1/Ce plot and Eq. (14), the value of K_L and q_m were calculated using the slope and intercept of the best fit line, respectively. The maximum adsorption capacity (q_m) values were found from the experimental result and Langmuir model. The deviation of q_m value obtained from the experiment to Langmuir model was determined.

The essential characteristics of the Langmuir isotherm may also be expressed in terms of a dimensionless separation factor of equilibrium (R_L) which may be calculated from Eq.(15)

$$RL = \frac{1}{1+KL*Co} \quad (15)$$

The parameter R_L is related to the shape of the isotherm according to the following characteristics: $R_L > 1$ represents unfavorable adsorption; $R_L = 1$ corresponds to a linear relationship; $0 < R_L < 1$ is favorable adsorption and $R_L = 0$ is irreversible.

3.8.2 Freundlich equilibrium adsorption isotherm

In 1906,Freundlich studied the Adsorption of a material on to activated carbon. The Freundlich isotherm model works based on the assumption that the adsorption of adsorbate occurs in multilayer on heterogeneous adsorbent surfaces since the active sites of adsorbent have heterogeneous surface energy.

The model is expressed linearly in Eq. (16) as follow that multilayer Cr(VI) adsorption occurs on heterogeneous surfaces of adsorbents (ALC).

$$qe = K_F C_e^{1/n} \quad (16)$$

Equation (16) yields Equation (17) on taking logarithms;

$$\text{Log}(q_e) = \frac{1}{n}\text{Log}(Ce) + \text{Log}(K_F) \quad (17)$$

where C_e is the equilibrium concentration of Cr(VI) in mg/L, q_e is the equilibrium adsorption capacity of adsorbent in (mg/g), q_m is the maximum adsorbate amount of Cr(VI) per mass of

adsorbent for complete monolayer coverage (mg/g), K_L is the Langmuir equilibrium adsorption constant related to the affinity of adsorption (L/mg), K_F is the Freundlich coefficient related to the adsorption capacity [(mg/g)(L/mg)], and 1/n is the adsorption of their respective regression coefficients (R^2). The isotherm that had R^2 value nearest to 1.0 was selected for modeling of the adsorption of Cr(VI) onto the adsorbent being considered.

3.9 Determination of adsorption kinetics (First and Second Order)

3.9.1 First order adsorption reaction kinetic model:

The kinetics of liquid-solid phase adsorption such as adsorption of Cr(VI) from aqueous solution onto activated carbon as presented by (Ho Y. S., 2004).can be described by a pseudo-first-order kinetic equation. Recently, first-order kinetics has been widely used to describe the adsorption of contaminants from wastewater, (Hameed; El-Khaiary, 2008b). Physically the first-order kinetic model expresses that adsorption reaction rate depends on one parameter such as the adsorbate concentration or the adsorbent dosage. The mathematical representation of the first-order kinetic model is as follows in Eq. (18).

$$\frac{dqt}{dt} = K_1(q_e - q_t) \qquad (18)$$

where q_e (mg/g) is the sorption capacity at equilibrium, q_t (mg/g) is the sorption capacity at time t (hr), and K_1 (hr) is the first-order rate constant for the kinetic model. Integrating Eq. (18) with the boundary conditions of q_t -1= 0 at t = 0 and $q_t = q_t$ at t = t, yields the following equation **(**Ho Y. S., 2004):

$$\ln\left(\frac{q_e}{qe-qt}\right) = k_1 t \qquad (19)$$

Equation (19) can be rearranged as follows,

$$\mathrm{Log}(q_e - q_t) = -\frac{K_1}{2.303}t + \mathrm{Log}(q_e) \qquad (20)$$

A plot was made following the first-order kinetic model of Eq. (20) by using the value of $\log(q_e - q_t)$ (mg/g) in the y- axis and the values of time, t (hr) in the abscissa which has shown later in the results section. The plot was used to determine the first order rate constant (K_1), equilibrium adsorption capacity (q_e), and regression coefficient (R^2). Conventionally, if the R^2 value is very

close to 1.0, the adsorption of Cr(VI) on to the adsorbent follows the first-order rate equation. Because the linearized first-order model has regression coefficient (R^2) value equal to 1. If R^2 value is not close to 1.0, the adsorption system is assumed not to follow the first order reaction rate. In this case, higher-order rate equations would be applied and tested for their applicability. For different initial concentrations of Cr(VI), adsorption capacity at a particular time (q_t) and equilibrium adsorption capacity (q_e) were found to be different.

3.9.2 Second order reaction kinetic model:

In the second-order kinetic model, the kinetics of the adsorption reaction depends upon the amount of metal ions (adsorbate amount) present on the surface of adsorbent at time t, and the amount of adsorbate species adsorbate at equilibrium. This means that the adsorption reaction rate is directly proportional to the number of active sites on the surface of adsorbent (Ho & McKay, 1998). In other words, physically a second-order kinetic model means that the adsorption reaction rate depends on two parameters such as adsorbate concentration and adsorbent dosage. The equation of the second-order kinetic model can be written as follows which has shown in Eq. (21).

$$\frac{d(p)t}{dt} = K2[Po-Pt]^2 \qquad (21)$$

where P_0 denote the amount of equilibrium sites available on the adsorbent, P_t denote the amount of active sites occupied on the adsorbent at time t, and k_2 is the second order adsorption rate constant in $g.mg^{-1}.h^{-1}$ (Ho; McKay, 1998). The value of (qe-qt) as defined previously is directly proportional to the available fraction of active sites (P_o–P_t), and substitution in the second order rate Eq. (21) yields the following equation:

$$\frac{dqt}{dt} = K2[qe - qt]^2 \qquad (22)$$

The expression in Equation 22 can be rearranged as follows:

$$\frac{dqt}{(qe-qt)^2} = K_2.dt \qquad (23)$$

Integrating Eq. (23) with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, yields the following equation:

$$\frac{1}{(q_e - q_t)} = \frac{1}{qe} + K_2 t \qquad (24)$$

Equation (24) can be rearranged as follows:

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{K_2 qe^2} \qquad (25)$$

Where q_e (mg/g) is the adsorption capacity at equilibrium, q_t (mg/g) is the adsorption capacity at a time t (hr), and K_2 is the second order adsorption rate constant in $g.mg^{-1}.h^{-1}$.To determine the second-order kinetic model of Eq. (25) parameters, the values of t/ q_t are plotted against time t, where, the values of t/ q_t and t were placed in the vertical axis and abscissa respectively, as it can be shown in the results section. The second order rate constant (K_2), equilibrium adsorption capacity (q_e), and regression coefficient (R^2) were calculated from the plot. When the R^2 value is found to be closer to 1.0, then the adsorption of Cr(VI) onto the adsorbent system is believed to follow the second-order rate equation. The theoretical values of equilibrium adsorption capacity (q_e) were found from the first and second order kinetic model were compared with the experimental (q_e) values, and deviation of these qe values in percentage units were calculated to suggest whether the adsorption system of Cr(VI) onto adsorbent follows the first-order or second order reaction kinetic model.

4. Results and Discussions

4.1 Evaluation of proximate analysis of lignite

The preliminary investigation of proximate analyses for LC and ALC was done to understand the performance of lignite coal for further studies. The obtained values are presented in Table (6).

Table 6: The proximate analysis result of lignite samples

Parameter Test	Result	
	LC	ALC
Bulk density	1.72 g/cm^3	1.65 g/cm^3
Moisture content	4.52 %	4.15 %
Volatile content	32.85 %	30.25 %
Ash content	39.9 %	19.95 %
Fixed carbon	22.73 %	45.65 %
Percentage of dry matter	95.48 %	95.85 %
Colour	Black	Black
Odour	odourless	Odourless
Appearance	Powdered solid	Powdered solid

4.1.1 Evaluation of bulk density of the lignite

On evaluation of surface characteristics of lignite, it was observed that the acid treated lignite had a high bulk density of 1.65 g/cm^3. Bulk density is an important physical parameter especially when an adsorbent is to be investigated for it filterability. Higher density provides greater volume activity and normally indicates high quality adsorbent (Kundu; Gupta, 2006). That is, it would be able to filter more liquid volume before available cake space is filled and it can be stabled or without degraded with the solution (Bai.*et al*,2006).

4.1.2 Evaluation of dry matter and moisture content of the lignite

The laboratory results of the moisture content of LC and ALC were determined to be 4.52 and 4.15 % respectively, where as dry matter content of both samples were determined to be 95.48 and 95.85 % respectively as shown in Table(6). The moisture content of a sample refers to the percentage of water content of the sample. These gave a tangible and substantial amount of organic matter needed for removal with acid solution to activated carbon by acid soaking process. Hence, the results obtained for lignite samples were good since the yield and quantity of the activated carbon produced can be enhanced by removal of moisture. The moisture content should be taken into account when evaluating the relative capacities of different carbon materials for the adsorption of a wide range of adsorbates.

4.1.3 Evaluation of ash content of the lignite sample.

On investigation the proximate analyses of LC and ALC as presented in Table (6) showed a treatment of lignite with acid solution resulted in the removal of the inorganic constituents and reduction of mineral matter of the raw material. The difference in ash removal by the acid was explained as a result of the ability of the acids to remove different inorganic components. When coal is exposed to water, mostly some organic and inorganic matters in coal may be leached out in water. The most common method of organic matter isolation is to dissolve the mineral fraction of the rock by attacking with HCl used (Chen*et al*, 1999). It was suggested that the observed weight loss with hydrochloric acid may be due to the removal of metal oxides and some organic matter such as the mineral sulphur, sulfides, and carbonates. The raw lignite coal contains various inorganic minerals in addition to the major organic components. Inorganic matter exists in two forms. One is the inherent mineral matter within the raw lignite coal particles, and the other is adventitious inorganic material remaining external to the coal particles (Chen*et al*,1999).

The percentage of ash content for LC and ALC samples were found to be 39.9 % and 19.95 %. The obtained value for lignite was favorable because the ash content serves as interference during the adsorption. The lower the ash content the better the starting material for adsorption (Khan *et al.*,2009).

4.1.4 Evaluation of volatile content of the lignite sample.

The percentage of volatile content for LC and ALC samples were reduced from 32.85 % to 30.25 % as shown in Table (6). The lower volatile content of the acid-washed lignite showed that some of organic molecules of the material was attacked and it is stable for adsorption experiment of Cr(VI) ions from aqueous solution.

4.2 Evaluation of agitation speed and contact time effect on Cr(VI) removal

Before evaluating the effects of selected experimental parameters, adsorption studies were carried out to determine the optimum agitation speed and equilibrium time for a known initial concentrations of the Cr(VI) ions solution. The value of optimum agitation speed and equilibrium contact time were chosen for further adsorption studies to investigate the effect of initial metal ion concentration, adsorption dosage and pH values.

4.2.1 Effect of agitation speed with different time parameter

Figure (4) shows the effect of agitation speed on percentage removal of Cr(VI) ions using lignite activated carbon by varying the agitation speed of 100–300 rpm with constant adsorbent dosage of 3.5 gm, initial Cr(VI) ions concentration of 100 mg/l and at pH 1.Themaximumpercentage removal of Cr(VI) ions was obtained at 200 rpm as shown in the Figure (4), percentage removal of Cr(VI) ions increased in this case may be due to the proper contact developed between metal ion in solution and the binding sites; in turn it promotes the effective transfer of Cr(VI) ions to the adsorbent sites. There was significant change in percentage removal of Cr(VI) ions using ALC while increased in agitation speed from 100 rpm to 200 rpm. But, there was no significant change in percentage removal of Cr(VI) ions while increase in agitation speed from 200 rpm to 300 rpm. Therefore, in this work for further studies of adsorption with other variable parameters the optimum agitation speed of 200 rpm for Cr(VI) ions removal was chosen.

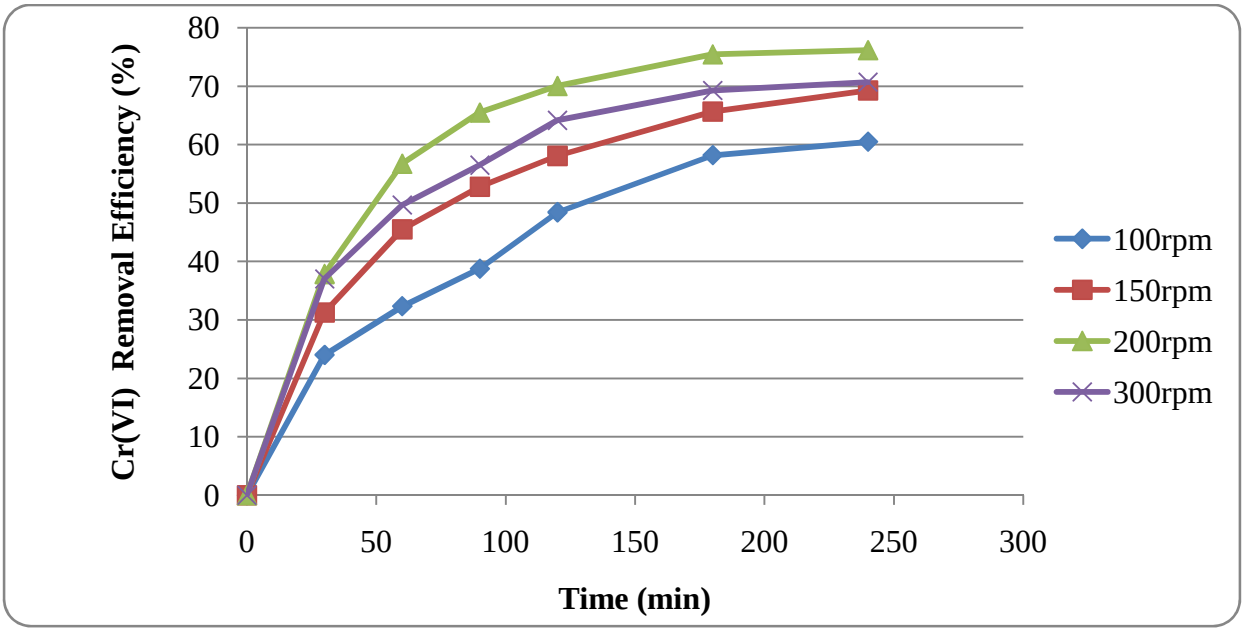


Figure 4: Effect of agitation speed on percentage removal of Cr(VI) ions (at m=3.5 g, Co =100 mg/l and pH=1).

4.2.2 Effect of contact time on Cr(VI) adsorption

The effect of contact time on adsorption capacity and removal efficiency of Cr(VI) ions using ALC were studied for 20, 60 and 100 mg/l of initial Cr(VI) ion concentration. The results are as shown in the Figure (5).The uptake of Cr(VI) from aqueous solution by ALC was observed that the rate of adsorption initially increased from 83 % to 98 %, when contact time was varied from 30 to 120 min for the initial concentration of 20 mg/l, when time was varied from 30 to 180 min adsorption increased from 55.13 % to 89 % for the initial concentration of 60 mg/l and also contact time was varied from 30 to 240 min adsorption efficiency was increased from 48.65 % to 76 % for the initial concentration of 100 mg/l and attained equilibrium after 120 min, 180 min and 240 min respectively for the three initial concentrations at constant agitation speed of 200 rpm.

In order to determine optimal adsorption time for activated carbon used in this study, effects of exposure time are determined at maximum adsorbent dosage of 3.5 g and at lower pH value of 1. It is clear that, in the beginning percentage of removal increased rapidly in few minutes, by increasing contact time, percentage of removal increased lightly and slowly till reach maximum.

The increase in adsorption of Cr(VI) with increase in contact time may be attributed to the increased intra-particle diffusion that occurred at longer shaking period. This can be explained on the basis that, initially a large number of vacant surface sites may be available for adsorption of Cr(VI) ions, and by time increased the surface sites become exhausted (Naeema H.Yarkandi, 2014). Therefore, for further studies of adsorption with other variable parameters the optimum time of 240 min for Cr(VI) adsorption was chosen for contact period.

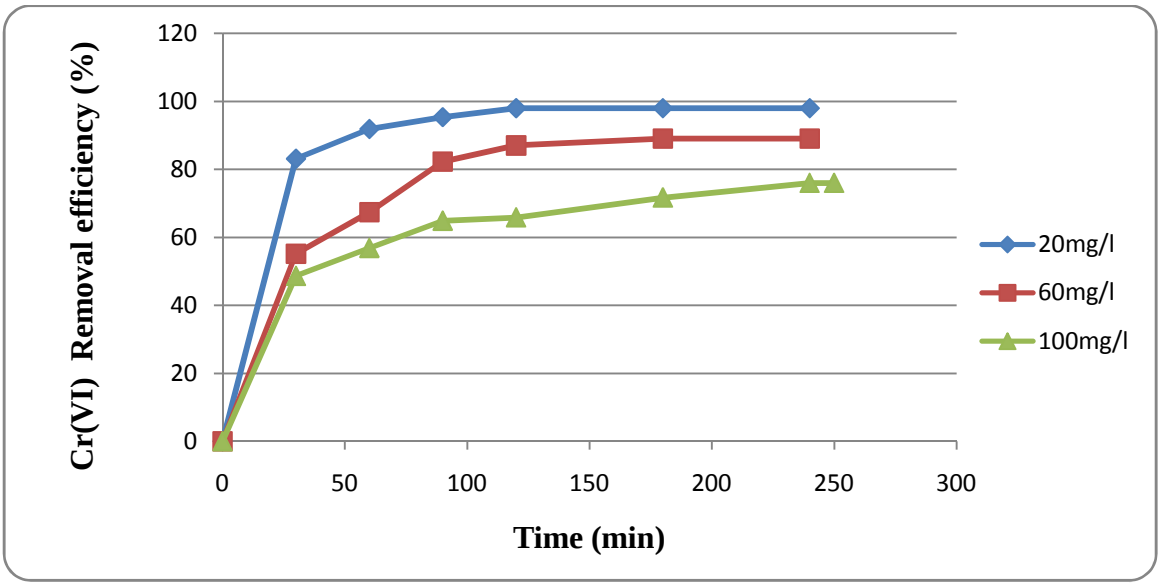


Figure 5: Effect of contact time on removal efficiency of Chromium ions (at m =3.5 g, pH=1 and Agitetion speed= 200 rpm).

4.3 Analysis of variance (ANOVA) for the design model

A total of 54 experiments with duplication of two were done to estimate the coefficients of each model using linear regression analysis. The single dependent output response of percentage removal (Y_1) was obtained from the independent input variables for GFFD and is presented in Appendix (V).The linear effects of three independent variables initial Cr(VI) concentration, adsorbent dosage, solution pH, each with three levels were chosen as independent variables with designated factors as A, B, and C, respectively, and the variables are presented in Table (7).

Table 7: Variables designed for the adsorption of Cr(VI).

Independent Variables	Factors	Range & Level Variables		
		Low Level	Medium Level	High Level
1. Initial Cr(VI) concentration (mg/l)	(A)	20	60	100
2. Adsorbent dosage (g)	(B)	0.5	2	3.5
3. pH	(C)	1	3	5

The 'Statistics'(ANOVA) on Cr(VI) ions percentage removal using ALC value with low probability P value ($P < 0.0001$) indicating that the model suggested by the software was highly significant. The Model F value of 155.82 implies that significant for percentage removal. In this case for percentage removal A, B, C, AB, AC, BC are statistically significant ($P<0.05$) model terms at the 95% confidence level. The non-significant value of lack of fit (F-value of 2.42) for the model showed that the developed model is valid (Biswajit Das *et al*., 2013). The ANOVA summary is given in Table (8)

Table 8: Analysis of variance(ANOVA) for percentage removal of Cr(VI) ions

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Significance
Model	12343.41	18	685.75	155.82	< 0.0001	Significant
A	1788.53	2	894.26	203.20	< 0.0001	
B	4141.55	2	2070.78	470.53	< 0.0001	
C	5876.30	2	2938.15	667.62	< 0.0001	
AB	67.22	4	16.81	3.82	<0.0112	
AC	191.08	4	47.77	10.85	< 0.0001	
BC	236.07	4	59.02	13.41	< 0.0001	
Residual	154.03	35	4.40			
Lack of Fit	64.26	8	8.03	2.42	0.0413	significant
Pure Error	89.77	27	3.32			
Cor Total	12497.45	53				

4.4 Evaluation of independent variables effect on Cr(VI) removal using ALC

4.4.1 Effect of initial Cr(VI)concentration

The adsorption of Chromium is influenced significantly by initial concentration of Cr(VI), in aqueous solutions. In this study, initial concentration of Cr(VI) was varied from 20 to 100 mg/l while maintaining other variable constant (adsorbent dose at 3.5 g, time at 4 hours and pH 1. The results of Figure(6) show the effect of variation of the initial concentration on the percentage of Cr(VI) removal. It was noted that the removal rate of Cr(VI) decreases from 98 % to 76 % when the initial concentration increases from 20 to 100 mg/l. The reduction in the removal efficiency of chromium was probably due to increased quantity of the Cr(VI) ions in the solution for the same number of sites and surface of adsorbent. This decrease in percentage adsorption may be attributed to lack of sufficient surface functional groups to accommodate much more metal ions present in the solution. At lower Cr(VI) ions concentration, all ions present in solution could interact with binding sites and thus percentage adsorption were higher than those at higher initial Cr(VI) ions concentration, lower adsorption yield is due to the saturation of adsorption sites. This is similar with the previous studies which was reported that the decreased in efficiency of metal ions removal with an increased metal ions was due to the decrease in the number of adsorption sites. This result supports the previous research which was done by (Devarasath *et al*., 2007). For the initial concentration value of 20 mg/l, the optimal values of Cr(VI) removal was found to be 98 % with other all parameters constant.

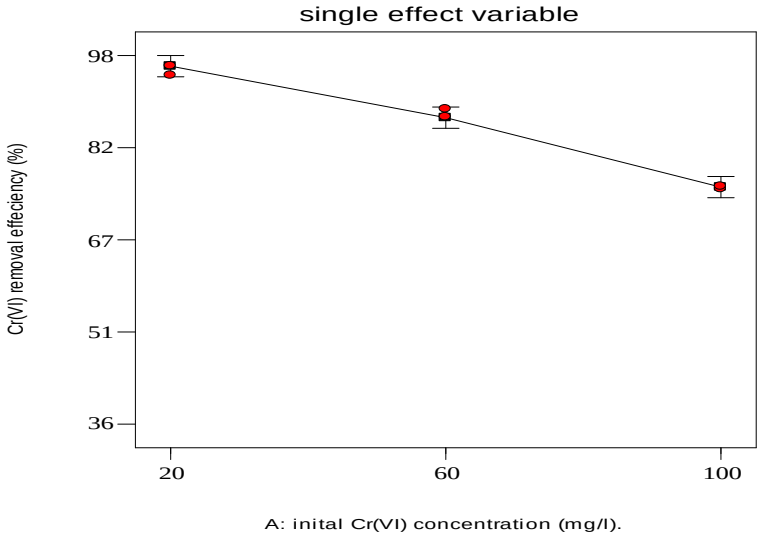


Figure 6: Effect of Initial Cr(VI) Concentration on percentage removal of Cr(VI)

4.4.2 Effect of adsorbent dosages

The study on the effect of the amount of adsorbent on the process of adsorption were carried out by varying adsorbent dose from 0.5 to 3.5 g with pH 1, contact time 4 hours and the higher initial concentration of Cr(VI) 20 mg/l. The graph obtained Figure(7) show that the removal efficiency of Cr(VI) increases from 68.45 % to 98 % when the amount of ALC increased from 0.5 to 3.5 g. With the increase of carbon dose the absolute amount of active centers increased, resulting in an increased of the overall adsorption efficiency of the systems. This is expected because higher dosages of adsorbent in the solution, increased the availability of exchangeable sites for the ions. It was earlier reported that the increases in efficiency of metal ions removal with an increases in the adsorbent dosage was due to the increased in the number of adsorption sites (Vinod *etal*.,2010). For this study under other constant parameters (pH 1,intial Cr (VI) concentration of 20 mg/l and contact time 4 hours), 3.5 g of ALC dose was found to be the optimum values for Cr(VI) removal efficient of 98 %.

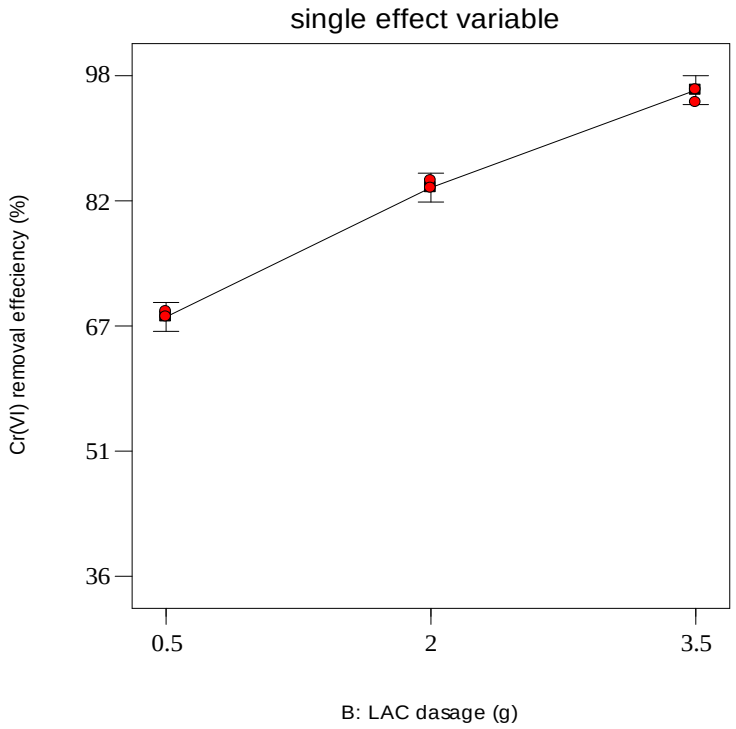
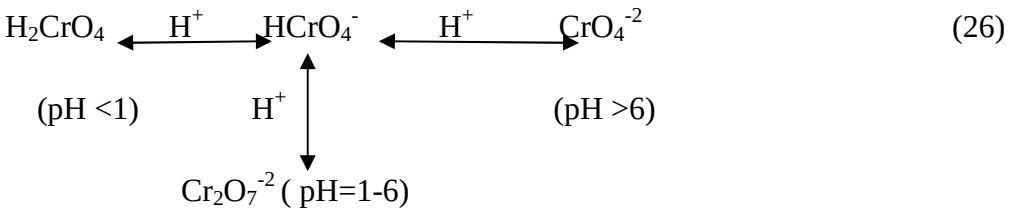


Figure 7: Effect of Adsorbent Dosage on Percentage Removal of Cr(VI)

4.4.3 Effect of pH

Many studies on heavy metal adsorption have shown that solution pH is the single most important parameter in the adsorption process (Nassima Tazrouti; Moussa Amrani, 2009). pH influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. So the pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption process (Azouaou *et al.*,2010; Gupta, 2008;Gupta; Rastogi, 2007).

In order to optimize the pH for maximum removal efficiency, adsorption experiment was conducted in the initial pH range from 1 to 5 with initial Cr(VI) concentration of 20 mg/l and adsorbent dose of 3.5 g, as shown in Figure(8). The maximum adsorption of Cr(VI) of around 98 %, 73 % and 63 % at the pH 1, 3 and 5 were observed respectively. The value at pH 1 was the highest removal efficiency obtained as compared to the efficiencies obtained at other pH values. With an increase of pH from 1 to 5, Cr(VI) removal efficiencies decreased. The negatively charged Cr(VI) can exist mainly as chromate (CrO_4^{-2}), dichromate ($Cr_2O_7^{-2}$),hydrogen chromate ($HCrO_4^-$) or chromic acid (H_2CrO_4) ions are the dominant species depending on the solution pH conditions, according to equation (26) (Nassima Tazrouti; Moussa Amrani, 2009;Brito *et al.*,1997). The surface of ALC at low pH surrounded by hydrogen ions (H^+). The negatively charged ions species were thus effectively adsorbed on positively charged active sites on adsorbent the interactions may be primarily electrostatic or coordinative in nature (sahin; ozturk,2005). With an increased in pH the binding of ions decreased on account of repulsive force between the ALC surface functional groups and Cr(VI) ions. $HCrO_4^-$ ions predominantly exist in the solution over $Cr_2O_7^{-2}$ at pH =(1- 6) and the ionic size of $HCrO_4^-$ is smaller than that of $Cr_2O_7^{-2}$ (Brito *et al.*,1997). Consequently, the $HCrO_4^-$ ions were diffused and adsorbed easily onto surface of the lignite, compared to $Cr_2O_7^{-2}$ ions. Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms ($CrO_4^{-2}$and $Cr_2O_7^{-2}$). It can be concluded that the active form of Cr(VI) that can be absorbed by the lignite in this study is $HCrO_4^-$.



Therefore, the optimum pH was considered as 1.0 for the highest removal of Cr(VI). Another study has also recommended the same optimum pH value for Cr(VI) removal (Hyder A. H. M. Golam, 2013). On the other hand, the removal efficiencies were improved slowly with time for each pH.

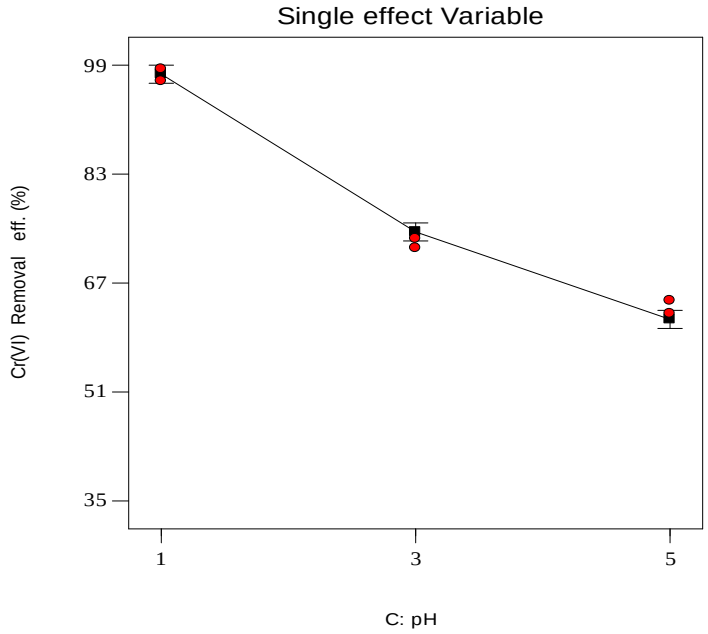


Figure 8: Effect of pH on percentage removal of Cr(VI) using ALC

4.5 Interaction effects of process variables on Cr(VI) removal

The interaction effect of process variables for percentage removal of Cr(VI) ions using ALC were visualized through contour and 3D plots of three dimensional views of response surface as a function of two independent variables, maintaining all other variables at fixed or different level. These plots can be helpful in understanding both the main and interaction effects of the independent variables on the response variable.

4.5.1 The interaction effect of Cr(VI) concentration and adsorbent dosages (AB)

The interaction effect of both factors (AB) was analyzed by checking the hot spotted formed in contour and 3D plotted. Figure(9) indicates the interaction effect of initial Cr(VI) ion concentration and adsorbent dosages on percentage removal of ions using ALC. The percentage

removal of Cr(VI) ions was increased with increased adsorbent dosage and with decreased Cr(VI) concentration.73.71 % Cr(VI) removal was obtained at Cr(VI) concentration of 60 mg/l, and adsorbent dose of 2 g at fixed pH 1. But, removal increased up to 96.54 % at Cr(VI) concentration decreased to 20.5 mg/l, and adsorbent dose increased to 3.01 g at fixed pH 1.The increased in percentage removal may be due to the complete utilization of all active sites in the adsorbent dosages by lower Cr(VI) metal ions in the solution. The reason increased in percentage adsorption with increased in adsorbent dose might be due to availability of more surface area and functional groups at higher mass of adsorbents (Naeema H. Yarkandi, 2014).

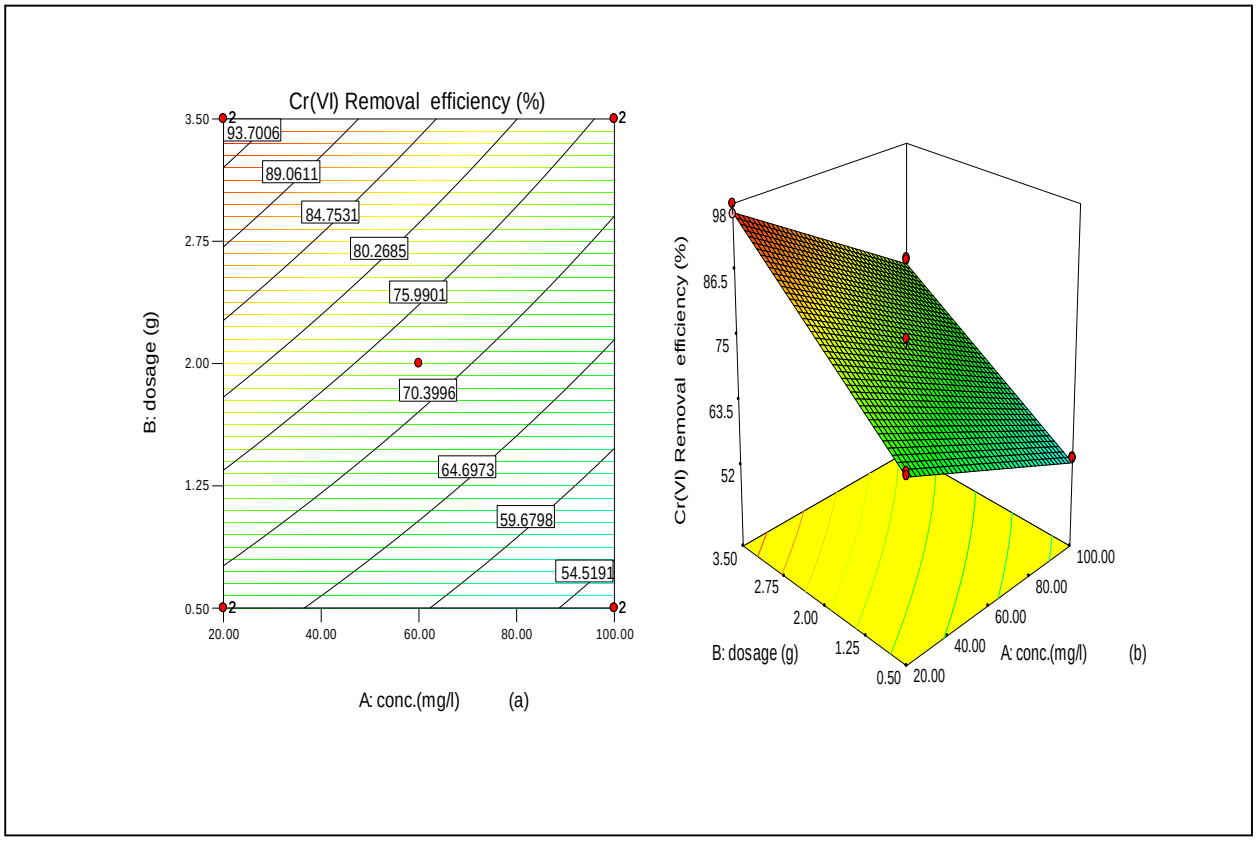


Figure 9: Contour (a) and 3D (b) plot of interaction effect of Cr(VI) ion concentration and adsorbent dosage (AB) on percentage removal of Cr(VI) ions using ALC

4.5.2 The interaction effect of Cr(VI) ion concentration and pH (AC)

Figure(10) (a), (b) represents the contour and 3D plot of the combined effect of initial metal ion concentration and pH value (AC) on percentage removal of Cr(VI) ions using ALC. The percentage removal of Cr(VI) ions was decreased with increased both initial metal ion concentrations and pH value. 49.94 % Cr(VI) removal was achieved at Cr(VI) concentration of 100 mg/l, and pH 5 at constant adsorbent dose of 3.5 g. But, at the same dosage (3.5 g) the Cr(VI) removal could be increased to 70.65 % by decreasing the initial concentration and pH value to 60 mg/l and 3, respectively. The decreased in percentage removal due to increasing initial concentration may be due to the limited number of actives sites in the specific adsorbent attained saturation above certain concentration. In another way, this might be due to the reason that at low concentration, the ratio of available surface to the Cr(VI) ions concentration is larger, so the removal is higher. However, in case of higher concentrations, this ratio is lower; hence the Cr(VI) ions removal was lesser (Naeema H Yarkandi, 2014). And also the decreased of percentage removal Cr(VI) ions at higher pH may be due to the increased negative charges on the adsorbent surface, which decreases the attraction of oxyanions of Cr(VI) ions on the adsorbent.

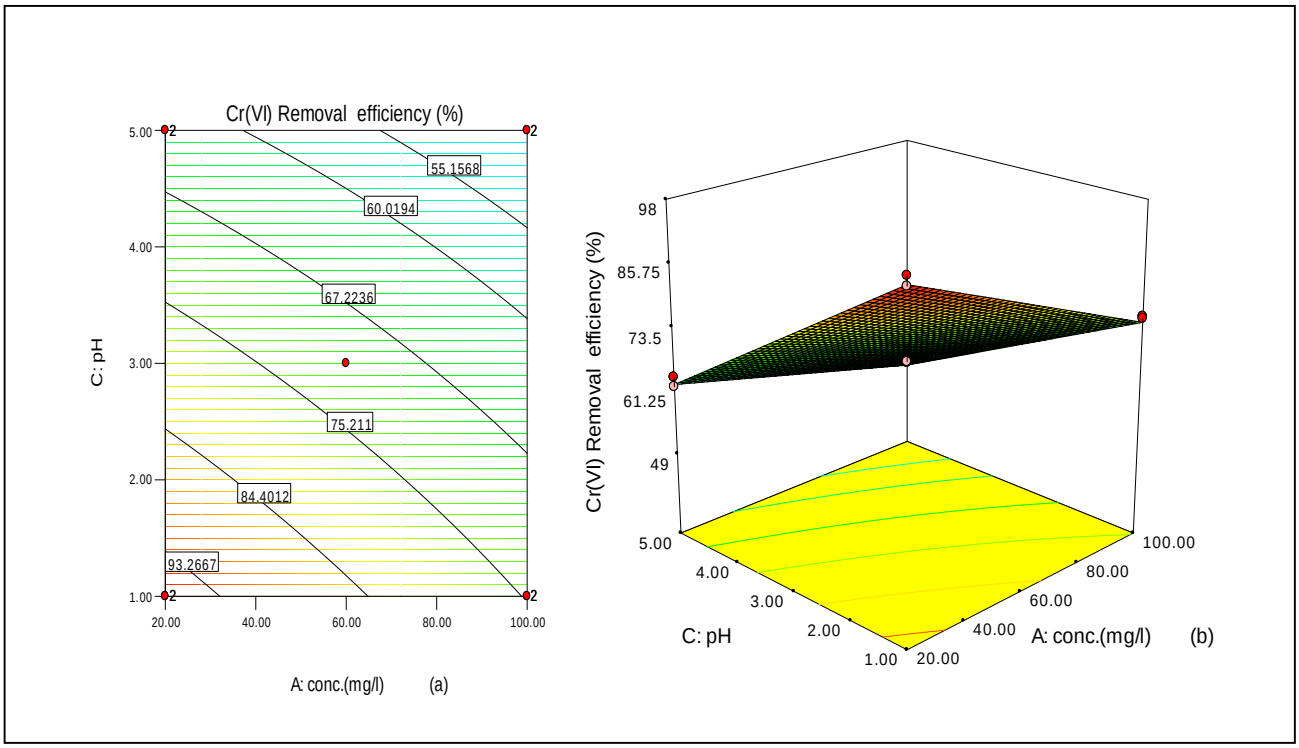


Figure 10: Contour (a) and 3D (b) the plot of interaction effect of Cr(VI)ion concentration and pH (AC) on percentage removal of Cr(VI) ions using ALC

4.5.3 The interaction effect of adsorbent dosage and pH (BC)

The interaction effect of adsorbent dosage and pH value on percentage removal of Cr(VI)ion using LAC is shown in Contour (a) and 3D (b) plot of Figure(11).The maximum percentage removal of Cr(VI) ion using ALC was obtained at lower pH and higher adsorbent dosage. The graph shows that the maximum adsorption (96.54 %) occurs under acidic conditions, pH 1.5 and adsorbent dose of 2.85 g. Increasing the solution pH from 1 to 5, decreasing removal to 42.44 %. This may be due to the surface positive oxygen-containing functional groups of the ALC adsorbent carried the oxyanions (negatively charged) of Cr(VI) ions by electrostatic force of attraction. At higher pH, the increased negative charges on the adsorbent surface decreased the attraction of oxyanions of Cr(VI) ions on the adsorbent.

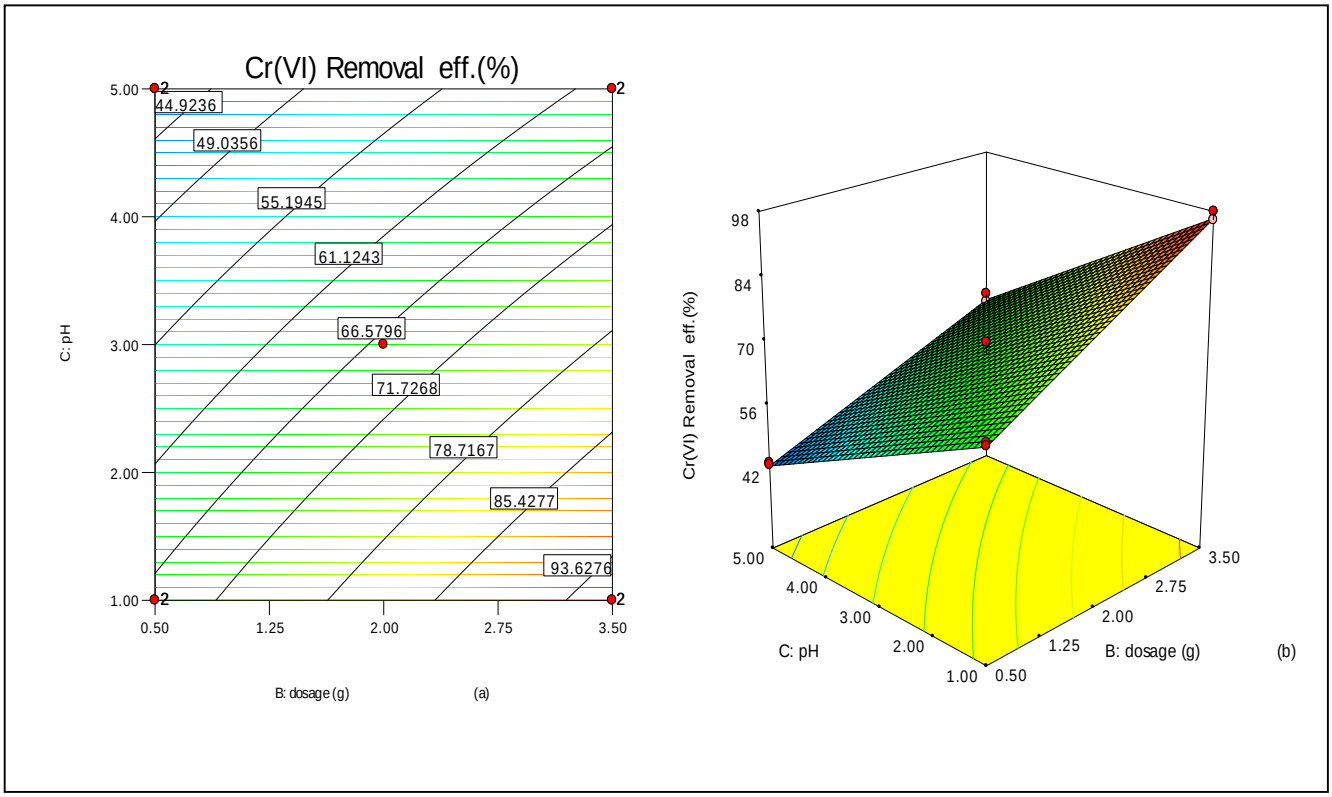


Figure 11: Contour (a) and 3D (b) plot of the interaction effect of pH and adsorbent dosage (BC) on percentage removal of Cr(VI) ions using ALC.

4.6 Development of regression model analysis

Based on the linear effect of the model designed from input variable, the comparison of RSM model of actual and predicted plots for percentage removal of Cr(VI) ions using ALC was estimated as shown in Figure(12).The relationship between actual values and predicted values indicate that the actual values are distributed relatively near to the straight line, indicating good fitness of the model. Again in Figure (13), the plot of studentized residuals versus run order was tested and the residuals were scattered randomly around ±3.00. This was an indication of better fitting of the model with the experimental data.

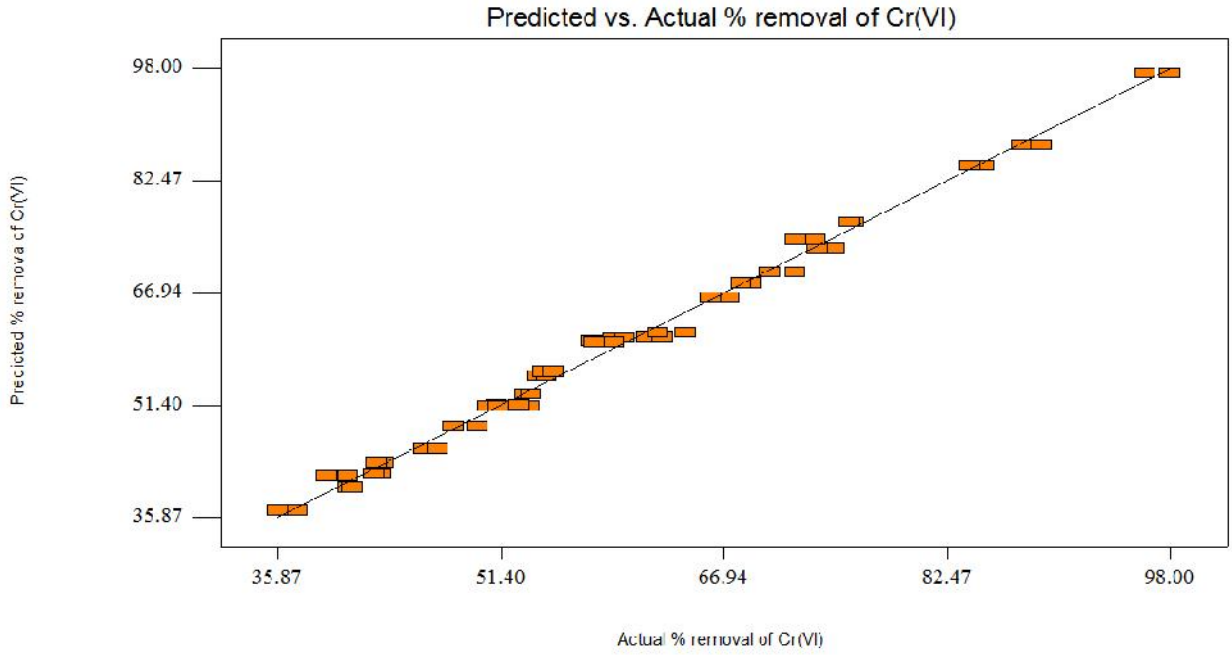


Figure 12: The actual and predicted plot for percentage removal of Cr(VI) ions using ALC

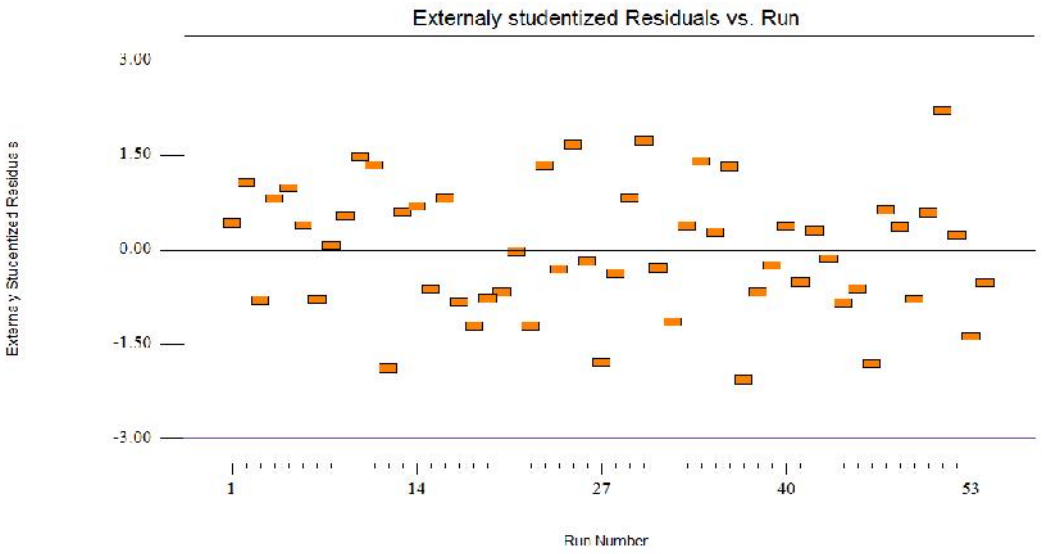


Figure 13: Plot of Studentized residuals versus experimental run number

The goodness of fit of the model was checked by the determination coefficient (R^2) as shown in the Table (9). The R^2 value provides a measure of how much variability in the observed response values can be explained by the experimental variable and their interaction. The R^2 value is always between 0 and 1. The closer the R^2 value is to 1, the stronger the model is and the better it predicts the response. In this case, the value of the determination coefficient (R^2=0.99) indicates that 98.77 % of the variability in the response could be explained by the model. In addition, the value of the adjusted determination coefficient (Adj R^2=0.98) is also very high to advocate for a high significance of the model. Also higher the value of correlation coefficient (R^2=0.97) justifies an excellent correlation between the independent variables. The response surface contour and 3D plots of percentage removal of Cr(VI) versus the interactive of initial chromium concentration (mg/l), adsorbent dosage (g), and pH are shown in the Figure (9) to (11).

Table 9: Model summary statistics for percentage removal of Cr(VI) ions using ALC

Std. Dev.	2.09	R-Squared	0.99
Mean	59.59	Adj R-Squared	0.98
C.V.	3.52	Pred R-Squared	0.97

4.7 Optimum conditions for Cr(VI) removal

According to RSM, the optimum conditions for the removal of Cr(VI)from aqueous solution using ALC are initial Cr(VI) concentration-20 mg/l, pH-1.00, and adsorbentdose-3.5g/200mL. At these conditions, the maximum removal of Cr(VI) was found to be 98 %.

4.8 Evaluation of adsorption capacity of ALC using optimum condition

4.8.1 Adsorption capacity of ALC at different adsorbent dosages

The study on the effect of the amount of adsorbent on the process of adsorption were carried out by varying adsorbent dose from 0.5 to 3.5 g in the maximum initial concentration of Cr(VI) 20 mg/l in solution of 200 mL with pH 1, contact time 4 hours. The adsorption capacity of Cr(VI) ions on ALC decreases from 5.5 to 1.12 mg/g when the amount of ALC increases from 2.5 to 17.5 g/L. This seems to be due to the binding of almost all ions to the adsorbent and equilibrium is reached between the ions bound to the adsorbent and those remaining unabsorbed in the solution.

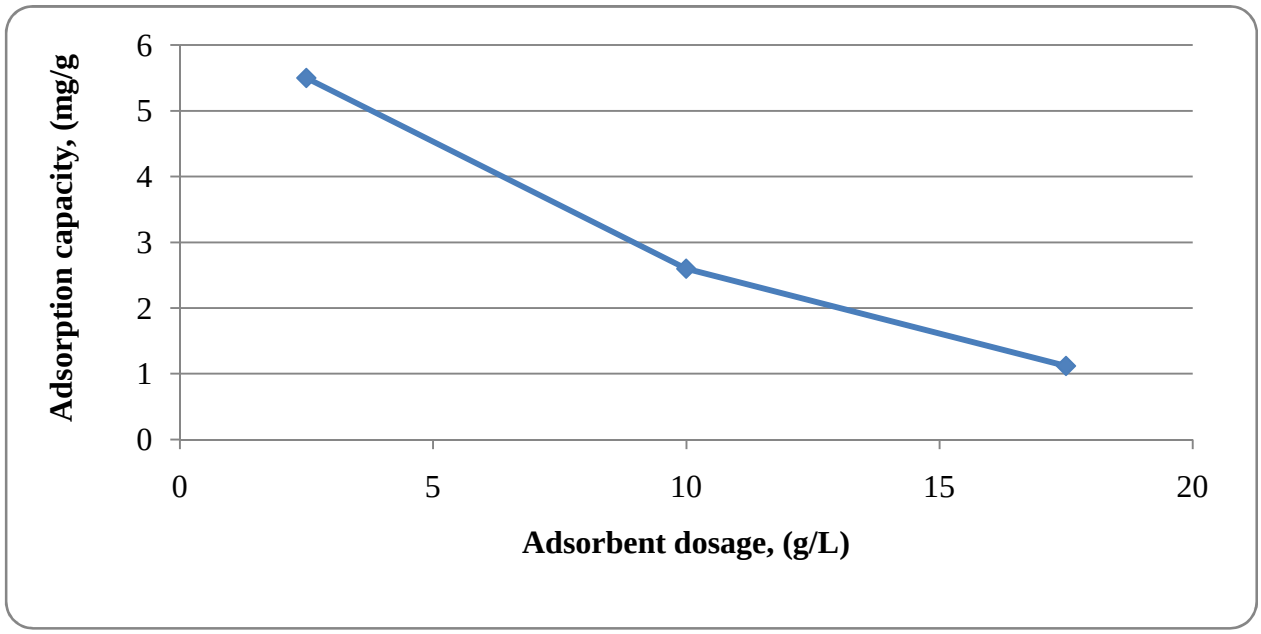


Figure 14: Effect of adsorbent dosage on adsorption capacity of Cr(VI) ions using ALC.

4.8.2 Adsorption capacity of ALC at different initial concentrations

The adsorption capacity of Cr(VI) is influenced significantly by initial concentration of Cr(VI), in aqueous solutions. In this study, initial concentration of Cr(VI) was varied from 20 to 100 mg/l while maintaining other variable constant (adsorbent dose at 0.5 g, time at 4 hours and pH 1).The results of Figure (15) show the effect of variation of the initial concentration on the adsorption capacity of Cr(VI). Adsorption capacity of Cr(VI) ions on ALC adsorbent increases from 5.5 to 21.34 mg/g with increases of Cr(VI) ions concentration. This may be due to the higher initial metal ion concentration provides increase a driving force to overcome all the mass transfer resistance of metal ions between the aqueous and solid phases resulting in a higher probability of collision Cr(VI) ions and the ALC adsorbent which results in increased adsorption capacity (Devarasath *et al*., 2007; Soroj; Surenda, 2008).

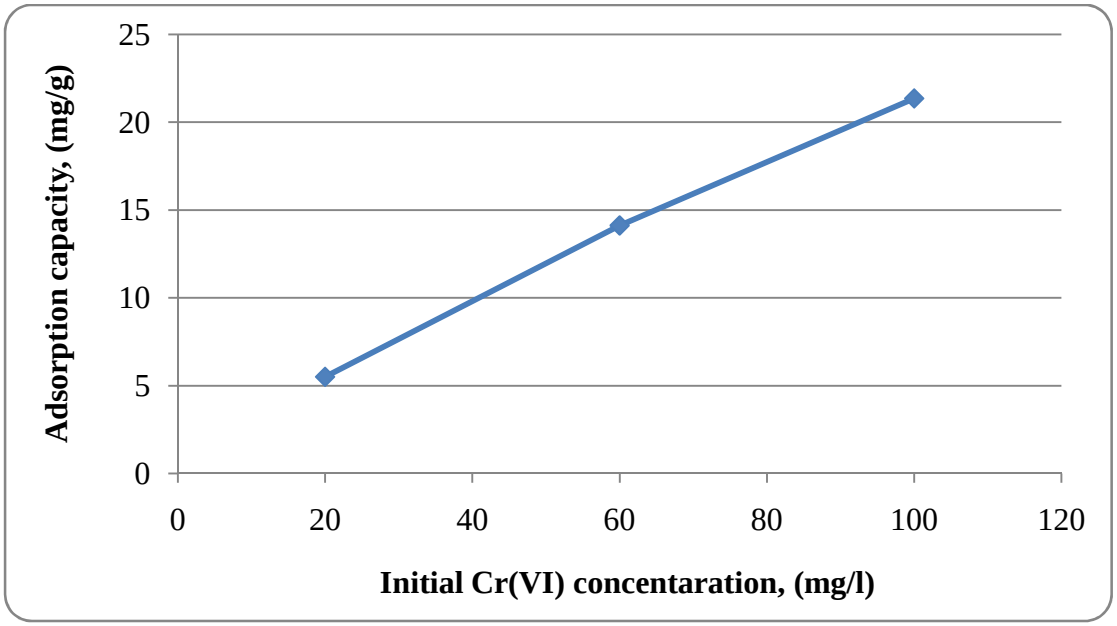


Figure 15: Effect of initial Cr(VI) concentration on adsorption capacity of Cr(VI)ions

4.8.3 Adsorption capacity of ALC at different pH.

In order to optimize the pH for maximum adsorption capacity of Cr(VI) ion, adsorption experiment was conducted in the initial pH range from 1 to 5 with constant initial Cr(VI) concentration of 100 mg/l and adsorbent dose of 0.5 g, as shown in Figure(16).The maximum adsorption capacity of Cr(VI) ion using ALC was obtained at lower pH value. The graph shows

that the maximum adsorption capacity of 21.34 mg/g occurs under acidic conditions (pH 1). Therefore, the optimum pH 1.0 was obtained for the highest adsorption capacity of Cr(VI) as the same effect on Cr(VI) removal efficiency (Dahbi *et al*., 1999). This due to at lower pH value the surface of the adsorbent becomes highly protonated and favours the uptake of Cr (VI) ions.

With increase in pH, the degree of protonation of the surface reduces gradually and hence adsorption capacity is decreased

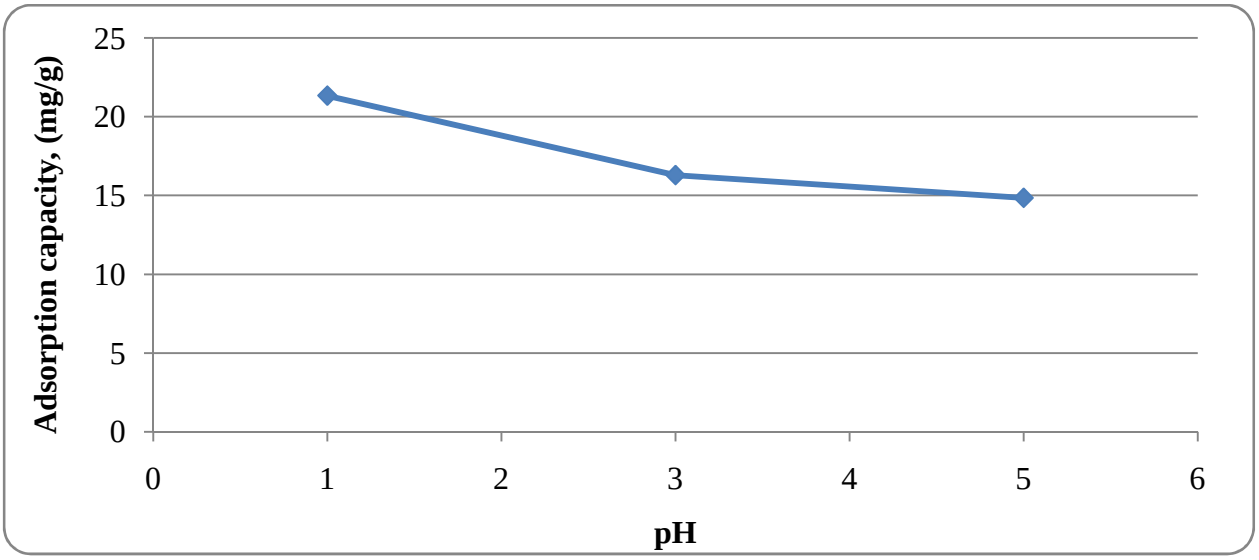


Figure 16: Effect of pH on adsorption capacity of Cr(VI) ions using ALC

4.9 Evaluation of equilibrium adsorption capacities (q_e)

The adsorption capacities of ALC after different reaction times with various initial concentrations of Cr(VI) ranging from 2 0 to 100 mg/l are shown Figure (17). With an increased of initial Cr(VI) concentrations, the adsorption capacities of the LAC (q_t) improved with time. For every particular initial Cr(VI) concentration (from 20 to 100 mg/l), the adsorption capacity increased up to a certain period and then tended to remain at a constant level at constant dosage of 3.5 g and pH 1. These constant adsorption capacities are interpreted as the equilibrium adsorption capacity (q_e). The lowest adsorption capacity of 0.95 mg/g was found after 0.5 hour for the lowest studied initial Cr(VI) concentration of 20 mg/l but the highest adsorption capacity of 4.34 mg/g was obtained after 4hours for the highest studied initial Cr(VI) concentration of 100 mg/l. However, the adsorption capacities reached constant (equilibrium) values at 1.12

mg/g after 2 hours, 3.05 mg/g after 3 hours and 4.34 mg/g after 4 hours for the three initial Cr(VI) concentrations of 20 mg/l, 60 mg/l and 100 mg/l, respectively. When the initial Cr(VI) concentration was low, the adsorptioncapacity (q_t) was low and became constant quickly. With an increased of initial Cr(VI) concentrations, adsorption capacities (q_t) increased and the time required to achieve the highest adsorption capacity was also increased. This might be due to the presence of sufficient Cr(VI) ions for adsorption by the active sites of ALC for the increasing initial Cr(VI) concentrations.

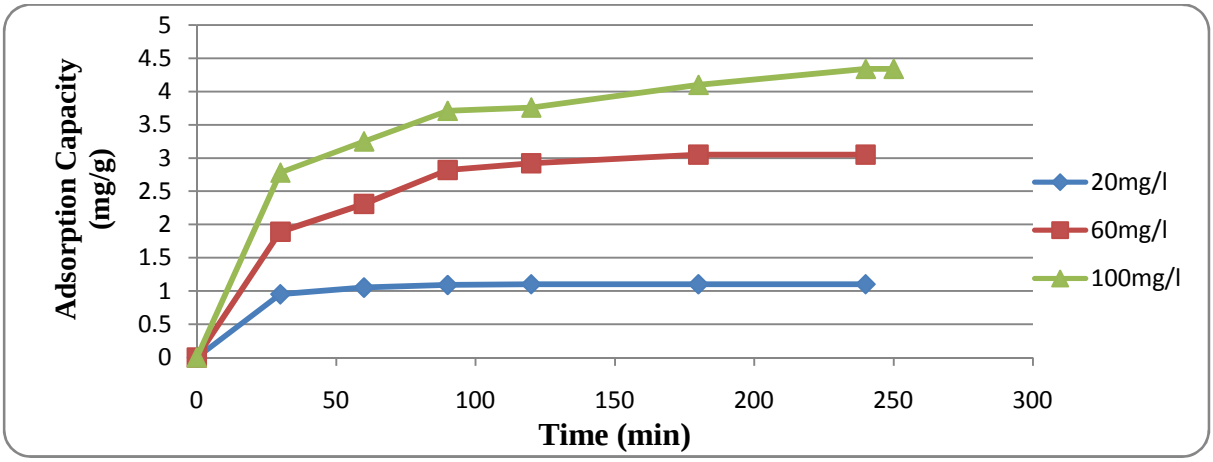


Figure 17: Adsorption capacities of ALC at any particular time for different initial Cr(VI) concentrations.

4.10 Evaluation of FTIR analysis

The FTIR spectra of Figure(18) illustrated for ALC and Cr(VI) loaded on ALC after adsorption process with its most abundant functional groups. As shown in Figure(18), the broad peak around 940 cm^{-1} was due to the C–O bending vibration of ketones, aldehydes and lactones or carboxyl groups (Ak Bajpai; Leena Rai, 2010). The bending peak at 1534.5 $cm^{-1}$was attributed to a C=O bending vibration of carboxylate (–COO-) or an N–H deformation vibration of amide I groups (Tan C.*et al.*, 2010). The bands around 2832.5 cm^{-1} was corresponded to the C–H symmetric stretch of the methylene groups (–CH) and deformation vibration of methyl groups (–CH) (Tan C., 2010). The broad peak at 3346 cm^{-1} was caused by the overlap of O–H and N–H stretching vibrations, indicating the presence of both surface free hydroxyl groups and chemisorbed water (Mohan S.V.*et al.*, 2008). Some of the bands shifted in wave numbers from 940 to 943.5, 1534.5 to 1547, 2832.5 to 2836 and 3346 to 3374 cm^{-1},were observed in the spectra

of ALC before and after use. These changes indicated interactions between functional groups of adsorbent and Cr(VI) ions. Generally, the FTIR spectral analysis of the both samples confirm: (i) the presence of functional group components in the adsorbent (ii) the change in band position of some functional groups of adsorbent after the adsorption of Cr(VI) ions indicating the important role of these groups in the adsorption of chromium.

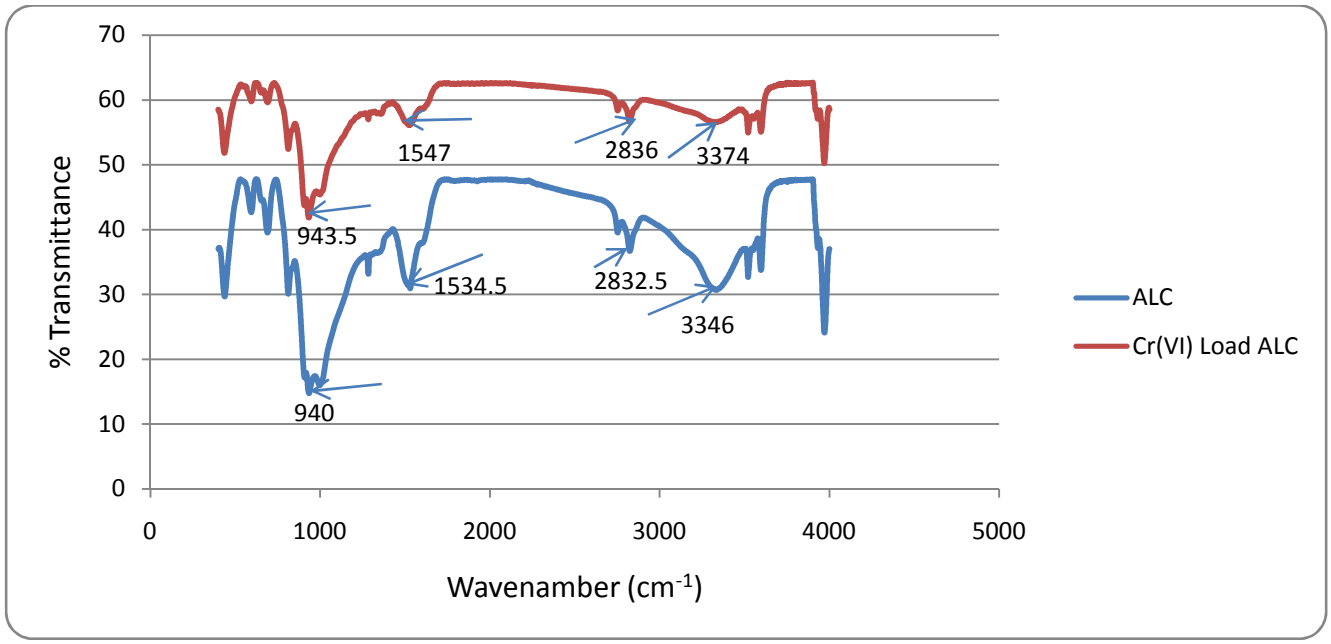


Figure 18: FTIR Spectra of unabsorbed LAC and Cr(VI) Adsorbed LAC.

4.11 Evaluation of the adsorption isotherm models of Cr(VI) on to ALC

4.11.1 Evaluation of the Langmuir Equilibrium adsorption isotherm model

The equilibrium adsorption data for Cr(VI) adsorption onto ALC was evaluated using the Langmuir model. The Langmuir model plot is shown Figure(19) which demonstrates a linearcorrelationbetween1/q_e and 1/C_e, and it represents not so linear correlation with R^2 of 0.992, that is lower than what was observed in the Freundlich model plot Figure(20).

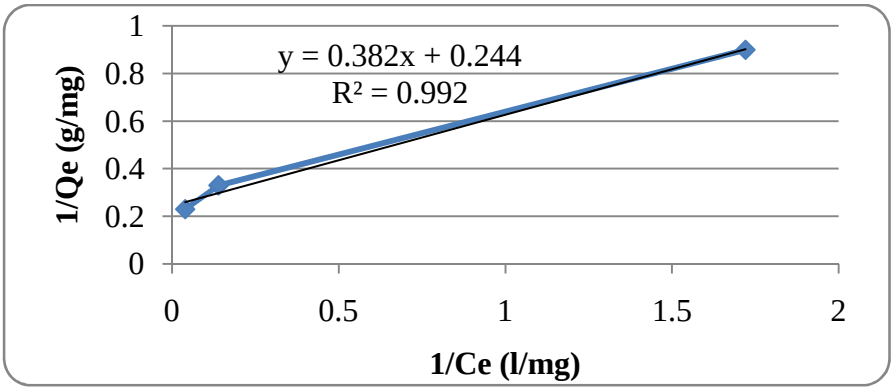


Figure 19: Langmuir equilibrium adsorption isotherm plot of Cr(VI) ions onto the ALC.

In this study, both isotherms have a better fitting, but Freundlich has a higher correlation regression coefficient (see Table 11). This indicates that, the applicability of multilayer coverage of the Cr(VI) on the surface of adsorbent (Adhena Ayaliew*et al.*, 2014). The R_L values falls in between $0<R_L<1$. As initial concentration increases, R_L value is closer to zero which is due to effect of pore diffusion adsorption process as it was calculated from Eq. (15). Therefore, the type of adsorption process of Cr(VI) on to acid treated lignite activated carbon is favorable as shown in Table(10).

Table 10: Regression constant values of ALC for removal of Cr (VI).

No	Co (mg/l)	$RL = \frac{1}{1 + KL * Co}$
1	20	0.0725
2	60	0.0254
3	100	0.0154

The values of the Langmuir equilibrium adsorption constant (K_L),the maximum adsorbed amount of Cr(VI) per mass of ALC for complete mono-layer coverage (q_m),and the regression coefficient (R^2) were estimated from Eq. (14) are given in the Table (11).

Table 11: Adsorption equilibrium isotherm model constants for Cr(VI) on the ALC

Langmuir isotherm constants			**Freundlich isotherm constants**		
q_m (mg/g)	K_L (l/mg)	R^2	K_F (mg/g)	1/n	R^2
4.10	0.64	0.992	1.40	0.368	0.996

The maximum adsorption capacity (q_m) found in the experimental result as 4.34 mg/g and the one predicted using Langmuir model as 4.10 mg/g. The deviation of q_m value obtained from the experiment to Langmuir model was 5.53 %.

4.11.2 Evaluation of the Freundlich equilibrium adsorption isotherm model.

The Freundlich model was used to evaluate the adsorption isotherm of Cr(VI) onto ALC. The plot of Freundlich model between $\log q_e$ and $\log C_e$ with R^2 of 0.996 (close to 1) was presented Figure (20). The values of the Freundlich adsorption capacity parameter (K_F), and the adsorption intensity factor (1/n) were estimated from Eq.(17) is listed in the Table (11). The adsorption isotherm analysis indicated that the adsorption of Cr(VI) onto ALC followed the Freundlich model as R^2 value is more closer to 1.0 than what was observed in the Langmuir model. The value of 1/n lying between 0 and 1 which in this case is 0.368, and the K_F value laying between 1 and 10, which in this case is 1.40, indicates a favorable condition for adsorption (Adhena Ayaliew*et al.*, 2014).

Thus, the results implied that adsorption of Cr(VI) took place on heterogeneous and multilayer surface energy of ALC, and Cr(VI) species did interact with each other during the adsorption process. Therefore, the Freundlich model indicates better linearity for the adsorption of Cr(VI) in heterogeneous condition. Similar results have been reported by other researchers in the study of Cr(VI) adsorption on multiwall carbon nano tubes and the activated carbon produced from waste rubber tires (Jung C.*et al.;* Gupta VK.*et al.*,2013).

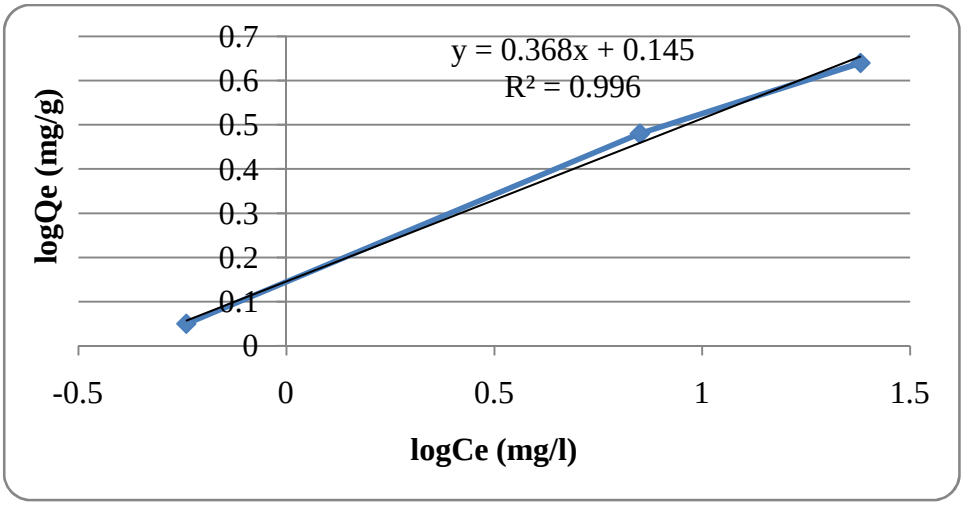


Figure 20: Freundlich equilibrium adsorption isotherm plot of Cr(VI) ions onto ALC.

4.12 Evaluation of the kinetic model of Cr(VI) adsorption onto ALC

4.12.1 Evaluation of the first order kinetic model

The first-order kinetic model plot for Cr(VI) adsorption onto the LAC is presented Figure (21). In order to draw this plot, the $\log(q_e - q_t)$ values were taken for the initial Cr(VI) concentration of 20 mg/l, because it was chosen as the optimum concentration. The best fit line of the plot of $\log(q_e-q_t)$ versus t was less or not linear, and showed a negative slope as expected from the governing kinetic equation.

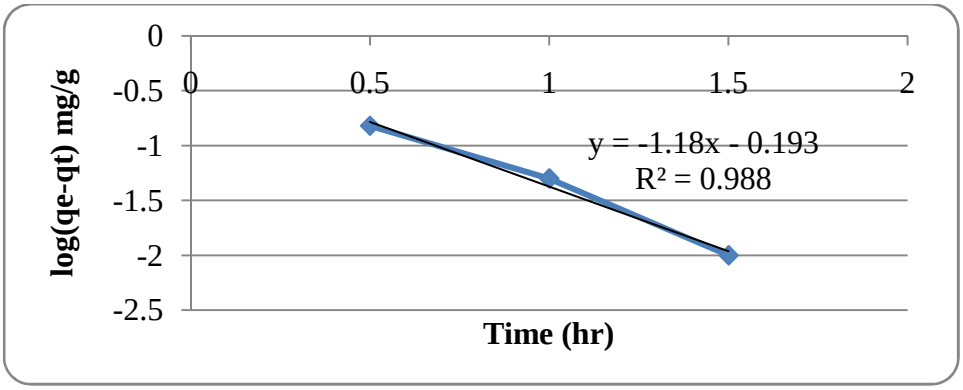


Figure 21: First order kinetic model for the Cr(VI) concentration of 20 mg/l adsorption.

According to the data from the plot, the values of the first order rate constant (K1), the equilibrium adsorption capacity (qe), and the regression coefficient (R^2) were calculated from Eq. (20) are given in the Table (12).

Table 12: Adsorption Reaction kinetic model parameters of Cr(VI) on the ALC

First Order Kinetic Parameters			Second Order Kinetic Parameters		
q_e (mg/g)	$K_1(hr^{-1})$	R^2	q_e (mg/g)	$K_2(g.mg^{-1}.h^{-1})$	R^2
0.64	2.72	0.988	1.18	7.01	1.0

4.12.2 Evaluation of the second order kinetic model

The second-order kinetic model plot for the experimental data is presented Figure (22). The plot clearly exhibits a linear correlation between the values of t/q_t and t with a positive slope as expected from the second order equation. This plot was drawn based on the data found for the initial Cr(VI) concentration of 20 mg/l adsorption, since this was the optimum concentration. The values of the second-order rate constant (K_2), the equilibrium adsorption capacity (q_e), and the regression coefficient (R^2) were calculated from Eq.(25) is listed in the Table (12).

Table 13: Deviation of q_e values for the first and second order kinetics.

q_e (mg/g)				
Experimental value	First order kinetic model value	Deviation (%)	Second order kinetic model value	Deviation (%)
1.1	0.64	41.8	1.18	7.3

The deviations of the equilibrium adsorption capacity (q_e) obtained from the experimental value to the first order kinetic model value and to the second order kinetic model value are shown Table(13). A deviation of about 41.8% was observed between the first order derived equilibrium adsorption and the experimental data larger deviation was observed. However, for the second-

order kinetic model smaller deviation of 7.3 % was observed between the experimental value of the equilibrium adsorption capacity (q_e) and the value was calculated from the second order kinetic model.

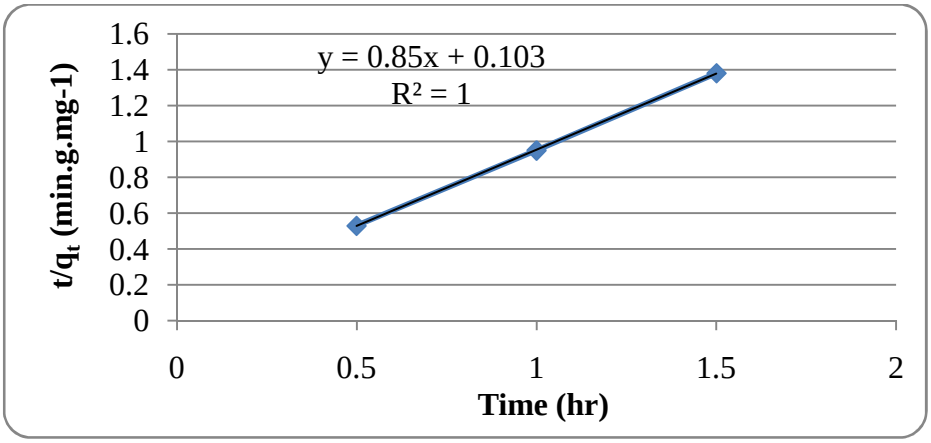


Figure 22: Second order kinetic model of the Cr(VI) concentration of 20 mg/l adsorption.

The results observed for the initial Cr(VI) concentration of 20 mg/l perfectly fit to second-order kinetics model, the same second- order kinetic model also was evaluated for the other initial Cr(VI) concentrations used in this study in order to verify whether the second order model fit like Cr(VI) concentration of 20 mg/l or not. The linear progressive correlation with positive slopes were found for all initial Cr(VI) concentrations ranging from 20 to 100 mg/l Figure(23). It was found that regression coefficient (R^2) values were very much closed to 1.0 for all these various concentrations. These regression coefficient (R^2) values indicate a strong support for the second order kinetic model for the adsorption of Cr(VI) on to the LAC at all initial concentrations studied. Therefore, it can be concluded that the kinetics of Cr(VI) adsorption on ALC fits best to the second-order model, which is in agreement with the previous reports on Cr(VI) adsorption (Luo C.*et al.*, 2013; Selvarani M.*etal.*, 2012). And also it can be interpreted that the kinetics of the Cr(VI) adsorption reaction onto ALC depends upon the concentration of Cr(VI) in the batch solution, and the amount of ALC needed to adsorb Cr(VI) ions from the batch solution at equilibrium.

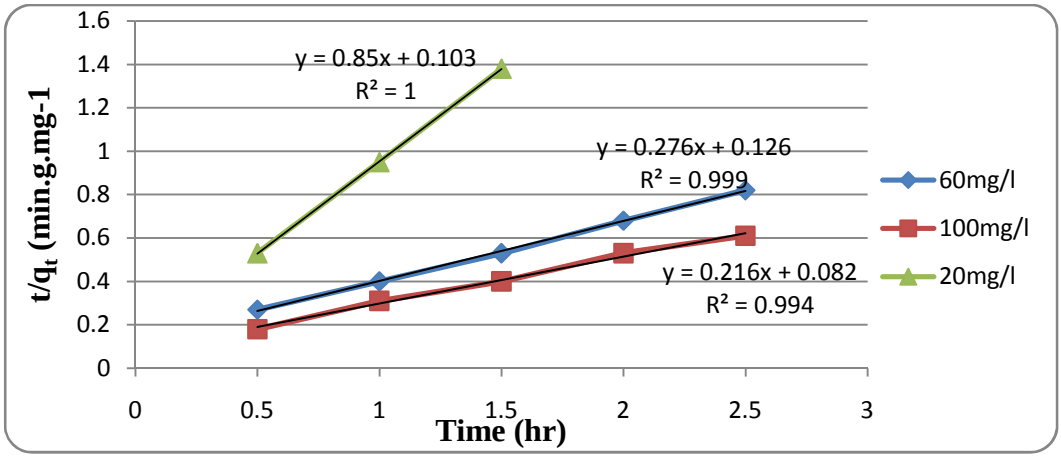


Figure 23: Second order kinetic model for Cr(VI) Adsorption onto the ALC at different initial concentrations.

5. Conclusions and Recommendations

5.1 Conclusions

The ALC produced from Ethiopian LC, as newly alternative adsorbent for Cr(VI) removal was investigated by making simple chemical modifications with hydrochloric acid. This ALC was characterized and utilized for removal of Cr(VI) from aqueous solution using batch adsorption techniques. The results indicate that the ALC is a good adsorbent. Thus Cr(VI) removal with ALC reached 98 % with dosages of 3.5 g for initial Cr(VI) concentration of 20 mg/l in 200mL volume of solution. Adsorption of Cr(VI) ion was highly pH-dependent and the results showed that the optimum pH for the removal was found to be strong acidic media (pH 1), at which Cr(VI) exists mostly as the most easily adsorbed form, $HCrO^-_4$, increases as the initial Cr(VI) concentration and contact time were found to increases the percentage removal of Cr(VI). The FTIR spectra analysis showed that this material contains many oxygen-containing functional groups namely: carboxyl, amine, methylene, and hydroxyl groups. These functional groups characteristics of ALC shows responsible for chromium binding onto surface of LAC within the pH range (pH 1-5) where chromium does not precipitate. The development of mathematical model for adsorption of Cr(VI) using statistical design of experiments appears to be a useful tool for prediction and understanding of interaction effects between process variables using general full factorial design.

The equilibrium data using both the Langmuir and Freundlich isotherm and the kinetics rate (first and second-order kinetic) models of Cr(VI) adsorption on the ALC were analyzed successfully. The adsorption data was better fitted by the Freundlich model adsorption isotherm followed by the Langmuir isotherm model over the concentration range studied and suggested that the surface is relatively heterogeneous surface energy in terms of functional groups. The second-order kinetic models provided better fit for the Cr(VI) adsorption rate onto LAC.

The studies data presented here inform that the adsorbent, ALC is locally available low-cost high carbonaceous containing raw material could be fruitfully employed as adsorbent for removal of chromium from aqueous solution, therefore it can be useful in the treatment of chromium contaminated wastewater before discharge into the aquatic environment without any sludge production.

5.2 Recommendations

In the future the following works should be explored on lignite coal for wastewater treatment:

- In this study synthetic wastewater was used to evaluate the batch test adsorption processes. However, in the future, use of real wastewater collected from the industries could be the great potential of the studies as synthetic wastewater does not contain other interfering substances such as other metal ions, micro-organism, and humic acid.
- Further research is needed to evaluate economic feasibilities on the lignite activated carbon production processes and utilization in the wastewater treatment system which has not been done in this work.
- Study the adsorption process using other metals like zinc, lead, arsenic among others.
- The saturated adsorbent which contains Cr(VI) is not safe for disposal due to the stringent environmental constraints. It is important and appropriate to propose a method for regeneration and reuse of adsorbent and recovery of Cr(VI) so as to reduce the load on environment in terms of disposal of polluted adsorbent.

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Appendixes

Appendix I: Evaluation of proximate analysis of lignite

1. Bulk Density (BD) Determination

Bulk Density (BD) = M_a / V_s (2)

BD= 2g/1.16 cm^3 =1.72 g/cm^3 for Raw lignite

BD= 2g/1.21 cm^3 =1.65 g/cm^3 for acid treated lignite

Where, M_a=weight of sample(g), V_s= volume of displaced (cm^3)

2. Moisture content (Mc%) and dry matter Determination

Moisture content (Mc%) = $Wo-W_1 / W_o$ x 100 % (3)

Mc=1.9096 - 0.0904/2*100= 4.52 % for raw lignite

Mc=1.917 - 0.083/2*100= 4.15 % for acid treated lignite

Where,

Mc= Moisture content

W_0= Initial weight of dry sorbent

W_1 = New weight of sorbent after drying /Oven dry weight

Dry matter [%] = $\frac{\text{Oven dry weight (g)}}{\text{Initial sample weight (g)}} \times 100$ (4)

Dm (%) = $\frac{1.909}{2} \times 100$ =95.48 % for Raw lignite

Dm (%) = $\frac{1.917}{2} \times 100$ =95.85 %for acid treated lignite

3. Ash Content (A_C %) Determination

Ash Content (A_C %) = $W_a / W_0 x$ 100 % (5)

A_C = 0.798/ 2x 100= 39.9% for Raw lignite

A_C = 0.399/ 2x 100= 19.95% for acid treated lignite

Where,

W_a=weight of ash after cooling

W_0=original weight of dry adsorbent

4. Volatile Content V_C(%) Determination

$V_C(\%) = [W_0 – W_a/ W_O] \times 100\ \%$ (6)

V_C =[41.149-40.492]/2 *100= 32.85 % for Raw lignite

V_C =[41.149-40.544]/2 *100= 30.25 % for acid treated lignite

Where,

V_C=volatile component in percentage

W_0 =the original weight of dry adsorbent

W_a=the weight of matter after cooling

5. Fixed Carbon (Fc%) Determination

Fc (%) = 100 –Vc– Ac-Mc (7)

F_C = 100 –32.85– 39.9-4.52 = 22.73 % for Raw lignite

F_C = 100 –30.25– 19.95-4.15= 45.65 % for acid treated lignite

Where,

V_C=volatile content

A_C=ash content

M_C= moisture content

Appendix II: Calculation of Potassium Dichromate Requirement

To Prepare 1000 mg/L of Cr(VI) Stock Solution we have to calculate how much $K_2Cr_2O_7$ is required to get concentration of Cr(VI) stock solution of 1000mg/L [1 g in1 L solution].

Potassium dichromate ($K_2Cr_2O_7$) has molecular weight= 2*39 + 2*52 + 7*16 =78+ 104 + 112= 294 g/mol, 104 g Cr(VI) is available in= 294 g of $K_2Cr_2O_7$. 1 g Cr(VI) in $K_2Cr_2O_7$ is ?

1 g Cr(VI) is available in= (294/104)*1 = 2.8269 g of $K_2Cr_2O_7$.

Appendix III: Dilution of Cr(VI) Stock Solution from 1000 mg/l

Let assume, Initial concentration of stock solution of Cr(VI), C1=1000 mg/l was diluted to the required working concentrations. Initial volume of stock solution of Cr(VI),V1 =?[have to find out]. Required diluted concentration of Cr(VI),C2= 20mg/l [can vary: 20-100 mg/l]. Required

diluted solution volume of Cr(VI), V2= 200mL [can vary to required volume]. According to them as balance equation, we know:

Mass of stock solution=Mass of diluted solution

$$C1*V=C2*V2 \quad (1)$$

which is V1 =(C2* V2)/C1 ;

V1 =(20mg/l* 200mL) / 1000mg/l= 4mL Required distilled water= Total volume of solution– Initial Volume of Cr(VI) = 200 – 4= 196 mL. Then,V1=4mL of Cr(VI) stock solution was taken from the Cr(VI) stock solution and was measured by a micropipette. This V1 amount of Cr(VI) stock solution was taken in a 200mL volumetric flux and then filled up there maining portion (up to 200mLmarks) of the volumetric flux with distilled water (196mL).

For Cr(VI) removal by lignite, all the batch tests was performed with solution volume of 200mL. Similar calculations described above was followed for dilution of Cr(VI) stock solution into the required working concentrations from 20-100 mg/l. According to Equation1 Cr(VI) stock solution was diluted to required working concentrations which is as follows:

For required working concentration of Cr(VI),C2=60 mg/l; was Calculated V1 =12mL

Required distilled water=Total volume of solution–Initial Volume of Cr(VI)=200–12 = 188mL

For required working concentration of Cr(VI),C2= 100 mg/l; was Calculated V1 = 20 mL.

Required distilled water=Total volume of solution–Initial Volume of Cr(VI) = 200 –20 = 180 mL

Appendix IV: Color change of the sample due to DPC

Figure 1: The color change of the samples due to DPC

Appendix V: Calibration Carve for standard solution

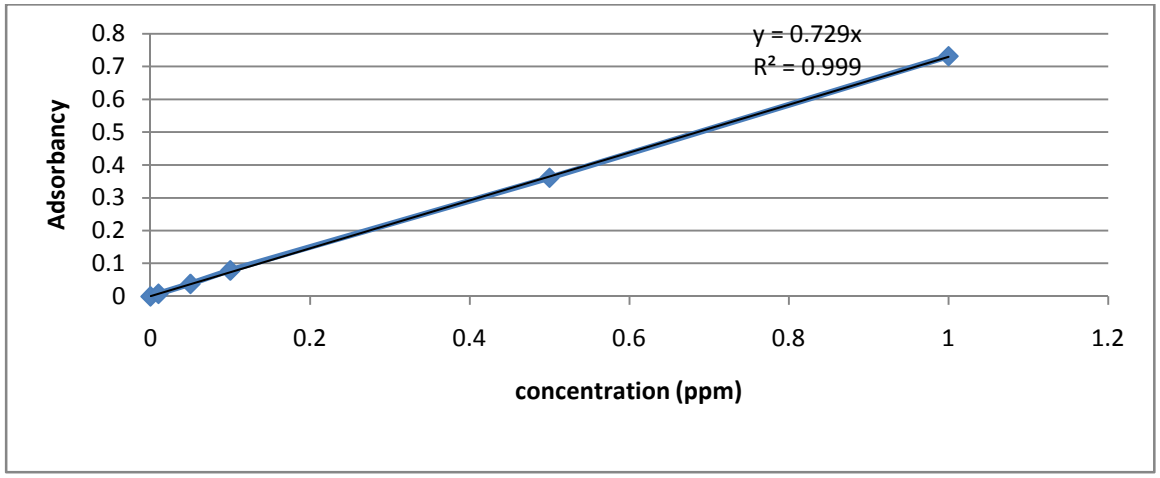

Figure 2: Calibration curve for UV measurement of Cr(VI) concentration

Appendix VI: Experimental design matrix and responses

Run	A: Conc. (mg/l)	B: Dosage (g)	C: PH	Y: Cr(VI) Removal eff. (%)
1	100	2	5	42.53
2	60	2	5	49.77
3	20	3.5	1	96.25
4	60	3.5	3	67.24
5	20	0.5	3	52.68
6	20	0.5	1	68.78
7	20	3.5	3	73.26
8	100	2	3	53.07
9	60	0.5	3	46.03
10	100	3.5	3	62.62
11	60	2	1	74.65
12	20	3.5	3	71.9
13	20	3.5	1	98
14	20	3.5	5	62.34
15	100	3.5	5	50.47
16	60	0.5	5	41

17	60	3.5	5	55.02
18	20	2	5	54
19	20	2	5	54.55
20	100	0.5	3	40.74
21	100	3.5	5	51.22
22	60	0.5	1	58.79
23	60	3.5	1	89
24	20	0.5	3	51.07
25	100	0.5	1	53.34
26	60	3.5	3	66
27	60	2	3	57.87
28	20	2	1	84.06
29	100	2	5	43.03
30	20	2	3	71.89
31	60	2	5	48.09
32	100	2	1	59.21
33	100	2	3	53.46
34	100	0.5	1	53.01
35	60	3.5	1	87.68
36	60	0.5	3	47
37	60	0.5	1	57.73
38	60	2	3	59.25
39	20	0.5	5	43.19
40	20	2	1	85
41	100	2	1	60
42	20	2	3	70.12
43	20	0.5	1	68.12
44	100	3.5	1	75.59
45	20	0.5	5	42.72

46	100	0.5	3	39.31
47	60	0.5	5	40.77
48	60	2	1	73.43
49	100	0.5	5	35.87
50	100	3.5	3	61.51
51	20	3.5	5	64.23
52	100	0.5	5	37.14
53	60	3.5	5	54.34
54	100	3.5	1	76

Appendix VII: Calculation of Removal efficiency and adsorption capacity

1. Calculation of chromium (VI) Removal efficiency

According to Equation 9 we can find the percentage removal of chromium (VI) at a particular time (t) from aqueous solution as follows:

$$\% \text{ Removal} = \left(\frac{Co - ct}{Co}\right) * 100 \qquad (9)$$

$$\% \text{ Removal} = \left(\frac{20 - 1.12}{20}\right) * 100 = 98\%$$

where;

C0 = initial concentration of Cr(VI) in the solution = 20 mg/l

Ct = final concentration of Cr(VI) = 1.12 mg/l at adsorption of time (t)=2 hr

Similar procedure was followed for other calculation. The values of Co and Ct or Ct can be found for different initial Cr(VI) concentrations with the variation of time using the LAC as adsorbent.

2. Calculation of Adsorption Capacity for Cr(VI) adsorption onto the ALC.

According to Equation (10) we can find adsorption capacity at a particular time (qt) in mg/g as follows:

$$qt = \left(\frac{Co - Ct}{m}\right) * v \qquad (10)$$

$qt=\left(\frac{20-3.375}{3.5}\right)*0.2 = 0.95$ mg/g

Where;

C0 = initial concentration of Cr(VI) in the solution = 20 mg/l

Ct = concentration of Cr(VI) at a particular time (t) in the solution = 3.375 mg/l at t = 0.5 hr

V = volume of the solution = 200 mL = 0.2 L

m = dry mass of adsorbent = 3.5 g of ALC.

According to Equation(11) we can determine the equilibrium adsorption capacity (qe) in mg/g as follows:

$$qe=\left(\frac{Co-Ce}{m}\right)*v \qquad (11)$$

$qe=\left(\frac{20-1.12}{3.5}\right)*0.2 = 1.1$ mg/g

where;

C0 = initial concentration of Cr(VI) in the solution = 20 mg/l

Ce = equilibrium concentration of Cr(VI) = 1.12 mg/l at a time (t)=2hr

V = volume of the solution = 200 mL = 0.2 L

m = dry mass of adsorbent = 3.5 g of ALC

Similar procedure was followed for other calculation. The values of Co and C_t or C_e can be found for different initial Cr(VI) concentrations with the variation of time using the ALC as adsorbent.

Appendix VIII: Calculation of Equilibrium Adsorption Isotherm Models

1. Calculation of the Langmuir Isotherm Parameters (K_L and q_m):

According to figure 19, the equation of the linearized Langmuir model was as follows:

$$Y=0.382X+0.244 \qquad (2)$$

According to Equation 14, the Langmuir model was expressed linearly as follows:

$$\frac{1}{q_e}=\frac{1}{q_m K_L}*\frac{1}{C_e}+\frac{1}{q_m} \qquad (14)$$

If we compare Equation 2 and 14, we can get

$\frac{1}{q_m}$ =0.1261 ; or q_m=4.10mg/g and $\frac{1}{q_m K_L}$ =0.382 ; or

$K_L = \frac{1}{4.10X0.382}$ =0.64 L/mg

Therefore, q_m= the maximum adsorbent amount of Cr(VI) per mass of ALC = 4.10 mg/g

K_L = the Langmuir equilibrium adsorption constant = 0.64 L/mg

2. Calculation of the Freundlich Isotherm Parameters (K_F and 1/n):

According to figure 20, the equation of the linearized Freundlich model was as follows:

Y= 0.368X + 0.145 (3)

According to Equation 17, the Freundlich model was expressed linearly as

$$Log(qe) = \frac{1}{n} Log(Ce) + Log(KF) \quad (17)$$

If we compare Equation 3 and 17, we can get

$\frac{1}{n} = 0.368$ and Log(**KF**)= 0.145; or K_F= 1.40 (mg/g)(L/mg) $^{1/n}$

Therefore, K_F = the Freundlich constant related to the sorption capacity = 1.40 (mg/g)(L/mg) $^{1/n}$

1/n = the adsorption intensity factor = 0.368 (unit less)

Appendix IX: Calculation of Kinetic model Parameters for Cr(VI) Adsorption

1. Calculation of the First Order Kinetic Model Parameters (K_1 and q_e):

According to figure 21, the equation of the linearized first order kinetic model was as follows:

Y= -1.18X -0.193 (4)

According to Equation 20, the first order kinetic model was expressed linearly as follows: $$Log(qe-qt) = -\frac{K1}{2.303} t + Log(qe) \quad (20)$$

If we compare Equation 4 and 20, we can get

$-\frac{K_1}{2.303} = -1.18$ or $K1 = 2.72\ hr^{-1}$ and Log(qe)= - 0.193 or qe=0.64mg/g

Therefore, K_1 = the first order rate constant = 2.72 hr^{-1} and

q_e=equilibrium adsorption capacity = 0.64mg/g

2. Calculation of the Second Order Kinetic Model Parameters (K_2 and q_e):

According to figure 22, the equation of the linearized second order kinetic model was as follows:

Y =0.85X + 0.103 (5)

According to Equation 25, the second order kinetic model was expressed linearly as follows:

$$\frac{t}{qt} = \frac{1}{qe}t + \frac{1}{K2qe^2} \qquad (25)$$

If we compare Equation 5 and 25, we can get

$\frac{1}{qe} = 0.85$ or qe = 1.18 mg/g

$\frac{1}{K2qe^2} = 0.103$ or $K2 = \frac{1}{0.103*(1.18)2} = 7.01\ g.mg^{-1}.h^{-1}$

Therefore, K2= the second order rate constant = 7.01 $g.mg^{-1}.h^{-1}$

qe=equilibrium adsorption capacity = 1.18 mg/

Appendix X: Some important photos shooted during experimental works.

(a)

(b)

1. LC collected from Yayo area (a), Size reduced to hydrolysis (soaked with 4M HCI solution mixing) after that hydrolytic Solid was washed out HCI solution with warm and distilled water

(b)

(a)

(b)

2. shaker for mixing the solution for required period of time (a) and Flasks after Adsorption(b)



3. The samples were collected, filtered, and stored for analysis.


4. Computerized UV-Spectrometer for Samples analysis