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Study on the Competitive Removal of Heavy Metals (Cr^{+6} and Pb^{+2}) from Wastewater By Using Activated Coffee Husk

By

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Declaration

I, the undersigned, declare that this thesis entitled "**Study on the Competitive Removal of Heavy Metals (Cr^{+6} and Pb^{+2}) from Wastewater By Using Activated Coffee Husk"** is my original work, and has not been presented by any other person for an award of a degree in this or any other University, and that all resources of materials used for this thesis have been duly acknowledged.

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Abstract

Due to the release of toxic heavy metals from various industries, water pollution has been a major challenge to environmental engineers today. Among various heavy metals, Pb(II) and Cr(VI) are considered as highly toxic due to their carcinogenicity and various health disorders. This study aimed was to investigate the competitive removal of heavy metal ions (cr^{+6} and pb^{+2}) from aqueous solutions by using activated carbon prepared from the coffee husk.

The initial work involves the optimization of process parameters involved in the preparation of activated carbon by chemical activation using H_3PO_4. The effects of activation temperature and concentration of H_3PO_4 at 2h contact times on the yield and MBN of prepared activated carbon were investigated. The highest yield (73%) of activated carbon was obtained at 400 0C temperatures and 30% H_3PO_4 concentrations while the highest removal efficiency (52%) was observed at 600 ^{0}C temperatures and 30% H_3PO_4 concentration. The prepared activated carbons were characterized for different physicochemical properties. The surface and structural properties of the adsorbent were studied using FTIR spectrometer and X- XRD analysis. The characterization result showed that the coffee husk-activated carbon has good properties and is compared favorably with other reference activated carbons.

A series of batch adsorption of Cr(VI), as a single component, on ACs were carried out and the effect of experimental parameters on the removal efficiency were studied. The maximum removal efficiency of Cr(VI) was 98.1%. The competition of ions to active sites was studied and the result showed that the removal efficiency of Cr(VI) from binary solution was decreased to 94.77% compared to the removal efficiency (98.1%) of Cr(VI) as a single component at the same conditions. The linear form of Langmuire and Freudlich models were applied to analyze adsorption data and the equilibrium data of Cr(VI) were well fitted to Langmuir isotherm model with R^2 of 0.98. Two kinetic models were used to determine the adsorption mechanism and the kinetic data were correlated (R^2 =0.998) well with the pseudo second order kinetic model for the adsorption study of Cr(VI) which implies that adsorption follows second order kinetics.

Key Words: Wastewater, Heavy Metals, Coffee Husk, Activated Carbon, Adsorption Isotherms, Adsorption Kinetics.

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List of Acronyms

AAS	Atomic Absorption Spectrometry
AC	Activated Carbon
ANOVA	Analysis of Variance
ASTM	American Society for Testing Materials
CAC	Commercial Activated Carbon
CHAC	Coffee Husk Activated Carbon
EMEP	European Monitoring and Evaluation Program
FAO	Food and Agriculture Organization
FTIR	Fourier Transform Infrared spectrometry
LCA	Low Cost Adsorbents
MB	Methylene Blue
MBN	Methylene Blue Number
MC	Moisture Content
MF	Microfiltration
RCH	Raw Coffee Husk
VC	Volatile Content
WHO	World Health Organization
XRD	X-Ray Diffraction spectroscopy

1. INTRODUCTION

1.1. Background

One of the most vital commodities, which man had exploited more than any other resources for the sustenance of his life is water. It is a chief natural resource essential for the existence of life and is a basic human entity. Almost all industries require water to function and living organisms cannot exist without water, however, severe contamination of this valuable resource become one of the worldwide challenges that society must address in the 21st century targeting to improve water quality and reduce human and ecosystem health impacts.

Several tons of liquid wastes are released globally, from point and non-point sources into both subsurface and surface water bodies every day (Corcoran, 2010). Only 8% undergo treatment of any kind, in low-income countries (Mena & Mateo-sagasta, 2017). Untreated wastewaters are a multifaceted admixture of several classes of pollutants like synthetic chemicals of many types, hydrocarbons, and heavy metals. Heavy metals pollution of water has become a significant environmental problem almost since the beginning of the agricultural and industrial revolution and today most water resources are still being contaminated with heavy metals released from domestic, industrial, and other man-made activities (Market, 2011).

The natural sources of heavy metals within the environment include weathering of metal-containing rocks and volcanic eruptions, while principal anthropogenic sources include industrial discharges, mining, smelting, and agricultural activities just like the application of pesticides and phosphate fertilizers (Ali, Khan, & Ilahi, 2019). Combustion of fossil fuels also contributes to the discharge of heavy metals like chromium (Cr) to the environment (Spiegel, 2002). Wastewater from many industrial activities, like plating facilities, mining operations, tanneries, metallurgical plants, and also the paint industry is often characterized by heavy metals contamination (Nurchi & Villaescusa, 2008).

Contamination of water resources by heavy metals remains a critical environmental issue that adversely affects plants, animals, and human health (Rezania, Taib, Din, Dahalan, & Kamyab, 2016). The threat of toxic and trace metals within the environment is more serious than those of other pollutants because of their non-biodegradable nature, accumulative properties, and long biological half-lives (Market, 2011). It is difficult to eliminate them from the environment once they enter into it (Aderinola, Clarke, Olarinmoye, Kusemiju, & Anatekhai, 2009). Heavy metal pollution may have overwhelming impacts on the biological balance of natural water bodies including the loss of aquatic diversity.

Most heavy metal ions in the environment are toxic to living organisms. According to many sources, heavy metals like chromium Pb (II) and Cr (VI) are considered as potential health hazards to humans, and it is listed by the Environmental Protection Agency (EPA) as priority pollutants (Toxicology & Medicine, 2011).

It is necessary to control the levels of those heavy metals in water intended for human consumption and also in industrial effluents because they are toxic to living organisms. For these reason, WHO has given recommendations that take into consideration maximum permissible concentrations of heavy metals in wastewaters as well as in drinking water (Kinuthia et al., 2020). Several works were focused on developing new technologies capable to reduce the concentration and effective adsorbent to obtain concentrations under the maximum permissible values of heavy metals in effluents.

Intensive research efforts are made to spot methods for the removal of such ions from aqueous solutions. Numerous technologies are present for the treatment of heavy metals having wastewaters. Among them, chemical precipitation, reverse osmosis, oxidation-reduction, electrodialysis, and solvent extraction are common. However, the conventional methods for the removal of toxic metal ions from wastewater aren’t economically feasible, especially at low concentrations, and have many disadvantages like incomplete metal removal, high reagent, and energy requirements, generation of toxic sludge, or other waste products that need disposal or treatment.

Adsorption, as compared to other methods, has seemed to be a simple attractive process in view of its high efficiency, easy handling, and cost-effectiveness as well as the accessibility of different adsorbents. Additionally, the recoveries of pure metal for recycling as well as reuse of the adsorbent are the added advantages (Esmael, Matta, Halim, & Azziz, 2013). Commercial activated charcoal has been studied as an adsorbent for the removal of heavy metal ions from waters for several years because of its great specific surface area and pore structure, but it is highly expensive. To beat this disadvantage, researchers carried out the studies towards the effective removal of varied heavy metals from solutions using natural adsorbents which are inexpensive, abundantly available, and renewable materials, as a precursor for the AC production, reduces adsorption processing costs (Bailey, Olin, Bricka, & Adrian, 1999) such as agricultural wastes, natural materials or industrial byproducts could be utilized as low-cost adsorbents.

Adsorption of several heavy metals from single metal solutions has been extensively investigated. However, scholars have seldom studied the competitive adsorption characteristics of heavy metal ions on coffee husk activated carbon (Dong & Lin, 2017). This is often a direct concern of the problem of experimentation and analysis involved in multicomponent adsorption studies, but it is an undeniable fact that natural water or wastewater effluents often contain over one heavy metal, which may potentially modify the kind of interactions (additive, synergetic, and antagonistic) between metal ions that leads to a contest for AC adsorption sites (Bohli, Ouederni, & Villaescusa, 2017).

Thus, it is important to grasp the details about these interactions to better understand the precise adsorption mechanism of heavy metal adsorption onto AC produced from the coffee husk in binary systems. In this work, adsorption of Cr (VI) in single and Pb (II) and Cr (VI) in binary systems onto coffee husk chemically activated carbon was studied. The analysis of interactions between metal ions in binary mixtures for binding adsorbent active sites was investigated by plotting isotherms of target metal-containing and varying initial concentrations of interfering metal.

Over the previous few decades, adsorption has increased importance as a purification, separation, and recovery process on an industrial scale. Activated carbon (AC) is maybe one of the most widely used adsorbents in the industry for environmental applications and it can be prepared from many carbonaceous materials (Ghani, Yusoff, & Andas, 2018). Activated carbon is a common term used to describe carbon-based materials that have a large surface area, highly developed pore structure as well as a wide range of oxygenated functional groups present on the surface (Zakaria, Jamaluddin, Zailani, & Bakar, 2021a).

Numerous studies have been dedicated to the preparation of low-cost high-quality carbon adsorbents for the decontamination of water and wastewater. Of particular interest is the preparation of low-cost activated carbons based on biomass for the purification of water from heavy metals such as Pb, Hg, As, and Cr (Ekinci, Industry, Company, & Grimm, 2006).

Activated carbons can be produced from the coffee husk, one of the agricultural by-products or wastes obtained from coffee processing unit which are considered as a low-cost adsorbent. Coffee husk is low-cost and an abundant adsorbent material on a large scale in many regions of Ethiopia, especially in Oromia. For this study, coffee husk was collected from coffee processing units which were used for the preparation of activated carbons to remove Cr (VI) and Pb(II) from aqueous solutions under different experimental conditions.

For preparations of activated carbons, there are two major activation methods: physical and chemical. The physical method involves two-stage processes of pyrolysis of the raw material in an inert atmosphere and activation of the solid residual product (char) at high temperature (900-1000 ^oC) in the presence of carbon dioxide or steam (Ekinci et al., 2006). Chemical activation of the raw material with a chemical activating agent followed by pyrolysis in an inert atmosphere at temperatures between 350-600 ^oC is the second method of activated carbon preparation. Activating agents, such as acids, bases, and salts, such as K_2CO_3 and $ZnCl_2$ are saturated into the biomass by mixing and stirring.

Important advantages of the chemical activation compared to the physical activation are lower treatment temperature and shorter treatment time. In addition to these, activated carbons obtained by chemical activation possess a larger surface area, well-developed microporosity, and has higher activated carbon yield, less environmental pollution (Feng, Li, Wang, & Xu, 2020). Chemical activation with H_3PO_4 has been studied using coffee husk as a low-cost adsorbent in the preparation of activated carbon, and the effect of preparation parameters such as chemical activating agent concentration and activation temperature on the characteristics of AC were investigated.

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1.2. Statement of the Problem

Heavy metals released into the marine environment from different sources have posed many problems worldwide. The existence of these heavy metals in wastewater has toxic effects on the human health and receiving environment. Wastewater containing heavy metals causes detrimental effects on all sorts of life upon direct discharge to the environment (Aksu, 2005). Unlike organic pollutants, heavy metal ions don’t degrade into harmless end products. So, heavy metals can provide a bad effect on the human body and also on the environment itself.

Many industries are producing multi-component wastewater that needs advanced treatment technologies to get rid of toxic heavy metals discharged from industries with high removal efficiency. However, those advanced treatment technologies for the removal of toxic metal ions from wastewater aren’t economically feasible, especially at low concentrations. Such advanced treatment methods are not widely used because of their high cost and also these processes involve the employment of chemicals and synthetic polymers which has an effect on the environment and have many disadvantages like incomplete metal removal, high reagent, and energy requirements, generation of toxic sludge or other waste products that need disposal or treatment.

Therefore, it’s urgently needed to use cost-effective and efficient treatment technology, increasing research interest by using alternative low-cost adsorbents, and effective removal of heavy metals from wastewater. Many researchers have done the research and found that adsorption is the most effective method to remove heavy metals and also there is some research done on heavy metals removal from aqueous solutions using coffee husk as a low-cost adsorbent. However, none of the studies provided due attention to interactions between metal ions (Pb^{2+} and Cr^{6+}) in binary mixtures for binding adsorbent active sites. Thus, the target of this study was to fill this knowledge gap.

In reality, the existence of multiple competing ions is more common than the existence of only one kind of ion. Therefore, assessing competition for adsorption sites is very important. Thus, this study was intended to study the competitive adsorption of heavy metal ions (cr^{+6} and pb^{+2}) from an aqueous solution using an activated coffee husk.

1.3. Objectives

1.3.1. General Objective

The main objective of this study was to investigate the competitive removal of heavy metal ions (Cr^{+6} and Pb^{+2}) from aqueous solutions using activated carbon prepared from coffee husk under a batch adsorptive experiment.

1.3.2. Specific Objectives

The specific objectives of the study are:

- To prepare chemically activated carbon from coffee husk.
- To remove Cr (VI) from the aqueous phase by prepared activated carbon and to study the effect of process parameters on the removal efficieny.
- To investigate the effect of interactions between metal ions Cr(VI) and Pb(II) in binary mixtures for binding adsorbent active sites.
- To evaluate the equilibrium isotherm of the activated coffee husk under batch adsorptive experiments.

1.4. Significance of the Study

Industrial activities and urbanization are increased rapidly and discharged a substantial amount of organic and inorganic contaminations into the water stream, in the last few decades according to different sources. Chief challenges of the many sectors, especially industrial sectors are finding solutions that equate to positive environmental and economic impacts regarding the treatment of their effluents. The activated carbon employed during this study can represent economic and environmentally friendly alternatives to conventional adsorbents since it was derived from natural sources (coffee husk) which are available in Ethiopia at low cost and their utilization is fortified in terms of solid waste management.

Additionally, the removal of heavy metal ions from wastewater reduces the tricky of cancer caused by contamination of water with heavy metal ions specifically, chromium and lead which are well-known human carcinogens. In real effluents different sources, the presence of one kind of ion is rare however the existence of multiple competing ions is more common. Therefore, understanding the adsorption mechanism of heavy metals adsorption onto activated carbon produced from the coffee husk in binary systems is a significant issue. Additionally, the information generated in this study may serve as baseline information for researchers to further develop the treatment process at pilot scale and full scale.

1.5. Scope of the Study

This study was focused on the preparation of activated carbon from locally available precursors i.e. coffee husk and adsorption capacity of coffee husk-based activated carbon as adsorbent for removal of heavy metal ions (cr^{+6} and pb^{+2}) from aqueous solutions at a laboratory scale. The main objective of this study is, to find out the effect of the adsorption parameters such as pH of the solution, adsorbent dosage, contact time, and initial concentration of the adsorbate on the adsorption capacity of coffee husk based activated carbon and also to investigate the adsorption of the heavy metals in a competitive environment.

A batch adsorption test was conducted to see the adsorptive nature of coffee husk in the batch process. Moreover, the relationship between metals adsorbed and the metals ion concentration at equilibrium was examined using the most widely used sorption isotherm models of which the Langmuir and Freundlich equations.

2. LITERATURE REVIEW

2.1. Water Pollution by Heavy Metals

Environmental contamination and pollution by heavy metals are a threat to the environment and are of significant concern (Ali, Khan, & Sajad, 2013). Heavy metals are often emitted into the environment by both natural and anthropogenic grounds. After release from both natural and anthropogenic sources, heavy metals contaminate natural water bodies, sediments, and soils (Ali et al., 2019).

Discharge of industrial effluents without treatment into the water bodies could be a major source of pollution of surface and groundwater (Afzal, Ashraf, & Nabeel, 2018). Contamination of water bodies with heavy metals is a major problem worldwide due to the environmental persistence, bioaccumulation, bio-magnification in food chains, and toxicity of those elements (Ali et al., 2019).

There are many definitions for heavy metals on different sources, however, they commonly defined as naturally existing elements that have a high relative atomic mass and a density at least five times more than that of water (Tchounwou, Yedjou, Patlolla, & Sutton, 2012). The most commonly known heavy metals are cadmium, lead, chromium, mercury, copper, nickel, iron, and zinc are commonly related to pollution and toxicity problems (Nagajyoti, Lee, & Sreekanth, 2010). These heavy metals are needed by several organs of both plants and humans to convey their normal functions but in very low quantity, however, they become toxic when their concentration surpasses the recommended level (Ur, Nazir, Irshad, & Tahir, 2020).

Heavy metals occur naturally in rock formation ore minerals and so a variety of normal background concentrations is linked with each of these elements in soils, sediments, waters, and living organisms (Bradl H., 2002). Heavy metals are also familiar in industrial usages such as in the manufacture of pesticides, batteries, textile dyes, alloys, electroplated metal parts, steel, mining, refining ores, fertilizers industries, paper industries, and others (Sud, Mahajan, & Kaur, 2008). Additionally, their multiple domestic, agricultural, medical and technological applications have led to their wide distribution in the environment; raising concerns over their potential pollution of water resources.

Beyond the permissible limit, all heavy metals have toxic effects on the environment and human health even though some heavy metals such as iron, copper, manganese, and zinc are nutritionally important for plants and animals in small quantities.

Table 1: Permissible limit of selected heavy metals by WHO

S.no:	Heavy metals	Concentration limit	Occurrences in drinking water
1	Arsenic	0.01 mg/litre	the range between 1 and 2 µg/liter
2	Cadmium	0.003 mg/litre	less than 1 µg/liter
3	Chromium (total chromium)	0.05 mg/L	less than 2 µg/liter
4	Copper	2 mg/litre	range from 0.005 to 30 mg/litre,
5	Lead	0.01 mg/litre	below 5 µg/liter
6	Mercury	0.006 mg/litre	below 0.5 µg/litre
7	Nickel	0.07 mg/litre	less than 0.02 mg/litre,

Source: (WHO, 2008)

2.2. Effects of Toxic Heavy Metals on Human Health

Heavy metals affect human health directly by inhaling dust containing heavy metals and indirectly by consuming contaminated food and drinking water (Pierzynski & Schwab, 1993). Heavy metals are the cause of various disorders and diseases because they can be easily stored in the body of living organisms without breaking down. The toxic heavy metals are gradually stored in the body of an organism and can result in bioaccumulation (Samuel, 2017). Bioaccumulation happens when an organism uptakes a toxic substance at a higher concentration than its release (Pierzynski & Schwab, 1993). As these heavy metals, cannot break down easily, the negative effects are worsened by the ecosystem of the environment (Nagajyoti et al., 2010). For example, Cd can be accumulated in the human body for up to 30 years, without being destroyed or becoming soluble like organic matter (Mohod & Dhote, 2013). Heavy metals such as Cd, Pb, Hg, and As deplete the major antioxidants of cells, particularly antioxidants and enzymes having the thiol group (-SH). Health consequences of heavy-metal exposure vary greatly depending on the specific element, the pathway of attack, and the vulnerability of the exposed population (Baker, Reeves, & Hajar, 1994). Chronic exposure to chromium (Cr), lead

(Pb), and other metals can be carcinogenic and can cause brain damage and nervous system disorders. Other heavy metals induce a range of health effects such as headaches, nausea, fatigue, eye irritation, and skin rash. At sufficient dosage, a large number of soil contaminants can cause death by direct contact, inhalation, or by ingestion of groundwater contaminated through the soil.

In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals (Tchounwou et al., 2012). Most products such as pharmaceutical products and dental products, some drugs, cosmetic products like shampoos, lipsticks, hair colors, and others contain heavy metals (Bocca, Pino, Alimonti, & Forte, 2014). The metals are transferred from these products to the environment, humans, and other living organisms and cause many health problems. Table 2 shows the Common uses and principal toxic effects of some heavy metals.

Table 2: Common uses, principal toxic effects of some heavy metals

Toxic Metals	**Uses**	**Toxicity Effect**	**Reference**
Arsenic	Pesticides, herbicides	Lung cancer and skin diseases	(Shaban, Abdou, & Hassan, 2016)
Cadmium	Electroplating, fertilizers, mineral processing, and Battery manufacturing	Cancer, lung insufficiency, Disturbances in the cardiovascular system, liver and kidney damage	Sharma, 1995
Chromium	Textile, Steel, Pulp and Paper, Petroleum Refining and Tanning	respiratory problem, producing lung tumors, kidney and liver damage, headache, weakened immune systems	FAO (2011)
Lead	Metal plating, textile, battery manufacturer, automotive, and petroleum industries	Spontaneous abortion, damage the nervous system, kidney, and brain damage	(Tunali et al., 2006)
Mercury	Metallurgy industries, chemical manufacturing, and metal finishing	Memory problems, increased heart rate, tremors, kidney, and brain damage	(Abia., 2006)
Manganese	Pesticides, batteries	Central nervous system effects	(Martin and Griswold, 2009)
Zinc	Pharmaceuticals, dyes, Batteries	Gastrointestinal disturbances and anemia	(Singhal, 1976)

2.3. Technologies for Removal of Heavy Metals from Wastewater

Heavy metals removal has become a burning issue in the industrialized as well as in the developing world where industrial use and discharging of heavy metals is gradually increasing (Hossain, 2013). The most commonly used methods for the removal of heavy metal ions from wastewater include physical, chemical, and biological methods used separately or inclusively based on need. The available methods are chemical precipitation, lime coagulation, adsorption, ion exchange, reverse osmosis, and solvent extraction (Areco, Hanela, Duran, & dos Santos Afonso, 2012). However, many of these conventional methods for treating wastewater have not been widely applied at a large scale, because of their high cost and disposal problems (Ahmaruzzaman, 2011a).

2.3.1. Chemical Precipitation

Chemical precipitation is the most widely used conventional method for heavy metal removal from wastewater discharged from different sources. Precipitation of metals is usually achieved by the addition of coagulants such as alum, lime, iron salts, and other organic polymers. In this method, the chemicals react with heavy metal ions to form insoluble precipitates (Agarwal, 2015). After the metal precipitates in the solution then it can be easily removed from the water by filtering or settling.

In chemical precipitation reagents such as hydroxide, carbonate, or sulfide are used for precipitation, especially lime and soda (Baveye, Vandervivere, Hoyle, DeLeo, & Sanchez de Lozada, 1998). The most common is precipitation by hydroxide formation because of its relative simplicity, low cost of precipitant, and ease of automatic pH control. The sulfide process is also effective for certain metals, such as mercury, which do not precipitate as hydroxides. Carbonate precipitation has also been used for the treatment of metal-containing wastewater. However, carbonate precipitation of metals using calcium or sodium carbonate is very limited (Patterson, 1975).

Despite its advantages, to reduce metals to an acceptable level for discharge, chemical precipitation needs a huge number of chemicals and produces a large amount of sludge containing toxic compounds during the process (Ahalya, Ramachandra, & Kanamadi, 2003). The produced sludge requires further treatment that increases the cost of sludge disposal. On another hand slow metal precipitation and the long-term environmental impacts of sludge disposal are other drawbacks of this method.

2.3.2. Ion Exchange

This is a method that uses an ion exchange resin or agent to exchange metal ions in dilute solutions to achieve the purpose of extraction or removal of certain metal ions (Nalenthiran & Sambandam, 2016). It is widely used for the recovery and removal of metals from process and waste streams in chemical process industries. The materials used for making ion exchange media are either natural zeolites or synthetic organic materials or inorganic polymeric materials. The modified zeolites like zeocarb and chalcarb have greater affinity for metals like Ni and Pb (Fernandez, Maranon, Castrillón, & Vázquez, 2005). The resins used in this method can be regenerated for re-use after their exchange capacity is exhausted. The limitations on the use of the ion exchange for wastewater treatment are primarily high cost and the requirements for appropriate pretreatment systems (Cont, 2017).

The other limitation of ion-exchange is that it cannot handle concentrated metal solutions because the matrix gets easily fouled by organics and other solids in the wastewater. Ion exchange is capable of providing metal ion concentrations to parts per million levels, however, in the presence of large quantities of competing ions such as Na and Ca, this method is almost ineffective. Moreover suitable ion exchange resins are not available for all heavy metals ions (Nalenthiran & Sambandam, 2016).

2.3.3. Membrane Separation

Membrane separation methods have received considerable attention for the treatment of inorganic effluent since they are capable of removing not only suspended solids and organic compounds but also inorganic contaminants such as heavy metals (Nalenthiran & Sambandam, 2016). The basis of these processes is that higher molecular weight organics cannot pass through when pressured wastewater is forced through the membrane (Belfort, 1984). Membrane processes usually consist of microfiltration, ultrafiltration, nanofiltration, electrodialysis, and reverse osmosis (Hossain, 2013). Different membrane separation technology has different separation mechanism and application range. Some common membrane separation processes are listed in Table 4.

Table 3: Some common membrane separation processes

Membrane Process	Membrane Pore Size	Driven Force	Separation Mechanism
Microfiltration	0.1-0.2μm	pressure difference 100kPa	mechanical screening
Ultrafiltration	0.05-1μm	pressure difference 0.1-1.0MPa	size and shape of molecules
Nanofiltration	0.5-10nm	pressure difference 0.5-1.0MPa	screening and certain selectivity
Reverse osmosis	<1nm	static pressure difference 1-10MPa	selectivity of reverse osmosis membrane
Electrodialysis	-	potential difference	selectivity of ion exchange membrane

Source: adapted from (Gao, 2016)

2.3.3.1. Microfiltration

Microfiltration employs a microporous membrane to remove micron-sized particles, bacteria, viruses, protozoa, contaminants, pollutants, etc., from a solvent/fluid/solution (Qasem & Mohammed, 2021). MF process is a low pressure-driven membrane process, whose membrane pores are in the range of 0.1-0.2μm.

2.3.3.2. Ultrafiltration

Ultrafiltration is the most common technique under membrane separation where the trans-membrane pressure required is relatively low (Verma, Balomajumder, Sabapathy, & Gumfekar, 2021). The aim of this method is to eliminate dissolved as well as colloidal particles and also used to remove water from wastewater containing emulsified oil, and exclude the metal particles. The major limitation of this method is the larger size of the pore and it needs to be cleaned and back-flushed regularly to operate efficiently and replaced periodically (Harland, 1994).

2.3.3.3. Nano-filtration

Nano-filtration is a membrane filtration-based method that uses nanometer-sized through-pores that pass through the membrane and is a kind of pressure infiltration membrane with an aperture between reverse osmosis and ultrafiltration membrane (Gao, 2016). It’s widely used for water softening, removal of heavy metals, organic substances and de-chlorination, purification, and wastewater discoloration. In this method, is the cost and maintenance of the membranes are the main disadvantage associated with this method.

2.3.3.4. Reverse Osmosis

Reverse Osmosis membranes possess dense thin selective layers with small free volume regions and are capable of rejecting almost all ions (Algieri & Chakraborty, 2021). For this reason, the reverse osmosis process is one of the main technologies used in water and wastewater treatment. However, membrane fouling determines a flux decrease and a reduced membrane life the feed pretreatments reduce the fouling. RO system requires high-quality feed for efficient operation, thus wastewater must be treated to remove solids before RO treatment (Hossain, 2013).

2.3.3.5. Electro-dialysis

Electro-dialysis is used to separates ions at the expense of electric potential difference and it uses different cation exchange membranes and anion exchange membranes, alternatively arranged in parallel, to separate ionic solutes (Qasem & Mohammed, 2021). Electro-dialysis can be applied for the removal of dissolved ionic substances and heavy metals from water and wastewater.

However**,** the application of the method described is limited because of pretreatment requirements, primarily, for the removal of suspended solids and heavy metals from water and wastewater. Additionally, this method is expensive and sophisticated, requiring a higher level of technical expertise to operate (Cont, 2017).

2.4. Adsorption

Adsorption is a surface process in which molecules or atoms of one phase (gas, liquid and solid) are accumulated on the other phase (Hossain, 2013), forming a molecular or atomic film. The processes can occur at an interface between any two phases, such as gas-liquid, liquid-liquid, or liquid-solid interfaces (Barakat, 2011a). The material getting adsorbed is known as the adsorbate and the material on which adsorbate is adsorbed is known as the adsorbent.

Many studies have been carried out on adsorption methods as important process in separation technology and are one of the more applicable methods for removing heavy metal ions from water and wastewaters, offering significant advantages like ease of operation, low cost, and efficiency (Demirbas, 2008). Adsorption is an economic method with great potential, compared to other wastewater treatment methods, for the removal of metals from wastewater (Salih & Salih, 2017).

It is an attractive option for the treatment of contaminated water and wastewater, especially if the adsorbent is reasonably cheap and does not need further pretreatment step before its application. Compared to the other techniques, adsorption is superior for water reuse in terms of simplicity of design, initial cost, flexibility, ease of operation, and insensitivity to toxic pollutants (Ahmaruzzaman, 2011b). Depending on the types of adsorbent and adsorbate bonds formed, adsorption can be classified into physical adsorption and chemical adsorption.

2.4.1. Physical Adsorption

It is a process in which the binding of adsorbate on the adsorbent surface is caused by van der Waals forces of attraction or hydrogen bonding. Physical adsorption is usually fast and reversible because the physical adsorption process involves the formation of weak bonds between the adsorbate and adsorbent, thus the adsorption bonds are easily formed and broken (Salih & Salih, 2017). Tsezos and Volesky (1982) verified that thorium and uranium biosorption by fungal biomass of Rhizopus is based on physical adsorption in the cell wall chitin structure. Physical adsorption is also responsible for the removal of copper, nickel, cadmium, zinc, and lead.

2.4.2. Chemical Adsorption

Chemical adsorption occurs as a result of a chemical interaction between the adsorbate molecules and the adsorbent surface (Salih & Salih, 2017). This kind of adsorption involves a strong interaction that results from the chemical reaction between the adsorbent and the adsorbate. This process is usually slow and irreversible because the chemisorption process involves the formation of strong bonds between the adsorbate and adsorbent and can change both the surface and adsorbate chemical character (Somorjai, 1993).

2.5. Factors Affecting Adsorption Process

Various factors such as particle size, pH, contact time, the dosage of adsorbent, temperature, and initial concentrations of metal ions can affect adsorption processes (Adib, Razi, Nur, & Mohd, 2017), and the effect of each factor is described below in detail.

2.5.1. Contact Time

Contact time affects the adsorption capacity, even though the time required for the adsorption process to reach equilibrium differs based on the adsorbent nature and the available adsorption sites. Generally, the removal rate increase with an increase in contact time to a certain extent (Adib et al., 2017) before equilibrium is reached. Due to the deposition of adsorbate on the available adsorption site on adsorbent material, any further increase in contact time will not increase the uptake (Ramesh, 2015). At this point, the amount of adsorbate desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of adsorbate being adsorbed onto the adsorbent. The time required to attain this state of equilibrium is termed as the equilibrium time and the amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions.

2.5.2. Adsorbent Dose

In the adsorption process, the adsorbent dose has a great effect on the removal efficiency of metal ions (Nejadshafiee & Islami, 2019). With more adsorbents dose present, the existing adsorption sites or functional groups present are also increased in principle. However, in practice at a small biomass dosage, the number of ions adsorbed per unit adsorbent weight is high. However, the overall solute adsorption per unit weight of adsorbent can decrease following the increase in adsorbent dose due to the meddling caused by the interaction of active sites of an adsorbent (Iftekhar, Lakshmi, & Srivastava, 2018).

2.5.3. The pH of the Solution

Due to the consequent change in the distribution of the surface charge of the adsorbent, as well as its degree of ionization and the speciation of functional groups, the amount of metal uptake by adsorbents is greatly affected by varying the pH of a solution (Rao, et al. 2013). In a highly acidic medium (pH≈2), it has been generally reported that, the removal of metal ions is almost insignificant and it increases by increasing the solution pH up to a certain limit (Abdelghani &

Elchaghaby, 2014). This is because at low pH the adsorbent is protonated by H^+ ions and the surface charge of the adsorbent is positive although the charge of the metal species is positive; hence creating forces of repulsion. In addition to this, at low pH, the concentration of the H^+ ions is high therefore the competition between the H^+ ions and the metal ions over the active sites on the surface of the sorbent decreases the adsorption efficiency (Soetaredjo, Kurniawan, Ki, & Ismadji, 2013). On the other hand, too high a pH value can cause precipitation of metal complexes. For different adsorption systems of metal ions, the optimal pH is different (Wang & Chen, 2009).

2.5.4. Initial Concentration

The initial metal concentration plays a pivotal role in the sorption process. It is generally approved that the adsorption capacity increases as the initial metal ion concentration increases, whereas the removal efficiency decreases by increasing the metal ion initial concentration (Abdelghani & Elchaghaby, 2014). In principle, the adsorption capacity increases as the initial metal concentration increase because it provides a driving force to overcome mass transfer resistance between the adsorbent and adsorption medium (Abbas, Ismail, Mostafa, & Sulaymon, 2014).

2.5.5. Effect of Temperature

Although depending on the types of adsorbent used, the temperature can affect the adsorption capacity of the adsorbent. In general principles of adsorption theory, adsorption decreases with an increase in temperature and molecules adsorbed earlier on a surface can desorb from the surface at higher temperatures. Temperature can change the adsorption equilibrium depending on whether the process is exothermic or endothermic. Kartikeyan et al. (2005) reported that the adsorption of Cr (VI) on activated carbon increases as the temperature increases and thus the adsorption reaction is endothermic.

The enhancement of adsorption capacity may be due to the chemical interaction between adsorbate ions and adsorbent, creation of some new adsorption sites, or increase in the intra-particle diffusion of metal ions into the pores of adsorbent at high temperatures (Science, 2020). But, as the temperature increases beyond a certain limit, desorption of heavy metals are observed and hence adsorption is decreased. However, the temperature has not been studied as a relevant variable in biosorption experiments. The tests are usually performed at approximately 25-30ºC.

2.5.6. Effect Other Factors

Adsorption is mainly used to treat wastewater where more than one type of metal ion would be present; the removal of one metal ion may be influenced by the presence of other metal ions (Ahalya et al., 2003). Wastewaters are contaminated with various contaminants, including different kinds of metals at the same time, which affects adsorption dynamics. The presence of other substances dissolved in a solute can inhibit the adsorption of metals. This is due to competitiveness between ions of metals that are removed and other ions for binding spots on the surface.

2.6. Adsorbents

The adsorbents such as commercial activated carbon and low-cost materials including natural mineral materials, industrial by-products, agricultural wastes/by products, and natural biomasses, have been recently developed and applied for metal ions adsorption from aqueous solutions. There are a large number of literatures relating to the performance of different adsorbents for the removal of a variety of heavy metals.

2.6.1. Commercial Activated Carbon

Commercial activated carbon is commonly used for industrial applications due to its richness in mesopores and micropores and the resulting large surface area and surface reactivity (Satyawali & Balakrishnan, 2009). Commercial activated carbon can be produced from any carbon-containing organic materials. Thus, CAC can be manufactured from those who have some original porosity and are simple to activate, such as coal, wood, petroleum coke, sawdust, nutshells, peat, lignite, etc (Marsh & Rodríguez-Reinoso, 2006).

Despite the high adsorptive capacity, the high costs of commercial activated carbon and 10-15% loss during regeneration limit its development all over the world. Moreover, commercial activated carbon also shows a high affinity towards organic molecules. As a result, these organic compounds will hinder the heavy metal ions from reaching the adsorbents bed. Due to these drawbacks, searching for alternative adsorbents from abundant and inexpensive sources is of extensive concern (Keng, Lee, Ha, Hung, & Ong, 2014). With the effort to lower costs, various types of CAC have been produced from agro-byproducts, such as pinewood, rice hull, palm shell, seed husks, coconut shell palm fruit for metal ions sorption (Kurniawan, Chan, Lo, & Babel, 2006b).

2.6.2. Low-Cost Adsorbents

Low-cost adsorbents from agricultural and industrial sectors have been recognized as sustainable solutions for wastewater treatment (De Gisi, Lofrano, Grassi, & Notarnicola, 2016). In a developing country like Ethiopia, materials that are locally available in large quantities such as agricultural wastes and industrial by-products can be utilized as low-cost adsorbents. Transformation of these materials into adsorbents would help to decrease the cost of waste disposal and deliver an alternative to commercial activated carbon (Kurniawan, Chan, Lo, & Babel, 2006a). Low-cost adsorbents like agricultural wastes and industrial by-products are found to be more promising in heavy metal removal due to the subsequent attention (Cont, 2017). They are metal selective, economical, regenerative, absence of toxic sludge generation, metal recovery, and highly effective.

Generally, an adsorbent can be assumed as “low cost” if it is abundant in nature, needs little processing, or is a by-product or waste material from another industry (Bailey et al., 1999). There are several studies that review low-cost adsorbents application for industrial wastewater treatment (Kurniawan et al., 2006a).

2.6.2.1. Coffee Husk as low-cost Adsorbent

Coffee husk, one of the by-products of industrial waste is an abundant and low-cost adsorbent material on a large scale in many African countries, especially in Ethiopia. Ethiopia is the homeland of coffee & the prominent producer of coffee in Africa and has many coffee processing units (Berhe, Ayele, Tadesse, & Mulu, 2015b). The enormous amount of coffee production and the rising number of coffee husk residue from processing units in the country shows the likely increase in amounts of coffee husk residue from processing units.

In recent years, there has been an increasing trend towards efficient utilization and value addition of coffee husks. Proposed alternative uses for coffee husks include employing this solid residue as a supplement for animal feed, direct use as fuel, fermentation for the production of a diversity of products, and removal of metal ions as adsorbent. This residue mainly consists of the pulp and hull of the coffee fruit; which presents an excessive concentration of carbohydrates (Franca and Olivier, 2013) of which lignin (18%), cellulose (45%), and hemicellulose (28%). Thus, the coffee husk is a cellulosic lignin material capable of excruciating heavy metals; dissolved in water by the porous structure and high cellulose content (Tien, Tuyen, & Chi, 2018).

2.7. Activated Carbon

According to many sources, AC is the most widely used adsorbent for water and wastewater treatment because of its amorphous structure and high porous character, and usually prepared in small pellets or a powder. AC is non-graphitizable carbon with a highly disordered microstructure, and it is well known for its high adsorption capacity due to its porosity and high surface area (Gottipati, 2012). It can remove a wide variety of toxic metals, because of these good characteristics.

2.7.1. Preparation of Activated Carbon

Generally, activated carbon can be prepared from various raw materials including agricultural and forestry residues (Gottipati, 2012). Most of the precursors used for the preparation of activated carbon are rich in carbon (Prahas, Kartika, Indraswati, & Ismadji, 2008). Because of the nature of the activation process, activated carbon can be prepared by two methods namely, physical and chemical activation depending on whether a gaseous or solid activating agent is used.

In the physical activation, two-step process are involved were the first process is the process of carbonization (pyrolysis) and the second is activation at high temperatures (between 800 and 1100 ^{o}C) in the presence of oxidizing gases like carbon dioxide or steam, whereas chemical activation involves mixing of the chemical activating agent with activated carbon and then followed by pyrolysis at moderate temperatures in the absence of air (Budinova et al., 2006).

2.7.2. Factors Affecting Carbonization of Activated Carbon

Activated carbon properties such as specific surface area, density, porosity, and mechanical resistance depend highly on the raw material used. However, it is possible to modify these parameters by changing the conditions in the pyrolysis process of the agricultural and industrial waste (lignocellulosic) materials. The surface area and pore size distribution are determined by the ratio between the mass of the chemical agent and the raw material. Besides, impregnation ratio, activation time, carbonization temperature, and heating rate are important preparation variables for obtaining ACs with specific characteristics (Mohamed et al., 2010).

2.7.2.1. Effects of Activating Agents

Porous structures and well-developed surface areas that render high adsorption capacity is necessary for the removal of heavy metals from wastewater by activated carbon. To prepare AC with a higher surface area and porous structure, activating agents play major roles in the preparation of activated carbon that renders high adsorption capacity, and various compounds used are reacted differently depending on the biomass type and the temperatures employed (Bedia et al., 2020). The lignocellulosic precursor is treated primarily with chemical activating agents, like H_3PO_4, H_2SO_4, HNO_3, NaOH, KOH, or $ZnCl_2$ by impregnation or physical mixture, and the resulting precursor is carbonized at temperatures between 400 and 800ºC under a controlled atmosphere, in the preparation of activated carbon (Gottipati, 2012).

The activation of carbon materials with phosphoric acid (H_3PO_4) has become an increasingly used method for the large-scale production of ACs because the use of this reagent has some environmental advantages like as low energy cost, ease of recovery, and high carbon yield (Hernández-Montoya *et al*. 2012).

2.7.2.2. Carbonization Temperature

During the activating process, carbonization temperature has the most influence over the activated carbon's quality. To ensure the complete transformation of organic compounds (present in agricultural and industrial waste (lignocellulosic) precursors) it must be at least 400°C into graphene structures. The degree of specific surface area development and porosity is incremented on par with the carbonizing temperature (Olivares-Marín, Fernández-González, Macías-García, & Gómez-Serrano, 2006).

2.7.2.3. Carbonizing Time

To obtain the maximum porosity development this parameter must be optimized while still minimizing the material's loss due to excessive combustion. Bouchette *et al*. 2008 have shown that the yield percentage decreases with an increase of activation temperature and hold time. Carbonization times ranging from 1 hr (up to 14hr (Pavan, Mazzocato, & Gushikem, 2008) have been used in charcoal production.

2.7.2.4. Mass Ratio of Precursor and Activating Agent

The overall saturation of agricultural and industrial by-product/waste (lignocellulosic) precursors must be ensured to develop the adsorbent porosity with the minimum activating agent consumption. This leads to a minimal consumption of chemical compounds and better removal of the excess during the carbon washing process. The effect of the increase in the proportion of the impregnation over the carbon porous structure is greater than the one obtained with the increase of carbonizing temperature (Olivares-Marín et al., 2006)

3. MATERIALS AND METHODS

3.1. Materials and Chemicals

The raw material used as a precursor for the preparation of activated carbon in this study was coffee husk obtained from the coffee processing unit. Lead nitrate (Pb(NO3)2 and potassium dichromate (K2Cr2O7) salts were used for preparing stock solutions of Pb(II) and Cr(VI) respectively. 1,5-Diphenylcarbazide and Phosphoric acid (H_3PO_4), were used as complexing agents and chemical activators respectively. Other chemicals such as 0.1MNaOH and 0.1MHCl were used to adjust the solution pH of the experiment. All chemicals and reagents used throughout the experiments were analytical grades.

3.2. Equipment

Equipment such as muffle furnace, pH meter, mass balance, oven, hot plate, desiccator, 250 and 500ml measuring cylinders, beakers, Erlenmeyer flasks, funnel, thermometer, filter paper (What man No.1, 18cm dia.), Orbital shaker, FTIR instrument, XRD, electrical mill, spoons, sieves, porcelain crucibles and UV/Visible Spectrophotometer were used for different purposes.

3.3. Preparation of Chemically Activated Carbon

The coffee husk, which is found in Ethiopia in abundance was collected from the coffee processing unit and was used for the preparation of activated carbon. The husks were washed with de-ionized water to remove surface impurities. After washing, it was sun-dried and thereafter oven-dried at 105 ^{o}C until a constant weight was obtained. Then the dried coffee husk sample was crushed and ground by using an electrical mill. The ground samples were sieved and those that had particle sizes between 0.71 and 1 mm were selected**.**

The selected coffee husk samples were then impregnated with phosphoric acid (H_3PO_4) activating agent for 24hr. For impregnation, 100ml of different concentrations of H_3PO_4 (10, 30, and 50 %) were mixed with 50g of coffee husk. After 1hr of stirring at 50^{o}C and 24h of aging at room temperature, the mixture was filtered and then dried at 105^{0}C overnight to prepare the impregnated sample. About 10g of the impregnated sample was exposed to thermal activation by varying temperatures from 400-600^{o}C for 2 h in a muffle furnace. Then the carbonized sample was cooled to room temperature. The resultant coffee husk-derived activated carbon was thereafter washed with 0.1M sodium hydroxide (NaOH) solution and then washed with deionized water until the pH became neutral, followed by oven drying at 105^0C for 2 h and then kept in a tightly covered bottle for further use.

Temperature and acid concentration were selected as the independent variables and were analyzed to estimate the effect on the yield and removal efficiency of the prepared activated carbon. The dependent variables which were served as the responses for this study were the yield and methylene blue number. The process variables involved in the activation/carbonization process and their experimental ranges are presented in Table 4.

Table 4: AC preparation conditions and ranges of study parameters at 2h

Factors	**Unit**	**Range**
Temperature	^{0}C	400-600
Concentration of activating agent (H_3PO_4)	%	10-50

3.3.1. Effect of Impregnation Ratio

The impregnation ratio was determined as the weight of the chemical activating agent to the weight of the precursor. The effect of impregnation of phosphoric acid (H_3PO_4), on the carbon yield and MBN, was analyzed. The concentrations of phosphoric acid ranging from 10-50% for impregnation were used. In this study, 100 ml of varied concentrations of phosphoric acid were impregnated with 50g of raw coffee husk.

3.3.2. Effect of Carbonization Temperature

Carbonization temperature is one of the most influencing factors for the development of porosity during the activation process (Gottipati, 2012). The effect of carbonization temperature on the carbon yield and MBN of the prepared activated carbon was investigated by varying temperatures from 400 to 600 ^{0}C.

3.4. Characterization of Activated Carbon

Various properties of prepared activated carbons were characterized by the following standard procedures.

3.4.1. Carbon yield

The total yield was determined after sample processing in terms of raw material mass by wet oxidation methods and loss ignition. The yield of AC is calculated as the percentage weight of the resultant activated carbon divided by the weight of dried coffee husk.

$$\mathrm{Yeild}(\%) = \frac{\mathrm{Wc}}{\mathrm{Wo}} * 100\% \tag{3.1}$$

Where: *Wc* is the dry weight (g) of final activated carbon and *Wo* is the dry weight (g) of precursor before chemical impregnation.

3.4.2. Determination of Methylene Blue Number

Methylene blue number (MBN) is an index that is normally used to express the specific surface area of an adsorbent (Latinwo, Alade, Agarry, & Dada, 2019a) and is defined as the maximum amount of dye adsorbed on 1.0 g of adsorbent. For this study, coffee husk AC (100 mg) was weighed and placed in contact with 100 ml of 10 mg/L of methylene blue solution for 1h at room temperature. The UV/V spectrophotometer was used to analyze the remaining concentration of methylene blue adsorbed. The amount of methylene blue adsorbed from each solution is calculated by using equation (3.2).

$$\mathrm{MBN}\left(\frac{\mathrm{mg}}{\mathrm{g}}\right) = \frac{(\mathrm{C_o} - \mathrm{C_e})}{\mathrm{M}} xV \ , \tag{3.2}$$

Where *MBN*, represents the quantity of MB dye per unit mass of adsorbent (mg/g); C_0 and Ce are the initial and equilibrium concentrations, respectively; V is the volume of MB dye solution in liters and m is the weight of AC adsorbent in grams.

3.4.3. Proximate Analysis

Proximate analysis was done to determine the amount of moisture, ash, volatile matter, and fixed carbon of the activated carbon.

3.4.3.1. Moisture Content

The moisture content of activated carbon was determined using the standard test method (ASTM D2867-91). A sample of activated carbon (5g) is put into a dry closed crucible of known weight and was weighed accurately. The crucible is opened and placed with the lid in a preheated oven at 110 ^{o}C and then the oven is closed and dried for 3 h. The sample was dried to constant weight and then removed from the oven with the crucible closed, cooled in portable desiccators, and weighed again accurately. Then the percent of moisture content was determined using equation (3.3).

$$\text{Moisture content}(\%) = \frac{((W_1+W_2) - (W_1 + W_3))\ \text{x}100}{W_2} \quad (3.3)$$

Where *W1* =weight of crucible in g

W2 =weight of original sample in g

W3 =weight of dried sample in g

3.4.3.2. Determination of Volatile Matter

Activated carbon volatile content determination was done according to the standard method (ASTM D5832 – 98). Dry AC sample (2g) was taken into the crucible with the cover of known weight and the covered crucible was transferred into a preheated muffle furnace regulated at 900^{o}C for 7min. Then the covered crucible was cooled to room temperature in a desiccator and weighed again. The percent of the volatile matter was calculated by using equation (3.4).

$$\text{Volatile matter } (\%) = \frac{\text{weight of volatile components (g)}}{\text{Oven dried weight (g)}} * 100\% \quad (3.4)$$

3.4.3.3. Determination of Ash Content

Ash content represents the quantity of the solid residue left after the biomass sample is completely burned. To determine the ash content, 2.5 g of dried AC sample was weighed and taken into the crucible of known weight. The crucible was transferred to a muffle furnace maintained at 600^{o}C for 2 hours. The crucible was then allowed to cool to room temperature in desiccators and weighed again. The percentage weight of the sample that remained is considered as ash content. The percent ash content (dry basis) was calculated as:

$$Ash\ (\%) = \frac{Wash}{Wo} * 100\% \quad (3.5)$$

Where W_o is the dry weight of the carbon sample before ashing and W_{ash} is the weight of the ash.

3.4.3.4. Fixed Carbon

Fixed carbon is the solid combustible residue that remains after biomass is heated and the volatile matter is expelled. Fixed carbon content in biomass is a calculated value and it is the resultant of summation of percentage moisture, ash, and volatile matter subtracted from 100, which is determined from the following equation.

$$\text{Fixed carbon (\%)} = 100 - (\text{Moisture \%} + \text{Ash \%} + \text{Volatile matter \%}) \qquad (3.6)$$

3.4.4. Bulk Density

The bulk density is the ratio of the mass of biomass particles to the total volume of biomass particles including the pore space volume between and within the biomass particles. The bulk density (ρ) of the AC was estimated by using a pycnometer. First, the sample is filled up to 50% volume of the pycnometer and the weight of the pycnometer with inserted AC sample ($m_o + m_{AC}$) was measured. Then the remaining volume was filled with distilled water. The volume of AC (V_{AC}) is the difference between the volume of water that fills the empty pycnometer V and volume V_{H2O}.

$$V_{AC} = V - V_{H2O} \qquad (3.7)$$

The density of AC was calculated as

$$\rho_{AC} = \frac{M_{AC}}{V_{AC}} \qquad (3.8)$$

Where $\rho_{AC,}$ the density of activated carbon, M_{AC}; the mass of activated carbon and $V_{AC;}$ the volume of activated carbon

3.4.5. Pore Volume

To determine pore volume, each AC sample of 1g was immersed in water and boiled for 15 minutes to displace air from the pores. The sample was then superficially dried and reweighed. The pore volume was calculated as the increase in weight (∂w) divided by the density (ρ_{H2O}) of water at 20°C using the following equation,

$$\text{Pore Volume} = \frac{\partial_w}{\rho_w} \qquad (3.9)$$

3.4.6. Determination of Porosity

The porosity of any porous material is defined as the ratio between the total void spaces within the solid porous material and the material bulk volume (Nyamful et al., 2020). To determine porosity, a cylinder and an aluminum plate were each weighed first. A sample of AC was placed into the cylinder, reweighed, transferred into the aluminum plate, and then oven-dried to a constant weight at a temperature of 105^oC for 1hr. The weights of the sample were recorded after drying. A cleaned, dried density bottle was weighed and a small quantity of sample of activated carbon was taken and gradually put into the density bottle with a little amount of water added and weighed. The volume of the void (Vv) was obtained by first determining the total volume of the cylinder used for the experiment and also determining the volume of the AC used. Porosity is calculated as

$$Porosity = \frac{volume\ of\ void}{Total\ volume} \tag{3.10}$$

3.4.7. X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis was carried out to determine the extent of graphitization in prepared ACs by X-ray diffractometer. Scans were run with a step size of 0.02^o /s of 2θ, typically in the angle range between 10^o and 60^o.

3.4.8. FTIR Analysis

The Fourier Transform Infrared Spectrometer was used to identify the functional groups present in the raw coffee husk and coffee husk activated carbon involved in Cr (VI) adsorption process. The instrument is used to record the FTIR spectra by FTIR instrument with kBr as reference. For this purpose 2 mg of each raw coffee husk and coffee husk AC were placed on the KBr disk and dissolved with 10 drops of paraffin. Then the KBr disk with the sample was immediately put into the sample holder. Then FTIR spectra were recorded in a spectral range of 400-4000cm^{-1}. FTIR was conducted before and after activation so that the organic and inorganic groups were determined by observing the change in frequency that occurred.

3.5. Batch Adsorption Experiments

3.5.1. Preparation of Standard Stock Solutions

Potassium dichromate and lead nitrate were used as the source for chromium and lead stock solution respectively. Stock solutions of 1000mg/L of Pb(II) and Cr(VI) were prepared by dissolving 1.6g of lead nitrate and 2.83g of potassium dichromate respectively in 1000ml distilled water in different 2000ml beakers. The stock solutions were diluted as required to obtain different concentrations of Cr (VI) and Pb (II) ions. Solution of 1, 5-Diphenylcarbazide the main complexing agent, was prepared by taking 0.25g of 1, 5-Diphenylcarbazide powder into a 100 ml volumetric flask and dissolving it with 50 ml acetone.

3.5.2. Single-Component Adsorption of Metal Ions

Batch mode adsorption studies for Cr (VI) ion removal were carried out to investigate the effect of different parameters such as adsorbent dose, agitation time, initial concentration, and solution pH by keeping other parameters constant. Adsorption of Cr (VI) ion on prepared activated carbons was conducted using a prepared aqueous solution. For each experimental run, a definite amount of AC (1-5g) was added to 100 ml of Cr (VI) solutions of known concentration (2-10mg/l) taken into 250 ml Erlenmeyer flasks and agitated at 150rpm in a mechanical shaker at predetermined time intervals (60-150min) and fixed temperature of 30°C. A range of solution pH (3-11) was used to study the effect of pH on the adsorption efficiency of AC. The adsorbate was decanted and separated from the adsorbent using What-man No.1 filter paper and the residual metals that were present in the solution were determined by UV/Vis spectrophotometer at 540 nm by complexing Cr(VI) with 1,5-diphenylcarbazide. Each experiment was conducted in duplicate and the mean values were considered.

The number of heavy metal ions adsorbed per unit mass of adsorbent or removing efficiency of coffee husk was calculated by equation (3.11).

$$Adsorption\ (\%) = \frac{(Co - C_f)}{Co} * 100\% \qquad (3.11)$$

The adsorption capacity of the activated carbon was the concentration of the metal ion on the adsorbent mass and was calculated based on the mass balance principle.

$$q_e = (\frac{C_O - C_f}{M})V \tag{3.12}$$

Where q_e= adsorption capacity of activated carbon (mg/g) V= the volume of reaction mixture (L) M = the mass of adsorbent used (g) C_o= initial concentration (mg/L) of the metal ions and

C_f = final concentration (mg/L) of the metal ions.

3.5.3. Effect of Solution pH

The effect of solution pH was investigated to determine the effect of solution acidity on the efficiency of adsorption and the pH of the solutions was adjusted between 3 to 11 and adsorption experiments were carried out by keeping other parameters constant.

3.5.4. Effect of Adsorbent Dose

The effect of adsorbent dosage was studied by varying adsorbent dose from 1 to 5g/l of activated carbon using 250 ml conical flask with metal ion concentration and contact times of 2 mg/l and 2h respectively. The adsorption efficiencies for different doses were studied with optimum pH and by keeping other parameters constant.

3.5.5. Effect of Initial Metal Concentrations

The effect of initial metal concentrations on adsorption of Cr(VI) onto prepared activated carbons were examined with optimum pH, doses, and contact time of 2h for 2-10mg/l Cr(VI) concentrations in 100 ml water. After filtering the water samples were analyzed for residual concentrations of metal. The optimum concentrations of metals were taken on in this study for proceeding experiments.

3.5.6. Effect of Contact Time

To analyze the effect of contact time on the adsorption efficiency of coffee husk-activated carbon, the agitation time was varied from 30 until equilibrium is achieved. For this experiment, an optimum pH, doses, and initial concentration of metal were used to examine the effect of contact time and to determine equilibrium time.

3.6. Competitive Adsorption

In reality, the presence of multiple competing ions is more frequent than the existence of only one kind of ion in wastewater. Therefore, to assess competition for adsorption sites, binary solutions were prepared and tested. Adsorption studies were carried out by keeping the concentration of the first metal constant and varying the concentration of another metal ion at optimum pH of the former metal ion obtained in the case of a single metal system. Binary adsorption of metal ions was conducted using the same operating conditions as for single-component adsorption.

3.7. Adsorption Isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and solid phase when the adsorption process reached an equilibrium state at constant room temperature. Adsorption isotherm is important to describe how solutes interact with adsorbents and is critical in optimizing the use of adsorbents. An adsorption isotherm study was carried out on two well-known isotherms: Langmuir Isotherm and Freundlich isotherm.

Langmuir isotherm is based on the assumptions that adsorption cannot proceed beyond monolayer coverage, all surface sites are equivalent and can accommodate only one adsorbate molecule, and the ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites (Gottipati, 2012). It can be represented by the equation:

$$q_e = \frac{q_m \, b \, C_e}{1 + b \, C_e} \tag{3.13}$$

This can be rewritten as:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{1}{q_m} Ce \tag{3.14}$$

Where q_e= mass of adsorbate adsorbed per unit mass of adsorbent, mg/g.

b = empirical constant

q_m = Maximum adsorption capacity (mg/g)

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/l

The Freundlich isotherm model assumes that the adsorption takes place on heterogeneous surfaces which have different adsorption energies. This can be defined as

$$q_e = K_f Ce^{1/n} \tag{3.15}$$

Can be written as,

$$logq_e = logK_f + \frac{1}{n} logCe \tag{3.16}$$

Where, q_e= mass of adsorbate adsorbed per unit mass of adsorbent, mg/g.

K_f = Freundlich capacity factor

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/l

1/n= Freundlich intensity parameter

To determine adsorption equilibrium isotherms on the prepared activated carbons, an experiment was carried out by varying initial concentration from 2 to 10 mg/l in 250ml solution of the metal ions using an adsorbent dose of 5g/L at constant temperature (30^{o}C) and agitation speed (120 rpm) for 3hrs of equilibrium time. The data from this experiment were fed into Langmuir and Freundlich adsorption isotherm model for analysis.

3.8. Kinetic Studies

Several researchers used different kinetic models, such as pseudo-first-order, pseudo-second-order, Elovich kinetic equation, and parabolic diffusion model, to predict the mechanism involved in the adsorption process. In the present study, kinetic data were analyzed against two kinetic models, pseudo-first-order and pseudo-second-order models, and the mechanism of the adsorption processes was established. To investigate adsorption kinetic, experiments were performed on different initial concentrations of Cr(VI) at pH 3, the temperature of 30^{o}C, and a dose of 5mg/l.

3.8.1. Pseudo-first-order Model

A general rate expression of pseudo-first-order equation takes the form:

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \tag{3.17}$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first-order sorption, q_e (mg/g) is the amount of metal ion sorbed on the adsorbent surface at equilibrium, and qt (mg/g) is the amount of metal ion sorbed at any time t (min).

Integrating the eq(3.15) with the boundary condition $q_t = 0$ at $t = 0$ and simplifies the equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (3.18)$$

The value of the sorption rate (k_1) can be calculated from linear regression analysis or the slope of the linear plot of experimental data in $\log(q_e - q_t)$ vs t.

3.8.2. Pseudo-second-order Model

The pseudo-second-order equation was used for the sorption of Cr(VI) from a liquid phase. The experimental data can also be tested for pseudo-second-order adsorption.

The commonly represented pseudo-second-order adsorption equation is:

$$\frac{dq_e}{dt} = k_2(q_e - q_t)^2 \qquad (3.19)$$

The linearized integral form of the model is represented as

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e}t \qquad (3.20)$$

Where, q_e and q_t (mg/g) are the amount of Cr (VI) that was adsorbed at the equilibrium and at time t (min), respectively, and k_1 is the pseudo-first-order rate constant of adsorption (g/mg min). The values of $\log(q_e - q_t)$ were linearly correlated with t. The plot of $\log(q_e - q_t)$ vs t gives a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

4. RESULT AND DISCUSSION

4.1. Evaluation of the Effect of Production Factors on the Yield and MBN

The adsorption capacity and carbon yield of activated carbon depend on various process parameters such as impregnation ratio, carbonization temperature, and holding time. Specifically, the effects of carbonization temperature and acid concentration at a constant holding time were discussed below.

4.1.1. Effect of Impregnation on the Yield of Coffee Husk AC

Figure 4.1 shows the effect of impregnation on the percentage yield of coffee husk AC at a constant temperature and activation time of 400 ^{o}C and 2hr respectively. The yield of AC increase with the increase of impregnation up to a certain value and then decreasing of yield with increasing impregnation was observed. This may happen because the activating agent reacts with the precursor and volatile matter then diffuses rapidly out of the surfaces of particles during the activation process (Ghani, Yusoff, & Andas, 2012). At elevated H_3PO_4 concentration, additional phosphoric acid could react with the carbon, and volatile matter diffuses out of the surface of the particles during the activation process.

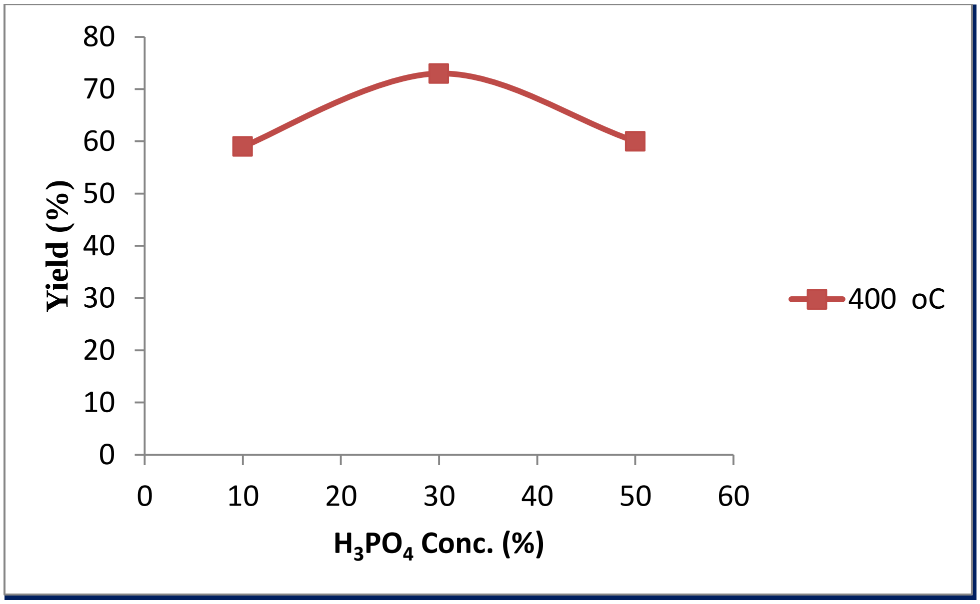

Figure 4.1: Effect of impregnation on yield of AC

The lower yield with the higher impregnation might be caused by the enhancement of carbon burn-off by an extra activating agent (Gottipati, 2012). Therefore, with high activating agent content, the gasification of surface carbon atoms became predominant, leading to an increase in weight loss and resulting in low carbon yield. A similar trend has been reported by (Gottipati, 2012) and (Latinwo, Alade, Agarry, & Dada, 2019b) in which an increase of yield to a certain value and then reduction in the yield of activated carbon was observed as the chemical concentration had been increased.

4.1.2. Effect of Impregnation on the MBN of Coffee Husk AC

The variation of MBN of the activated carbons prepared at different H_3PO_4 concentrations keeping other parameters constant is shown in figure 4.2. By fixing the activation temperature and contact time at 600 ^{o}C and 1h respectively, an increase in the H_3PO_4 concentration from 10% to 30% contributed to a gradual increment in the adsorption capacity of MB dye from 48.8 to 52.58 mg/g. Further increase in the H_3PO_4 concentration to 50%, a slight decrease in the adsorption capacity to 43.52 mg/g was observed. The decrease in methylene blue number at high concentrations of phosphoric acid may be caused by the degeneration of porous structures of activated carbons due to excessive dehydration.

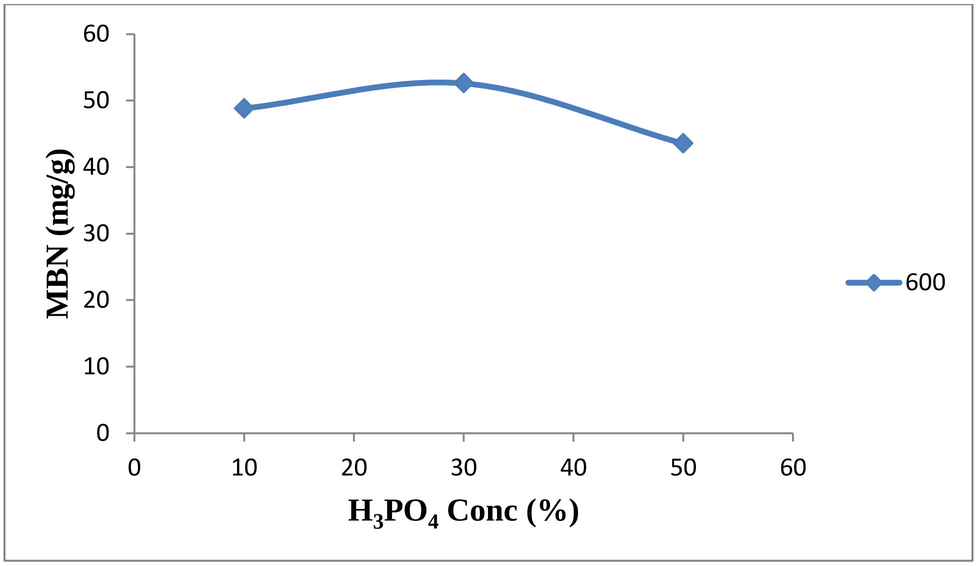

Figure 4.2: Effect of impregnation ratio on MBN of AC

4.1.3. Effect of Temperature on the Yield of Coffee Husk AC

The effect of temperature on the coffee husk activated carbon yield was investigated by varying temperatures from 400 to 600 °C at a fixed H_3PO_4 concatenation (30%) and activation time of 2hr. Figure 4.3 shows the effect of activation temperature on the yield of coffee husk-activated carbon prepared by chemical activation. The percentage yield obtained was decreased from 73% to 28% with the increase of temperature from 400 to 600 ^{0}C. The increasing temperature was contributed to the mass losses. The decrease in the yield of activated carbon is due to a reaction with the dehydrating agent (H_3PO_4), providing elimination and dehydration reactions, breaking the C-O-C and C-C bonds of the raw material (Bhungthong, Aussawasathien, & Hrimchum, 2018).

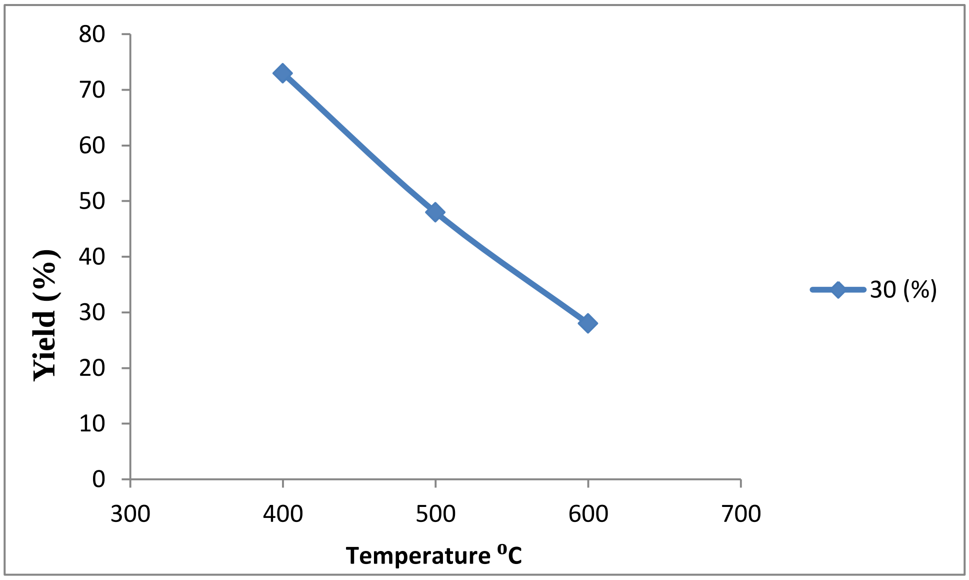

Figure 1.3: Effect of activation temperature on the yield of prepared ACs

4.1.4. Effect of Temperature on the MBN of Coffee Husk AC

Methylene blue number indicates mesopore distribution in the activated carbon. The variation of methylene blue number of activated carbons as a function of carbonization temperature keeping other parameters such as carbonization time and concentration of phosphoric acid constant is shown in Figure 4.4. It is clear that methylene blue number increases from 24.28 to 52.58 mg/g as temperature increases from 400 to 600 ^{0}C. However, an increase in temperature from 400 °C to 500 °C is more significant than that from 500 to 600 ^{0}C. The results indicate that the carbonization temperature has a significant effect on the pore structure of activated carbon which ultimately determines the adsorption capacity of activated carbon. The highest value of methylene blue number is obtained at 600 °C. This may be due to the widening of some micropores are caused by escaping out of more volatile matters at high temperatures (Shrestha, 2016).

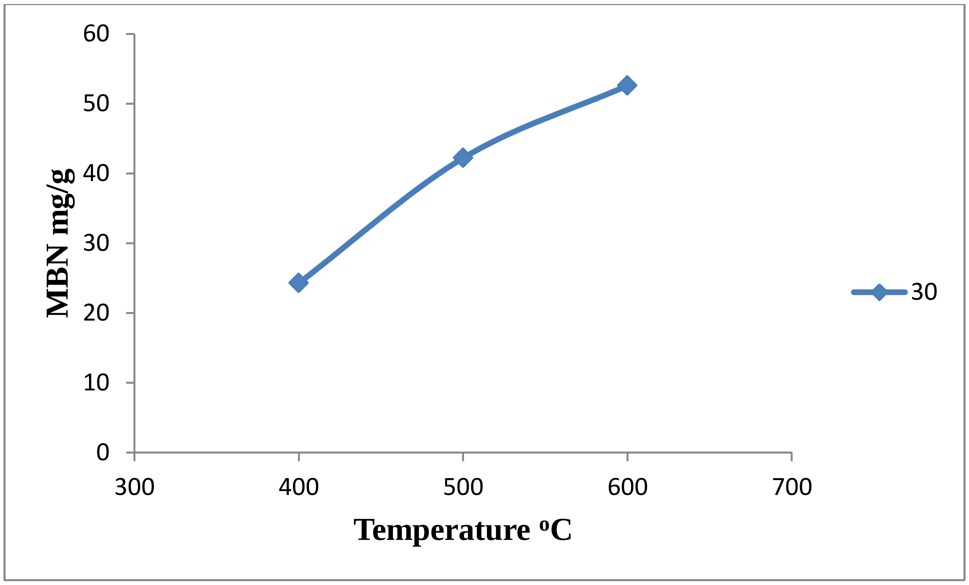

Figure 4.4: Effect of activation temperature on the MBN of prepared AC

4.2. Selected Parameters for Preparation of AC

The production of AC is based on the quantity and the quality of products obtained. Thus, it is necessary to prepare AC with a high adsorption capacity and higher yield. However, from current study experimental data, the carbon yield and MBN were responds opposite to each other with the two factors studied. So, to find the middle ground of these two factors, optimization by using software is very important but, in this study the optimum conditions were selected only based on MBN result since MBN is more important.

An activation time of 2h, an activation temperature of 600 °C, and an H_3PO_4 concentration of 30 % was identified as the optimum set of synthesis parameters that provide the most optimum methylene blue number among the rest of the parameters. Activated carbon prepared using this set of parameters was characterized in the subsequent sections and used for adsorption of heavy metals (Cr^{+6} and Pb^{+2}) from aqueous solutions.

4.3. Characterization of Prepared AC

4.3.1. Proximate Analysis

The various physicochemical composition of coffee husk activated carbon was characterized and compared with other activated carbons produced from low-cost precursor investigations (Table 6). As shown in the table, the moisture content of coffee husk activated carbon was tended to be low (5.2%) showing that this adsorbent was properly prepared and handled. Moisture content, according to Aziza et al., (2008) has a relationship with the porosity of a given adsorbent, and activated carbon with lower moisture content has been reported to have more adsorption efficiency (Elelu, 2019). Table 6 provides a summary of the proximate analysis and methylene blue number as well as pore volume, and bulk density of activated carbon from the coffee husk.

The percentage of the volatile content of coffee husk activated carbon was 13.6 % as shown in Table 6. The higher volatile content of coffee husk-activated carbon showed that some of the organic molecules of the material were attacked and it is stable for adsorption of metal ions from aqueous solutions.

In most cases, ash content is considered as the measure of inorganic impurities in the carbons (Bansode et al., 2003). In this study, ash contents (6.3%) of coffee husk activated carbon as presented in Table 6 showed that coffee husk activated carbon contains a small number of inorganic constituents that show the better adsorbent characteristics of activated carbon.

Generally, a less amount of moisture, ash, and volatile matter, and a high value of fixed carbon indicate a high graphitization grade and low amount of functional groups. This in turn shows that activated carbon can be an excellent raw material for adsorbents to be used in the removal of heavy metals (Awugchew, 2015).

4.3.2. Bulk density

Table 6 shadowed that coffee husk-activated carbon has a bulk density of 0.58 g/ml. This property is an important physical parameter, especially when an adsorbent is to be studied for its filterability. Greater density affords better volume activity and normally indicates high-quality adsorbents for wastewater treatment (Kundu; Gupta, 2006).

Table 5: Physico-chemical property of coffee husk activated carbon

S/N	Characteristics	Unit	values
1	Moisture content (MC)	%	5.2
2	Ash content (AC)	%	6.3
3	Volatile content (VC)	%	13.6
4	Fixed carbon	%	74.9
5	Bulk Density	g/ml	0.58
6	Porosity	%	54.24
7	MBN	mg/g	52.58

4.3.3. X-ray Diffraction (XRD) Analysis

The XRD patterns for raw coffee husk and coffee husk ACs prepared at optimum conditions were demonstrated in Figures 4.5. The samples with broad peaks and the absence of sharp peaks revealed the amorphous structure of carbons, which is an advantageous property for well-defined porous adsorbents (Gottipati, 2012). Higher peaks and broadness were observed in the coffee husk AC sample than in the raw coffee husk sample. Broad peaks found at around 25° in coffee husk AC confirm that the samples are non-graphitized and can have a high microporous structure and hence good adsorption capacity (Onukwuli & Okey, 2015).

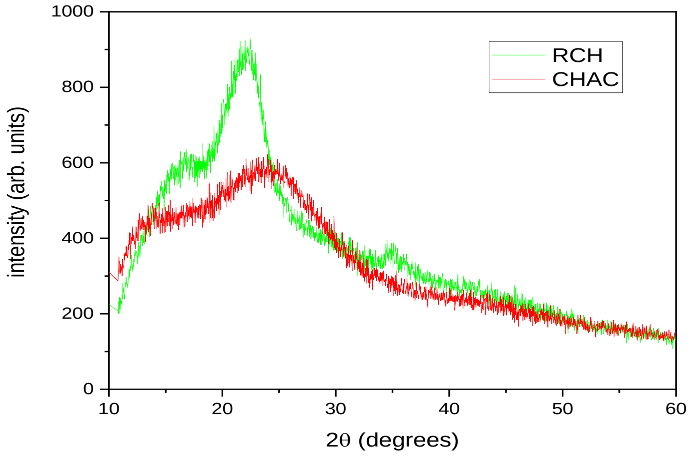

Figure 4.5: XRD patterns of the raw coffee husk and coffee husk ACs

4.3.4. Fourier Transform Infrared spectroscopy (FTIR)

The adsorption capacity of AC is defined not only by its pore structure but also by the chemical nature of its surface. Biosorbents consist of complex organic and inorganic materials such as proteins, lipids, carbohydrate polymers, and sometimes metals. Chemisorptions and ions exchange mostly depend on the available functional groups in a particular bio-sorbent and eventually, metals biosorption depend on it (Hossain, 2013).

To investigate the surface functional groups on the raw coffee husk and AC of the coffee husk FTIR was used and the fundamental structure of those surface functional groups can be determined by the spectral locations of their IR absorptions as chemical bonds absorb infrared energy at certain frequencies (or wavelengths).

The surface functional groups of the raw coffee husk were compared with the H_3PO_4 activated sample and are shown in figure 4.6. It showed that raw coffee husk consists of several functional groups which include amines, hydroxyl groups, various unsaturated hydrocarbons, carbonyl compounds, and others. Whereas, activated carbon made from coffee husk shows that most of the functional groups on the surface of the samples were mostly eliminated during the carbonization or activation process and consisted of a considerable number of peaks or functional groups.

In the case of raw coffee husk, the broad peak observed at 3327 cm $^{-1}$ is due to the presence of hydroxyl groups (O-H stretch) on the surface and H-bonded groups (Lü et al., 2010). The peaks observed at 2927 cm^{-1} and 2855 cm^{-1} are due to the asymmetric and symmetric stretching of methylene (C-H) groups, respectively (Gottipati, 2012). Carbonyl group (C=O stretch) was found for 1760-1665 cm^{-1}band (Awugchew, 2015). Amines group was found between 1650 - 1580 cm^{-1} band. The weak band observed at 1236 cm^{-1} might be due to the existence of in-plane bending of primary or secondary OH groups. The peak found at 1013 cm^{-1} was due to primary hydroxyl groups (Hossain, 2013).

In the case of coffee husk activated carbon similarly different peaks or functional groups were found but some of the functional groups on the surface of the samples were mostly eliminated as shown in figure 4.6. The OH groups (adsorbed moisture) on the surface observed in the raw material were disappeared in the case of activated coffee husk. This could happen due to the evaporation of the water content at the time of physical activation, where the space that was occupied by the free and bonded water molecules becomes empty so that the sorbent adsorption capacity increases (Series & Science, 2018). The peak at around 2920 cm^{-1} was assigned to the presence of C-H stretching. Bands due to the presence of silane (Si – H) groups can be observed in the range of 2100 – 2360 cm^{-1}(Gottipati, 2012). The existence of amine groups is also proved by the peaks observed at 1570 cm^{-1}.

Therefore, amines, silane, and C-H stretching groups of ACH can be very effective in capturing cations such as Cr(VI), Pb(II), and Zn(II) ions from wastewater (Sheng et al., 2004).

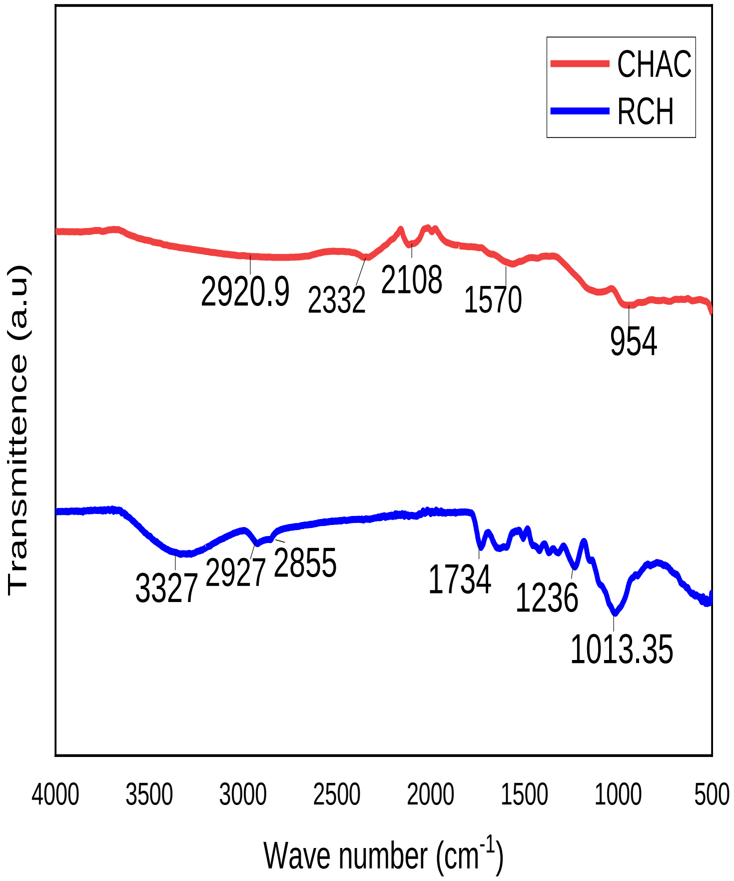

Figure 4.6: FTIR spectra of raw coffee husk and activated coffee husk

4.4. Batch Mode Adsorption Studies

Batch adsorption studies for Cr(VI) ions removal were carried out to study the effect of different parameters such as adsorbent dose, initial metal concentration, contact time, and pH by keeping other parameters constant.

4.4.1. Effect of Solution pH

It's one of the most significant parameters for any adsorption process as it influences the solubility of the metal ions, the ionic form in which it was presented in the solution, and the type and ionic state of the functional groups at the sorbent surface (Lodeiro *et al.,*2005). The effect of pH on the amount of adsorption of the Cr(VI) onto the coffee husk AC was studied by varying the pH in the range 3 to 11 with metal concentration 2 mg/L and shown in figure 4.7. The results in Figure 4.7 illustrated clearly that Cr(VI) adsorption efficiency decreases with an increase in pH. It is reasonable from the figure that the percentage adsorption is higher at acidic pH (3), reaching a maximum of about 98.41%, however, it decreased gradually with the increase of pH up to a certain point. This is evident that the dependence of Cr(VI) adsorption on pH can mainly be related to the type and ionic state of the functional groups present on the surface of the adsorbent. Therefore, the high adsorption efficiency of Cr(VI) at lower pH can be attributed to the availability of Cr(VI) in different forms and the surface groups of the adsorbent (Palmer and Puls, 2004) but at higher pH, there can be the formation of precipitation of metal complexes.

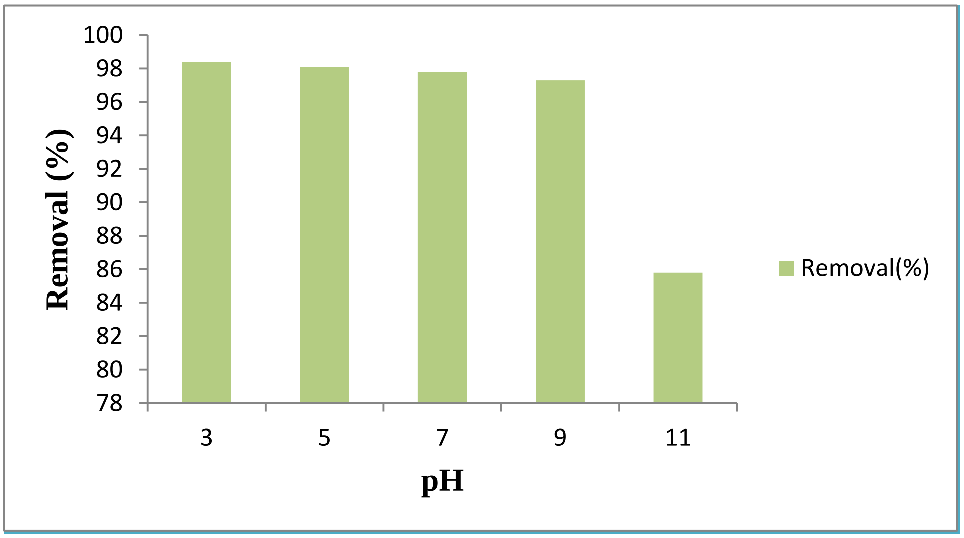

Figure 4.7: Effect of pH on Cr(VI) removal by CH-ACs (at initial chromium concentration = 2 mg/L, adsorbent dose =3.0 g/L, contact time = 2.0 h, and temperature =30 ^{o}C)

4.4.2. Effect of Adsorbent Dose

The effect of the adsorbent dose on Cr(VI) removal by activated coffee husk was studied at room temperature by varying the adsorbent doses from 1 to 5 g/l. To study the effect of adsorbent dose, initial concentration of Cr(VI), pH, agitation speed, and contact time was kept constant. Figure 4.8 shows the removal efficiency of different doses of the activated coffee husk as adsorbent.

The result revealed that the removal efficiency increases from 82.62% to 90% with an increase in adsorbent dose from 1.0 to 2.0g/l. This can be attributed to an increased number of sorption sites available for sorbent solute interaction. With a further increase of adsorbent dose from 2.0 to 5.0 g/l, the percent adsorption increases less significantly compared with the initial stage. From this result, it can be ascribed to the fact that a number of the adsorption sites stay unsaturated after the coffee husk activated carbon and the metal ion were together and it is rational that with a higher dosage of adsorbent, there would be a greater number of exchangeable sites for metal ions (Berhe, Ayele, Tadesse, & Mulu, 2015a). Maximum Cr (VI) removal was found at 5 g/l dose and pH 3 and therefore adopted this dose and pH for the rest of the studies; however, it needs optimization because as a large number of adsorbents are consumed for removal the cost of adsorbent is a big matter.

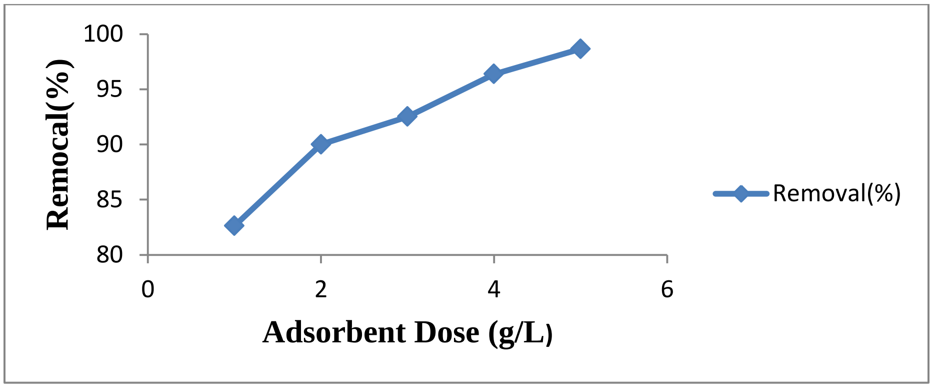

Figure 4.8: Effect of adsorbent dose on the Cr (VI) adsorption efficiency (at Co = 2ppm, pH = 3, agitation speed = 150 rpm and contact time = 2 hr)

4.4.3. Effect Initial Concentration

Outcomes of the study on the effect of initial Cr (VI) concentration on the removal efficiency of the activated coffee husk are shown in figure 4.9. The obtained result indicated that the removal efficiency of activated coffee husk increased initially and then decreased from 97.96 % at 4 mg/L to 94.81% at 10 mg/L of Cr (VI). This is maybe due to that, at lesser concentrations; the number of chromium ions is small relative to the available adsorption sites on the adsorbent. However, at higher concentrations, most of the adsorption sites will be occupied by chromium ions and the available sites of adsorption become fewer, hence the percentage removal of chromium ion which depends on the initial concentration decreases.

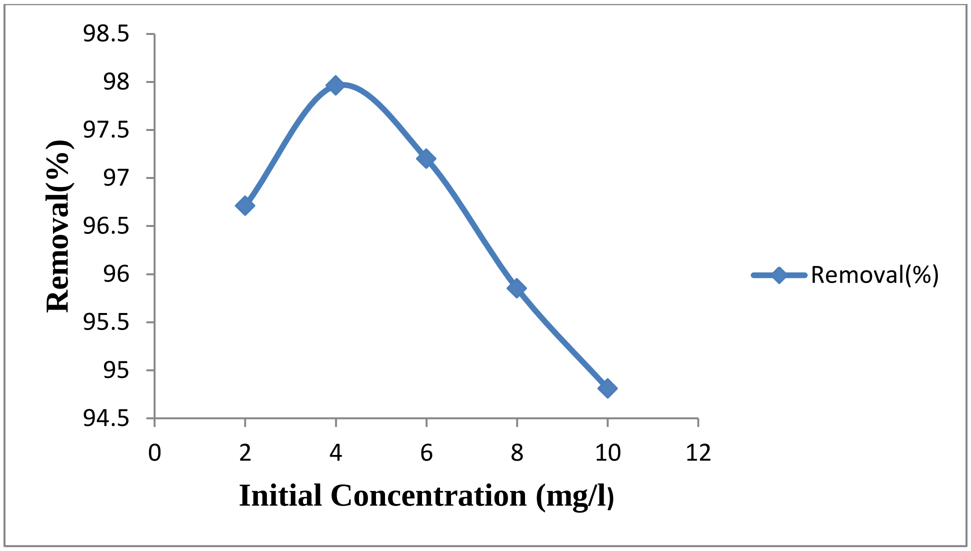

Figure 4.9: Effect of Initial concentration on chromium (VI) removal by CH-AC(at pH=3, adsorbent dose = 5.0 g/L, contact time =2 h, and temperature = 30 ^{o}C)

4.4.4. Effect of Contact Time

The effect of contact time on the Cr(VI) adsorption efficiency of activated coffee husk was shown in figure 4.10. The results indicated that the percentage removal of Cr(VI) has rapidly increased while increasing the time in the first stage. However, the second stage represented slower progressive adsorption.

The rapid initial adsorption may be attributed due to the increase of the available biosorption surfaces and sites (Hossain, 2013). From the result, it is evident that the process in the second stage became slower with the progressive occupation of these sites. With the gradual occupation of these sites, the process in the second stage became slower and this has happened after 90 min. This is following the observations of another similar study by (Qaiser, 2009) and others.

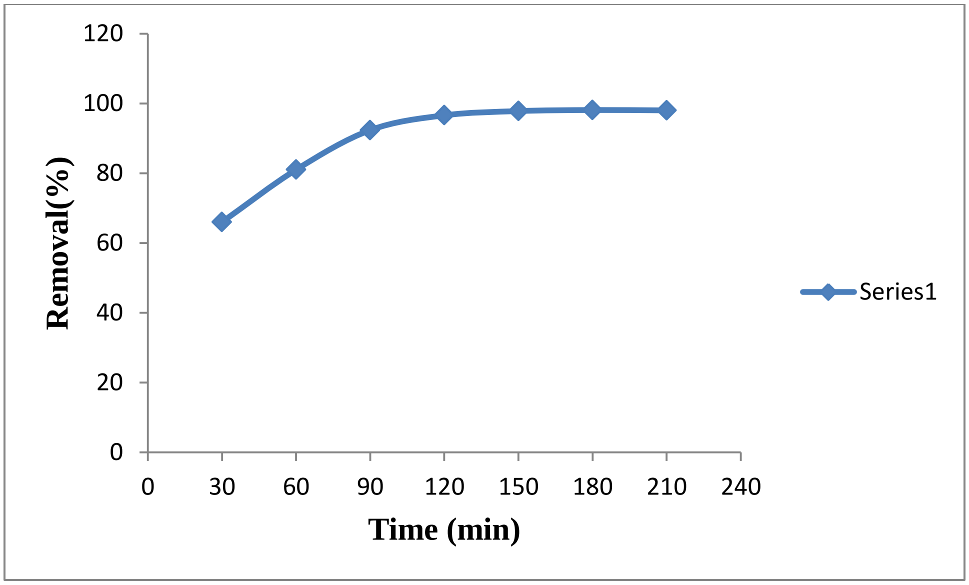

Figure 4.10: Effect of contact time on Cr(VI) adsorption by CH-AC (at pH=3, adsorbent dose =5.0 g/L, Cr(VI) concentration =4.0 mg/L, and temperature =30 ^{o}C)

4.9. Competitive Adsorption of Cr (VI) and Pb(II) Ions in Binary Metal Solution

The competition features of Cr (VI) and Pb(II) ions for the active site in binary metal solution were studied, and the results are shown in figure 4.11. The adsorption tests were performed by varying the concentration of Cr(VI) from 2-10mg/l with fixed concentration (2mg/l) of Pb(II), to evaluate the joint effects of the coexisting Cr(VI) and Pb(II) ions on their respective adsorption on the coffee husk AC, and the result was compared with chromium removal efficiency as a single component.

From the results, we can observe that the removal efficiency of chromium in a binary solution was lower than the removal efficiency of chromium as a single component. The Cr(VI) adsorption on coffee husk AC was genuinely prevented when they coexisted with Pb(II). The adsorption efficiency of Cr(VI) by coffee husk AC in the binary-metals system at different initial concentrations were all lower than those in the single-metal system and the gap in adsorption efficiency between them was decreasing with the initial concentration of Pb(II) increasing.

Specifically, adsorption efficiency for Cr(VI) in the single-metal system at the initial metal concentration of 2mg/L was 96.71%, while it dropped to 90.34% in the binary-metals system. This difference suggested that at a lower initial concentration of Cr(VI) more Pb(II) ions were adsorbed than at a higher concentration of Cr(VI). Hence, in a binary-metals system with a low concentration of heavy metals, the available adsorption sites on coffee husk AC were occupied by Pb(II) preferentially, resulting in the fact that Cr(VI) adsorption was inhibited, but the uptake of Pb(II) almost decreased as Cr(VI) initial concentration increases.

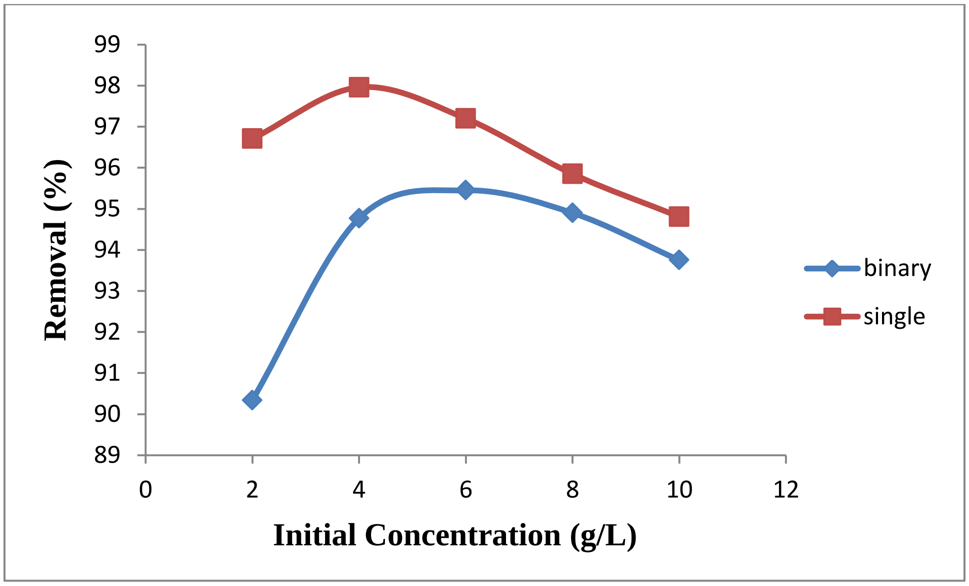

Figure 4.11: Competion effect on chromium(VI) removal by CH-AC **(**at pH = 3, adsorbent dose = 5.0 g/L, contact time - 2h, and temperature 30 ^{o}C, Pb(ii) initial concentration = 2mg/l)

4.5. Study of Adsorption Isotherm

To compare the adsorption capacity of different bio-sorbents under different operating conditions, modeling of the equilibrium data is very important. Besides, adsorption isotherm is required for the design of adsorption systems and provides information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions such as initial pH of the metal solution, initial metal ion concentrations, and amount of bio-sorbent. There are many equilibrium models in use but the most common models are Langmuir and Freundlich models. In this study evaluation of equilibrium of the adsorption process was carried out by introducing the experimental results into Langmuir and Freundlich isotherm models.

4.5.1. Langmuir Isotherm

In this isotherm model, it assumed that the maximum adsorption capacity corresponds to a saturated monolayer of adsorbate molecules into the adsorbent surface. The equation of the Langmuir isotherm model can be expressed in the following non-linear form (equation 4.1).

$$q_e = \frac{q_m\, b\, C_e}{1 + b\, C_e} \tag{4.1}$$

The above equation can be written in the linear form as follows;

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} Ce \tag{4.2}$$

Where,

q_e = Milligram of adsorbate/gram of adsorbent @ equilibrium,

q_m = Maximum adsorption capacity (mg/g)

C_e = Equilibrium concentration (mg/L)

b = Langmuir Isotherm constant (L/mg)

For the Langmuir isotherm, the linearized graph of C_e/q_e was plotted against C_e to obtain a straight line with a slope of $1/q_m$ and a y-intercept of $1/bq_m$. Figure 4.12 presents the linearized Langmuir isotherm for the adsorption of Cr(VI) on the coffee husk-activated carbon at room temperature. The plot of C_e/q_e versus C_e is linear and it could be seen that the adsorption of Cr(VI) on coffee husk activated carbon was well fitted reasonably to the Langmuir isotherm model by comparing the regression coefficients (R^2 : 0.98 and 0.96) obtained from two sorption models. Langmuir equation is reasonably applicable in all of the cases with correlation coefficients (R^2) in the range of 0.94-0.99 (Zakaria, Jamalluddin, Zailani, & Bakar, 2021b).

From the plotted graph, the constants were calculated from the slope $1/q_m$ and intercept $1/bq_m$, and the Langmuir constants obtained are summarized in Table 8. The maximum adsorption capacity by activated coffee husk was obtained as 7.4 mg/g. This means, one gram of the activated coffee husk can absorb 7.4 mg of Cr(VI).

The other important characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant, separation factor (R_L), which is represented as,

$$R_L = 1/(1 + bC_o)$$

The determination of the value of R_L is important to verify if the adsorption in the system is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). It could be seen from (Table 20) that the value of R_L (0.149) is between 0 and 1 indicating the adsorbents prepared are favorable for adsorption of the metal ions under conditions used in the study.

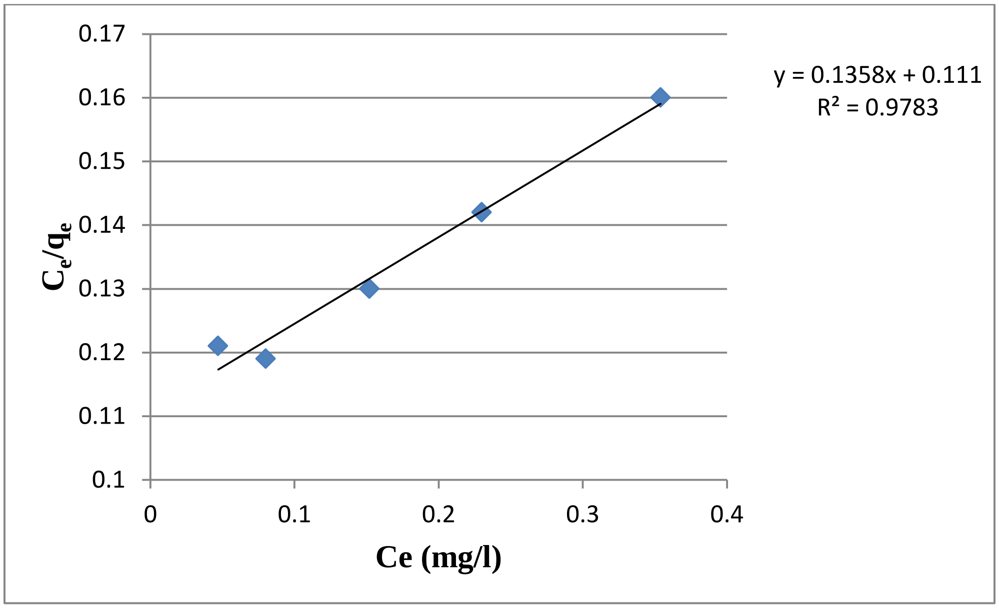

Figure 4.12: Plot of Langmuir Isotherm for Cr(VI) adsorption onto CH-AC (at volume of solution = 100mL, Cr(VI), pH=3, adsorbent dose = 0.5g, contact time = 3h at room temperature).

4.5.2. Freundlich Isotherm

Freundlich isotherm assumes that the multilayer adsorption occurs on heterogeneous surfaces at sites with different energy of adsorption and with non-identical adsorption sites that are not always available (Zakaria et al., 2021b). The Freundlich isotherm is given by Equations

$$q_e = K_f + {C_e}^{1/n} \tag{4.3}$$

This is linearized as,

$$\log q_e = logk_f + \frac{1}{n} logC_e \tag{4.4}$$

Where: q_e = Amount of adsorbate adsorbed at equilibrium, (mg/g)

C_e = Equilibrium concentration of adsorbate, (mg/L)

K_F = Freundlich constant, (mg/g) $(L/mg)^{1/n}$

n = Freundlich heterogeneity factor

To determine the values of n (heterogeneity factor) and K_f (Freundlich constant), the graph of log q_e was plotted against logC_e. The values of K_f and n were calculated from the intercept and slope of the graph as shown in Figure 4.13. The adsorption of Cr(VI) on coffee husk-activated carbon demonstrated a correlation coefficient (R^2) of 0.9677. The slope and y-interception were determined to be 0.773 and 0.904 respectively.

The value of 1/n is a measure of surface heterogeneity or adsorption intensity if it ranges between 0 and 1, but it becomes more heterogeneous as its value gets closer to zero (Haghseresht, 2006). If the value of the slope (1/n) is lower than 0, it should be noted that the system is believed to be operated under a normal Langmuir. If the value of the slope (1/n) is higher than 1.0, the system is supposed to be cooperative adsorption.

As observed from Figure 14 the values of 1/n obtained from Freundlich's equation was 0.773, which implies that the adsorption of Cr(VI) on coffee husk-activated carbon was somewhat heterogeneous. Based on the slope and y-interception obtained from the Freundlich plot, the values of n and K_f were 1.294 and 8.01 L/mg, respectively (Table 8).

The heterogeneity factor (n) could be used to indicate whether the adsorption process is linear (n=1), a chemical process ($n < 1$), or a physical process ($n > 1$)(Gottipati, 2012). Since the value of n determined from the slope was 1.294 ($n > 1$), the adsorption of Cr(VI) on coffee husk-activated carbon is thought to be a physical process under the coffee husk-activated carbon-system.

Overall, the correlation coefficient (R^2) for Langmuir and Freundlich isotherms were 0.98 and 0.967, respectively. Greater R^2 value indicated that the adsorption of Cr(VI) on the coffee husk activated carbon fitted-well to the Langmuir isotherm, to imply that significant monolayer adsorption of Cr(VI) was taken place on the surface of the prepared activated carbon.

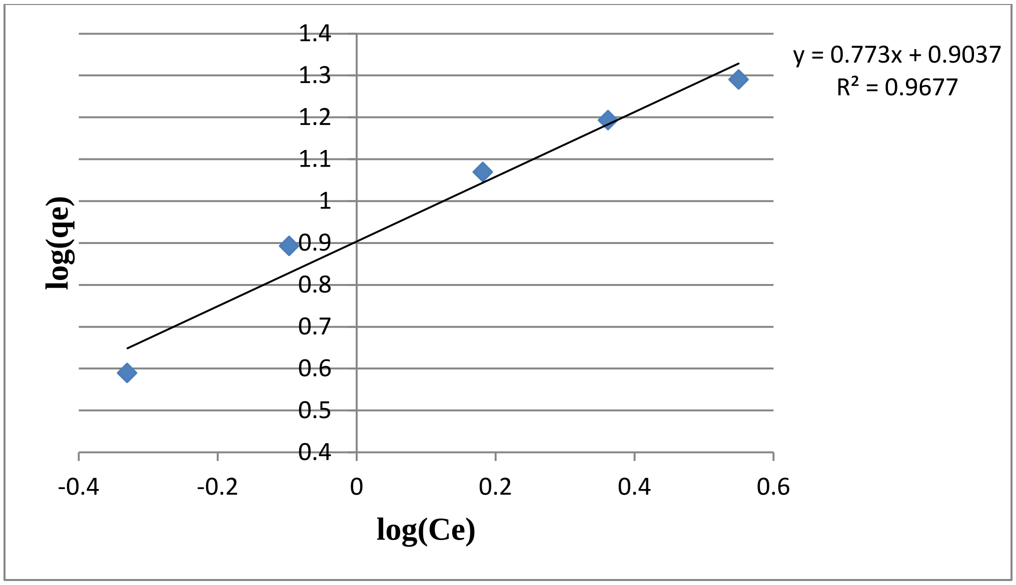

Figure 4.13: Freundlich isotherms for the Cr(VI) adsorption of on coffee husk activated carbon (at volume of solution = 100mL, Cr(VI) concentration= 4mg/L, pH=3, amount of coffee husk activated carbon = 0.5g, contact time = 3h at temperature of 30^{o}C).

Table 6: Langmuir and Freundlich isotherm constants for the Cr(VI) adsorption on prepared activated carbon

Adsorption isotherms	Parameters	Values
Langmuir isotherm	q_m	7.4
	b	1.22
	R^2	0.98
Freundlich isotherm	K_f	8.01
	n	1.294
	R^2	0.967

4.6. Comparison of Adsorption Capacity with Other Low-Cost Adsorbents

The adsorption capacity of Cr(VI) onto coffee husk-activated carbon was compared with other low-cost adsorbents reported in the literature and is shown in Table 9. It can be observed that the activated carbon produced from coffee husk compares well with the activated carbons from most of the raw materials listed and the coffee husk activated carbon can be considered to be a feasible adsorbent for the removal of Cr(VI).

Table 7: Cr (VI) adsorption capacity of previously reported low cost activated carbons

Adsorbent	Maximum q_m(mg/g)	Reference
Coffee husk activated carbon	7.4	Current study
Trapa natans husk	11.83	Liu et al. (2010)
Pre-boiled sunflower stem	5.37	Jain et al. (2009)
Sawdust	2.2899	Hamadi et al. (2001)
Coconut tree sawdust	3.46	Selvi et al. (2001)
Modified peanut husk	29.14	Li et al., 2007
Na-montmorillonite	9.6	Abollino,2003
Fly ash	17.2	Alinoor., 2007

4.7. Adsorption Kinetics

Pseudo-first-order and pseudo-second-order were used to analyze batch adsorption data, in order to examine the adsorption mechanism, and calculate kinetic parameters, because of their good representation of the experimental data (Inbaraj et al., 2002). The best fit models among the two models were selected based on the linear regression correlation coefficient (R^2).

4.7.1. Pseudo First-Order

The adsorption based on the sorption capacity of solids is mainly expressed by a pseudo-first-order kinetic model (Lagergren, 1898) which assumes that one metal ion is sorbed onto one sorption site. The pseudo-first-order equation is generally expressed as follows:

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \tag{4.5}$$

After definite integration within the conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t, the integrated form becomes,

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{4.6}$$

Where, q_e and q_t (mg/g) are the amount of Cr (VI) that was adsorbed at the equilibrium and at time t (min), respectively, and k_1 is the pseudo-first-order rate constant of adsorption (min^{-1}). The values of $\log(q_e - q_t)$ were linearly correlated with t. The Pseudo-first order rate constants, K_1, and q_e were determined from the slope and intercept of the plot of Log(qe-qt) versus t as presented in figures 4.14. The results of the q_e and K_1 were evaluated and listed in Table 10. A significantly lower correlation coefficient (R^2) obtained suggests that the adsorption of Cr(VI) on prepared activated carbon does not follow the pseudo-first-order kinetics. Besides the inconsistency between q_e experimental and calculated, indicating its unsuitability in explaining adsorption mechanism here. This suggested a poor fit between the kinetics data and the pseudo-first-order model.

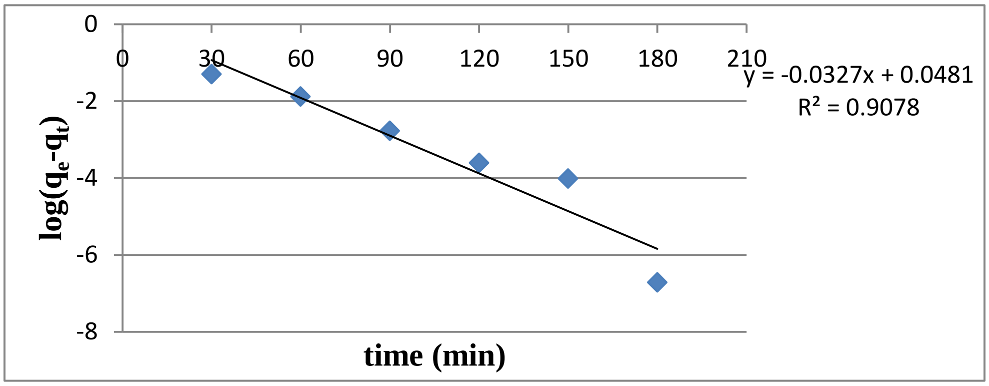

Figure 4.14: Pseudo first order plots for adsorption of Cr(VI) on onto coffee husk activated carbon (at conditions of: volume of solution = 100mL, initial Cr(VI) concentration= 4mg/L, pH=3, amount of coffee husk activated carbon = 0.5g, contact time =3h at room temperature).

4.7.2. Pseudo-Second-Order Kinetic Model

The pseudo-second-order kinetic model also describe adsorption kinetics (Gottipati, 2012). It assumes that the rate-limiting step of adsorption may be chemical sorption which involves sharing or exchange of electrons between the bio-sorbents, and heavy metal ions thus offering the best consistent data for the heavy metal ions (Hossain, 2013). The linear integral form of this model can be represented as;

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e} t \qquad (4.7)$$

Where, q_t and q_e (mg/g) are the amounts of Cr (VI) adsorbed at time t (min), and at the equilibrium respectively. k_2 is the rate constant of the pseudo-second-order (g/mg min). The equilibrium adsorption capacity (q_e) and the pseudo-second-order rate constants (k_2), h ($k_2q_e^2$), were determined from the slope and intercept of the plot t/q_t versus t and given in table 10. Figure 4.15 shows the graph of the linearized form of the pseudo-second-order of Cr(VI) adsorption on activated coffee husk.

The conformity between experimental data obtained and the model predicted values were decided according to correlation coefficients (R^2) (Özsin, Kılıç, Apaydın, Ayşe, & Pütün, 2019). Based on the result presented, the pseudo-second-order kinetic model fitted very well with the dynamic behavior adsorption of Cr(VI) ions on the coffee husk AC with higher regression coefficients (R^2 >0.99). The regression (R^2) values obtained are very close to unity and the adequate fitting of the plots confirmed that the adsorption of Cr(VI) by the prepared AC followed the pseudo-second-order kinetics. This means that pseudo second order equation can more precisely predict the rate of adsorption process (Zaidi, Khan, Azam, & Farooqi, 2021). This states that the rate-limiting step on the transportation of metal ions to the solid surface may be chemical sorption rather than diffusion (Abbas et al. 2014; Semerjian 2018).

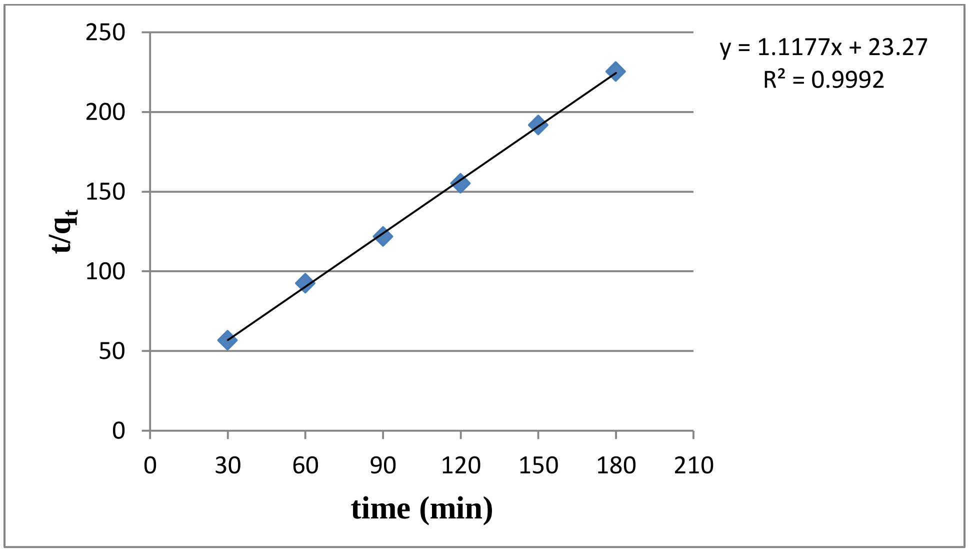

Figure 4.15: Pseudo second order plots for adsorption of Cr(VI) on onto coffee husk activated carbon (at conditions of: volume of solution = 100mL, initial Cr(VI) concentration= 4mg/L, pH=3, amount of coffee husk activated carbon = 0.5g, contact time =3h at room temperature).

Table 8: Adsorption kinetic rate constants for Cr(VI) on coffee husk ACs

Kinetic models	Parameters	Values
Pseudo first order	k_1(1/min)	7.5 x10^{-2}
	q_e(mg/g)	1.12
	R_l	0.149
	R^2	0.98
Pseudo second order	K_2 (1/min)	5.4 x 10^{-2}
	q_e (mg/g)	0.895
	h(mg/g min)	0.043
	R^2	0.999

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Coffee husk, which is considered as waste at the coffee processing unit showed a potential precursor for the preparation of activated carbon. The effect of H_3PO_4 concentration and carbonization temperature on yield and MBN of coffee husk AC were investigated and showed significant effects. The maximum yield (73%) was attained at 30% impregnation and 400 ^oC, while the maximum MBN (52.58mg/g) of AC was attained at 30% impregnation and 600 ^oC temperature.

FT-IR and XRD techniques were used for the characterization of activated carbon prepared from the coffee husk. The result from the FTIR analysis showed that the CHAC has functional groups groups which are accountable for higher adsorption of Cr(VI) from aqueous solution. The result of the XRD analysis also showed that the CHAC has an amorphous structure of carbons, which is an advantageous property for well-defined porous adsorbents.

The adsorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time, and adsorbent dosages. The adsorption of Cr(VI) on chemically produced AC by H_3PO_4 is found to be affected by pH, adsorbent dose, initial metal concentration, and contact time. Adsorption of Cr(VI) on prepared AC increased with decreasing pH from 11.0 to 3, while the percentage of Cr(VI) removed increased with increase in adsorbent dosage due to increased adsorption surface area and an increasing contact times also increases the percentage removal of Cr(VI). Increasing initial metal concentration increases the removal efficiency of Cr(VI), however, further increasing of initial metal concentration results in decreasing of Cr(VI) adsorption. The competition effect was also investigated, and the result showed that the removal efficiency of Cr(VI) from binary solution was decreased from 98.1% to 94.77% at optimum conditions.

Comparison of the equilibrium models shows that the Langmuir model fits with the experimental data better than the Freundlich isotherm, which indicates monolayer adsorption. The kinetic data correlated (R^2 =0.99) well with the pseudo-second-order kinetic model for the sorption studies of Cr(VI) which implies that adsorption follows second order kinetics.

5.2. Recommendation

The result of the CHAC adsorbent indicates that the adsorbent has capable of removing Cr(VI) ions from an aqueous solution. Therefore, from the knowledge gained during the course of this work, the following recommendations are made in the production and application of activated carbon from coffee husk for the removal of Cr(VI) from wastewater as a result of the outcome of the study.

- Comparative study of coffee husk activated carbon with commercial activated carbons in terms of both adsorption capacity and cost is important.
- To investigate the economic aspects, and to approve the applicability of this adsorbent under real conditions, such as the industrial effluent treatment, more studies are required to optimize the process from the regeneration point of view.
- The current study only evaluates the removal efficiency of the coffee husk-activated carbon under batch adsorption experiments and this can be compared with continuous column experiments.
- The performance of removal of heavy metals along with organic pollutants can be evaluated by using the developed adsorbent.
- Further research is needed to evaluate economic feasibilities on the preparation of activated carbon and utilization in the wastewater treatment system and to investigate the recovery of activating agents for further use.
- A pilot-scale column with the developed adsorbent can be conducted for real wastewater.
- Activation and adsorption parameters should require optimization in order to evaluate the feasibility of the process.

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Appendices

Appendix I: Preparation of Coffee Husk Activated Carbon (CH-AC)

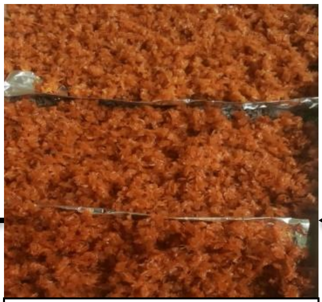
Raw coffee husk (after washing)

Size reduction

Separation by sieves

Size distribution

(500µm-1mm)



Impregnation with 10, 30 and 50 % H_3PO_4

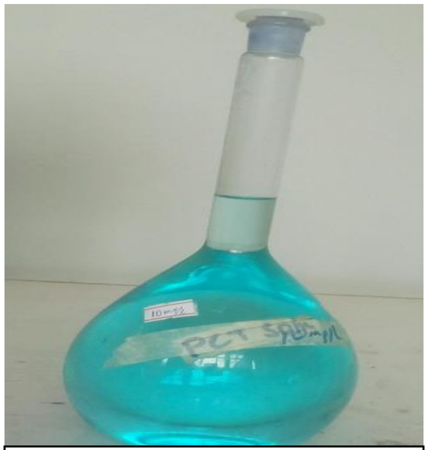
After drying at 110 ^{O}C for 2 hrs

Activation in muffle furnace at 600 ^{O}C for 2 hrs

Coffee husk activated carbon ready for use

Appendix II: **Preparation of methylene blue dye for characterization of CH-AC**

To prepare 10 mg/l of methylene blue dye, 10 mg of methylene blue dye was weighed and added into 1000 ml of distilled water. Then 10 mg of coffee husk activated carbon was added to 100 ml of dye solution of 10 ppm in the 250 ml menyer flask. Finally the solutions were filtered and the filtrate was analyzed by spectrophotometry to determine the final concentration of the dye left after adsorption.



10 mg/l of methylene blue

Methylene blue dye after adsorption

Table 9: Experimental result of CH-AC yield and methylene blue number

	Factor 1	Factor 2	Response 1	Response 2
Run	A: Impregnation (%)	B:Temperature (^{o}C)	Yield (%)	MBN (mg/g)
1	30	600	28	52.58
2	50	400	60	44.28
3	10	600	27	48.82
4	30	400	73	24.28
5	10	500	47	21.34
6	50	600	17	43.52
7	50	500	46	32.63
8	10	400	59	15.19
9	30	500	48	42.20

Appendix III: Calculations of Potassium Dichromate and Lead nitrate Requirement

To Prepare 1000 mg/L of Cr(VI) and Pb(II) stock solutions, we have to calculate the amounts of $K_2Cr_2O_7$ and Pb(NO3)2 required to get concentration of Cr(VI) and Pb(II) stock solution of 1000mg/L [1 g in1 L solution] respectively.

Potassium dichromate ($K_2Cr_2O_7$) has molecular weight= 2*39 + 2*52 + 7*16 =78+ 104 + 112= 294 g/mol. From this, 104 g Cr (VI) is available in 294 g of $K_2Cr_2O_7$. But what amount of $K_2Cr_2O_7$ is required to get 1g Cr(VI)? So, from the above, 1 g of Cr(VI) is available in $K_2Cr_2O_7$ is (294/104)*1 = 2.8269 g of $K_2Cr_2O_7$.

Similarly, lead nitrate $Pb(NO_3)_2$ has molecular weight= 207.2 + 2*14 + 6*16 =207.2+ 28 + 96 = 331.2g/mol. From this, 207.2 g Pb(II) is available in 331.2g of Pb(NO3)2. But what amount of $Pb(NO_3)_2$ is required to get 1g of Pb(II)? 1 g Pb(II) is available in= (331.2/207.2)*1 = 1.6 g of $Pb(NO_3)_2$.

Appendix IV: Dilution of Cr (VI) and Pb(II) Stock Solution from 1000 mg/l

Initial concentration of prepared stock solution of Cr(VI) and Pb(II), were (C_1=1000mg/l) and diluted to the required working concentrations by using the following eqn.

$$C_1V_1 = C_2V_2$$

Where, C_1 and C_2 were initial and final concatenations of Cr(VI) or Pb(II) respectively, V_1 and V_2 were volumes of stock solutions of Cr(VI) or Pb(II). V_1 was calculated depending on required diluted concentration of Cr(VI) or Pb(II), by making V_2 constant. In this study (C_1 = 1000mg/l), (C_2 = 2, 4, 6, 8 and 10 mg/l), and (V_2 = 1000ml). Accordingly V_1 was calculated for each required concentrations in presented in table below.

Table 10: Dilution of Cr (VI) and Pb(II) stock solution

S/N	C_2(mg/l)	C_1(mg/l)	V2(ml)	V_1(ml)(calculated)	Volume of distilled water (ml)
1	2	1000	1000	2	998
2	4	1000	1000	4	996
3	6	1000	1000	6	994
4	8	1000	1000	8	992
5	10	1000	1000	10	990

Appendix V: Standard Solutions of Cr(VI) and their respective absorbance

Table 11: Standard solutions of Cr(VI) and its respective absorbance

S/N	Standard Solutions ppm	Absorbance
1	0.1	0.044
2	0.2	0.088
3	0.4	0.176
4	0.6	0.264
5	0.8	0.352

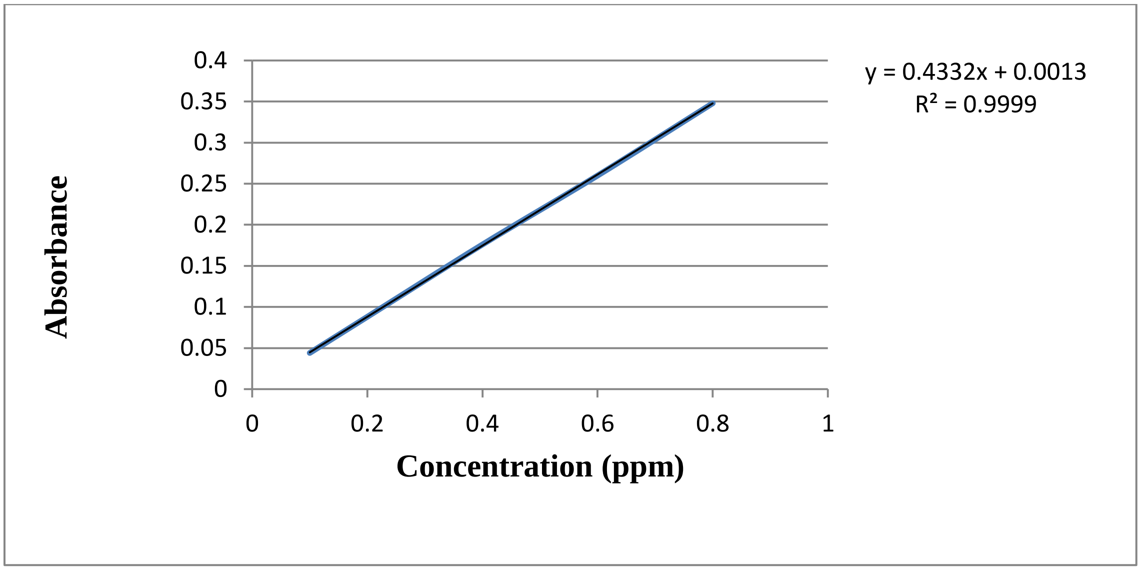


Figure 5.1: Calibration curve for Cr(VI)

Appendix VI: Stock solutions of Cr (VI) and Pb(II) prepared from $K_2Cr_2O_7$ and Pb(NO3)2 and 1,2-Diphenylcarbazide

$K_2Cr_2O_7$ and $Pb(NO_3)_2$

Cr (VI) and Pb(II), 1000ppm

1,5-Diphenylcarbazide

Cr (VI), 1,5-Diphenylcarbazide complex after adsorption

Appendix VII: Results of Batch Adsorption Experiments

Table 12: Effect of pH on the removal of Cr(VI) on coffee husk activated carbon (at constant adsorbent dose = 5g/l, Initial conc. = 2mg/l contact time = 120 min and temperature of 30^oC).

S/N	Factor/s		Response/s	
	Initial conc. (mg/l)	pH	Final concentration(mg/l)	Removal efficiency (%)
1	2	3	0.0318	98.41
2	2	5	0.038	98.1
3	2	7	0.044	97.8
4	2	9	0.054	97.3
5	2	11	0.284	85.8

Table 13: Effect of adsorbent dose on the removal of Cr(VI) on coffee husk activated carbon (at constant pH = 3, Initial conc. = 2 mg/l, contact time = 120 min and temperature of 30^oC).

S/N	Factor/s		Response/s	
	Dose g/l	Initial conc. (mg/l)	Final concentration(mg/l)	Removal efficiency (%)
1	1	2	0.3476	82.62
2	2	2	0.2	90
3	3	2	0.15	92.5
4	4	2	0.0726	96.37
5	5	2	0.0272	98.64

Table 14: Effect of initial concentration on the removal of Cr(VI) on coffee husk activated carbon (at constant pH = 3, adsorbent dose = 5g/l, contact time = 120 min and temp of 30^oC).

S/N	Factor/s		Response/s	
	Dose g/l	Initial conc. (mg/l)	Final concentration(mg/l)	Removal efficiency (%)
1	5	2	0.0658	96.71
2	5	4	0.0816	97.96
3	5	6	0.168	97.2
4	5	8	0.332	95.85

5	5	10	0.519	94.81

Table 15: Effect of competition on the removal of Cr(VI) on coffee husk activated carbon(at the presence of lead concentration(2mg/l) and constant pH = 3, adsorbent dose = 5g/l, contact time = 120 min and temperature of 30^{o}C).

S/N	Factor/s			Response/s	
	Dose (g/l)	Pb(ii) initial conc. (mg/l)	Cr(VI) initial conc. (mg/l)	Final concentration(mg/l)	Removal efficiency (%)
1	5	2	2	0.1932	90.34
2	5	2	4	0.2092	94.77
3	5	2	6	0.273	95.45
4	5	2	8	0.404	94.9
5	5	2	10	0.625	93.75

Table 16: Effect of contact times on the removal of Cr(VI) on coffee husk activated carbon(at constant pH = 3, initial concentration = 4mg/l, adsorbent dose = 5g/l, contact time = 120 min and temperature of 30^{o}C).

S/N	Factor/s			Response/s	
	Time (min)	Initial conc. (mg/l)	Final concentration (mg/l)	Removal efficiency (%)	Removal capacity (q_t)(mg/g)
1	30	4	1.36	66	0.528
2	60	4	0.76	81	0.648
3	90	4	0.3064	92.34	0.738
4	120	4	0.1368	96.58	0.773
5	150	4	0.088	97.8	0.782
6	180	4	0.076	98.1	0.7848
7	210	4	0.08	98.0	0.784

Appendix VIII: Results of Adsorption Isotherms

Table 17: Results for Cr(VI) adsorption isotherms

S/N	Factor/s		Response/s				
	Initial conc. (mg/l)	Final concentration(mg/l)	Removal efficiency (%)	q_e	Ce/qe	Log(Ce)	Log(qe)
1	2	0.047	97.65	0.388	0.121	-0.33	0.589
2	4	0.08	98.0	0.781	0.102	-0.097	0.893
3	6	0.152	97.47	1.172	0.13	0.182	1.069
4	8	0.23	97.13	1.56	0.147	0.362	1.193
5	10	0.354	96.46	1.953	0.181	0.55	1.29

Table 18: R_L values for Cr(VI) adsorption at different concentration

S/N	Initial concentration C_o(mg/l)	b (constant)	R_L=1/1+bC_o
1	2	1.22	0.29
2	4	1.22	0.17
3	6	1.22	0.12
4	8	1.22	0.093
5	10	1.22	0.075
Average			**0.1496**

Appendix IX: Results of Adsorption Kinetics

Table 19: Results for Cr(VI) adsorption kinetics

S/N	Factor/s			Response/s			
	Time (min)	Initial conc. (mg/l)	Final concentration Ce(mg/l)	Removal efficiency (%)	Removal capacity (q_t)(mg/g)	ln(qe-qt)	t/q
1	30	4	1.36	66	0.528	-1.302	56.82
2	60	4	0.76	81	0.648	-1.884	92.59
3	90	4	0.3064	92.34	0.738	-2.78	121.95
4	120	4	0.1368	96.58	0.773	-3.612	155.239

5	150	4	0.088	97.8	0.782	-4.02	191.82
6	180	4	0.076	98.1	0.7848	-6.73	225.34