

JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY



M.Sc.THESIS

ON

**EVALUATION OF CHROMIUM (VI) REMOVAL FROM AQUEOUS SOLUTIONS
USING NATURAL BITUMINOUS COAL**

By

EMMANUEL PAPETI PAMATH KWODJOK

OCT, 2017

JIMMA, ETHIOPIA

**EVALUATION OF CHROMIUM (VI) REMOVAL FROM AQUEOUS SOLUTIONS
USING NATURAL BITUMINOUS COAL**

**A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES JIMMA
UNIVERSITY, COLLEGE OF NATURAL SCIENCES DEPARTMENT OF
CHEMISTRY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE IN CHEMISTRY (ANALYTICAL)**

By

EMMANUEL PAPETI PAMATH

ADVISORS

FEKADU MELAK (M.Sc., Ph.D PURSUING)

MENBERU YITBAREK (M.SC., Ph.D PURSUING)

OCT, 2017

JIMMA, ETHIOPIA

Table of Contents

Contents	page
List of tables.....	IV
List of figures.....	V
Abbreviations	VI
Acknowledgement.....	VII
Abstract.....	VIII
1. Introduction.....	1
1.1. Background of the Study.....	1
1.2. Statement of the Problem	3
1.3. Objectives of the Study	4
1.3.1. General Objective	4
1.3.2. Specific Objectives	4
1.3.3. Significance of the Study.....	4
2. Literature Review	5
2.1. Occurrence of Chromium.....	5
2.2. Applications of Chromium.....	5
2.3. Effect of Chromium to Human Health.....	5
2.4. Adsorption.....	6
2.4.1. Principles of Adsorption.....	6
2.4.2. Types of Adsorption	7
2.5. Chromium Removal Technologies.....	7
2.5.1. Granular Activated Carbon (GAC).....	8
2.5.2. Ion Exchange	9

2.5.3. Membrane Filtration	9
2.5.4. Starch-Based Material	9
2.5.5. Other Adsorptive Materials	10
3. Materials and Methods	12
3.1. Chemicals and Materials	12
3.2. Instrumentations	12
3.3. Collection of Adsorbents and Characterization	13
3.4. Preparation of Adsorbent	13
3.5. Preparation of Stock Solutions.....	13
3.6. Construction of Standard Calibration Curve.....	14
3.7 Experimental Procedures.....	14
3.7.1. Study of pH of Adsorbents	14
3.7.2. Determination of Bulk Density.....	14
3.7.3. Determination the Moisture Content	15
3.7.4. FTIR Spectral Analysis Procedure	15
3.8. Batch Adsorption Experiments	16
3.8.1. Effect of Contact Time.....	16
3.8.2. Effect of pH.....	16
3.8.3. Effect of Adsorbent Dose	17
3.8.4. Effect of Initial Chromium (VI) Concentrations.....	17
3.8.5. Effect of Temperature	17
3.8.6. Determination of Adsorption Removal Efficiency	18
3.9. Adsorption Isotherm	18
3.10. Kinetic Experiments.....	20
3.11. Thermodynamics Study	21

3.12. Column Studies	21
3.13. Quality Assurance	22
4. Results and Discussions	23
4.1. Characterization of adsorbent.....	23
4.1.1. Physiochemical Properties of Adsorbent	23
4.1.2. FTIR Analysis	24
4.2. Effect of Time	26
4.3. Effect of pH.....	27
4.4. Effect of Adsorbent Dose.....	29
4.5. Effect of Initial Concentrations	30
4.6. Effect of Temperature	31
4.7. Adsorption Isotherm Investigation.....	32
4.7.1 Langmuir Isotherm	33
4.7.2 Freundlich Isotherm.....	33
4.8. Adsorption Kinetic Studies	35
4.9. Adsorption Thermodynamics Studies.....	37
4.10. Column Studies.....	39
4.11. Comparison of Chromium (VI) Adsorption with other Adsorbents.....	41
5. Conclusion and Recommendations	42
6. References	43
7. Annex	52

List of tables

Table: 1 Effect of Cr (VI) On Human Health.....	6
Table: 2 The Physical Properties of Adsorbents.....	23
Table: 3 Chemical Compositions of Natural Bituminous Coal	24
Table: 4 Results oIsotherm Models for The Adsorption of Cr (VI) Ions onto Bituminous Coal at Constant Temperature of 25 °C.....	34
Table: 5 Kinetic Parameters For Adsorption of Cr (VI) Ions onto Adsorbents at Constant Temperature of 25 °C.	37
Table: 6 Thermodynamic Parameters Calculated for the Adsorption of Cr (VI) Ions onto Bituminous Coal at Different Temperatures.	38
Table: 7 Comparison of Adsorption Capacities of Cr (VI) Ion with other Adsorbents Reported In Various Studies.....	41

List of figures

Fig 1: FTIR for Natural Bituminous Coal Before -A (NBCB) and After Adsorption Process-B (NBCA).	25
Fig 2: Effect of Shaking Time on the Cr (VI) Removal on Natural Bituminous Coal.	26
Fig 3: Effect of pH on the Percentage Removal of Cr (VI) on Natural Bituminous Coal.	27
Fig 4: Effect of Dose on the Percentage Removal of Cr (VI) on Natural Bituminous Coal.	29
Fig 5: Effect of Initial Concentrations on the Percentage Removal of Cr (VI) onto Natural Bituminous Coal.	31
Fig 6: Effect of Temperature on the Percentage Removal of Cr (VI) on Natural Bituminous Coal.	32
Fig 7: Freundlich Adsorption Isotherm For Cr (VI) on Natural Bituminous Coal.	34
Fig 8: Pseudo-First Order Plot For Cr (VI) Adsorption onto Natural Bituminous.	36
Fig 9: Pseudo-Second Order Plot for Cr (VI) Adsorption onto Natural Bituminous Coal.	36
Fig 10: Graphical $\text{Log}q_e/C_e$ Versus $1/T$ For Determination of ΔH° , ΔS° , ΔG°	38
Fig 11: Effect of Flow Rate on Breakthrough Curve for Adsorption of Cr (VI) on Bituminous Coal.	40

Abbreviations

AC	Activated Carbon
COD	Carbon Oxygen Demand
DPC	Diphenylcarbazine
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared Spectrometer
GAC	Granular Activated Carbon
IARC	International Agency for Research on Cancer
LDLs	Low Density Lipoproteins
NBC	Natural Bituminous Coal
NF	Nano-Filtration.
NIOSH	The National Institute for Occupational Safety and Health
RO	Reverse Osmosis.
UF	Ultrafiltration
WHO	World Health Organization

Acknowledgement

Firstly, I would like to offer praise and glory to Almighty God; I take immense pleasure to express my sincere and deep sense of gratitude to my advisors Fekadu Melak (M.Sc., Ph.D, pursuing) and Menberu Yitbarek (M.Sc., Ph.D, pursuing) for their endless guidance, motivation and editing the draft from the beginning of the work to the end. My special thanks go to Department of Chemistry, College of Natural Sciences, Jimma University, for its financial support. I am thankful to all staff members and laboratory technicians for their assistance as well as encouragement in all aspects during the periods of my study. I wish to extend my acknowledgement to ministry of Education Federal Republic of Ethiopia for sponsoring my M.Sc. study, to also Delibi share mining company for providing coal, special thanks to Mr. Ermaius.

I convey my thankfulness to my batch class mate and my best friend, Mr. Ababe Dero for his unforgettable help in terms of working materials. My special genuine gratitude goes to my dearest friends Mr. Paulino Achuil, Ms.Josphina Yowin, Mr.Yohanes Kimo, Hakim Yohanes and Mr. Dak Olami for their kindness, concern, encouragement, prayers and cooperation when their help were necessary.

My most honest gratefulness goes to my parents my mother and my late father who have disciplined and reared me to arrive at this level with their continuous follow ups and lovely guidance. I would have not arrived at this stage without their genuine help. My brothers as well as my sisters are all acknowledged for their enduring love, motivation and encouragement throughout my life.

Finally, my deepest affection and appreciation goes to my beloved wife, Juliana Temsha, who has encouraged me to pursue my study by shouldering all our family burdens for the last two years. Juliana, your patience, motivation and understanding during the stresses, ups and downs we have passed through, are greatly appreciated and unforgettable in my life. May almighty God reward for your all good deeds!! All my Kids should also deserve great appreciation for their patience, love, understanding and motivation throughout my study period. There are so many others whom I may have unintentionally left out and I sincerely thank all of them for their support.

Abstract

The existence of chromium (VI) in water causes significant environmental problems. In the present study, the performance of natural bituminous coal (NBC), which is locally available in Ethiopia, was evaluated for the removal of Cr (VI) from aqueous solutions. Batch and column adsorption experiments were performed in order to examine the removal process under various parameters. The parameters optimized at batch scale include contact time, pH, initial concentration, adsorbent dose and temperature. The Cr (VI) ion uptake was pH dependent and reached optimum at pH 3.0. The adsorbents were characterized using FTIR and XRF. The capacity of NBC at equilibrium calculated to be 1.54 mg/g. The isotherm study revealed that Freundlich isotherms explain the adsorption process better than Langmuir. It was determined that removal of Cr (VI) was well-fitted by second-order reaction kinetic over Pseudo-first order. Thermodynamic of the adsorption of Cr (VI) onto the adsorbent were also investigated and ΔH and ΔS found negative indicating exothermic adsorption. Results of column experiments indicated that NBC could be suitable to treat low concentration of Cr (VI) contaminated water at slow flow rate 1.25 mL/min. Therefore, the batch and column studies showed that NBC are favorable adsorbent for removal of Cr (VI) from aqueous solution.

Key words: Chromium (VI), Natural bituminous coal, Adsorption efficiency, Adsorption isotherms, Batch, Column.

1. Introduction

1.1. Background of the Study

Chromium is 21st most abundant element in earth's crust and the sixth most abundant transition metal [1]. Chromium in water bodies typically comes from industrial pollution sources, including leather tanning factories, steel fabrication, photographic material, corrosive painting, cement, wood preservation, and artificial fertilizers, from anthropogenic sources chromium is commonly released as liquid or solid wastes which may contain combination of Cr (III) or Cr (VI) with various solubility [2].

It's one of the major heavy metal pollutants in the environment and it is widely known that the toxicity and biological activity of the element not only depends on the total amount, but also on its chemical form [3]. Chromium has been considered as one of the top 16th toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public. It has become a serious health concern, due to large use of chemical agents and produce in electroplating, chromate preparation and the tanning industries [4, 5].

Chromium species exist mainly in two different oxidation states in environmental water Cr (VI) and Cr (III), the toxicity of those species differs significantly, the oxidation state of the chromium has a significant effect on the transport and fate of chromium and on the type and cost of treatment required to reduce chromium concentrations less than regulatory health-based standards. Cr (VI) is far more mobile than Cr (III) and more difficult to remove from water [6], the most common Cr (VI) forms are chromate (CrO_4^{2-}), and hydrogen chromate (HCrO_4^-) also called bichromate ($\text{Cr}_2\text{O}_7^{2-}$) can occur. The relative amount of these two species depends on pH, The equilibrium concentration of dissolved Cr (III) in natural water is small compared to Cr (VI) concentration [6, 7]. Therefore, Cr (VI) have different physiological effects in human due to its toxicity while Cr (III) is considered as an essential trace element for the maintenance of an effective glucose, lipid, and protein metabolism in mammals, in addition to insulin, which is accountable for reducing blood glucose levels, its control certain cases of diabetes, It has also been found to reduce blood

cholesterol levels by diminishing the concentration of low density lipoproteins“LDLs” in the blood [1, 5, 8].

General use of chromium results in large quantities of chromium containing effluents which need difficult treatment. The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard [5]. Cr (VI) is of particular concern because of its toxicity; the recommended limit of Cr (VI) in potable water is only 0.05 mg/L [9] The Cr (III) and Cr (VI) are commonly in ground water contaminants at industrial and military installations. Chromium was classified by the IARC to be a powerful carcinogenic agent that modifies the DNA transcription process causing important chromosome aberrations [5, 8]. Thus, Increasing levels of heavy metals in the environment cause serious threats to water quality, human health and living organisms, In epidemiological studies, an association has been found between exposure to Cr (VI) by the inhalation and lung cancer, the IARC, NIOSH and WHO has classified Cr (VI) in Group 1 (toxic to animal and human) [9-11]. Chromium contamination of soil and water is a major environmental problem. The toxicity of chromium varies greatly among a wide variety of chromium compounds, its oxidation state and its solubility in water [11, 12]. Therefore, very sensitive techniques are used for the determination of chromium in water samples WHO has considered, chromium, to be of most immediate concern [13].

In Ethiopia according to literatures reported the presence of Cr (VI) in surface waters such as streams and rivers around leather industries, in the water bodies of Ethiopian rift-valley lakes, in six rivers (their inflows), and in effluents from two factories chromium Cr (VI) was reported to be in ranges between 0.104 and 0.121 mg/L[14], Whereas Cr (VI) level was reported to be 0.092 mg/L in Firewoini and 0.158 mg/L in Mekelle, which are all above the WHO standard limit of chromium in drinking water (0.05 mg/L) [15]. However, the less toxic Cr (III) can easily be oxidized to chromium Cr (VI) in the presence of oxidizing impurities. The concentration of chromium in discharged effluents depend mainly on the amount and state of chromium compounds utilized in the industrial process, pH, and the presence of other organic and inorganic processing wastes [16].

Adsorption is an efficient and cost-effective method of chromium removal from water and wastewater. Recently, the use of low-cost adsorbents has been considered to reduce chromium concentration from industrial waste effluents [17].

In this study the natural bituminous coal was investigated for the removal of Cr (VI) by NBC, Bituminous coal is the type of coal created by long time natural process and it's a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. However; there is no literature report on the chromium Cr (VI) removal using locally materials such as natural bituminous coal in Ethiopia, NBC considered as environmentally friend. The objective of the present investigation was to find out the optimum conditions for removing the chromium Cr (VI) ions from aqueous solutions by adsorption on natural bituminous coal and evaluate the effects of different parameters including contact time, adsorbent doses, pH, temperature and initial concentration of Cr (VI), and therefore examine its potential to be used in wastewater treatment systems.

1.2. Statement of the Problem

Chromium is one of the major focuses in worldwide due to their toxicity causing lung cancer, liver and kidney damage [18]. Chromium contamination of water bodies is the questions that continue to arise regarding the safety of the drinking water supply, In some areas in Ethiopia, researchers investigated the presence of Cr (VI) in surface waters such as streams and rivers around leather industries which indicated that the level of chromium in water above permissible limit [14-15]. The presence of chromium at different concentration levels in water have direct or indirect impact, As a result, continuous investigation of different adsorbent is very important in order to solve problems of chromium contaminated water. Therefore, there is a need for the development of simple and available local materials such as natural bituminous coal, which could be used to eliminate Cr (VI) from water bodies. Moreover, understanding these methods is very essential to reduce chromium concentrations in environment and avoid water pollution, this hence, the development of simple, rapid, and effect adsorbents. Thus in this study the removal of Cr (VI) from aqueous solutions using natural bituminous coal has been investigated.

1.3. Objectives of the Study

1.3.1. General Objective

To evaluate Cr (VI) removal from aqueous solutions using natural bituminous coals as adsorbent.

1.3.2. Specific Objectives

- ✓ To optimize parameters such as pH, mass of adsorbents, initial concentration, contact time and temperature on the adsorption efficiencies of adsorbents.
- ✓ To describe the responsible adsorption isotherm models.
- ✓ To assess the kinetics and thermodynamic of the adsorption of Cr (VI) onto the adsorbent.
- ✓ To determine the adsorption efficiencies of natural bituminous coal for the removal of Cr (VI) ion from aqueous solutions.
- ✓ To investigate the efficiency of packed column method for adsorption of Cr (VI) ion from aqueous solutions.

1.3.3. Significance of the Study

It is known that chromium used in many industries, such as leather tanning factories, steel works, wood preservation and artificial fertilizers. However, an intensive and uncontrolled uses of these result in the contamination of the water. Therefore, development of efficient and effective method for the removal of Cr (VI) is crucial. In general, the findings of this study will have the following significances:

- ✓ The obtained results could be used as background information regarding the removal techniques for Cr (VI) from aqueous solutions.
- ✓ The investigated method provides data to explore low-cost technology and the use of local material to solve problem related to chromium removal from various water sources.
- ✓ The finding could also serve as resource materials to carry out future research on similar method.

2. Literature Review

2.1. Occurrence of Chromium

The principal chromium ore is ferric chromite, FeCr_2O_4 , found mainly in South Africa (with 96% of the world's reserves), Russia and the Philippines. Less common sources include crocoite, PbCrO_4 , and chrome ochre, Cr_2O_3 [1]. In rocks and soil, Cr (III) is a common trace mineral, found as amorphous Fe (III), Cr (III) hydroxides, eskolaite ($\text{CrO}_3(\text{s})$), and chromite ($\text{FeCr}_2\text{O}_4(\text{s})$), all Cr (III) forms. There are a wide natural variation in chromium concentrations in soils and rocks. River materials and soils with fine grain sizes have the highest concentrations, whereas granite carbonates, and large grained (sandy) sediments have the lowest concentrations [6-7]. In acidic media Cr (VI) exists in the form of oxyanions such as HCrO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_3\text{O}_{10}^{2-}$. At pH 1, the chromium ions exist in the form of H_2CrO_4 , while in the pH range of 1–6 different forms of chromium ions such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ coexist, of which HCrO_4^- predominates. As pH increases this form shifts to CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. Chromium exists in different oxidation states and the stability of these forms depends upon the pH of the system [19].

2.2. Applications of Chromium

Chromium is used in many industrial; including leather tanning factories, steel works, cement, artificial fertilizers, metal finishing and chromate preparation [2- 4]. Cr (VI) is used extensively in industrial processes such as electroplating, textile dyeing, corrosion inhibition and wood treatment, all of which produce discharge of chromium-containing waste matter [20].

2.3. Effect of Chromium to Human Health

Chromium has both beneficial and harmful properties for human being; Cr (III) is an essential trace element in mammalian metabolism. It is responsible for reducing blood glucose levels, and is used to control certain cases of diabetes; it also reduces blood cholesterol levels. Furthermore, Cr (VI) is hazardous by all exposure method [1] their effects on human health are summarized in Table (1).

Table: 1 Effect of Cr (VI) on human health

Level of Cr(VI) in different sources	Effect on human health	References
In water in general (<1 mg/L)	Cause carcinogenic and teratogenic (Fetal malformations)	[5,6]
In soil 5 to 100 mg/ kg	Mutagenic and carcinogenic effects on biological organisms	[20]
In water < 0.1 mg/L and Cohort workers	Nasal septum , skin lesions, asthma, dermatitis and other allergic reactions	[20]
Worker exposures	Lungs cancer, kidney , liver damage and even death	[18]
In drinking water < 0.1 mg/L	Nose irritates, intestinal, stomach upsets and ulcers.	[20]
In animal lab < 0.1 mg/L	Sperm and male reproductive system	[21]

2.4. Adsorption

Adsorption is usually used as an effective physical method of separation in order to eliminate or lower the concentration of wide range of dissolved pollutant both organic and inorganic in the effluent [22]. The important of adsorption is seen in the requirements for choosing an effective adsorbent for adsorption or purification needs due to high effluents waste water disposed to environments; therefore determination of adsorption capacity is necessary advantage for selection of adsorbent [23].

2.4.1. Principles of Adsorption

Adsorption” is a well established and powerful technique for treating domestic and industrial effluents. In water treatment, the most widely method is “adsorption” onto the surface of activated carbon. The basic principle of operation for carbon adsorption is the mass transfer and adsorption of a molecule from a liquid or gas into solid surface. Activated carbon is manufactured in such a way as to produce extremely porous carbon

particles whose internal surface area is very large. This porous structure attracts and holds organic molecules as well as certain metal and inorganic molecules [6].

2.4.2. Types of Adsorption

On the basis of type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into two types: physical adsorption or chemical adsorption. Physisorption: is the adsorption in which the forces involved are intermolecular (i.e., van der Waals, hydrogen bonding) of the same kind as those responsible for the non-ideality of real gases and the condensation of vapours and which do not involve a significant change in the electronic orbital patterns of the species involved. Chemisorption: is a chemical process in which a reacting molecule forms a definite chemical bond with an unsaturated atom, or a group of atoms (an active centre) on a catalyst surface, and electron transfer is involved [6].

2.5. Chromium Removal Technologies

Removal of toxic metal ion from waste water is an important and widely studied in research area. This reduces the problem of sludge disposal and renders the system economically viable, especially when the adsorbents used are also of low cost. Adsorption process is used in a variety of important industrial applications and now it is increasingly used on large scale as an economical and efficient separation technique for metal ion removal from wastewater [24].

Several treatment technologies have been developed for the effective removal of chromium and others heavy metals from solutions using natural adsorbents which are economically practicable such as agricultural wastes including sunflower stalks, Eucalyptus bark, maize bran, coconut shell, rice straw , tree leaves , saw dust, sand, clay mineral, charcoal, and various agricultural by products like peanut shell, wheat husk, sugarcane bagasse, biosorption, magnetic beads, carbon nanotubes, *Sinorhizobium meliloti* 1021 exopolysaccharide, polyacrylic acid, ionic polyamino acid block copolymers, albumins synthetic polyacrylamide, etc [9,17], These methods were been examined and practiced by many scientists for their chromium removal efficiencies in different parts of the world. In addition to that there are different reports on the use of natural zeolite utilization in metal

effluent treatment, Zeolites, modified by ion exchange [25], natural zeolite and nanozeolite from natural clinoptilolite and aluminum sulfate were also reported [26, 27], and Chitosan coated carbon [28]. In general, a wide range of adsorption methods have been reported in literature to eliminate the Cr (VI) from water and wastes include chemical precipitation, ion exchange, membrane separation, electrocoagulation, solvent extraction, sedimentation, reverse osmosis, dialysis, electrodialysis, cementation, air stripping, steam stripping, and flocculation [4,29-31]. Therefore due to their limitations of these methods alternative adsorbents have been proposed for removing Cr (VI), in order to save money and/or recycle waste material. Some of disadvantages of chemical precipitation are not major removal mechanism and less practices, ion exchange it's selective only toward aromatics solutes, sensitive and expensive whereas the membrane separation and reverse osmosis depends on high pressure and their difficulty be regenerated [6]. Carbon and activated carbon is usually derived from charcoal is used as excellent low cost adsorbent for removal of toxic metal ions from industrial waste water. Due to its high level of micro porosity, a surface area in excess of 500 m²/g, sufficient activation for useful applications may come exclusively from the high surface area, though further chemical treatment often enhances the adsorbing properties of the material [28].

2.5.1. Granular Activated Carbon (GAC)

Granular Activated Carbon (GAC) is a well-established technology for removing organics from water supplies and has been demonstrated to remove heavy metals as well, including (Cr) [6], GAC has an extremely high internal surface area, on the order of 1000 m²/g. Cr (VI) is removed by two different mechanisms electrostatic adsorption to GAC surfaces and reduction to Cr (III) [6]. While the activated carbon is the most effective adsorbent which have, very high surface areas, porous sorbent, great capacity to absorb a wide range of pollutants, high capacity and high rate of adsorption used, but it is expensive and the higher quality, the greater the cost their performance dependent on the type of carbon [1].

2.5.2. Ion Exchange

Ion exchange is a physical process in which an ion with a high affinity for the resin material of the ion exchange column replaces an ion with a lower affinity that was previously bound to the column resin. As water flows through, dissolved Cr (VI) ions bind to the resin and displace the previously bound ions (usually Cl^- or OH^- ions). The resins used for chromium sequestration are typically either a naturally occurring inorganic zeolite or a synthetic weak base or strong base anion exchanger resin. Ion exchange resins are capable of reducing Cr (VI) concentrations to less than the detection limit [6]. Ion exchange characterized in wide range of pore structure and physicochemical characterization, good surface area, effective sorbent and excellent selectivity towards aromatic solutes, but expensive and sensitive to particle, its performance dependent on the type of resin used [1].

2.5.3. Membrane Filtration

Semi permeable membrane filters are used in water treatment to filter soluble compound anions and cations from water, including HCrO_4^- and CrO_4^{2-} . The flux of water through the membrane is proportional to the pressure that is applied. The flux of solute chromium can be related to the flux of water, the concentration of Cr and other empirically derived membrane parameters. Membrane filtration systems are categorized by pore size. From largest to smallest pore size, these include microfiltration, ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Although RO membranes can achieve the highest effluent water purity, they must operate at higher pressure. For this reason, nanofiltration has attracted increasing attention [6].

2.5.4. Starch-Based Material

This type of adsorbents has the following advantages: good removal of wide range of pollutants, important selectivity for different concentrations, fast kinetics, amphiphilic cross linked adsorbent and applicable to a wide variety of process an easy regeneration if required [1].

2.5.5. Other Adsorptive Materials

These include, activated alumina; activated carbons; other natural and synthetic adsorbents they are greater accessibility, low cost, simple operation, availability of wide range of adsorbents but high efficiency often demand adjustment and readjustment of pH [32]. Some other alternative sorbents have been proposed for removing Cr (VI), in order to save money and/or recycle waste material. Researchers have tested living and dead biosorbents, including bacteria, yeasts, milled peat, microalgae, fungi and seaweed. Natural materials tested include clays, peat moss, and plant litter low cost sorbents are not regenerated, but are disposed off as soon as significant breakthrough occurs [33]. The use of fired clay soils to remove Cr (VI) from aqueous solution was investigated in Jimma zone. It's showed that the removal efficiencies ranging 64 to 97% and adsorption capacity ranging 0.67 to 0.83 mg/g were achieved for a 1 % increase in clay content and maximums calculated by Langmuir was at range of 4.74, 4.81 and 8.77 mg/g respectively [34]. Various biomasses adsorbents prepared from avocado kernel seeds (AKS), Juniperus procera sawdust (JPS) and papaya peels (PP) were reported which shows as good adsorbents for the removal of Cr (VI), their capacities were found to be 16.03, 10.08 and 7.16 (mg/ g) respectively [35].

Several literature survey use of different biomass for removal of Cr (VI) in aqueous solutions as well in wastewater sample, with their good adsorption capacity such as neem leaves powder with 0.85 mg/g [36], The adsorption capacity for the GAC strongly depends on pH of solution and salinity, with maximum values around 7.0 mg/g at neutral pH and low salinity [37], The use of waste material like cooked waste tea as adsorbent was applied for chromium removal which was reported with high capacity of 30.39 mg/g and potato peel waste (8.012 mg/g) [38,39], formaldehyde treated sunflower (7.85 mg/g) [40] , Bael fruit (*Aegle marmelos correa*) shell (17.27 mg/g) [41], The Rice bran a, b their capacities range were 0.069 and 12.341 mg/g respectively [42,43]. Whereas the application of ash and others waste material such as Pre-boiled sunflower stem was reported to be 4.9 mg/g [44], Adsorption isotherms of chromium ions in aqueous solution on Char of South African coal (CSAC) shows a smaller adsorption capacity, about 0.3 mg/g, which slightly decreases by increasing pH [45], Sawdust a, Sawdust b (20.70, 15.823) mg/g [46,47] and different Turkish brown coals with variation in their adsorption capacity of 11.2 mg/g for Ilgin

(BC₁), 12.4 mg/g for Beys_ehir (BC₂) and 7.4 mg/g for Ermenek (BC₃) respectively [48]. Chemically modified Chitosan (CTS 205 mg/g) [8], Olive stones (OS-S) and commercial active carbon (CAC-S) by sulfuric acid were been reported for chromium uptake where (OS-S) show a very abundant agricultural by-product with good adsorptive properties and hardness. At initial pH 1.5 for a 50 mg/L Cr (VI) solution (OS-S) with maximum capacity of 71 mg/g and (CAC-S) 25.5 mg/g respectively [49].

3. Materials and Methods

3.1. Chemicals and Materials

All chemicals and reagents that were used in this study were analytical reagent grade, ($K_2Cr_2O_7$ 99.5 % Riedel-deHaen, Germany) purchased from a commercial technical grade solid (Sigma-Aldrich). HNO_3 69 % LOBA, chem. india (NaOH) 99.0 % and (HCl) 37 %, were purchased from BDH Chemicals Ltd, both reagents were used throughout the work to adjust the pH of the solutions. 1, 5 diphenylcarbazide DPC (BDH laboratory supplies, poole, England), H_2SO_4 97% and acetone from (BDH Chemicals Ltd) filters paper (0.125 mm) from machinery –NAGEL-Germany) were used for filtration.

Equipments which used in this study comprise; sampling containers, funnel, pH (353 ATC pH METER.UK), digital analytical balance type Kern ABS Germany, thermostatic water bath shaker (Grant GLS 400, Germany), sieve (ASTME ELE international laboratory test sieve), Oven (Model N50 C, GENLAB WIDNES, England), stirrers and classical glass wares.

3.2. Instrumentations

FTIR spectrophotometer type (Shimadzu 8201 PC) spectrophotometer using KBr) was used for determination of functional groups by KBr disc method; Elemental analysis for NBC was evaluated using X-ray Fluorescence (Philips PW 1390). Temperature controlled shaking water bath type (Grant GLS 400, Germany), digit balance type Kern ABS Germany, JENWAY 6031 colorimetric, and pH meter 353 ATC pH METER were used throughout this work. The amount of chromium in the effluent solutions after adsorption was determination by colorimetric method of detection of Cr (VI). Three replicate determinations were carried out on each sample and the mean was used for further data analysis.

3.3. Collection of Adsorbents and Characterization

In this study, coal as adsorbents sample was collected from Delbi, Ethiopia. The Delbi coal mine is located in Oromia regional state, Jimma Zone, Dedo Wereda, Southwest of Ethiopia which is 400 Km from Ethiopia's capital, Addis Ababa while its mining concession covers a 39.2 square kilometer lot with an estimated coal deposit of 11.4 billion tonnes. Delbi Coal Mining is set to extract 30,000 tonnes of coal in Ethiopia [50]. Physical and chemical compositions of the adsorbent natural bituminous coal were studied through FTIR and XRF.

3.4. Preparation of Adsorbent

In this study, natural bituminous coal adsorbent sample which was taken from Delbi coal mining site, Ethiopia was washed several times with distilled water to remove fine impurities and dried in air. Then, after drying the adsorbent was washed with warm distilled water and dried at 105 °C for 24 hours in an oven. Finally, the adsorbents sample were crushed with a mortar and pestle to fine powder and sieved to the mesh size of < 250 µm and the grinded product were stored in a plastic container for further use. The physicochemical analysis of coals was carried out [51].

3.5. Preparation of Stock Solutions

Stock of (1000 mg/L) Cr (VI) was prepared by dissolving 2.829 g potassium dichromate ($K_2Cr_2O_7$) in 1000 mL volumetric flasks and filled to the marked with distilled water. The working solution was prepared by diluting the stock solution with distilled water to give the appropriate concentration (3 mg/L) of the solution. The pH of the test solution was adjusted by 0.1 M hydrochloric acid and/or 0.1 M sodium hydroxide and measured using a pH meter. A 1,5 diphenylcarbazide (DPC) was prepared by dissolving 0.25 g of DPC in 50 mL of acetone, and stored in brown bottle according to literatures [52-54].

3.6. Construction of Standard Calibration Curve

Calibration standards of the desired concentrations were prepared by serial dilution of the stock solution. Cr (VI) of different concentrations 0.05, 0.1, 0.2, 0.4, 0.8 and 1.6 mg/L were prepared in 100 mL volumetric flask from working solution. The pH of the solution adjusted to 2.0 ± 0.5 by 0.5 M H_2SO_4 . Then, 2 mL of the diphenylcarbazide solution was added to standard and the mixture was allowed to stand for 10 minutes to obtain full color development and then colorimetric was set to zero absorbance with the reference solution (Distilled water) and their absorbance were recorded by colorimetric [54]. The data and calibration curve are shown in annex, Cr (VI) react with color reagent DPC based on the following reaction mechanism in equation (1) the reaction consists of the simultaneous oxidation of diphenylcarbazide to diphenylcarbazone, reduction of Cr (VI) to Cr (III), and the chelation of Cr (III) by diphenylcarbazone. The actual structure of the chelate is not known [55].



Where H_4L =Diphenylcarbozide and H_2L is diphenylcarbazone

3.7 Experimental Procedures

3.7.1. Study of pH of Adsorbents

1.0 g of natural bituminous coal was weighed and transferred into a 250 mL beaker and then 100 mL of distilled water was added and stir for 1 hr using magnetic stirrer. The mixed was allowed to stabilize and then the pH was measured [51].

3.7.2. Determination of Bulk Density

The bulk density of the adsorbent coal was determined using Archimedes's principle by weighing a 25 cm^3 measuring cylinder before and after filling with the samples. The measuring cylinder was then dried and the sample was packed inside the measuring cylinder, leveled and weighed. The weight of the sample packed in the measuring cylinder was determined from the difference in weight of the filled and empty measuring cylinder. The volume of water in the container was determined by taking the difference in weight of

the empty and water filled measuring cylinder. The bulk density was determined using the equation (2) [56].

$$\text{Bulk density} = \frac{W_2 - W_1}{V} \quad (2)$$

W_1 = Weight of empty measuring cylinder W_2 = Weight of cylinder filled with sample,
 V = Volume of cylinder

3.7.3. Determination the Moisture Content.

This was done by weighing 5g of natural bituminous coal into a crucible, Then NBC placed in the oven and heated for 24 hours at constant temperature of 105°C. The sample was then removed and re-weighed. The difference in the mass constitutes the amount of moisture content of the adsorbent was measured [16].

$$\text{Moisture} = \frac{(w_2 - w_3)}{(w_2 - w_1)} \times 100 \quad (3)$$

W_1 = Weight of crucible, W_2 = Initial weight of crucible with sample, W_3 = Final weight of crucible with sample.

3.7.4. FTIR Spectral Analysis Procedure

0.125 g of the solid coal sample was taken by a micro-spatula and 0.25-0.50 teaspoons of KBr. Then mixed thoroughly in a mortar while grinding with the pestle, enough samples were placed on spl. to cover bottom in pellet die. The sample was placed in press and press at 5000-10000 psi. Afterward the sample removed from press sample die and placed in the FTIR sample holder. The FTIR spectrums of the magnetite powder were recorded using FTIR instrument in the region 400-4000 cm^{-1} with a spectral resolution of 2 cm^{-1} , using a pressed KBr pellet technique.

3.8. Batch Adsorption Experiments

3.8.1. Effect of Contact Time

The adsorption of Cr (VI) ions by the adsorbents were studied at various adsorption periods as follows, (30, 60, 90, 120, 150 and 180 min). This was done by weighing 0.25 g of each of the adsorbents bituminous coal into an acid washed polyethylene 150 mL plastic flasks containing 25 mL of 3 mg/ L of Cr (VI) ion solutions at the optimized pH 3 and the flasks were shaken in thermostatic water bath shaker at 200 rpm (25 °C) for various periods of time. Then, solution was filtrated at each interval time through a filter paper with a diameter of 0.125 mm. The pH of the filtered sample solutions was adjusted to 2.0 ± 0.5 using 0.5 M sulfuric acid. Then 1 mL of the diphenylcarbazide solution was added to each sample and the mixture was allowed to stand for 10 min until red violet full color developed. The filtrates were analyzed using colorimetric instrument at a wavelength of 540 nm and the absorbance was recorded [52-54].

3.8.2. Effect of pH

The study of pH on the adsorption of the metal ion was conducted by adjusting the pH from 2-9. The pH of each solution was adjusted to the desire values by drop wise addition of 0.1 M HCl and/or 0.1 M NaOH, and after 0.25 g was added to 25 mL of working solution. The flasks containing the mixture were left in a thermostatic water bath shaker at 200 rpm and 25 °C for 180 min. The adsorbents were removed from the solution by filtration. Then after equilibrium time of each the pH of solution was adjusted to 2.0 ± 0.5 using 0.5 M sulfuric acid. Then 1 mL of the DPC solution was added and the mixture was allowed to stand for 10 min until red violet full color developed. The residual metal ion concentration left in the solutions was analyzed followed colorimetric methods. Then the optimum pH was determined as the pH with the highest adsorption efficiency of Cr (VI) ion.

3.8.3. Effect of Adsorbent Dose

The adsorption of Cr (VI) ion was investigated using the following adsorbent doses: 10-80 g/L by keeping other variables constant (at optimal pH of 3, shaker speed 200 rpm, contact time 180 min and temperature 25 °C). After adsorption time was completed the adsorbents were removed from the solution by filtration and the concentrations of residual metal ion in each solution were determined.

3.8.4. Effect of Initial Chromium (VI) Concentrations

Batch adsorption study was made to determine the effect of initial Cr (VI) concentration on the adsorption efficiency. Various chromium concentrations (3, 5, 25, 50, 75, 100, 125 and 150 mg/L) were studied at the optimum conditions: pH of 3, adsorbent dose 80 g/L, shaking speed (200 rpm), contact time (180 min) and temperature (25 °C). After adsorption equilibrium was completed, the adsorbents were removed from the solution by filtrations and the concentration of residual metal ion in each solution was quantified using DPC which form red violet complex whose intensity was read at a wavelength of 540 nm, proper dilution was made and dilution factor used in the calculation for concentrations of 50, 75, 100, 125 and 150 mg/L.

3.8.5. Effect of Temperature

The batch adsorption process was investigated at different temperatures (20, 25, 30, 35, 40 and 45 °C) by keeping other parameters constant (pH of 3, adsorbent doses 10 g/L and 3 mg/ L of Cr (VI) ion at 200 rpm for 180 min). Then after equilibrium time of each the pH of solution was adjusted to 2.0 ± 0.5 using 0.5 M sulfuric acid. Then 1 mL of the DPC solution was added to each sample and the mixture was allowed to stand for 10 min until red violet full color developed. The filtrates were analyzed using colorimetric at a wavelength of 540 nm and the absorbance was measured.

3.8.6. Determination of Adsorption Removal Efficiency

The adsorption efficiency studies were carried out after adjusting the pH values before and after adding a measured mass of the adsorbent of interest into 25 mL of the metal ion solution and shaken in thermostatic water bath shaker at the speed of 200 rpm. Depending on the parameters under study, the pH was adjusted by pH meter with diluted 0.1 M HCl and/or 0.1 M NaOH solution, adsorbent dose, initial metal ion concentration, contact time or temperature was varied to study the adsorption efficiencies. The residue was filtered after the equilibrium time of adsorption had been completed. The final concentration of chromium left in the filtrates was analyzed [52-54]. Then the adsorption efficiency (%), the amounts of Cr (VI) adsorbed at equilibrium, q_e (mg/g) and at time t (min), q_t (mg/g), were calculated according to the equations 4-5 [4, 22].

$$\% \text{Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (4)$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (5)$$

Where q_e is the amount of Cr (VI) removed from solution (mg/g); C_0 is initial concentration of Cr (VI) (mg/L) in solution before mixing with adsorbent (mg/L); C_e is the equilibrium concentration of Cr (VI) left in the solution after the experiment (mg/L); V is the solution volume (L), and m is adsorbent dosage (g).

3.9. Adsorption Isotherm

The study of isotherms was carried out by varying the concentration of metal ion solution (3,5,25,50,75,100,125 and 150 mg/L) but keeping the volume (25 mL), adsorbent dose 2 g, pH (3), time interval (180 min), and temperature (25 °C) of the Cr (VI) solution constant. The adsorption equilibrium data were analyzed in terms of the Freundlich and Langmuir isotherm models, The Langmuir isotherm equation could be written as;

$$\frac{q_e}{q_m} = \frac{K_L C_e}{1 + K_L C_e} \quad (6)$$

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

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} \quad (7)$$

Where q_e the equilibrium concentration on adsorbent (mg/g) is, C_e is equilibrium concentration in solution (mg/L), q_m is maximum adsorption capacity (mg/g), and K_L is adsorption equilibrium constant (mg/L) [11, 17].

The Langmuir isotherm is based on the assumption that the forces of interaction between adsorbed molecules are negligible and once a molecule occupies a site no further adsorption takes place [9]. The Freundlich equation could be described by assuming a heterogeneous surface with adsorption on each class of sites. Although this expression is empirical, $1/n$ reflects the curvature in the isotherm and may represent the energy distribution of adsorption sites. The linearized form of Freundlich adsorption isotherm [4, 22] is:

$$q_e = K_F C_e^{1/n} \quad (8)$$

By plotting $\ln q_e$ versus $\ln C_e$, K_F and n can be determined if a straight line is obtained.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (9)$$

Where q_e is the equilibrium concentration on adsorbent (mg/g), C_e is equilibrium concentration in solution (mg/L), K_F is adsorption capacity, and n is reaction energy.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L which is given as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (10)$$

Where K_L is Langmuir constant and C_0 is the highest initial Cr (VI) ion concentration (mg/L). The value of R_L provides information as whether the adsorption is irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [57].

3.10. Kinetic Experiments

Batch studies were carried out to determine the time profiles of Cr (VI) adsorption onto natural bituminous coal. The samples were collected from the polyethylene bottle after 30, 60, 90, 120, 150, and 180 minutes and filtered, the filtered, were analyzed for chromium concentrations followed the colorimetric methods [52-54]. The pseudo-first order and pseudo-second order models are the most popular kinetic models to study the adsorption equilibrium: The pseudo-first order model is described as equation 11 [58]:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (11)$$

Where, q_e and q_t are the amounts of adsorbent (mg/g) at equilibrium and time (min), respectively. K_1 is the constancy of the adsorption rate (1/min). Integration of equation (10) at the boundary of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ leads to equation (12):

$$\log\left(1 - \frac{q_t}{q_e}\right) = -\frac{k_1}{2.302t} \quad (12)$$

The pseudo-second order model is written as equation 13 [58]:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad (13)$$

Where K_2 is the constancy rate (mg/g).The linear form of equation (13) at the boundary of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ can be described as equation (14):

$$\frac{dq_t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e t} \quad (14)$$

3.11. Thermodynamics Study

In order to study the thermodynamics of sorption of the metal ion on adsorbent, three basic thermodynamic parameters, free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) of sorption were calculated using the following equations [60, 61].

$$\Delta G^0 = -2.303 RT \log K_c \quad (15)$$

$$K_c = \frac{q_e}{C_e} \quad (16)$$

$$\text{Also, } \Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (17)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (18)$$

Where R is universal gas constant (8.314 J/mol K).

3.12. Column Studies

Column adsorption experiments were performed using a glass column with 1.4 cm internal diameter, length of 30 cm and 5 g of the adsorbent natural coal with bed heights of 7.4 cm was used, the column was washed with distilled water followed by 3 mg/L of Cr (VI) solution at pH 3.0 was passed through the column. Then a glass column was packed with cotton at bottom and filled with a known amount of adsorbent (mesh size < 250 μm), the experiments was run out in a down flow mode at a flow rate of 1.25 mL/min, 2 mL/min and 4 mL/min respectively. Effluent flow was adjusted manually with a clip at the bottom of the column at specific time using stop watch. The column runs were carried out up to the point where the breakthrough capacity was consumed. Effluent samples were taken at different intervals time and analyzed for residue chromium in the solution using colorimetric method [62, 63] and average value was reported.

The breakthrough point is identified as the number of bed volumes of treated water to reach the point where the effluent concentration exceeds 0.05 mg/L of Cr (VI). The number of bed volumes (BV) is calculated as the ratio shown in Eq. (19).

$$BV = \text{Volume of the solution treated} / \text{Volume of the adsorbent bed} \quad (19)$$

The filtration rates of the packed column were determined at each flow rate of 1.25 mL/min, 2 mL/min and 4 mL/min respectively using equation (20) [63] as:

$$FR = \frac{Q}{A} \quad (20)$$

$$A = 4\pi d^2 / 4 \quad (21)$$

Where FR is filtration rate cm/min, Q flow rate, A is cross sectional area, d is column dimension.

3.13. Quality Assurance

To establish the accuracy of the collected data, all batch experiments tests were recorded in triplicate and average values only are reported. Blank tests have been run in parallel. All polyethylene bottles and lab ware were washed with detergent, followed by repeated rinsing with distilled water and soaked overnight in 10% HNO₃ for 24 h and finally rinsed three times with distilled water and oven dried.

All the chemicals used in this work are AR grade from different supplies. Experimental runs have been performed by using chromium containing working solution prepared from stock. The experiments confirm that the initial chromium concentration, the pH and the Cr (VI) ratio changed during the experiment due to interaction between adsorbent and adsorbate. The accuracy of analytical techniques has been checked by determination of the standard deviation (S.D.) of the filtered sample analysis. Regression analysis and Chi of experimental data has been carried out with the Microcal origin 6.0 soft ware. The correlation coefficient (R^2) and the standard error in parameter evaluation have been investigated to characterize the precision of optimal data fitting analysis.

4. Results and Discussions

In this study, batch adsorption experiment and column study were carried out, different parameters such as contact time, pH, dose, effect of initial concentration of chromium Cr (VI) and temperature were evaluated in order to determine the efficiency of adsorbent. The data obtained from these studied were used to describe responsible adsorption isotherm models, to assess the kinetics and thermodynamics of the adsorption of Cr (VI) onto natural bituminous coal, the adsorbent characterization was also studied.

4.1. Characterization of adsorbent

The physicochemical analysis of natural bituminous coals was carried out by X-ray Fluorescence. The results of analysis were presented in Table (2), and the chemical compositions of NBC are given in Table (3). It is noted that the sum of iron, aluminum, magnesium and calcium oxides are significantly high and together amounted to nearly 45.38 wt.%, plus relatively higher amount of carbon content was the reason which could lead to high adsorption of Cr (VI) anion. Similar results have observed with similar adsorbents percentage [64].

4.1.1. Physiochemical Properties of Adsorbent

The physical properties of the studied adsorbents such as pH, moisture contents and bulk density were investigated and results are shown in Table (2).

Table: 2 The Physical properties of adsorbents

Adsorbent	pH	Moisture content %	Bulk density g/cm ³
Natural bituminous coal (NBC)	5.2	4.21	1.88

Table: 3 Chemical compositions of natural bituminous coal

Total elements	Percentage	Ash chemistry /Oxides	Percentage
Carbon	47.20	Fe ₂ O ₃	7.07
Hydrogen	4.51	Al ₂ O ₃	34.80
Sulfur	0.45	MgO	0.71
Oxygen	10.09	CaO	2.80
Nitrogen	1.09	SiO ₂	52.26
		SO ₃	0.88

Source: Raw data taken from Dilbi Coal Mining Share Company (Ethiopia, 2008 and 2010 data) with permission letter.

4.1.2. FTIR Analysis

The FTIR spectroscopy is a known method for detection of functional groups and quantitative analysis of the sample to determine the changes in vibration frequency in the functional groups of the adsorbents due to metal sorption. Fourier transforms infrared spectroscopy of the bituminous coal before and after adsorption process has been studied using FTIR Analysis Instruments. The spectra were recorded in the region 400-4000 cm⁻¹ with a spectral resolution of 2 cm⁻¹, using a pressed KBr pellet technique. The FTIR results are shown in Fig. 1 (A and B).

It is quite clear from the spectra Fig (1, A and B) the absorption broad peak at 3428 cm⁻¹ indicated the presence of both band is generally attributed to the (O-H) vibration of phenolic group or water which tend to show a band width difference before and after sorption. Other peaks observed at 2922 cm⁻¹ could be due to the asymmetric stretching vibration of CH₃ for the aliphatic group. 1620 cm⁻¹ is assigned to aromatic carbonyl and carbonyl motion in carboxyl groups similar result have reported at 1615 cm⁻¹ [48, 65], while the peaks at 1384, 1033, and 544 cm⁻¹, C-N, C-C and C-O stretching, respectively. The rest 1384 could be symmetric deformation of -CH₂- (bending) or aliphatic bending modes and the peaks in 1300-1000 cm⁻¹ could be due to the phenolic deformation C-O-C

(stretching). Whereas, bands observed at 544 shifted to 540 cm^{-1} this may be due to metal oxygen stretching. These bands were sharp and of strong intensity thus indicating the high degree of crystallinity of the sample [65, 66]. A strong absorption at 1033 cm^{-1} NBC can be ascribed to the presence of the mineral quartz. The most relevant signals on the FTIR spectrum for coals are the absorption bands in the region between 850 and 650 cm^{-1} . The bands near to 840 and 780 cm^{-1} are attributed to AlO_4 groups; the bands around 720, 685, 640 and 570 cm^{-1} are ascribed to AlO_6 groups [67]

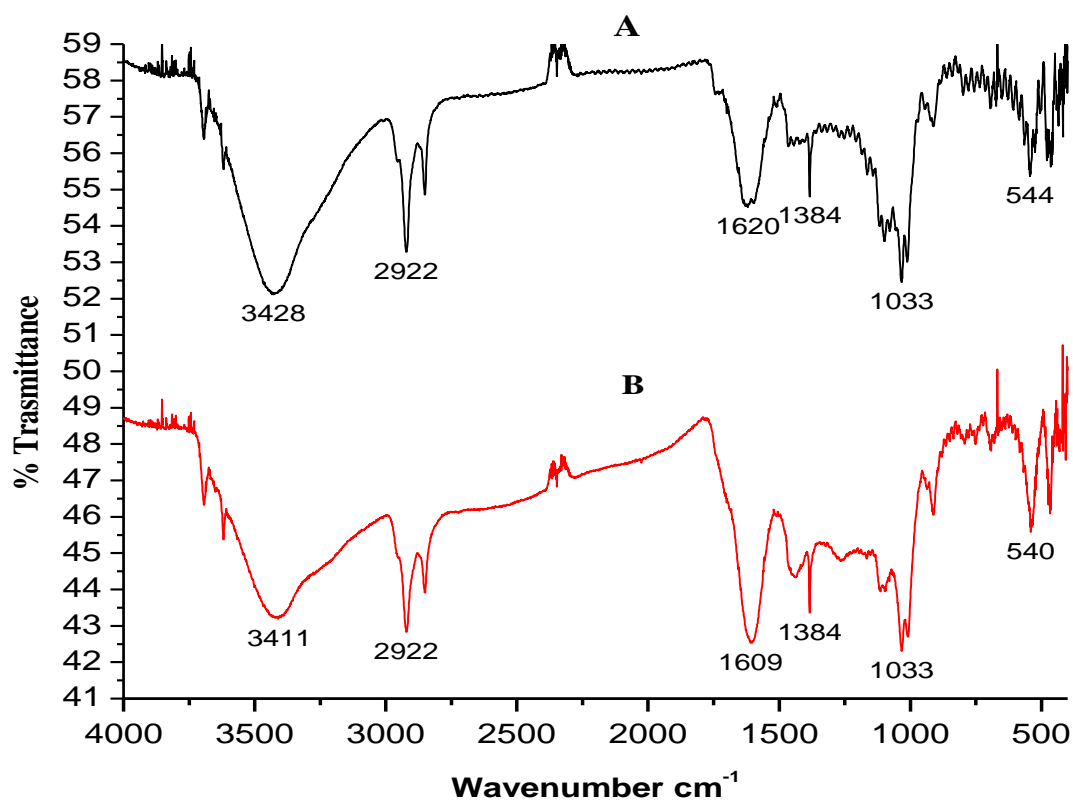


Fig 1: FTIR for Natural bituminous coal before -A (NBCB) and after adsorption process-B (NBCA).

Therefore, the effect of metal cations on loading on the FTIR spectra of the samples showed that the functional groups play a major role in the uptake of Cr (VI) ion, these observed in Fig (B) loaded after adsorption of Cr (VI) onto natural bituminous coal, where the band at 3428 cm^{-1} before adsorption process shifted in position and shape to 3411 cm^{-1} and 1620 to 1609 cm^{-1} respectively. This indicate strong reasonable for binding metal ion.

4.2. Effect of Time

The effect of shaking time on the percentage removal of Cr (VI) ions by the adsorption on coal is an importance parameter in which the equilibrium kinetics can be obtained as shown in Fig.(2). Its evidence that Cr (VI) removal increases with increasing contact time and approximately 60.3-94.3% of maximum Cr (VI) removed is attained in 150 min and the maximum adsorption is attained in about 180 min. It is clear that, before equilibrium the greater the contact time the greater will be the adsorption and accordingly, the greater will be the percentage removal. The initial rapid rate of adsorption may be due to the availability of the positively charged surface of the adsorbent for anionic Cr (VI) species present in the solution [68]. These results indicate that the NBC have a strong capacity for adsorption of Cr (VI) ions in solutions. Then from the results obtained the optimum contact time 180 min was chosen for adsorption process onto adsorbents since the efficiency removal became constant after this contact time and the kinetics study were investigated after.

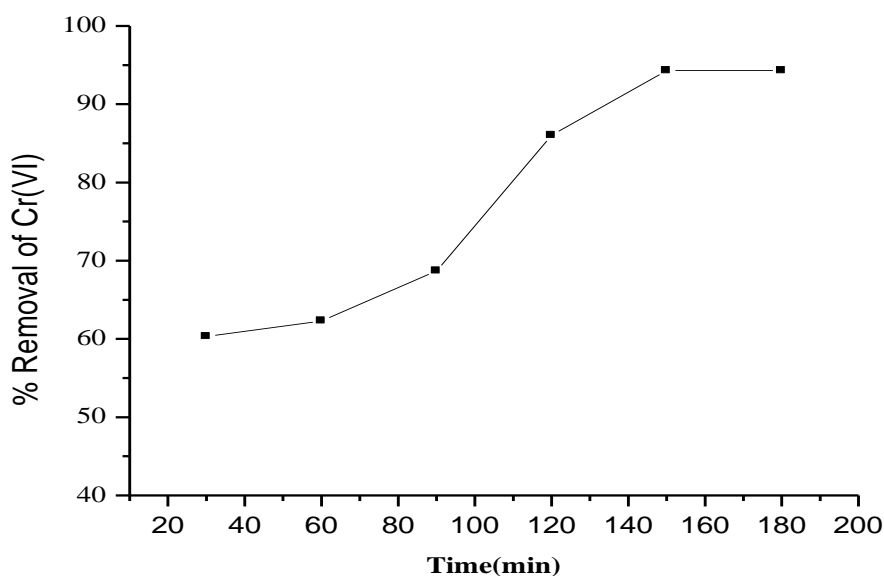


Fig 2: Effect of shaking time on the Cr (VI) removal on natural bituminous coal, Cr (VI) initial 3 mg /L, pH of 3, adsorbent dose: 10 g/L, shaking speed: 200 rpm, and temperature: 25 °C, n = 3.

4.3. Effect of pH

The pH value of the solution is an important factor that controls the uptake of Cr (VI) during the adsorption process; hence it become necessary to determine at what pH, Maximum adsorption will takes place [69]. The interaction of Cr (VI) with bituminous coal was investigated at different pH values. The experimental results revealed that the percentage removal of Cr (VI) decrease with increase in pH values. The maximum removal efficiency was 95.1% at pH 2 and 94.3% at pH 3 as shown from Fig. (3). The Chromium removal was higher at lower pH values. Therefore the bituminous coals are able to absorb Cr (VI) ion, it would seem due to the presence of a multitude of anionic sites and the removal of Cr (VI) could be attributed to the physical adsorption mechanism, especially at low pH, as can be seen from Fig. (3), the adsorption of Cr (VI) uptake is in all cases pH-dependent showing a maximum at equilibrium pH values between 2.0 and 3 similar result reported by researchers at pH 2 and 3.2 respectively [70].

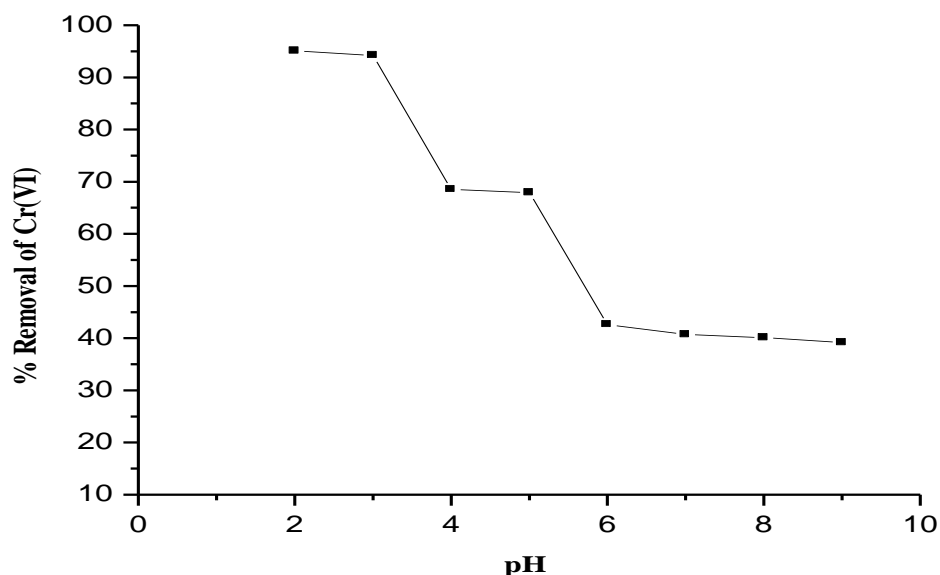
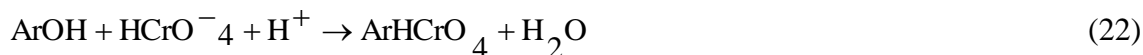


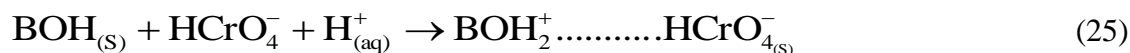
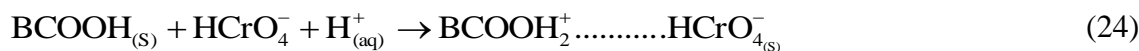
Fig 3: Effect of pH on the percentage removal of Cr (VI) on natural bituminous coal, Cr (VI) initial 3 mg/L, and shaking speed: 200 rpm, adsorbent dose: 10 g/L, and temperature: 25 °C, n = 3).

When examining the effect of pH on adsorption of Cr (VI) different mechanisms must be considered, such as electrostatic forces, ion exchange, and chemical complexation. Electrostatic attraction/repulsion between adsorbent and adsorbate is the most commonly proposed mechanisms. Thus, the increase of Cr (VI) adsorption at acidic pH should be due to the electrostatic attraction between positively charged groups of bituminous coal surface and the HCrO_4^- anion, which is the dominant species at low pH due to high protonation. Moreover, the decrease of the sorption with increasing pH could be due to the decrease of electrostatic attraction and to the competitiveness between the chromium anionic species (HCrO_4^- and CrO_4^{2-}) and OH^- ions in the bulk for the adsorption on active sites of the sorbent. From these assumptions, it can be suggested that Cr (VI) removal takes place by physical adsorption [71, 72].

The surface charge of adsorbent is positive at low pH, and this may promote the binding of the negatively charged HCrO_4^- ions. The HCrO_4^- species are most easily exchanged with OH^- ions at active surfaces of adsorbent under acidic conditions as shown in Eq. 22 (Ar is adsorbent surface) [73].



Some reports suggested that amino, carboxyl, and hydroxyl groups of biomaterials such as coal are suspected to bind anionic Cr (VI) ions with the support of protons in aqueous phase [74-76] as follows:



Thus it was found that removal of Cr (VI) ions from solution was pH dependent and in view of these observations, the pH 3 was taken as the optimum pH for further studies.

4.4. Effect of Adsorbent Dose

The amount of the adsorbent doses was varied from (10-80 g/L) and equilibrated for 180 min at an initial Cr (VI) concentration of 3 mg/L; these were considered to see the effect on Cr (VI) adsorption keeping other parameters at optimum conditions (Fig.4). The result showed that the removal efficiency of chromium ion increases with increasing adsorbents dose significantly from 94.3 to 99.6 % with maximum capacity of 0.284 mg/g, the increase in the adsorption efficiency with an increase in the adsorbent dose can be attributed to the increase due active adsorption sites. Whereas chromium ion adsorption capacity decreases with an increase of adsorbents amount [77]. At lower dosage of adsorbents, there are insufficient active sites that the adsorbate can easily occupy. However, at higher dosage, active sorption sites are sufficiently available for the adsorbate to occupy. Similar results have been reported in the study on adsorption of Cr (VI) onto avocado kernel seeds, Juniperus procera sawdust and papaya peels [35].

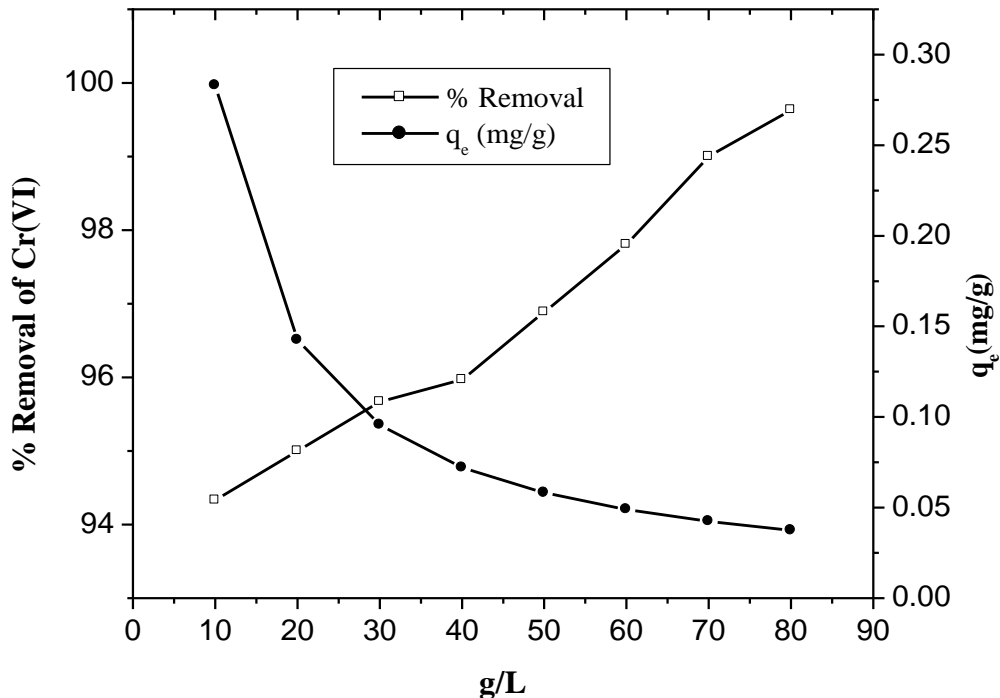


Fig 4: Effect of dose on the percentage removal of Cr (VI) on natural bituminous coal, Cr (VI) initial 3 mg/L, pH of 3 and shaking speed: 200 rpm and temperature: 25 °C, n = 3).

4.5. Effect of Initial Concentrations

The effect of initial concentrations of Cr (VI) adsorption was studied in batch experiments (pH 3, 80 g/L as selected dose optimum and other parameter constant) the initial Cr (VI) ion concentrations of 3, 5, 25, 50, 75, 100, 125 and 150 mg/L. The equilibrium curve shows that the overall percentage removal of Cr(VI) from solution decreases with an increase in initial Cr(VI) concentration as shown in Fig(5). The final percentage removal for an initial chromium concentration of 3, 5, 25, 50 and 75 mg/L saw a removal of 99.7 % , 99.6%, 97.2%, 86.4% and 82.3%, respectively whilst initial concentration of 100, 125, 150 mg/L were remain constant at 82 %. This may be due to lack of sufficient surface area to accommodate much more Cr (VI) ions presence in the solution. It is evident that the amount of chromium removed from solution increases with an increase in concentration of Cr (VI). This is probably due to the higher interaction between the metal ions and metal sequestering sites of the bituminous coal. This trend was also found by other investigators [78]. The decrease in removal efficiency can be explained by the fact that all adsorbents had a limited number of active sites, which would have become saturated above a certain concentration.

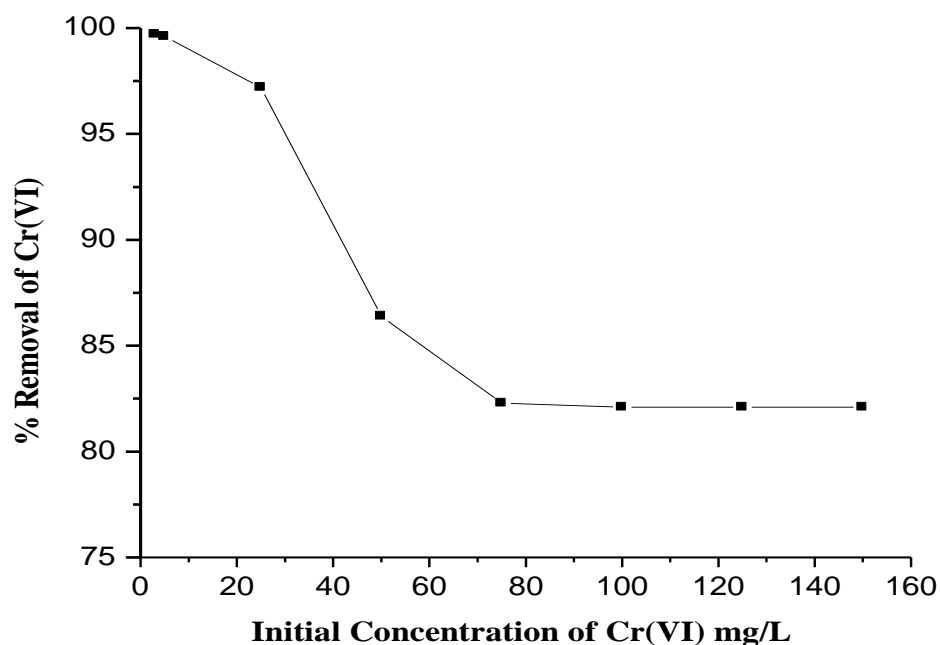


Fig 5: Effect of initial concentrations on the percentage removal of Cr (VI) onto natural bituminous coal, pH of 3 and shaking speed: 200 rpm, adsorbent dose: 80 g/L, and temperature: 25 °C, n = 3).

4.6. Effect of Temperature

Temperature is an important variable that determines the thermodynamic of adsorption process. From the Fig.(6), it has been observed that the percentage removal of Cr (VI) rapidly increase from 20- 25 °C with efficiency removal of 77% - 94.3% at 25 °C and slightly increased (94.3-97.7%) with an increase of temperature from 25°C to 45 °C and other conditions were kept constant. The increase in the adsorption capacity for some range of temperature may be attributed to the chemical interaction between adsorbate and adsorbents, formation of some new adsorption sites or enlargement of pore size and activation of the sorbent surface with rise in temperature. Additional increase in temperature increases the mobility of the metal ions and reduces the swelling effect in biosorbent, thus, enabling the metal ions to penetrate further [79]. The results also indicate that the adsorption of Cr (VI) onto natural bituminous coal is an exothermic process [80].

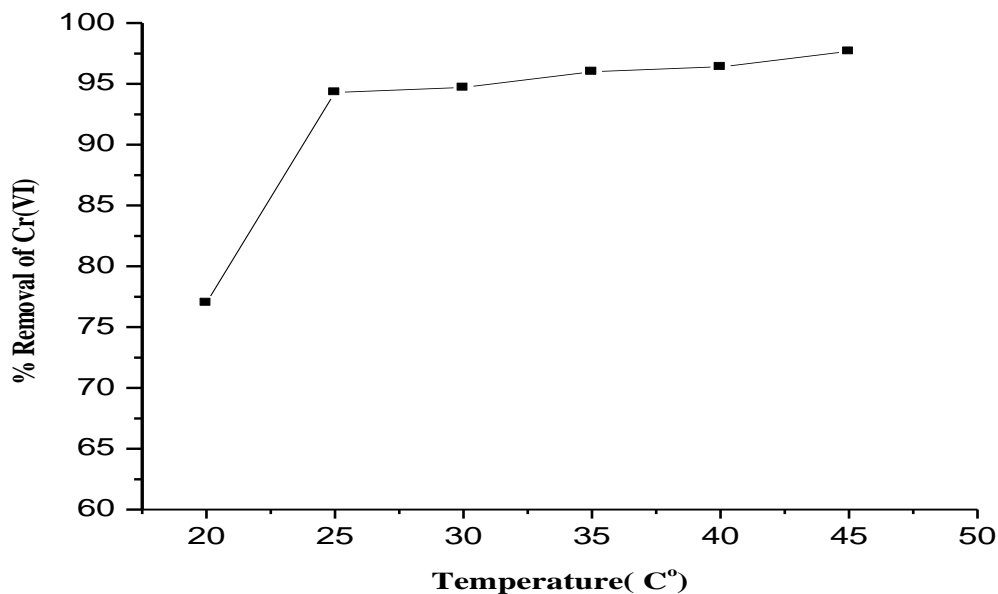


Fig 6: Effect of temperature on the percentage removal of Cr (VI) on natural bituminous coal, Cr (VI) initial 3 mg/L, pH of 3 and shaking speed: 200 rpm, adsorbent dose: 10 g/L, n = 3 and contact time 180 min).

4.7. Adsorption Isotherm Investigation

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species [27]. Adsorption data are usually described by adsorption isotherms, such as Langmuir and Freundlich model are mostly used by many researches. The equilibrium adsorption of Cr (VI) onto bituminous natural coal was studied for different initial concentrations of 3, 5, 25, 50, 75, 100, 125 and 150 mg/L adsorbate at 25 °C, 80 g/L and the data obtained was fitted by Langmuir and Freundlich isotherm using nonlinear.

4.7.1 Langmuir Isotherm

According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at the site [11]. The Langmuir isotherm is given by equation (7), from nonlinear analysis the Langmuir isotherm does not fit well the equilibrium data with weak the correlation coefficient. In the present study, R_L was found to be 0.053 meaning in the ranges ($0 < R_L < 1$), which indicates that natural bituminous coal is good adsorbents for Cr (VI) ion removal.

4.7.2 Freundlich Isotherm

Freundlich isotherm model was also used to explain the observed phenomenon. This is commonly used to describe the adsorption characteristics for the heterogeneous surface [27, 81]. The Freundlich isotherm is represented by Equation (8) and K_f and n are constant incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. A plot of q_e vs C_e (Fig.7) a nonlinear trace with a slope of $1/n$ and intercept of $\log K_f$. K_f and n calculated from the intercept and slope of the plots were found to be 0.11851 and 0.76496 respectively. The magnitudes of K_f and n show easy separation of chromium ions from the aqueous solution and indicate favorable adsorption. The intercept K_f value is an indication of the adsorption capacity of the adsorbent; the slope $1/n$ indicates the effect of concentration on the adsorption capacity and represents adsorption intensity. As seen from Table (4), n value was found high enough for separation. The Freundlich isotherm is more widely used to describe heterogeneous surface but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. The Freundlich isotherm fitted well the equilibrium data with the correlation coefficient of 0.98379.

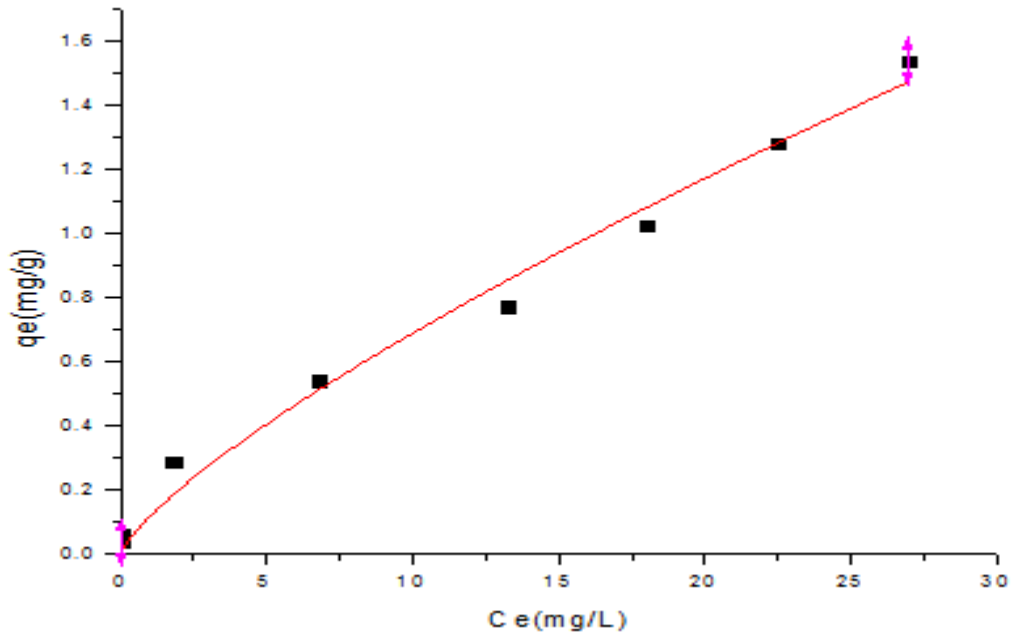


Fig 7: Freundlich adsorption isotherm for Cr (VI) on natural bituminous coal, pH = 3, T= 25°C, adsorbent dose = 80 g/L, Time = 180 min and SD = 0.08076

Table: 4 Results of isotherm models for the adsorption of Cr (VI) ions onto bituminous coal at constant temperature of 25 °C.

Freundlich model	N	K_F (mg/g)	R²	q_{e(cal)} (mg/g)	q_{e(exp)}	Chi	R_L
Value	0.76496	0.1185	0.98379	1.473	1.538	0.0123	0.053

In order to determine the best-fit isotherm for each system adsorption of Cr (VI) onto NBC, two error analysis methods were used to evaluate the data, the linear coefficient of determination which is the widely used approach in evaluating the fit between experimental data and the two isotherm models, and closeness of the fit is determined by (R²) while the Chi-square statistic test for determination of a non-linear model base on normality assumptions of standard least squares [82, 83]. The chi-square test statistic is basically the

sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from the models. The equivalent mathematical statement is:

$$\chi^2 = \sum (q_e - q_{e,m})^2 / q_{e,m} \quad (26)$$

Where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is the experimental data of the equilibrium capacity (mg/g). If the data from the model are similar to the experimental data, χ^2 will be a small number, and if they are differ; χ^2 will be a large number. Therefore, the data set were analyzed using the non-linear chi-square test to confirm the best-fit isotherm for the sorption system [82-84]. The χ^2 values are calculated using Eq. (26) and are given in Table 5. Based on the values of the R^2 and the results of chi-square analysis, Cr (VI) adsorption by NBC can be best described by the both isotherm model given high value of R^2 and the χ^2 values of both the isotherms are comparable and hence the adsorption of chromium onto NBC follows both Langmuir and Freundlich isotherms. The smaller χ^2 values confirm a better correspondence between experimental data and isotherm model [85]. Results indicated that the Chi-square test provided a better determination for the sets of experimental data confirmed that χ^2 from non-linear model of Freundlich isotherm was found to be small (0.0123).

4.8. Adsorption Kinetic Studies

The kinetics data of adsorption process provide key information about the efficiency of adsorption. Clearly, the fast reaction period shall facilitate smaller reactor volumes ensuring effectiveness, economy as well. The kinetic parameters obtained were evaluated at different contact time and keeping other parameter at optimum conditions, Pseudo-first order and pseudo-second-order models were tested to analyze the adsorption kinetics [30]. The pseudo-first-order and second order equation are expressed in equation 12 and 14. The values of K_1 (the first-order reaction rate constant of adsorption (min^{-1})) and q_e were calculated from the slope and intercept of the plot of $\log (q_e - q_t)$ versus t while the values of K_2 (the pseudo-second-order rate constant of adsorption ($\text{mg} / \text{g min}$)) and q_e were evaluated from the intercept and slope of a plot of t/q_t versus t , respectively [39].

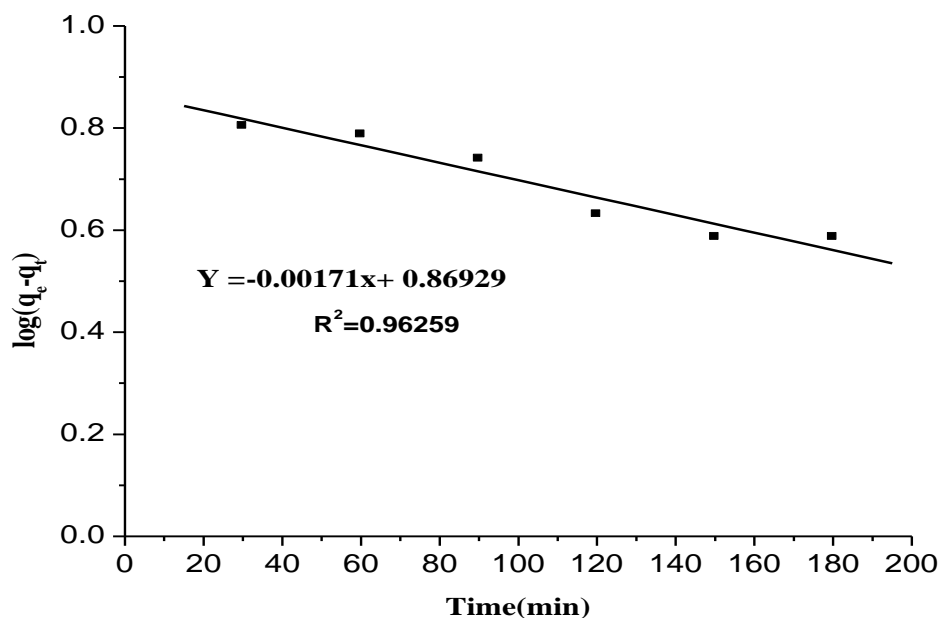


Fig 8: Pseudo-first order plot for Cr (VI) adsorption onto natural bituminous

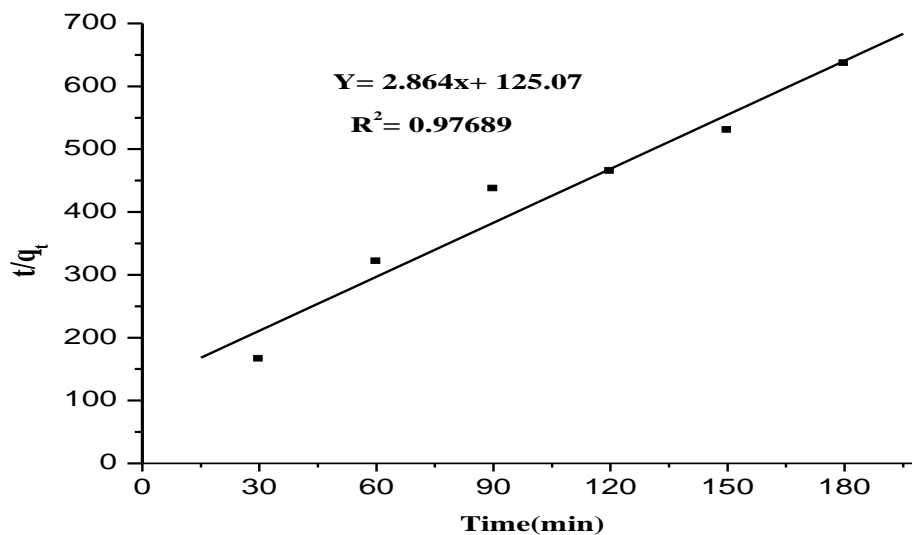


Fig 9: Pseudo-second order plot for Cr (VI) adsorption onto natural bituminous coal.

Both adsorption kinetic models have been used to understand the adsorption kinetics and the correlation coefficient, R^2 , were calculated from these plots. These pseudo-first-order and Pseudo-second-order models were calculated by using equations (12) and (14).

However, the correlation coefficient, R^2 , values showed that the pseudo-second-order model fits better (Fig. 9 and Table 5) to the experimental data than the pseudo-first order model (Fig.8 and Table (5)). Here the observed rate constant (K_1 , K_2) was considerably greater than or compared with some reported value for chromium adsorption on the variety of adsorbents [28, 35, 49, 79], which indicate that the NBC was an efficient adsorbent for Cr (VI) removal from aqueous solutions.

Table: 5 Kinetic parameters for adsorption of Cr (VI) ions onto adsorbents at constant temperature of 25 °C.

Pseudo-first-order			Pseudo-second-order		
$K_1(\text{min}^{-1})$	$Q_e(\text{mg/g})$	R^2	$K_2 (\text{mg/g.min})$	$Q_e(\text{mg/g})$	R^2
508.35	1.15	0.96259	0.0228	0.349	0.97689

4.9. Adsorption Thermodynamics Studies

Thermodynamic parameters such as enthalpy change (ΔH^0), entropy change (ΔS^0) and free energy change (ΔG^0) for Cr (VI) sorption onto bituminous coal were evaluated using Eq. 15, 16 and 17. The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of $\log q_e/C_e$ versus $1/T$ (Fig. 10). Table (6) shows the thermodynamic parameters for metal ions adsorption onto natural bituminous coal. The negative values of ΔG^0 indicate the spontaneous nature of the process and more negative value with increase of temperature reflected that an increased in temperature favors the adsorption process [77]. The negative value of ΔH^0 (-11.24 kJ/ mol) indicates exothermic nature of the process of the Cr (VI) adsorption onto the natural bituminous coal. While the negative (-283.68 KJ/Kmol) ΔS^0 corresponds to a decrease in the degree of freedom of the adsorbed species [86].

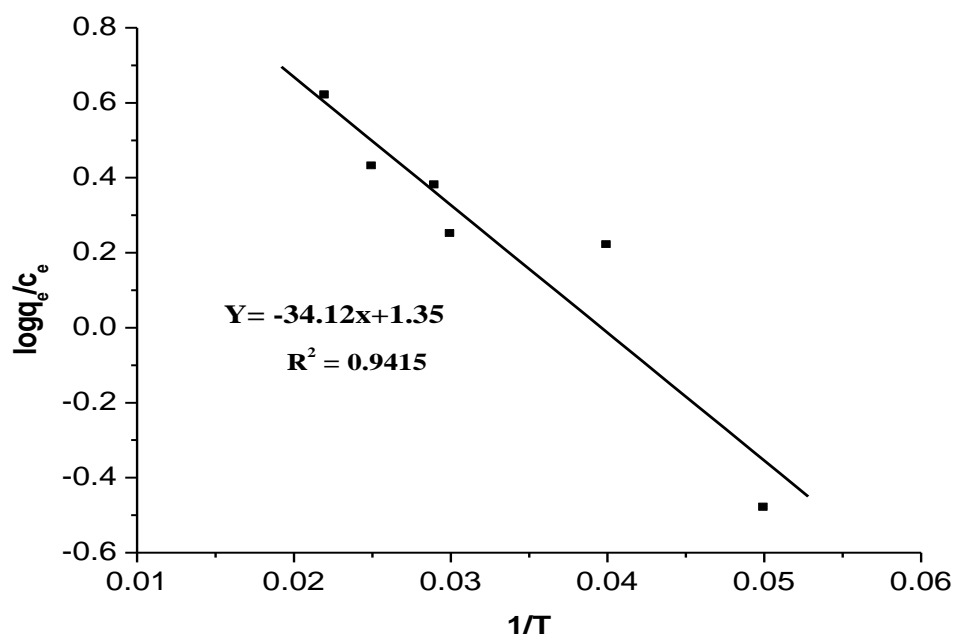


Fig 10: Graphical $\log q_e/c_e$ versus $1/T$ for determination of ΔH° , ΔS° , ΔG° and $SD = 0.14285$, $N= 6$, $P < 0.00503$.

Adsorption process is generally considered as physical if $\Delta H^0 < 25$ kJ/mol and as chemical when $\Delta H^0 > 40$ kJ/mol [87, 88]. The value of ΔG^0 for sorption of metal ions was negative, indicating spontaneous sorption. Similar results have been reported for the Cr (VI) adsorption onto activated carbon [89]. This may be attributed to a relative increase in escaping tendency of the solute from the adsorbent phase to the bulk phase with the rise in the temperature of the solution.

Table: 6 Thermodynamic parameters calculated for the adsorption of Cr (VI) ions onto bituminous coal at different temperatures.

ΔH° (kJ/mol)	ΔS° (kJ/Kmol)	ΔG° (kJ/mol)	20 °C	25 °C	30 °C	35 °C	40°C	45 °C
-11.24	-283.68		79.82	-45.73	-62.36	-110.58	-143	-231.97

4.10. Column Studies

The effect of flow rate on breakthrough curves for the adsorption of Cr (VI) onto the natural bituminous coal was varied to achieve the maximum removal of the adsorbate at flow rates of 1.25 mL/min, 2 mL/min, and 4 mL/min with column bed height 30 cm, 5 g dose, at an inlet concentration of 3 mg/L, it was found that the maximum uptake of Cr (VI) was achieved at flow rate 1.25 and 2 mL/min. About 92–98.3% chromium is removed at lower flow rates 1.25 mL/min after 170 min, while this decreases with increased flow rate for 2 mL/min at 110 min and 4 mL/min. A plot of C/C_0 versus time is shown in Fig. (11), where C is the effluent concentration and C_0 is the influent concentration 3 mg/L. The breakthrough point of Cr (VI) according to WHO standard of 0.05 mg/L occurred at about 1760 and 2700 cm^3 for the flow rate of 1.25 mL/min and 2 mL/min at bed volumes (BV) of 4.22 and 6.47 cm^3 respectively, BV was calculated base on equation (19). A higher Cr (VI) uptake was observed at slow flow rate with height of 7.4 cm may be due to the present of enough amount of adsorbent which provided more active binding sites for adsorptions process with better distribution of adsorbates. Increase in bed volume and contact time also observed in most of the previous studies [62, 63, 90, 91].

The low flow rate 1.25 mL/min reduces concentration of Cr (VI) 3 mg/L to permissible level 0.05 mg/L at the fixed time and the maximum of 0.72 mg/L. Thus the flow rate 2 mL/min minimize the used concentration to 0.05 mg/L with maximum concentration of 0.56 mg/L, meanwhile the faster flow rate decrease the 3 mg/L to 0.20, 0.23, 0.24 and 0.26 mg/L.

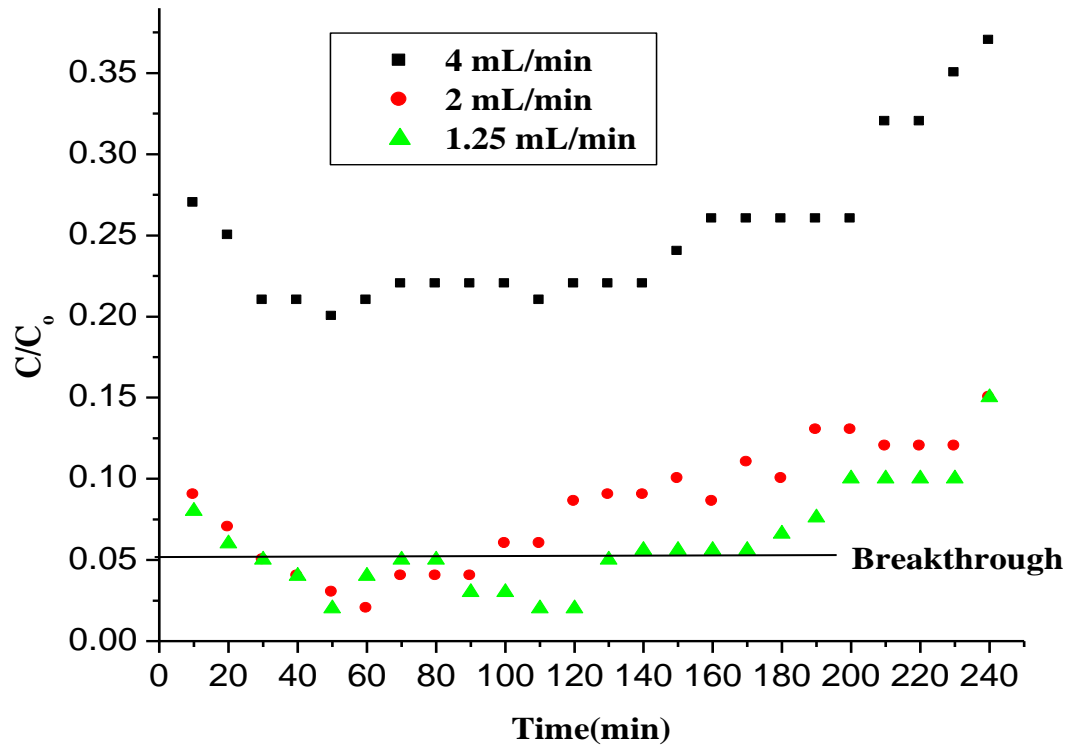


Fig 11: Effect of flow rate on breakthrough curve for adsorption of Cr (VI) on bituminous coal, at initial Cr (VI) concentration of 3 mg/L, pH 3, dose 5 g , and flow rate of 4 mL/min, 2 mL/min ,and 1.25 mL/min.

It's seen from Fig (11) that the breakthrough occurred at a comparatively faster and slow flow rate time less time was taken to reach the saturation breakthrough. This can be explained from the mass transfer surrounding area, the rate of mass transfer gets increased at higher flow rate leading to faster saturation [65]. The filtration rate (FR) for flow rate 1.25 mL/min, 2 ml/min, and 4 ml/min were calculated according to the equation (19), And the FR was found to be 0.54cm/min, 0.27cm/min, and 0.16 cm/min respectively.

4.11. Comparison of Chromium (VI) Adsorption with other Adsorbents

The adsorptive capacities of the adsorbents used in this work have been compared with those of others reported in the literature and the values of adsorption capacity and the pH as presented in Table (7). The experimental data of the present investigation were compared with reported values. Results of investigation showed that the adsorbents have high adsorption capacity compared to Neem leaves powder, Rice bran (a), Fired clay soils, Chitosan coated carbon, Char of South African coal (CSAC). Whereas Turkish brown coals such as Ilgin (BC₁) and Beys-ehir (BC₂), untreated papaya peel (PP) and powder of potato peelings showed higher capacity than this work. The difference in adsorption capacity of the natural bituminous coal in this paper to those previously reported could be due to different pH, the doses, adsorbents types and others experimental conditions.

Table: 7 Comparison of adsorption capacities of Cr (VI) ion with other adsorbents reported in various studies.

S/No.	Adsorbents	pH	Q _m (mg/g)	References
1.	Chitosan coated carbon	5	0.688	[28]
2.	Granular activated carbon (GAC)	2	7.0	[30]
3.	Fired clay soils	2	0.67 - 0.83	[34]
4.	Untreated papaya peels (PP)	1	7.16	[35]
5.	Neem leaves powder	2	0.85	[36]
6.	Rice bran a	2	0.069	[42]
7.	Char of South African coal (CSAC)	2	0.3	[45]
8.	Turkish brown coals	2 -3.2	6.8,7.4,	[48]
9.	Modified oak sawdust	3	1.7	[73]
10.	Powder of potato peelings	2.5	3.28	[78]
11.	Animal bone charcoal	2	16.5	[92]
12.	Natural bituminous coal (Ethiopia)	3	1.54	This work

5. Conclusion and Recommendations

The aim of this study was intended to evaluate the potential use of natural bituminous coal for the elimination of Cr (VI) from aqueous solutions. The obtained results revealed that the locally available adsorbents is an effective for removal of Cr (VI) with efficiency 94.3 % within 180 minutes at initial concentration 3 mg/L of pH 3 and the uptake was found to be dependent on the different parameters such as contact time, pH, adsorbent dose, concentrations and temperature. Chromium Cr (VI) was rapidly adsorbed when higher adsorbent dose were applied, Thus the percentage removal of adsorption increases to 99.7% with the increase in adsorbent dose (2 g), The FTIR spectra showed that the functional groups were the appropriate site for chromium binding due to shift which occur in their positions. The experimental data for the adsorption process were well fitted Freundlich adsorption isotherm model with good correlations. Relatively high correlation coefficients (R^2) for the pseudo-second-order model over the pseudo first order kinetic models can adequately describe the kinetic process of Cr (VI) adsorption onto NBC. Thermodynamic data confirmed that the adsorption process is feasible, spontaneous and exothermic in nature at a temperature range of 20 °C - 45 °C. From findings of this research it is possible to conclude that the natural bituminous coal which is readily available in Ethiopia was found to be a simple, effective and economical adsorbent for uptake of Cr (VI) ion in both batch experiments as well as column studies at low concentration. Therefore developed method could be useful in the treatment of chromium contaminated waste water in industrial and other sources of effluents before released into the aquatic environment under investigated conditions. Further evaluation of the adsorbents (NBC) for removal of Cr (VI) in waste water in field is required to express that they could be capable for practical in treatment of real sample.

6. References

1. Dinesh, M.; Charles, U.; Pittman, J. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *Journal of Hazardous Materials*. **2006**, *B137*, 762–811.
2. Radovic, L.; Moreno-Castilla, C.; Rivera-Utrilla, J. Carbon materials as adsorbents in aqueous solutions, in: L.R. Radovic (Ed.), *Chemistry and Physics of Carbon*. Marcel Dekker, Inc. New York. **2000**. 27.
3. Dinesh, M.; Singh, K.; Singh, V. Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth. *Journal of Industrial and Engineering*. **2005**, *44*, 1027–1042.
4. Rengaraj, S.; Cheol, J.; Younghun, K.; Jongheop, Y. Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H. *Journal of Hazardous Materials*. **2003**, *B102*, 257–275.
5. Tasrina, R.; Choudhury, P.; Nurul, A.; Ali, M.; Quraishi, S.; Mustafa, A. Adsorption of Cr(III) from aqueous solution by groundnut shell. *Journal of Environmental Science and Water Resources*. **2012**, *16*, 144 – 150.
6. Elisabeth, L.; Hawley, R.; Deeb, C.; James, J. Treatment Technologies for Chromium (VI). Chromium(VI) Handbook . **2004**. 274
7. Richard, F.; Bourg, A. Aqueous geochemistry of chromium. *A review, Water Resources*. **1991**, *25*, 807–816.
8. Jun, D.; Fenglian, R.; Chun, T. Adsorption of Cr(VI) and Speciation of Cr(VI) and Cr(III) in Aqueous Solutions Using Chemically Modified Chitosan. *International Journal of Environmental Research and Public Health*. **2012**, *9*, 1757-1770
9. Vandana, S.; Nishi, A.; Radha, T. Sorption of Cr(VI) and As(V) on HDTMA –Modified Zeolites. *International Journal of Scientific and Engineering Research*. **2011**, *2*, 5.
10. Marshal, S. Hazardous and Toxic effects of Industrial Chemicals, NDC Publication, USA, **1979**, 137.
11. Tashauoei, R.; Movahedian, H.; Kamali, M.; Amin, M.; Nikaeen, M. Removal of Hexavalent Chromium(VI) from Aqueous Solutions using Surface Modified Nanozeolite. *Journal of Environmental Science and Water Resources, Summer*. **2010**, *4*, 491-500.

12. Salimi, A.; Amini, N.; Danyali, H.; Hallaj, R. Electrocatalytic reduction of chromium (VI) by thionin: electrochemical properties and mechanistic study. *Electroanalysis*. **2006**, *17*, 1664–1671.
13. Baig, M.; Mehmood, B.; Matin, A. Removal of chromium Cr(VI) from industrial effluents by sand filtration. *Electron Journal of Environmental, Agriculture and Food*. **2003**, *2*, 374–379.
14. Gebrekidan, M.; Nicholas, Pearce, J. Concentrations of heavy metals and related trace elements in some Ethiopian rift-valley lakes and their in-flows. *Hydrobiologia*. **2003**, *492*, 171–178.
15. Gebrekidan, M.; Samuel, Z. Concentration of heavy metals in drinking water from Urban Areas of the Tigray Region, Northern Ethiopia. *Momona Ethiopian Journal of Science*. **2011**, *3*, 105-121.
16. Igwe, J.; Abia, A. A bioseparation process for removing heavy metals from waste water using biosorbents. *Africa Journal of Biotechnol*. **2006**, *5*, 1167–1179.
17. Agaje, B.; Bhagwan, C.; Feleke, Z. Removal of trivalent chromium from aqueous solution using aluminum oxide hydroxide. *SpringerPlus*. **2016**, *5*, 1-11.
18. Cole, P.; Rodu, B. Epidemiologic studies of Chrome and Cancer mortality. A series of meta- analysis. *Regular Toxicological of Pharmacology*. **2005**, *43*, 225-231.
19. Nameni, M.; Moghadam, M. A.; Arami, M. Adsorption of hexavalent chromium from aqueous solutions by wheat bran. *International Journal of Environmental Science and Technology*. **2008**, *5*, 161–168.
20. Nezha, T.; Hanane, S.; Wifak, B.; Nai'ma, E. Mechanisms of Hexavalent Chromium Resistance and Removal by Microorganisms. *Springer International Publishing Switzerland*. **2015**, *233*, 45-68.
21. Wei, L. Trace Heavy Metal Analysis in Animal Feed by ICP-MS. Office of the Texas State Chemist, **2011**.
22. Okeola, F.; Odebunmi, E. Freundlich and Langmuir isotherm parameter for adsorption of methylene blue of activated carbon derived from Agro wasters. *Advances in Natural and Applied Sciences*. **2010**, *4*, 281-288.
23. Ansari, R.; Mohammed, K. Activated Charcoal: preparation, Characterization and application review article. *International Journal of Technology Research*. **2009**, *1*, 859-864.

24. Zvinowanda, C.; Okonkwo, J.; Shabalala, P.; Agyei, N. A novel adsorbent for heavy metal remediation in aqueous environments. *International Journal of Environmental Science and Technology*. **2009**, *6*, 425-434.
25. Covarrubias, C.; Arriagada, R.; Y'añez, J.; García, R.; Angélica, M.; Barros, S.; Arroyo, P.; Sousa-Aguiar, E. Removal of chromium (III) from tannery effluents, using a system of packed columns of zeolite and activated carbon. *Journal of Chemical Technology & Biotechnology*. **2005**, *80*, 899–908.
26. Kesraoui-Ouki, S.; Cheeseman, C.; Perry, R. Natural zeolite utilization in pollution control: a review of application to metal's effluents. *Journal of Chemical Technology and Biotechnology*. **1994**, *59*, 121–126.
27. Kamali, M.; Vaezifar, S.; Kolahduzan, H.; Malekpour, A.; Abdi, R. Synthesis of nanozeolite A from natural clinoptilolite and aluminum sulfate; Optimization of the method. *Powder Technology*. **2009**, *189*, 52-56.
28. Souundarrajan, M.; Gomathi, T.; Sudha, P. Adsorptive removal of chromium (VI) from aqueous solutions and its kinetics study. *Archives of Applied Science Research*. **2012**, *4*, 225-235.
29. Namasivayam, C.; a Ranganathan, K. Waste Fe (III)/Cr (III) hydroxide as adsorbent for the removal of Cr (VI) from aqueous solution and chromium plating industry wastewater. *Environmental Pollution*. **1993**, *82*, 255-261.
30. Rengaraj, S.; Younghun, K.; Yeon, S.H. Removal of chromium from water and wastewater by ion exchange resins. *Journal of Hazardous Materials*. **2001**. *87*, 273–287.
31. Rengaraj, S.; Younghun, Kim.; Yeon, S.Y.; Kang, J.Y.; Kim, K.-W. S. Studies on adsorptive removal of Co(II), Cr(III) and Ni(II) by IRN77 cation-exchange resin. *Journal of Hazardous Materials*. **2002**, *92*, 185–198.
32. El-Gohary, F.; Tawfik, A.; Mahmoud, U. Comparative study between chemical coagulation/precipitation (C/P) versus coagulation/dissolved air flotation (D/DAF) for pre-treatment of personal care products (PCPs) wastewater. *Desalination*. **2010**, *252*, 106–112.
33. Bailey, S.; Olin, T.; Bricka, R.; Adrian, D. A review of potentially low-cost sorbents for heavy metals. *Water Resources*. **1999**, *33*, 2469–2479.
34. Dessalew, D.; Alemayehu, S.; Singh, K.; Dejene, T. Assessment of the Adsorption Capacities of Fired Clay Soils From Jimma (Ethiopia) For the Removal of Cr(VI) from

- Aqueous Solution. *Universal Journal of Environmental Research and Technology*. **2012**, *2*, 411-420.
35. Elsay, M.; Menberu, Y.; Tesfaye R. Kinetic and thermodynamic studies of the adsorption of Cr(VI) onto some selected local adsorbents. *South Africa Journal of Chemicals*. **2015**, *68*, 45–52.
36. Jain, R.; Patil, S.; Lal, D. Adsorption of Cr-(VI) from aqueous environment using Neem leaves powder. *International Journal of Research in Engineering and Technology*. **2014**, *3*, 25-28.
37. Gholipour, M.; Hashemipour, H.; Mollashahi, M. Hexavalent chromium removal from aqueous solution via adsorption on granular activated carbon: adsorption, desorption, modeling and simulation studies. *Journal of Engineering and Applied. Science*. **2011**, *6*, 10–18.
38. Dhanakumar, S.; Solaraj, G.; Mohanraj, R.; Pattabhi, S. Removal of Cr(VI) from aqueous solution by adsorption using cooked tea dust, *Indian Journal of Science and Technology*. **2007**, *1*, 1–6.
39. Abdullah, M.; Devi, P. Kinetic and equilibrium studies for the biosorption of Cr(VI) from aqueous solutions by potato peel waste. *International Journal of Chemical Engineering Research*. **2009**, *1*, 51–62.
40. Jain, M.; Garg, V.; Kadirvelu, K. Chromium removal from aqueous system and industrial wastewater by agricultural wastes. *Bioremediation Journal*. **2013**, *17*, 30–33.
41. Anandkumar, J.; Mandal, B. Removal of Cr(VI) from aqueous solutions using bael fruit (*Aegle marmelos correa*) shell as an adsorbent. *Journal of Hazardous Materials*. **2009**, *168*, 633–640.
42. Hsu, N.; Wang, S.; Liao, Y.; Huang, S.; Tzou, Y.; Huang, Y. Removal of hexavalent chromium from acidic aqueous solutions using rice straw-derived carbon, *Journal of Hazard Materials*. **2009**, *171*, 1066–1070.
43. Singha, B.; Das, S. Biosorption of Cr(VI) ions from aqueous solutions: kinetics, equilibrium, thermodynamics and desorption studies. *Colloids and surfaces B: Biointerfaces*. **2011**, *84*, 221–232.

44. Jain, M.; Garg, V.; Kadirvelu, K. Chromium (VI) removal from aqueous system using *Helianthus annuus* (sunflower) stem waste. *Journal of Hazardous Materials*. **2009**, *162*, 365–372.
45. Di-Natale, F.; Lancia, A.; Molino, A.; Musmarra, D. Removal of chromium ions from aqueous solutions by adsorption on activated carbon and char. *Journal of Hazardous Materials*. **2007**, *145*, 381–390.
46. Bhattacharya, A.; Naiya, T.; Mandal, S.; Das, S. Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents. *Chemical Engineering Journal*. **2008**, *137*, 529–541.
47. Dakiky, M.; Khamis, M.; Manassra, A.; Mer'eb, M. Selective adsorption of chromium (VI) in industrial wastewater using low cost abundantly available adsorbents. *Advanced Environmental Research*. **2002**, *6*, 533–540.
48. Gulsin, A.; Erol, P. Batch removal of chromium(VI) from aqueous solution by Turkish brown coals. *Bioresource Technology*. **2007**, *98*, 2836–284.
49. Attia, A.; Khedr, S.; Elkholy, S. Adsorption of chromium ion (VI) by acid activated carbon. *Brazilian Journal of Chemical Engineering*. **2010**, *27*, 183–193
50. Delibi share company official web: <http://www.2merkato.com/news/energy-and-mining/64> (accessed on 12 April, 2017)
51. Merga, R.; Fekadu, M.; Wondessen, B.; Esayas, A. Defluoridation of Water Using Natural and Activated Coal. *International Advanced Research Journal in Science, Engineering and Technology*. **2016**, *3*, 1-7
52. Marjorie, D. Determination of Hexavalent Chromium in Waters by A Colorimetric Method, Laboratory Methods Manual, **1999**, Version 02, 1-4.
53. Sandell, E. Colorimetric determination of Traces of Metals (2nd Ed), New York, Interscience Publishers. **1950**, 260.
54. Aniruddha, P. Determination of Hexavalent Chromium in Toys by using UV/Vis Spectrometry. *PerkinElmer, Inc. Shelton, USA*. **2009**, CT 06484.
55. Thermo Scientific technical Note 26. Determination of Cr (VI) in Water, Wastewater, and Solid Waste Extracts. *Thermo Fisher Scientific Inc*, **2016**, 1-5

56. Shinogi, Y.; Kanri, Y. Pyrolysis of Plant, Animal and Human Wastes; Physical and Chemical Characterization of the Pyrolytic Product. *Bioresource Technology*. **2003**, *90*, 241-247.
57. Malik, P. Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. *Journal of Hazardous Materials*. **2004**, *113*, 81–88.
58. Acemioglu, B. Batch kinetic study of sorption of methylene blue by perlite. *Chemical Engineering Journal*. **2005**, *106*, 73–81.
59. Azizian, S. Kinetic models of sorption: a theoretical study. *Journal of Colloid Interface Science*. **2004**, *276*, 47–52.
60. Gupta, V.; Rastogi, A. Biosorption of hexavalent chromium by raw and acid-treated green alga *Oedogonium hatei* from aqueous solutions. *Journal of Hazardous Materials*. **2009**, *163*, 396–402
61. Gupta, V.; Sharma, S. Removal of zinc from aqueous solutions using bagasse fly ash—a low cost adsorbent. *Industrial and Engineering Chemical Research*. **2003**, *42*, 6619–6624
62. Tsegaye, G.; Jeriffa, D.; Kim, V.; Dejene, A.; Fekadu, F.; Christian, V.; Gijs, D. Uptake of arsenate by aluminum (hydr)oxide coated red scoria and pumice. *Applied Geochemistry* *accepted manuscript*. **2016**, *S0883-16*, 2927-30156 -1.DOI: 10.1016/j.apgeochem.2016.12.013.
63. Vinod, K.; Gupta, A.; Arunima, N. Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. *Journal of Colloid and Interface Science*. **2010**, *342*, 135–141.
64. Akinyemi, S. A.; Akinlua, A.; Petrik, L. F.; Gitari, W. M. Mineralogy and Geochemistry of Sub-Bituminous Coal and Its Combustion Products from Mpumalanga Province, South Africa, in: *Analytical Chemistry*. **2012**, *56*.
65. Pehlivan, E.; Arslan, G. Comparison of adsorption capacity of young brown coals and humic acids prepared from different coal mines in Anatolia. *Journal of Hazardous Materials*. **2006**, *B138*, 401–408.
66. Namdeo, M.; Bajpai, S. Investigation of Hexavalent chromium uptake by synthetic magnetite Nanoparticles. *Electronic Journal of Environmental, Agricultural and Food Chemistry*. **2008**, *7*, 3082-3094.

67. Akinyeye, R.; Perea, O.; Petrik, L.; Olaofe, O. Comparative Chemical and Trace Element Composition of Coal Samples from Nigeria and South Africa. *American Journal of Innovative Research and Applied Sciences*. **2016**, *2*, 391-404.
68. Ghosh, U.; Goswami, S. Studies on adsorption behaviour of Cr (VI) onto synthetic hydrous stannic oxide. *Water SA*. **2005**, *31*, 597-602.
69. Babu, B.; Gupta, S. Adsorption of Cr(VI) using activated neem leaves: kinetic studies. *Adsorption*. **2008**, *14*, 85-92.
70. Gulsin, A.; Erol, P. Batch removal of chromium(VI) from aqueous solution by Turkish brown coals. *Bioresource Technology*. **2007**, *98*, 2836-2845
71. Sharma, D.; Foster, C. Removal of hexavalent chromium using sphagnum moss peat. *Water Resources*. **1993**, *27*, 1201-1208.
72. Sharma, D.; Foster, C. A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents. *Bioresource Technology*. **1994**, *48*, 257-264.
73. Argun, M.; Dursun, S.; Ozdemir, C.; Karatas, M. Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *Journal of Hazardous Materials*. **2006**, *141*, 77-85
74. Park, D.; Yun, Y.; Park, J. Studies on hexavalent chromium bisorption by chemically-treated biomass of ecklonia SP. *Chemosphere*. **2005**, *60*, 1356-1364.
75. Park, D.; Lim, S.; Yun, Y.; Park, J. Development of a new Cr(VI)-biosorbent from agricultural biowaste. *Bioresource Technology*. **2008**, *99*, 8810-8818.
76. Yang, L.; Chen, J. Biosorption of hexavalent chromium onto raw and chemically modified sargassum SP. *Bioresource Technology*. **2008**, *99*, 297-307.
77. Attia, A.; Khedr, S.; Elkholy, S. Adsorption of chromium ion (VI) by acid activated carbon. *Brazilian Journal of Chemical Engineering*. **2010**, *27*, 183-193
78. Farai, M.; Olga, K.; Pardon, K. Removal of Cr(VI) from Aqueous Solutions Using Powder of Potato Peelings as a Low Cost Sorbent. *Bioinorganic Chemistry and Applications*. **2014**, *10*, 973153-973160
79. Salah, A.; Abdel, M.; Ahmedb, M.; Mamdouh, A. Adsorption studies on the removal of hexavalent chromium contaminated wastewater using activated carbon and bentonite. *Asian Journal of Chemistry*. **2013**, *25*, 8245-8252.
80. Saroj, S.; Surendra, N.; Pradip, R. Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust. *Biochemical Engineering Journal*. **2006**, *31*, 216-222.

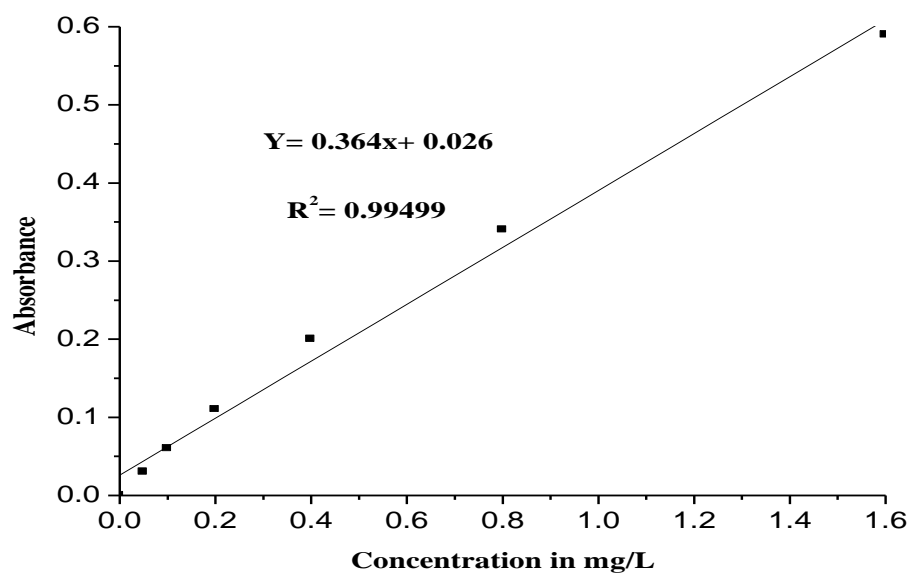
81. Kumar, P.; Kirthika, K. Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder. *Journal of Engineering Science and Technology*. **2009**, *4*, 351 – 363
82. Ho, Y.; Chiu, W.; Wang, C. Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. *Bioresource Technology*. **2005**, *96*, 1285-1291.
83. Ncibi, M. Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis. *Journal of Hazardous Materials*. **2008**, *153*, 207-212
84. Meenakshi, S.; Viswanathan, N. Identification of selective ion-exchange resin for fluoride sorption, *Journal of Colloid Interface Science*. **2007**, *308*, 438–450.
85. Chi-Chuan, K.; Aldwin, H.; Kim, K.; Renato, O.; Mark, D. Hexavalent chromium removal from aqueous solution by adsorbents synthesized from groundwater treatment residuals. *Sustainable Environment Research*. **2017**, *27*, 163-171.
86. Kadirvelu, K.; Thamaraiselvi, K.; Namasivayam, C. Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith. *Separation and Purification Technology*. **2001**, *24*, 497–505.
87. Gupta, V.; Jain, R.; Mittal, A.; Mathur, M.; Sikarwar, S. Photochemical degradation of the hazardous dye Safranin-T using TiO₂ catalyst. *Journal of Colloid Interface Science*. **2007d**, *309*, 464–469.
88. Gupta, V.; Al Khayat, M.; Singh, A.; Pal, M. Nano level detection of Cd (II) using Poly (Vinyl Chloride) based membranes of Schiff bases. *Analalica Chimica Act* .**2009**, *634*, 6–43
89. Leyva-Ramos, R.; Juarez-Martinez, A.; Guerrero-Coronado, R. Adsorption of chromium (VI) from aqueous solutions on activated carbon. *Water Science and Technology*. **1994**, *30*, 191–197.
90. Saha, S.; Sarkar, P. Arsenic mitigation by chitosan-based porous magnesia-impregnated alumina: performance evaluation in continuous packed bed column. *International Journal of Environmental Science and Technology*. **2016**.*13*,243-254.
91. Liu, J.; Huang, X.; Liu, J.; Wang, W.; Zhang, W.; Dong, F. Adsorption of arsenic (V) on bone char: batch, column and modeling studies. *Environmental Earth Sciences*.**2014**. *72*, 2081-2090.

92. Animesh, A.; Puneet, K. Adsorption study of Cr(I) from aqueous solution using animal bone charcoal as low cost adsorbent. *International Journal of Engineering Technology, Management and Applied Sciences*. **2015**, 3, 2349-4476

7. Annex

Calibration standards data for Cr (VI) quantifications

Conc	Abs 1	Abs 2	Abs 3	Average Abs
blank	0	0	0	0
0.05	0.03	0.03	0.03	0.03
0.1	0.06	0.07	0.06	0.06
0.2	0.12	0.11	0.11	0.11
0.4	0.2	0.21	0.21	0.20
0.8	0.34	0.36	0.35	0.34
1.6	0.59	0.59	0.58	0.59



The standard calibration curve for Cr (VI) ion.