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REMOVAL OF LEAD FROM WASTE WATER USING CORN COB ACTIVATED CARBON AS AN ADSORBENT

BY

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Declaration

I, the undersigned, declare that this thesis entitled “Removal of Lead from Wastewater Using Corn Cob Activated Carbon as an Adsorbent” 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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ACRONYMS

CCAC	Corn cobs activated carbon
IN	Iodine number
FTIR	Fourier Transform Infrared spectrometry
MC	Moisture content
AC	Ash content
VC	Volatile content
UNWWDR	United nations world water development report
DOF	Design of Experiment
WHO	world health organization
ANOVA	Analysis of variance
EPA	Environmental Protection Agency
IR	Impregnation ratio
BET	Branauer, Emmett, and Teller
ASTM	American Society for Testing and Materials
GTP	Growth and Transformation Plan
MoFED	Ministry of Finance and Economic Development
GDP	Gross Domestic Product
CRGE	Climate Resilient Green Economy
ADLI	Agricultural Development Led Industrializations

ABSTRACT

Industrial development has caused the release of various pollutants including heavy metals into the environment. These toxic compounds are extremely dangerous to living beings and the environment due to their non-biodegradability, severe toxicity, carcinogenicity, the ability to be accumulated in nature and the ability to contaminate groundwater and surface water. The aim of the present research was to provide an appropriate and cost-effective adsorbent to remove one of these heavy metals namely lead from waste water. The activated carbon was produced from the dried corn cob. Batch experiments were performed on synthetic samples at room temperature. The effect of pH, adsorbent dose, initial concentration, and contact time were studied, and the adsorption isotherms of heavy metals were determined.

The optimum conditions for corn cobs activated carbon preparation were determined as impregnation ratio of 1.5, carbonization temperature of 450^{o}C, activation time of 120min, and acid concentration 60% by weigh. The result of the characterization showed that the corn cob activated carbon has good properties as compared with other reference activated carbons.

The maximum removal efficiency of heavy Pb^{2+}ions by activated carbon adsorbent prepared from corn cobs was obtained optimum pH 5, optimum adsorbent dose of 3g, and the optimum contact time of 120 min; in these optimum conditions the removal efficiency was 96.8%. Greater adsorption amount of 10.7mg/g occurs at smaller adsorbent dose of 1g.

The results were also confirmed that the adsorption process follows Langmuir isotherm model with a better sorption fit and supported for the monolayer adsorption of Pb^{+2}ions on corn cobs activated carbon. The kinetic model of this study shows a pseudo-second order kinetic model with good correlation coefficient. Based on the results obtained, the activated carbon produced from corn cob has a good capability in removal of the lead ions from the aqueous solutions.

Key words: corn cobs activated carbon; adsorption of lead (Pb^{2+}); optimal conditions.

1. INTRODUCTION

Water is a limited natural resource and fundamental for life and health (UNWWDR, 2002). About 97.5% of all water on earth is salt water and the remaining 2.5% is fresh water. Around 70% of fresh water is frozen in the Antarctica and Greenland icecaps. Only 1% of the earth's fresh water is accessible for extraction and human use (Corcoran, 2010). Water is important for life and for processing various materials in industry. Living organisms cannot exist without water, and almost all industries require water to operate. However, in the 21st century the growing population and industrial sector have contributed significantly to a reduction in quality of water and its availability through discharge of untreated wastewater to the environment; thus becoming the concern of many nation across the world (Kapanji, 2009; Sato et al., 2013).

Globally, every day more than two million tons of liquid waste are released from point and nonpoint sources into both subsurface and surface water bodies without treatment (Corcoran, 2010).

For example, in Ethiopia has used 18% of 49 million m^3 of its wastewater generated in volume per annum without treatment for agricultural production and other purposes, while the remaining wastewater is discharged into nearby water bodies such as rivers, springs, streams, and lakes (Corcoran, 2010; GTP-MoFED, 2010; Sato et al., 2013). In Addis Ababa, around 390 hectares of land for vegetable farming is irrigated with the contaminated Akaki river, reported to contain high amounts of toxic heavy metals (Ni, Cd, Cr, Zn, Cu, Mn and Pb), and found in the tissues of vegetables (lettuce, swiss chard, cauliflower, cabbage and kale). This shows that, industrial wastewater needs to be treated before being used for irrigation purposes (Itanna, 2002; and Beyene, 2011). The sustainability of the environment has become a critical global issue (Dişli, 2010) and the protection of fresh water bodies from various contaminants has become a major challenge facing the planet earth (Chaturvedi 2014). Among the major causes of environmental pollution is the discharge of untreated industrial wastewater containing toxic chemicals such as heavy metals (Kulkarni 2014). A direct industrial wastewater discharge into fresh water bodies is a usual practice particularly in less developed countries like Ethiopia, where no stringent environmental regulations have been enacted (Asfaw, 2007; Zinabu, 2011; Belay and Sahile, 2013).

The release of toxic chemicals from industrial wastewater into the environment degrades water quality and is hazardous for human beings, as well as, other living organisms such as aquatic life (Ahluwalia and Goyal, 2007).

The composition of heavy metals from industrial wastewater is a major concern for the environment, based on the rich of copper (Cu), lead (Pb), chromium (Cr), cadmium (Cd), (Zwain et al., 2014). Population growth, an increase in development and the expansion of investment in the industrial sector has led to the rise in demand for industrial products. The expansion and development of various types of industries can result in generating huge volumes of wastewater along with complex toxic chemical compositions which demand advanced technological treatment techniques (Corcoran, 2010; Keng et al., 2013; Zwain et al., 2014). Subsequently, most industries in less developed countries discharge huge volumes of raw wastewater to water bodies, causing environmental and health damage to the local population.

As a result of industrialization and urbanization, the volume of wastewater generated from the Ethiopian industrial sector has increased rapidly. From 1980 to 1990, the toxic load discharged per unit of industrial output increased by 1.8, which was about 1.3 times higher than sub-Saharan African countries such as Swaziland, Seychelles and others (UNIDO, 2001; Sato et al., 2013; Tegegn, 2014). Investment inflow into Ethiopia to establish industries is increasing for example, the contribution to Gross Domestic Product (GDP) from industry is expected to increase to 19.1% at the end of the Growth and Transformation Plan (GTP) 2014/15 from 8.1% in 2004/05 (GTP-MoFED, 2010; FDRE-CRGE, 2011). As a consequence to prevent increasing environmental and health related problem, Ethiopia faces a challenge to effectively treat the industrial wastewater discharge. As with other developing countries, Ethiopia cannot afford to use advanced technologies for the treatment of contaminated water. Accordingly, it is crucial to explore locally available materials for the treatment of industrials wastewater. The adsorption principles are cost-effective, simple to design and operate locally available materials corn cob activated carbon (CCAC) will be investigated for adsorptive removal of Pb^{2+} from synthetic wastewater under batch experiments. The findings of this study will used an input for the exploring and development of low-cost adsorptive removal techniques for the effective treatment of industrial wastewater.

1.1. Statement of the Problem

Agricultural Development Led Industrializations (ADLI) is the basic road map for Ethiopian development (GTP-MoFED, 2010; FDRE-CRGE, 2011). Development of the country is currently based on ADLI. So far, industrial development is beginning to be realized in the leather industry and other agriculturally based processing industries, such as beverages and food, textiles, and the sugar industry. During future implementations of the Growth and Transformation Plan (GTP-MoFED, 2010; FDRE-CRGE, 2011) important strategies will be enacted into promote environmentally sustainable, agriculturally based processing industries. Others industries, such as chemical, textile, cement, pharmacologic and metal industries are also rapidly growing. Continued population growth and rapid industrialization are found to be the cause of wastewater discharge into the environment, affecting the environment, human health and compromising the life of future generations.

In the capital city, Addis Ababa, an estimated annual volume of 49 million m^3 total wastewater is discharged, of which about 4 million m^3 is industrial wastewater, with only 4% of the wastewater being treated and reused (Gupta, 2003; Qadir et al., 2010; Van Rooijen et al., 2010; Krishna, 2011). The techniques are currently being implemented in Ethiopia are conventional treatment methods. However, these conventional treatment processes require large investments making their application unaffordable for developing countries, like Ethiopia (Mandal, 2014).

The liquid waste discharged from industries contains heavy metals toxic to living organisms (Barakat, 2011). Heavy metals of urgent environmental concern are lead, chromium, mercury, cadmium, copper, zinc, and iron. Among these heavy metals, Lead (Pb^{2+}) is hazardous and carcinogenic and discharged from most industries above permissible limited set by Ethiopian environmental protection agency. A number of technologies have been developed over the years to remove toxic heavy metals from waste water.

One of the most commonly used techniques involves the process of adsorption, which is the physical adhesion of chemicals onto the surface of solid. Adsorption as a process, employed due to its low cost and applicability on large scales. Adsorption is commonly being done using activated carbon, which adsorbs dissolved organic substances in the water treatment and although activated carbon has several advantages, such as its effectiveness in removing high concentrations or organic and inorganic compounds. (Agbozu & Emoruwa, 2014)

Unfortunately, like other developing countries, Ethiopia cannot afford to use advanced treatment technologies to deal with toxic industrial wastewater, therefore, it is crucial to explore locally easily available agricultural waste corn cob as an activated carbon for removal of lead ions. Since corn crop is the second most grown cereals for wide variety of applications in Ethiopia and the corn cobs often leaves in the fields has very low economic value. The efforts of using the corn cobs as a biomass fuel has not given very promising results primarily because of the low calorific value of corn cobs. Another alternate route to convert these waste corn cobs to high economic value product can be to convert them into more commonly called as activated carbon for treatment of industrial pollution is promising contribution for developing country like Ethiopia to treat their waste water before discharged into the environment. The use of various precursors such Coffee husk, Bamboo steam and lignite coals for producing activated carbon has been studied in detail by several researchers. However, no sufficient research to investigate these issues particularly in Ethiopia Corncobs activated carbon as potential adsorbent to remove heavy metal lead from wastewater. Therefore, the research is conducted to treat the lead contaminant before discharge into environment using a locally available corn cobs activated carbon (CCAC).

1.2. General Objectives

The main objective of this research is to study the application of corn cob activated carbon as an adsorbent in the removal of Pb^{+2} ions from synthetic waste water.

1.2.1. Specific Objectives

- To find optimal operational conditions such as acid concentration (H_3PO_4), Impregnation ratio, and activation temperature during corn cob activated carbon preparation process.
- To characterize corn cob activated carbon.
- To determine the effect of initial concentration of the adsorbates, pH solutions and adsorbent dose by using a batch adsorption technique.
- To analysis the adsorptive capacity and equilibrium isotherm of corn cobs activated carbon under batch adsorptive experiments.
- To generate statistical models that fit the experimental data through the use of a full factorial design analysis approach.

1.3. Significance of Study

A major challenge of many industries is finding solutions that equate to positive environmental and economic impacts regarding the treatment of their effluents. Solution to this challenge is of uttermost importance to enable improvement of water quality. Since the activated carbons employed in this study are derived from natural sources, they can represent economic and environmental friendly alternatives to conventional adsorbent (commercial activated carbon).

The study can also provide fundamental information in the adsorption of lead metal ions, from aqueous solution. Knowledge of the mathematical models employed in this study could serve as a useful guide for further experimental work, provide predictions of the performance of the adsorption process under different operating conditions and again provide essential information in the design of adsorption treatment system for the treatment of heavy metal bearing effluents.

1.4. Structure of the Thesis

Introduction: This mainly presents the background of the thesis research rational, objectives and the necessity of this project.

Literature Review: This is dedicated to illustrate the relevant literatures and the recent works related to the study and the literature review of studies conducted by other researches, in which this research was referred too.

It consists of background of the theory of the topics involved, providing a background on the uses and applications. The chapter emphasizes the advantages of using adsorption and low cost materials in terms of cost, time, and efficiency and illustrates the applications of using it on wastewater.

Materials and Methodology: The materials used and methodologies adopted for the study is described in this chapter. The study parameters and test methods are given briefly in this chapter and also present the methodology employed to achieve the objectives of the thesis. It discusses the experiments that were conducted. It consists of procedures, methods, equipment, apparatus, and other relevant information that was used for conducting the experiments.

Results and Discussion: presents the results that were obtained during the experimentations. It consists of discussion of the results obtained, and presents favorable and unfavorable scenarios for the best experiment results. The chapter emphasizes on obtaining optimal conditions that lead to the best conditions for the most efficient adsorption, as well as fitting the experimental data with both Freundlich and Langmuir Adsorption Isotherms and kinetics study. The analysis of test results, tables and figures are presented in this chapter and finally the conclusion of study and recommendations are given.

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2. LITERATURE REVIEW

Environmental pollution due to development in modern industrial practice is one of the most significant problems of this century. Of this the contamination of water resources by hazardous pollutants has attracted much serious attention in the last few decades. This is particularly due to their toxic, acute and chronic health effects.

2.1. Waste water

Wastewater is used water generated from homes, public and private institutions, rural areas, urban areas, farms, industries and others point and non-point sources (Majeed et al., 2014).Billions of gallons of liquid waste from agricultural, industrial, domestic and commercial sources are discharged into fresh surface water bodies every day (Renge et al., 2012). Worldwide, between 300 to 400 million tons of liquid, hazardous waste to living organisms are discharged annually into nearby surface water bodies from industries (Palaniappan, 2010; Pizanoet al., 2010; UNEP, 2010). Similarly, approximately two million tons of liquid wastewater are released each day from non-point sources like agricultural areas, and from point sources like industries to surface water bodies across the globe (Corcoran, 2010). The release of untreated wastewater into the environment can lead to the contamination of rivers, streams and other surface water bodies. Industrial wastewater contains harmful suspended and dissolved matter, like heavy metals, and inorganic matters, which when released untreated greatly affects the environment and causes serious health problems to living organisms. According to available evidence, including the World Health Organization, (Shahmohammadi-Kalalagh et al., 2011), heavy metals of urgent environmental concern are lead, chromium, mercury, cadmium, copper, zinc, and iron. The industrialization drive of most developing countries like Ethiopia has attracted foreign investments but has led to heavy pollution of water bodies due to the discharge of untreated industrial waste. This pollution has been of great concern to governments and other stakeholders, and therefore, exploring low-cost and effective treatment techniques is the focus of many researchers and scientists across the globe.

2.2. Heavy metals in the environment

The term “heavy metal” denotes any metallic element that has a relatively high density and is toxic or poisonous even at low concentration. (Agbozu & Emoruwa, 2014) “Heavy metal” is a general collective term, which generally applies to a group of metals and metalloids with an atomic density greater than 4g/cm3 (Kaakani, 2012), However, chemical properties of heavy metal are more important than its density. Examples of heavy metals are lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe), and the platinum group elements.

Most of the heavy metals are classified as hazardous pollutants due to their toxicity. It has been established beyond any doubt that dissolved heavy metals escaping into the environment pose serious health hazard. They accumulate in living tissues throughout the food chain, which has humans at its top (Volesky,1999). Removal of heavy metal ions from wastewater is essential due to their extreme toxicity towards aquatic life and humans. The increasing environmental pressures have led to stricter regulations with regard to metal discharges particularly in developing countries. In a global context, the major problem of surface water pollution is heavy metal discharge from industrial activities (Alfarra et al., 2014; Pawar et al., 2014). The development of industrial sector in the African continents is the primary cause of heavy metals being released into water, air and soil in all countries, including Ethiopia (Table 2.1)

Table 2-1; Pollution of water with heavy metals in African countries

Country	Source	Heavy metal concentration in mg/l							Reference
		Pb	Cd	Hg	Cu	Co	Zn	Cr	
Ethiopia	River	0.069	0.0076	-	-	0.067		0.09	Mersha(2008)
Ghana	River	0.075	0.041	-	-	-	2.45	-	Fianko (20070
Cameron	River	20.3	2.8	-	42.8	-	28.8	94.7	Ekengele(2008)
South Africa	Water	16.3	72	-	42.6	-	27.6		Fatoki(2001)
Nigeria	Water	0.046	0.0044	-	0.0033	0.018	0.14	-	Mombeshora (1998)

Most industries are the point source of heavy metals (Pehlivan, 2008); these industries include electroplating, chemical and petrochemical, metal and mining, leather, textile, ceramic, cement, fertilizer, tanneries, batteries, paper, pesticides and others. These industries release their wastewater containing various harmful heavy metals without treatment into the environment (Fasinu and Orisakwe, 2013). These harmful toxic chemicals include elements such as uranium (Ur), selenium (Se), zinc (Zn), silver (Ag), gold (Au), nickel (Ni), cadmium (Cd), mercury (Hg), copper (Cu), chromium (Cr), arsenic (As), lead (Pb) and others (Ahalya et al., 2003). The presence of these harmful heavy metal elements, even at low concentrations, affects the health of humans and other living organisms (Duruibe et al., 2007). The fact that these elements are highly soluble in water and not easily degradable by soil, makes their presence in water bodies more alarming (Kurniawan et al., 2006b). Therefore, it is important to treat heavy metals discharge from industrial wastewater, with affordable and technically feasible methods.

This initiates the need for exploring cost-effective, simple and efficient removal techniques using locally available materials.

2.2.1.Health Effects of Heavy Metals

Excess levels of heavy metals in the environment are harmful to the health of human beings and other living organisms. The gradual accumulation of toxic chemicals in the body of a living organism can result in bioaccumulation. Bioaccumulation happens when an organism uptakes toxic substance at a higher concentration than its release (Renge et al., 2012).

Therefore, the storage of these chemicals in the body of a living organism is greater than their release may occur gradually. As these elements cannot biodegrade or break down easily, the negative effects are worsened by the ecosystem of the environment (Abas et al., 2013). 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 and Dhote, 2013). According to the study conducted by Biney and Ameyibor (1992) untreated industrial wastewater containing heavy metals (Cd, Cu, Zn, Pb, Hg and Fe) released into fresh water bodies can also be stored in the bodies of aquatic organisms, for example in Pink Shrimp. Therefore, the need to treat wastewater is of great importance in order to safeguard the environment and reduce associated health problems.

According to the World Health Organization (WHO) reports and other studies (Shahmohammadi-Kalalagh et al., 2011), the heavy metals which are of greatest concern with regard to human health are Pb, Cd, Hg, Cr, Cu, Zn and Fe. Most products such as pharmaceutical products and dental products, some drugs, and Unani drugs, cosmetic products like shampoos, lipsticks, hair colors and others contain heavy metals (Bocca et al., 2014).

The metals are transferred from these products and the environment to humans and other living organisms by the food chain or food web and by coming in contact with the skin. In the food chain process, heavy metals are absorbed into the body of the organism through eating food that contains high levels of heavy metals, or by drinking water, inhalation, skin and eye contact and through other sense organs (Yadanaparthi et al., 2009). Small amounts of these elements, beyond allowable limits, have serious effects and are unsuitable for living organisms because of their high energy particle output (Ghiloufi et al., 2014). Due to this, wellbeing of living organisms' is compromised (Ghiloufi et al., 2014; Pawar et al., 2014), and living organisms are easily exposed to different diseases and associated problems such as carcinogens, schizophrenic like behavior, dyspnea, mental disorders, kidney damage, lung fibrosis, liver disease, high blood pressure, headaches, intestinal problems and others (Renge et al., 2012). Therefore, it is important to eliminate heavy metals from contaminated water.

2.3. Wastewater Treatment

Wastewater treatment is the method of purifying wastewater. This operation is highly important due to the fact that some contaminants or pollutants are difficult to manage after release from point source pollution to environments (Handa,1983). A conventional wastewater treatment process is divided into three various stages; primary, secondary and tertiary. These stages depend on the characteristics of wastewater discharge, and the amount of harmfulness, and cost effectiveness. Accessibility of land for construction of treatment plants is main factors in the process

2.3.1. Waste Water Treatment Options for Heavy Metal Removal

Heavy metals are the cause of various disorders and diseases due to that fact that they can be easily stored in the body of living organisms without breaking down. Therefore, it is important to remove heavy metals from polluted water using conventional techniques. There are many conventional methods for the removal of toxic chemicals/heavy metals, including the following; ion exchange processes; membrane filtration; adsorption; electrochemical treatment; photochemical oxidation; zonation and biological processes (CROSTAT, 2012).

These technologies have been widely applied for some time and can be classified into three clusters: physical, chemical and biological treatment techniques (Abas et al., 2013). However, these heavy metal removal technologies have their own disadvantages such as their expensive due to initial and operational costs; are less efficient, carry high costs for disposal; consist of complex processes and require large land areas (Ahmaruzzaman, 2011).

The ion-exchange process, electronic coagulation, irradiation, chemical and biological techniques for the removal of heavy metals. These techniques are not widely used because they are less feasible for small scale industries, as well as having high expenses (Ghiloufi et al., 2014). They also produce a harmful sludge and have been found to be not ecologically-friendly mainly because the technology requires high energy for operation (Abas et al., 2013) In addition, these technologies were reported to be complex to control (Alfarra et al., 2014), and do not completely remove the heavy metals from the contaminated water (Ahalya et al.). In contrast, due to it being inexpensive, environmentally friendly and efficient, the adsorption technique has been chosen as a method of wastewater treatment with a special interest in the removal of heavy metals from contaminant water (Li etal., 2007). The adsorption technique is also found to be simple and easy to operate, effective and efficient in eliminating heavy metals (Tajrishy, 2012; Hua and Li, 2014). Generally, in developed countries toxic heavy elements discharged from different industrial areas along with polluted liquid waste, have been successfully removed by high resolution and costly treatment methods (Abas et al., 2013). However, in developing countries the application of such advanced technologies for wastewater treatment is technically complex and expensive (Yadanaparthi et al., 2009)

2.4. Adsorption Process

Adsorption refers to the attachment of substances from a liquid or gaseous phase to solids. The solid is referred to as the adsorbent. The substance taken up is called the adsorbate. In adsorption there is a fundamental difference between Physisorption and Chemisorption

In Physisorption the attachment of the adsorbate is based on physical forces (Van der Waals forces). In contrast, during chemisorption the adsorbate enters into a chemical bond with the molecules of the adsorbent. Adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutants removal.(Abdualaziz, Hamza, Hammad, & Eltayeb, 2013) When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface. The solute retained (on the solid surface) in adsorption processes is called adsorbate, whereas, the solid on which it is retained is called as an adsorbent. This surface accumulation of adsorbate on adsorbent is called adsorption. The term loading of an adsorbent means the mass of adsorbate that has been adsorbed by one gram of adsorbent. The loading is therefore stated in units of mg/g. As the adsorption progress, an equilibrium of adsorption of the solute between the solution and adsorbent is attained (where the adsorption of solute is from the bulk onto the adsorbent is minimum). Other definition of adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions. Adsorption with activated carbon was the most sought-on process, where the carbon was used as a "polishing process" to remove a fraction of the existing dissolved substances in the water after treatment.(Yahya, Al-Qodah, & Ngah, 2015)

Adsorption has been used for centuries. It is thought that the idea was first conceived in ancient times. However, first results or observations weren't documented until the late 1700's. At that time, adsorption was used to test the ability of charcoals and clays to uptake gases. With more research, by 1814 it was concluded by de Saussure, that all types of gases can be taken up by porous substances such as asbestos, cork, sea-foam, in addition to charcoal. By the early 1900's, the Freundlich equation was developed but was not theoretically justified. (Ekpete, Harcourt, Chemistry, & Harcourt, 2011)

2.4.1. Factors affecting adsorption process

Adsorption is one of the top wastewater treatment methods in the globe (Chaturvedi and Sahu, 2014). during the adsorption process the sewage is free from inorganic and organic elements like heavy metal effluents (Du et al., 2014). The adsorption process generally depends on the following:

2.4.1.1.Contact time

The removal efficiency increased with an increase in contact time before equilibrium is reached. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions (Mohammad Mehdi et al., 2011).

2.4.1.2. pH

The pH of the solution was clearly an important parameter that controlled the adsorption process (Gupta 2008; Gupta and Rastogi, 2007).The effect of pH in turn depends on the charge on the adsorbent surface.

2.4.1.3.Initial Metal Concentration

Different initial metal concentrations and a fixed concentration of biomass were used to calculate adsorption capacity. The initial and final concentrations of the solutions were measured by Atomic absorption spectrophotometer. These data were used to calculate the adsorption capacity of the adsorbent (Mohammad Mehdi et al., 2011).

2.4.1.4.Adsorbent Dose

The adsorbent dosage is an important parameter because this determines the capacity of an adsorbent. The removal of metal ions increases with an increase in the adsorbent dosage. The effect of adsorbent dosage on adsorption was studied by varying the amount of adsorbents and keeping the other parameters constant (Azouaou et al., 2010; EI-Said et al., 2010; Saifuddin and Kumaran, 2005).

2.4.1.5.Adsorbent particle size

Due to their relationship, adsorbent particle size is important to the process of adsorption. For example, when the number of particles' size is small, the adsorption capacity increases and surface area of adsorbents increases. Particle size increases with adsorption decrease, although the surface area decreases (Gao et al., 2009). The adsorption capacity is inversely proportional to the size of the adsorbent particle (Gao et al., 2009). On the other hand, the adsorbate surface area is directly proportional to the adsorption capacity (Gao et al., 2009). Similarly, the surface area of adsorbents has great importance for the adsorption process due to physicochemical properties (Long et al., 2009)

2.4.2. Types of adsorbents

Different types of adsorbents are classified into natural adsorbents and synthetic adsorbents.Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores.

These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities. Synthetic adsorbents are adsorbents prepared from Agricultural products and wastes, house hold wastes, Industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Many waste materials used include fruit wastes, coconut shell, scrap tyres, bark and other tannin-rich materials, sawdust, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore mineral.(Polytechnic, 2008)

Activated carbons as adsorbent for organic pollutants consists in their adsorption a complex process and there still exists considerable difficulty. The main cause of this difficulty results from the large number of variables involved. These include, for example, electrostatic, dispersive and chemical interactions, intrinsic properties of the solute (for example solubility and ionization constant), intrinsic properties of the adsorbent (such pore size distribution), solution properties (in particular, pH) and the temperature of the system. (Zayat & Smith, 2006)

Activated carbons (AC) (both granular activated carbon (GAC) and powdered activated carbons (PAC)) are common adsorbents used for the removal of undesirable odor, color, taste, and other organic and inorganic impurities from domestic and industrial waste water owing to their large surface area, micro porous structure nonpolar character and due to its economic viability.

The major constituent of activated carbon is the carbon that accounts up to 95% of the mass weight in addition; active carbons contain other hetero atoms such as hydrogen, nitrogen, sulfur, and oxygen. These are derived from the source raw material or become associated with the carbon during activation and other preparation procedures.(Franca et al., 2013)

2.4.2.1.Low cost adsorbents

Adsorption is a low-cost process as it uses relatively cheap materials. Low-cost adsorbents are naturally available materials/ adsorbents, and are defined as waste product from agriculture, industries and domestic use. These materials are, less expensive (Renge et al., 2012), affordable (Lim and Aris, 2014), environmentally friendly as well as abundant (Kurniawan et al., 2006b; Kırbıyık, 2012; Lim and Aris, 2014) and cheap (Kurniawan et al., 2006a; Carvalho et al., 2011). They have a high treatment efficiency for the elimination of toxic chemicals, heavy metals (Tajrishy, 2012). These cheap/low-cost adsorbents are simply gathered from agricultural waste, industrial byproducts, clay soil, food waste and seafood (Bailey et al., 1999; Jain et al., 2013). Hence, they are economically affordable and copiously available (Li et al., 2007; Kaushal, 2013). For example, the cost of bagasse fly ash adsorbent available atUS$0.002 kg-1including the transport payment to the adsorption process site, energy used and other things. The final, total cost of this bagasse fly ash is around 0.009 US dollars per kilogram (Srivastava, 1995).

The method to obtain and prepare the materials is effortless and does not require the use of other resources, chemicals, or processes. Low cost material that only requires thorough washing and drying to remove moisture before being sieved is the latest research material being employed for successful adsorption. (Ali et al., 2014), Evaluation of tree leaves, coffee husk, barks, agricultural waste , maize corn , saw dust , has been done to test adsorption capability on different metals at different conditions. Conditions that are tested for include obtaining optimal pH, contact time, agitation speeds, and initial concentrations of metals and dosage of adsorbent. Different conditions yield different results for different metals and adsorbents. Hence, what may apply for a certain combination of experimental conditions, metals, and adsorbents, may not apply for another.(Geetha & Belagali, 2013)

2.4.2.2.Use of corn cobs activated carbon

In last few years the growth of corn crop has increased considerably in the Ethiopia because of the government's policy of promoting alternative agricultural practice and there is a huge supply of waste corn cobs. However, after the use of corn for wide variety of applications the corn cobs often leave in the fields as very low economic value agricultural waste. Due to their abundance in the region, they are very inexpensive and easily obtained, hence, resulting in their desirability to be used for this research. The efforts of using the corn cobs as a biomass fuel has not given very promising results primarily because of the low calorific value of corn cobs.(Adie et al., 2010) Another alternate route to convert these waste corn cobs to high economic value product can be to convert them into more commonly called as activated carbon. Hence using them for experimental purposes yields no cost, no adverse environmental effect. The use of various precursors such as saw dust, Coffee husk, and lignite coals for producing activated carbon has been studied in detail by several researchers.(Narayanan, 2014) .

One of the excellent precursors for activated carbon could be corn cob because of its botanical origin similar to coconut shells and olive pits. Since the yield of the activated carbon production is usually very low, the cost and availability of the raw material is a very important factor in the economic production of activated carbon. Coconut shell, wood, lignite coals which are often used for commercial production of activated carbon have high price as compared to agricultural waste such as corn cob. Corn cob is available in abundance and is relatively cheap. Also the chemical compositions of corn cobs suggest that it has less mineral matters, which are often responsible for preferential gasification during the activation process resulting in pore. The elemental analyses of corn cobs which show high promises of its use as precursor of nanoporous carbon production because of its carbon content up to 45%. Because of this reasons corn cobs could be an excellent precursor for the commercial production of activated carbon. (Abdel-Ghani et al., 2007)

Table 2-2; Elemental analysis of corn cob:

Elements	%
Carbon	43.5
Nitrogen	0.21
Oxygen	48.4
Hydrogen	7.9
Sulphur	0.013
Ash	1.2
Moisture	10+/-2
Lignin	6.8
Cellulose	47.1
Hemicellulose	-

Parag S. Shah(August ,2007).

2.5. Adsorption Experiments and models

2.5.1. Batch adsorption

Most of the research conducted on adsorption of metals using waste materials underwent batch tests to analysis how the adsorbate and adsorbent perform under various conditions.

These conditions include pH levels, initial concentration of metal solution concentration of adsorbent, temperature, agitation speed, and contact time. (Khan et al., 2015)

All of these conditions produce different results once changed; however, the magnitude and significance of change alters between the different conditions as each has a different effect on the adsorption process. As adsorption is a process which involves reactions between the adsorbate and adsorbent, varying the conditions may improve or exacerbate the rate and amount of adsorption. pH affects adsorption reactions through H+ and OH- ions that are emitted into the solution. A more acidic pH releases more H+ ions that may react with the adsorbent or adsorbate, hence affecting results. Likewise, an alkaline pH solution releases OH which may also react with the adsorbent or adsorbate.(Anagement, 2014), Hence, it is crucial when performing batch tests to evaluate the process at different pH levels. Hence, tests need to be performed to determine the most efficient value of pH. Like pH, contact time is another crucial factor to consider when performing tests. This is also significant as the adsorbents used are organic materials, which may release additional organic materials in the system. Not allowing for enough contact time will not effectively complete the adsorption process, hence, results obtained will be incomprehensible and void. The greater the contact time, the greater the possibility that equilibrium has been reached, and hence, adsorption has reached its potential. Agitation speed is another important criterion to be test, as this either speeds up or slows down adsorption. However, a higher agitation speed does not necessarily mean a higher rate of adsorption. Adsorption is highest at a certain speed that needs to be determined through experimentation. Different initial concentrations of the metal solution evaluate the capacity of the adsorbent in its ability to adsorb and remove the metals from the solution. Usually, the lower the concentration of the metal, the better the adsorption, as there is less adsorbate for the adsorbent to remove. However, some adsorbents perform extremely well in high initial concentrations of adsorbate, and hence, have a higher adsorption capacity.(Kyzas & Kostoglou, 2014) .

2.6. Adsorption isotherm model

The adsorption isotherm is known as Freundlich equation, due to Freundlich’s emphasis on the importance of the equation, which developed its extended use, although it was believed the equation was developed in the empirical form a decade earlier by Boedecker. Other equations were also developed and included Langmuir, Euckena, and Polanyi. Langmuir’s equation was originally developed for monolayer adsorption.

It is this equation that is considered as the practical equation that corresponding to an ideal and localized monolayer. Branauer, Emmett, and Teller (BET) proposed the multilayer isotherm. The

BET equation uses the same assumptions as Langmuir, and assumes that Langmuir's equation applies to every adsorption layer. It was the BET theory that was the initial endeavor at creating a universal theory of physical attraction. The Langmuir and BET theories and equations are the most widely used equations for monolayer and multilayer adsorption.(Aeisyah et al., 2014)

There are two most used equations for water and wastewater treatment: Langmuir and Freundlich. The capacity of the adsorbents determines the amount of heavy metal that was adsorbed onto the adsorbent.

An adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at constant temperature. Langmuir and Freundlich adsorption isotherms are commonly used for the description of adsorption data.

This mathematical description is based on Herbert Freundlich (1880 - 1941). Therefore, these types of isotherms are known as Freundlich isotherms. The Freundlich isotherm describes heterogeneous surface adsorption. The energy distribution for adsorptive sites (in Freundlich isotherm) follows an exponential type function which is close to the real situation. The rate of adsorption/desorption varies with the strength of the energy at the adsorptive sites. The Freundlich equation is expressed as(Scholar, 2013)

The Freundlich isotherm is based on the following equation:

$$\mathrm{q_e = K_f c_e{}^{n_f}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .2.1$$

Where

$\mathrm{q_e}$ = Equilibrium loading in mg/ g

$\mathrm{c_e}$ = Equilibrium concentration in mg/L

$\mathrm{K_f}$ =Freundlich constant in mg/g

$\mathrm{n_f}$ = Freundlich exponent

The Freundlich isotherm is an empirical equation and not a physical, chemical or thermodynamic principle. Normally Freundlich isotherms are displayed in a logarithmic scale. By taking the logarithmic function of Formula above the Freundlich isotherm can be represented as a linear equation:

$$\log \mathrm{q_{eq}} = \log \mathrm{k_f} + \frac{1}{\mathrm{nflog\ Ce}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .2.2$$

With an intercept of $\mathrm{k_f}$ and a straight lined-slope of $\frac{1}{n}$ where $\mathrm{k_f}$ roughly indicates the adsorption capacity, and $\frac{1}{n}$ the adsorption intensity.

The Freundlich exponent $\mathrm{n_f}$ has a decisive influence on the profile of the adsorption isotherm. In the field of water treatment, we are usually aiming for very low equilibrium concentrations. In this case, the equilibrium concentration corresponds to the maximum permitted adsorbate concentration in the treated water.

As such, in the case of Freundlich exponents < 1 we also talk about a favourable isotherm curve.

Accordingly, in Freundlich exponents > 1 there is an unfavourable curve.

The Freundlich exponent therefore allows us to express how well a substance can be adsorbed.

Where: The smaller the Freundlich exponent, the better the adsorbate can be adsorbed.

Langmuir's Adsorption Isotherm may be used for monolayer adsorption onto a surface containing a finite number of identical sites, and assumes uniform energies of adsorption on the surface, in addition to no transmigration of the adsorbate in the plane of the surface.(Davis & Gietka, 1994), The Langmuir isotherm model determines the maximum capacity of the adsorbent from complete monolayer coverage of the adsorbent surface. Langmuir's isotherm non-linear equation is.(Abdel-Ghani et al., 2007)

$$\mathrm{q_e} = \frac{\mathrm{q_o\, bC_e}}{1 + \mathrm{bC_e}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots .. 2.3$$

q_e is the amount of the substance adsorbed at equilibrium per amount of the adsorbent (mg/g), q_o is the saturation monolayer adsorption capacity (mg/g), and b is the equilibrium adsorption constant (l/mg).

Mathematically its linear form of equation 2.12 is expressed as

$$\frac{\mathrm{C_e}}{\mathrm{q_e}} = \frac{1}{\mathrm{K_a q_0}} + \frac{\mathrm{C_e}}{\mathrm{q_o}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots .. 2.4$$

Where $q_e$is the amount of the metal adsorbed for the complete monolayer (mg/g), $\boldsymbol{K_a}$is the Langmuir adsorption equilibrium constant. The plot of $\boldsymbol{\frac{C_e}{q_e}}$ versus $\boldsymbol{C_e}$enables the determination of isotherm constants. Where $\mathrm{q_o}$, $\frac{1}{intercept}$ and b equal to intercept *$\frac{1}{\mathrm{slope}}$.

Adsorption equilibrium studies are important to determine the effectiveness of adsorption. In addition to this, it is also necessary to identify the adsorption mechanism.

2.7. Adsorption kinetic model

Kinetic models can be exploited to investigate the mechanism of biosorption and its potential rate-controlling steps that may include mass transport and chemical reaction processes. In addition, to select the optimum condition for full -scale removal processes, information on the kinetics of metal uptake is required. Adsorption kinetics is expressed as the solute removal rate. In practice, kinetic studies were carried out in batch systems by using various initial sorbate concentrations, sorbent doses, particle sizes, agitation speeds, pH values and temperatures along with different sorbent and sorbate types. Then data regression was used to determine the best -fitting kinetic rate equation. The linear least-square method can also be applied to the linearly transformed kinetic rate equations for fitting the experimental data to determine the rate constant. (Masoud et al., 2012) To understand the adsorption kinetics and rate-limiting step, several kinetic models have been proposed in the literature. Examples include pseudo-first and pseudo second order rate models. The pseudo first and second-order kinetic models are the most appreciated models to study the biosorption kinetics of heavy metals and quantify the extent of uptake in biosorption kinetics (Tnbaraj & Sulochana, 2002)

A study of the kinetics of adsorption is desirable as it provides information about the mechanism and characteristics of adsorption, which is important for efficiency of the process The adsorption of the lead (II) from wastewater was tested by using pseudo first-order and pseudo-second-order kinetic models. The Pseudo-first-order and second-order kinetic models were tested at different concentrations in this study to determine which model is in good agreement with experimental (adsorption capacity) value, thus suggesting which model the sorption system follows. Mathematically pseudo-first order is expressed as:

$$\log(q_e - q_t) = log q_e - \frac{k_1 t}{2.303} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 2.5$$

Where ; q_e is the equilibrium adsorption capacity (mg/g), q_t is the adsorption capacity at time t, k_1 is pseudo-first-order rate constant (g/mg h) which can be evaluated by plot between $\log(q_e - q_t)$ and t.

Mathematically pseudo-second-order kinetic model is expressed as:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots .2.6,$$

Where; $q_e$the equilibrium adsorption capacity (mg/g) is, q_t is the adsorption capacity at time t, k_2 is pseudo-second-order rate constant (g/mg h). The value of q_e is evaluated by plot between $\frac{t}{q_e}$ and t.

2.8. Current status of wastewater treatment in Ethiopia

The industries in the country are rapidly growing from year to year due to the policies of the country. For example, chemical, metal processing, agro-processing and others industries are increasing and expanding throughout the regions of Ethiopia. (Alemayehu, 2014).

Increased industrialization in Ethiopia has contributed significantly to the great in Gross Domestic Product (GDP) of the country. However, wastewater discharge from this industrial sector is increasing from year to year and is being discharged into the environment without treatment. It is affecting the health of living organisms both biotic and abiotic. Therefore, treatment of these toxic heavy metals is becoming a critical issue in the country. Moreover, there is limited information on treatment options available which are suitable for application in the country.Industrial wastewater containing heavy metals are released every day to surface water bodies like rivers, streams and are significantly affecting the quality of water (Ogedengbe, 2004). The effect is exponentially raised every year because most countries tend to be industrialized. Similarly, in Ethiopia different industries discharge their wastewater into nearby surface water bodies. For example, in Hawassa town wastewater from the textile industry is released into the Tikur Wuha river (Mekuyie, 2014). Kombolcha is one of the main industrial corridors of Northern Ethiopia and the few existing industries are steel products, textiles, tannery, and brewery, meat processing (ELFORA) and flour production. These industries release contaminated wastewater containing toxic heavy metals into the nearby rivers, namely the Borkena, Worka and Leyole rivers (Zinabu, 2011). Domestic and municipal wastewater is discharged into the Huluka river of Ambo. The amount of the wastewater released into the Huluka river differs from 10,000 to 15,000 l.day-1(Padanilly et al., 2008).

Wastewater containing harmful elements from non-point source of pollution flows into the Awetu and Kitorivers at Jimma town, and like other towns, urbanization and the increase population and industrial growth increases pollution in the water bodies (Haddis et al., 2014). The socio political and industrial corner of Ethiopia, and the capital Addis Ababa generates an estimated annual volume of 49 million m^3total wastewater from which about 4 million $m^3$is industrial wastewater (Van Rooijen et al., 2010). Rivers in Addis Ababa are contaminated with heavy metals because more than two thousand industries in the town are established along the river ways. According to Environmental Protection Authority (EPA) three quarters of the industries in Ethiopia are established in Addis Ababa, around 90% of these industries release their waste directly into these water bodies. Others have some degree of on-site treatment plant, and subsequently discharge effluents into adjacent streams (Leta, 2004).

Most toxic heavy metals are found in industrial waste (Schmuhl et al., 2004). For example, in Ethiopia at Ejersa area of East Shoa, textile and tannery industries release waste that contains heavy metals including cadmium (Cd), lead (Pb), iron (Fe), chromium (Cr), copper (Cu), and zinc (Zn) (Asfaw, 2007). The Akaki river in Addis Ababa, around 390 hectares of land irrigates vegetables such as potatoes which have some toxic elements such as zinc, nickel, mercury, copper, cadmium and chromium, as does red beet and onions containing chromium (Gebre et al., 2009). For a long time, it has been known that intake of food that contains high levels of heavy metals, poses risks to human health .These toxic hazardous elements have a significant effect on biotic, abiotic and other living organisms (Sarı et al., 2007). Disease include asthma, malarial, respiratory infections, skin infections, pregnancy problems, cancer and mortality (Gebre et al., 2009; Zinabu, 2011). It is important to remove toxic hazardous elements from contaminated water discharged into nearby surface water bodies by using low-cost locally available materials. Examples are minerals like clay, industrial byproducts, agricultural waste and other easily available materials (Kurniawan et al., 2006a). Generally, the discharge from industries of untreated effluent wastewater contains heavy metals, and the main source of water pollution in developing countries like Ethiopia.

2.8.1. Volume of wastewater discharge in Ethiopia

In Addis Ababa 90-96%, of industries discharge their wastewater without treatment into nearby water bodies (Getachew, 2006). The daily wastewater discharge from industries is increasing, while, on the other hand, the amount of wastewater treated has decreased annually (Krishna, 2011). This indicates that, it is becoming a crucial issue requiring the introduction of low-cost treatment techniques that use local abundantly available raw materials.

3. METHODOLOGY

3.1. Materials

3.1.1. Chemical reagents

The chemicals used for the study is Analytical grade Pb(II)NO_3 for standard metal ion sample preparation, Nitric acid for preservation of the samples, Hydrochloric acid and Sodium hydroxide for pH adjustment. H_3PO_4: used as activating agent of corn cob activated carbon production process.Na_2Co_3- To remove any residual acid char and all experiments were used distilled water. Hydrochloric acid (HCl) and Sodium hydroxide (NaOH) for p^H adjustment. All experiments used distilled water.

3.1.2. Instruments

Excella E 24R model incubator shaker: was used to agitate the corn cobs activated carbon with initial metal ion concentration. Precisa model 900 pH meters combined with a glass electrode to measure the pH of the solution. Filter paper (Advantec, 45µm) to filter the content of the flasks. Analytical balance model Mettler Toledo (PB 602-S): to weigh the samples. Perkin Elmer model 3110 Atomic Absorption Spectrometer (AAS) operating with air acetylene flame: were used to measure metal ion after reaching sorption equilibrium. The analysis on the AAS on each sample was carried out in triplicate.

Tubular furnace: -used for pyrolysis/carbonization of the corn cobs and oven was used for subsequent moisture removal and dying.

3.2. Methods

3.2.1. Adsorbent preparation

Since corn cob was the selected adsorbent for the preparation of activated carbon. Corn cobs were collected from local community house in Agarfa, Ethiopia. They were then washed in distilled water to avoid having any ions from regular water contributing to variations in results and well-scrubbed using a sponge and distilled water, subsequently dried in the oven at 105°C for 24 h to remove the moisture content. The dried corn cob was crushed and sieved to the size of 1-2 mm then preserved in clean containers for carbonization step.(Awugchew.T , 2015)

3.2.2. Carbonization of the adsorbent

The dried corn cobs was carbonized in a horizontal cylindrical furnace with continuous Nitrogen flow in nitrogen atmosphere at a activation temperatures of400,450 and 500℃, activation time of 2, then carbon was then left to cool for 24 h and the carbonized corn cob was ground with the aid of grinder and there after sieved using Sieve of 1-2 mm.(Awugchew .T ;2015)

3.2.3. Activation of the Adsorbent

The carbons obtained from corn cobs of the waste materials were subjected to chemical activation prior to use. The corn cob carbons were prepared chemically using phosphoric acid as activation agent. One hundred grams of the corn cob carbon were mixed with 100ml of solution (85% phosphoric acid) at different impregnation ratio of 1:1,1: 1.5, and 1:2 and Concentration of activating agent (H_3PO_4) 30, 60 and 90% by weight. The mixture was heated in a mechanical heating mixer at a temperature 120℃ for 1 h to vapourize the water, after which the content was extracted and dried for 12h. Then the carbonized adsorbent was washed with distilled water until the washing was free of acid, and then the pH of the washed adsorbents was close to neutral. The washed adsorbents were dried for 24h, later sieved with 1-2 mm sieve and then stored in air tight containers for use.

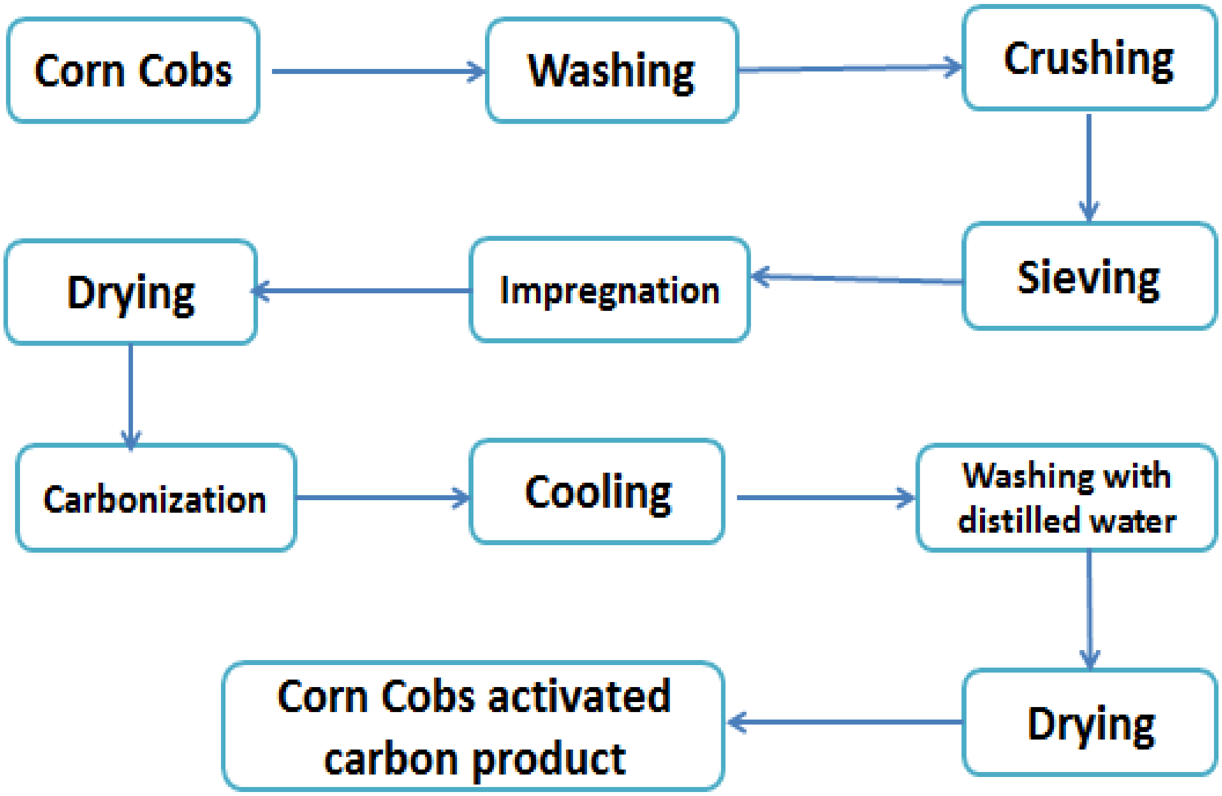


Figure 3-1; Flow sheet for the development of activated carbon from corn cobs

3.2.4. Characterization of corn cobs activated carbon

Characterizing parameters determined were: surface area, pore or void volume, ash content, moisture content, fixed carbon, bulk density, carbon yield, iodine number and porosity.(Baysal, Ozbek, & Akman, 2013)

3.2.4.1.Iodine Number

The quality of the finished activated carbon is measured by its ability to adsorb a liquid (iodine). Iodine number calculations which corresponds to the amount of milligrams iodine one gram of activated carbon can adsorb. Iodine number is the most fundamental parameter used to characterize activated carbon performance. It is the standard measure for liquid phase applications.

The iodine number is determined according to the (ASTM D4607-94) method. The iodine number is defined as the milligrams of iodine adsorbed by 1.0 g of carbon when the iodine concentration of the filtrate is 0.02 N (0.02 mol L^{-1}). A standard iodine solution is treated with three different weights of activated carbon under specified conditions.

The experiment consists of treating the activated carbon sample with 10.0 mL of 5% HCl. This mixture is boiled for 30 s and then cooled. Soon afterwards, 100.0 mL of 0.1 N (0.1 mol L^{-1}) iodine solution is added to the mixture and stirred for 30 s. The resulting solution is filtered and 50.0 mL of the filtrate is titrated with 0.1 N (0.1 mol L^{-1}) sodium thiosulfate, using starch as indicator. The iodine amount adsorbed per gram of carbon (X/M) is ploted against the iodine concentration in the filtrate (C), using logarithmic axes. If the residual iodine concentration (C) is not within the range of 0.008 to 0.04 N (0.008 to 0.04 mol L^{-1}), the whole procedure should be repeated using different carbon masses for each isotherm point. A least squares fitting regression is applied for the three points. The iodine number is the X/M value when the residual concentration (C) is 0.02 N (0.02 mol L^{-1}). The X/M and C values are calculated by the Equations 3.1and 3.2 respectively.

$$X/_M = \frac{(N_1 * 126.93 * v_1) - [(V_1 + V_{HCl})/v_F]}{M_c} * \frac{(N_{Na2S2O3*126.93)} * v_{Na2s2O3}}{M_c} \ldots\ldots..3.1$$

$$C = (N_{Na2s2O3*}\, V_{Na2s203}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2\,.$$

Where : N_I is the iodine solution normality, V_I is the added volume of iodine solution, V_{HCl} is the added volume of 5% HCl, V_F is the filtrate volume used in titration, $N_{Na2S2O3}$ is the sodium thiosulfate solution normality, $V_{Na2S2O3}$ is the consumed volume of sodium thiosulfate solution and M_C is the mass of activated carbon.

3.2.4.2.Carbon Yield

The total yields were determined after sample processing in terms of raw material mass. The dried weight, Wo of each pre-treated sample was determined using Metler balance and the carbon yield calculated as;

$$Y = \frac{w_f}{w_o} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . 3.3$$

Where: w_o is dry weight before carbonization and w_f is dry weight of produced corn cob activated carbon.

3.2.4.3. Moisture Content

- Crucible was weighed empty (B).
- Crucible was weighed with 2g of the corn cob samples (C).

- Crucible with corn cob was put in the oven at $105℃$ for 1 hrs.
- The sample was left to cool to room temperature in a desiccator.
- The sample was weighed with the crucible (D) and the moisture content was determined in weight % according to Equation.

$$\%\ (M_c) = 100 * \left(\frac{C-D}{C-B}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..3.4 \qquad (\text{ASTM, 2010})$$

Where: M_c = moisture content

3.2.4.4.Ash Content

- Crucible was weighed empty (B).
- Crucible was weighed with 2g of the corn cobs samples (C).
- Crucible with corn cobs was put in the muffle furnace at $600℃$ for 3 hrs.
- The sample was left to cool to room temperature in a desiccator.
- The sample was weighed with the crucible (D) and the ash content is determined in % according to Equation :

$$\text{Ash content}(A_c) = 100 * \left(\frac{D-B}{C-B}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.3.5 \qquad (\text{ASTM,2010})$$

3.2.4.5.Volatile content

- Crucible was weighed empty (B).
- Crucible was weighed with 2g of the corn cobs sample (C).
- 2g of the sample was heated to about $900℃$ for 7 minutes in the muffle furnace.
- The sample was left to cool to room temperature in a desiccator.
- The sample was weighed with the crucible (D) and the volatile matter content (VM) was determined in % according to equation 3.5and 3.6 where E is weight loss in % and M_c is moisture content in % as defined in Equation 3.3.

$$\text{Weight loss in \% (E)} = 100 * \left(\frac{C-D}{C-B}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..3.6$$

$$V_c = E - M_c \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.3.7 \qquad (\text{ASTM, 2010})$$

3.2.4.6.Bulk Density and Porosity

The bulk density of the adsorbent (corn cobs powder) was carried out in the laboratory; the method described in European standards, CEN/ TS, (2005) was employed. This was done by measuring the volume of water displaced when a known weight of the raw sample was dropped into a graduated measuring cylinder. A cylinder and an aluminum plate were each weighed. A sample of activated carbon was placed into the cylinder, reweighed and transferred into the aluminum plate and then oven dried to a constant weight at a temperature of 105℃ for 60 mins. The weight of dry sample was recorded after drying. A cleaned, dried well-cooked density bottle was weighed. A small quantity of sample of activated carbon was taken and ground to powder; sieved using 110 µm mesh size, and gradually put into the density bottle with a little amount of water added and weighed. The volume of void (V_v) was obtained by first determining the total volume of the cylinder used for the experiment and also determining the volume of the AC used:

The volume of void ($\mathbf{V_v}$) was obtained as;

$$V_v = V_{Cylinder-}V_{activated\ carbon} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..3.8$$

$$\text{Bulk Density(BD)} = \tfrac{Ma}{Va} * 1000\tfrac{Kg}{l} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..3.9$$

$$\text{Porosity}(\eta) = \frac{\text{volume void}}{\text{total volume}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.3.10$$

Where

M_a= weight of sample

V_a= volume of water displaced.

3.2.4.7. Fixed Carbon Determination

The fixed carbon content was determined using the formula:

$$F_c(\%) = 100 - A_c - M_C \ldots\ldots\ldots\ldots\ldots.3.11$$

Where

V_c = volatile content

A_c= ash content

M_c= moisture content

3.2.4.8. pH determination

10g of activated carbon sample was dissolved into a 250 mL beaker and 100 mL of distilled water was added and stirred thoroughly and then filtered then supernatant measured using an electronic pH meter.

3.2.5. FT- IR (Fourier Transform Infrared spectrometry)

The FTIR study was conducted on activated adsorbent sample to determine the various organic and inorganic groups on the surface before adsorption and then FTIR was also conducted after adsorption so that the organic and in organic group which participate in the adsorption process was determined by watching the change in frequency occurred due to adsorption of Lead on adsorbent using spectrum 65 FT-IR (Perkinelmer) model in rang of 4000-400 cm^{-1} using KBr pellets.

3.3. Batch Adsorption Experiments

3.3.1. Preparation of Standard Solutions for batch test

The wastewater that was used was artificially prepared in the laboratory. This was due to the fact that the effect of studying lead (Pb^{2+}) ions metal alone was required, as having other soluble and insoluble substances in the water would make it difficult to assess the effect of corn cobs activated carbon on the adsorption behaviour of the metal. Distilled water was used to dissolve metal crystals. This was performed to eliminate the disturbances of other soluble substances located in regular tap or drinking water. $Pb(II)NO_3$, was used to obtain lead solution.

The adsorption equilibrium of Pb(II) on CCAC was reached within approximately 120minute under the experimental conditions according to a preliminary test. Therefore, an equilibrium time of 2 hr was selected for all batch adsorption experiments. A lead stock solution with 1000 mg/L prepared from 1000ppm of $Pb^{2+} ions$ was prepared by dissolving 1.5985g of lead nitrate, $Pb^{2+}(NO_3)2$ in distilled water and the volume was made to the mark in l000ml volumetric flask using distilled water and was used to prepare the working solutions with various initial lead concentrations by serial dilution.

Batch experiments were conducted to investigate parametric effect of pH, dose of adsorbent and $\mathrm{Pb}^{2+} ions$ initial concentration on removal efficiency and adsorption capacity corn cobs activated carbon (CCAC) heavy metal Lead (Pb^{2+}) from synthetic waste water.

The experiment was carried out in a batch mode for the measurement of adsorption capabilities. Different initial metal ion concentrations of 10, 55 and 100 ppm of lead ions measured from the standard stock solution were used. For this study Pb^{2+}solution with this initial metal ion was taken in 250mL Erlenmeyer flask with different dose of adsorbent 1, 2 and 3 g and the effect of pH on the Pb^{2+} adsorption onto corn cobs activated carbon was studied at pH range of 4, 5, and 6 was used for all experiments.

The three factors selected are, metal initial concentration, dose of CCAC and pH factors were conducted through batch experiments to study, the effects of each main factors and their interaction on removal efficiency and adsorption capacity were investigated and evaluated. To obtain optimal conditions for each independent factors and response variables design of experiment was used. Adsorption is a process which takes place on the surface. It depends upon the physical and chemical properties of adsorbent and adsorbate. Effect of various parameters like initial concentration of the adsorbate, adsorbent dose, and pH were studied in this work

Throughout the experimental work, 250 mL of Erlenmeyer flasks were used. Each of flask contained lead solution of required concentrations. Desired pH was adjusted by using 0.1 M HCl and 0.1 M NaOH with different amount of adsorbent in each flask. All the experiments were carried out at 25 ^{0}C. Flasks containing samples were agitated by using Wise shake flask shaker at 150 rpm for all experiments. The samples were filtered by using whatman filter papers and supernatant was analyzed for Pb^{2+} ion by atomic absorption spectrometer. The blank adsorption experiments were also carried out. The equilibrium adsorption capacity, removal efficiency and adsorption capacity at time t were determined by using:

$$\mathrm{q_e} = \frac{(\mathrm{c_o} - \mathrm{c_e})}{\mathrm{m_{ac}}} * \mathrm{V} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . . 3.12$$

$$\mathrm{q_t} = \frac{(\mathrm{c_o} - \mathrm{c_t})}{\mathrm{m_{ac}}} * \mathrm{V} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.13$$

$$E(\%) = \frac{(c_o - c_e)}{c_o} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .3.14$$

Where q_e (mg/L) is the equilibrium adsorption capacity, c_o (mg/L) is the initial concentration of lead ions in the solution, c_e (mg/L) is the equilibrium concentration of the lead ions in the solution, c_t is the concentration of lead ions in the solution at time t, V (L) is the volume of the lead solution, m_{ac} (g) is weight of activated carbon or the adsorbent. E(%) ;Removal efficiency

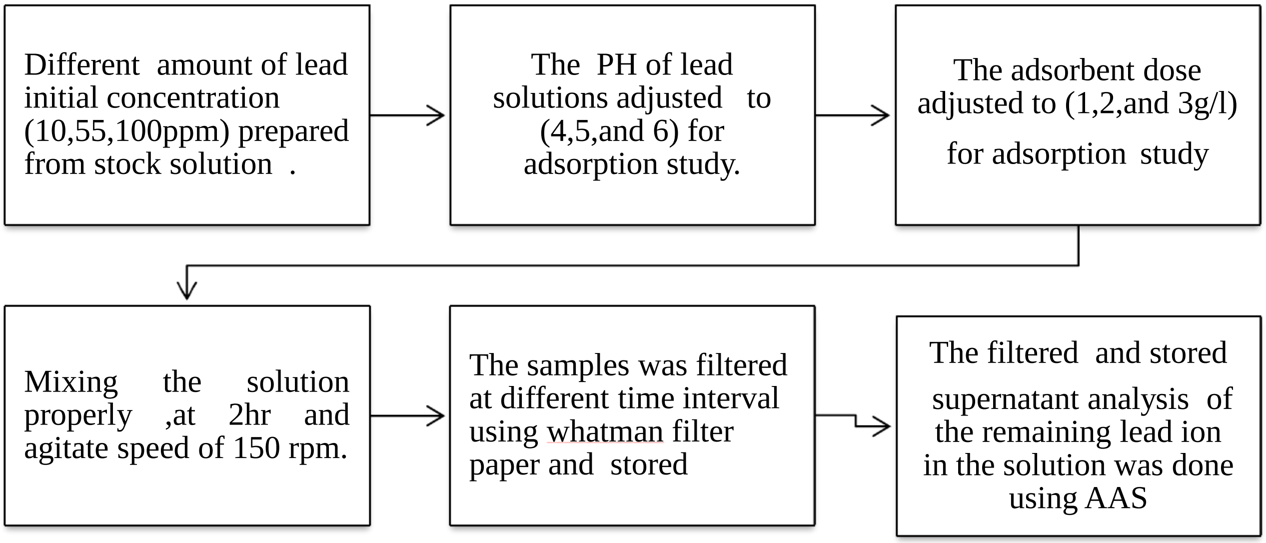


Figure 3-2; Experimental set up for determination of optimum pH, initial concentration and adsorbent dosage

3.4. Experimental design

The experimental data were analyzed using a statistical software Design Expert software version 7.0.0. For regression analysis and also for the evaluation of the statistical significance of the equations developed.

Design of experiments (DOE) is defined as a statistical technique or approach that is used for the design and the analysis of experiments. The use of DOE is required in designing experiments in order to draw valid and accurate conclusions about any set of experiments. In DOE, a series of tests are made where certain changes are imposed to the input factors, so that the causes of the main changes in the output or response are identified. DOE is a statistical tool used to explore new processes and gain understanding of the existing processes. This helps researchers to optimize such processes. DOE is about following a particular pattern of experiments in order to generate a great deal of information about a certain process while using the absolute minimum of actual experiments or runs needed to get this information. (John Wiley and Sons, 2005.)

In most research areas, the majority of experiments are designed by studying the effects of two or more inputs on the output or the response variable rather than the effect of the individual factors. A full factorial design study is about studying the effect of each of the selected factors on the desired response variable or output. For full factorial designs, three levels of each factor are studied. The use of factorial design is more advantageous than studying the effects of individual factors or the one-factor-at-a-time analysis approach. (John Wiley and Sons, 2005.).

3.4.1. Factorial Design Methodology

The sets of experimental data that were generated on CCAC production and characterization study are examined using full factorial designs. For the full factorial design three levels considered with three factors (acid concentration (%) ,activation temperature (℃) and impregnation ratio (IR) are considered as the main effects and carbon yield and iodine number as the response variable.

However, for the full factorial design, batch adsorption studies three factors, initial concentration of lead, pH and adsorbent dose are considered to study the main effects and interactions on the removal efficiency of lead from waste water and adsorption capacity as response variables. The main objective of this study is to investigate the effects and the interactions between the studied factors, so that invalid and inaccurate conclusions can be avoided about the process. Results found are also verified by studying and generating the analysis of variance or ANOVA. This statistical approach is used to determine the most important operating conditions on the CCAC production and lead removal efficiency from waste water**.** One way to understand and represent the interactions between the tested factors is through generating their related predictive regression models. The regression model for a factorial experiment is expressed as:

3.5. Adsorption Isotherms

Adsorption equilibrium is the most significant and helpful data in an adsorption system. It is also helpful in model prediction for analysis and design of an adsorption process.

Several equilibrium isotherm equations namely, Langmuir, Freundlich, etc. have been evaluated to represent the experimental sorption isotherm data.The results obtained for the batch tests were then best fitted into both the Langmuir and Freundlich isotherms.

3.5.1. Langmuir Isotherm

The assumptions of Langmuir equation include the followings: a) maximum absorption occurs when the adsorbent surface is covered by a single molecular layer of soluble material. b) The absorption energy is fixed and identical at all the points. c) The molecules of adsorbed material cannot move in the adsorbent surface

$$\mathrm{q_e} = \frac{\mathrm{q_o\,bC_e}}{1+\mathrm{bC_e}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..3.15$$

q_e is the amount of the substance adsorbed at equilibrium per amount of the adsorbent (mg/g), q_o is the saturation monolayer adsorption capacity (mg/g), and b is the equilibrium adsorption constant (l/mg).

Mathematically its linear form of equation 3.13 is expressed as

$$\frac{\mathrm{C_e}}{\mathrm{q_e}} = \frac{1}{\mathrm{K_a q_o}} + \frac{\mathrm{C_e}}{\mathrm{q_o}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..3.16$$

Where $q_e$is the amount of the metal adsorbed for the complete monolayer (mg/g), $\boldsymbol{K_a}$is the Langmuir adsorption equilibrium constant. The plot of $\frac{\boldsymbol{C_e}}{\boldsymbol{q_e}}$ versus $\boldsymbol{C_e}$enables the determination of isotherm constants. Langmuir isotherm is also used to calculate the dimensionless constant known as separation constant or equilibrium parameter (R_L) which gives information about the favorability of the adsorption of metal ions on the adsorbent. Mathematically it is expressed as:

$$R_L = \frac{1}{1+K_a c_o} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 3.17$$

Where R_L is the separation factor, $\boldsymbol{K_a}$ is the Langmuir adsorption equilibrium constant and $\boldsymbol{c_o}$ (mg/L) is the initial concentration the lead (II) ions.

3.5.2. Freundlich Isotherms

The Freundlich equation expresses adsorption on a heterogeneous surface in terms of adsorption, and it can be expressed as follows.

$$\mathrm{q_e = K_f c_{eq}}^{\mathrm{n_f}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..3.18$$

Where

$\mathrm{q_e}$ = Equilibrium loading in mg/ g

$\mathrm{c_{eq}}$ = Equilibrium concentration in mg/L

$\mathrm{K_f}$ =Freundlich constant in mg/g

$\mathrm{n_f}$ = Freundlich exponent

The Freundlich isotherm is an empirical equation and not a physical, chemical or thermodynamic principle. Normally Freundlich isotherms are displayed in a logarithmic scale. By taking the logarithmic function of Formula above the Freundlich isotherm can be represented as a linear equation:

$$\log \mathrm{q_{eq}} = \log \mathrm{k_f} + \frac{1}{\mathrm{nf} \log \mathrm{Ce}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.3.19$$

3.6. Adsorption Kinetics

A study of the kinetics of adsorption is desirable as it provides information about the mechanism and characteristics of adsorption, which is important for efficiency of the process The adsorption of the lead (II) from wastewater was tested by using pseudo first-order and pseudo-second-order kinetic models. The Pseudo-first-order and second-order kinetic models were tested at different concentrations in this study to determine which model is in good agreement with experimental (adsorption capacity) value, thus suggesting which model the sorption system follows. Mathematically pseudo-first order is expressed as:

$$\log(q_e - q_t) = log q_e - \frac{k_1 t}{2.303} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.20$$

Where ; q_e is the equilibrium adsorption capacity (mg/g), q_t is the adsorption capacity at time t, k_1 is pseudo-first-order rate constant (g/mg h) which can be evaluated by plot between $\log(q_e - q_t)$ and t.

Mathematically pseudo-second-order kinetic model is expressed as:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.21$$

Where; $q_e$the equilibrium adsorption capacity (mg/g) is, q_t is the adsorption capacity at time t, k_2 is pseudo-second-order rate constant (g/mg h). The value of q_e is evaluated by plot between $\frac{t}{q_e}$ and t.

4. RESULT AND DECISSION

Evaluation of the performance of corn cob activated carbon heavy metal lead (II) removal efficiency and adsorption capacity with regards to the results of experiments are presented and discussed below based on the sequence on methodology section in this chapter.

4.1. Preparation of activated carbon and effect of processing parameters

The experimental result of the activated carbon is tabulated below in Table4.1.

Table 4-1; the experimental result of corn cobs activated carbon prepared:

	Variables			Response	
Run	Activation Temperature(^oC)	Acid concentration (%)	Impregnation ratio(W/W)	Yield (%)	IN(mg/g)
1	400	30	1	41.8	227
2	450	30	1	37.4	251
3	500	30	1	43.65	211
4	400	60	1	41.5	283
5	450	60	1	43	317
6	500	60	1	34	242
7	400	90	1	36	291
8	450	90	1	27.8	331
9	500	90	1	25	244
10	400	30	1.5	36	296
11	450	30	1.5	38	339
12	500	30	1.5	40	247
13	400	60	1.5	41	309
14	450	60	1.5	55.7	528
15	500	60	1.5	41	247.8
16	400	90	1.5	43	325
17	450	90	1.5	48	368
18	500	90	1.5	41.3	251
19	400	30	2	40	359
20	450	30	2	47	412
21	500	30	2	43	255
22	400	60	2	40.56	378
23	450	60	2	47.7	453
24	500	60	2	42.83	272
25	400	90	2	44	421
26	450	90	2	49	472
27	500	90	2	43.57	278

As illustrations figures 4.1-4.4 shows the effect of phosphoric acid concentration, activation temperature and impregnation ratio on some properties of the prepared activated carbons.

As it can be discerned from figure 4.1, the carbon yield of the sorbent increases first rapidly (from 25 to 55.7%) with an increase of acid concentration range 60- 85% H_3PO_4. A concentration of 60% H_3PO_4 it might to be the most suitable for the development of a high carbon yield of the adsorbent material.

The corn cob activated carbon yield in this study for phosphoric acid activation were 55.7% These results are in agreement with the findings of others researchers who reported carbon yield of 39.99 to 55.44% for most corn cobs activated carbon raw materials. (Birbas, 2011), It can be seen that the local raw materials studied in this present work have high carbon yield. Product yield is an important measure of the feasibility for preparing activated carbon from corn cob.

The effect of (H_3PO_4)concentration on the yield of corn cob activated carbon at constant activation temperature of 450℃,impregnation ratio 1.5 w/w and activation time of 2h showed in figure 4.1.

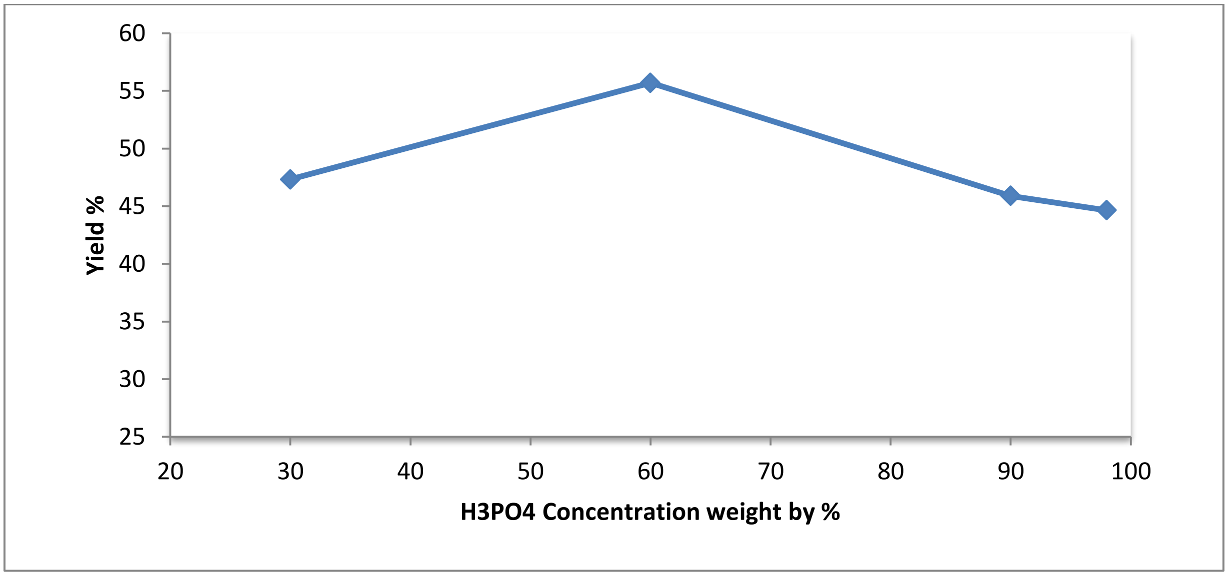


Figure 4-1; Effect of (H3PO4) concentration on the yield of corn cob activated carbon

The effect of activation temperature on the yield of CCAC (figure4.2) showed that the yield of carbon begin to increase with an increase of the temperature from 400 to 450 ℃ , and then decrease when the temperature exceeds 450 ℃ .thus , keeping the activation temperature at around 450 °C leads to a better development of the sorbent porosity.

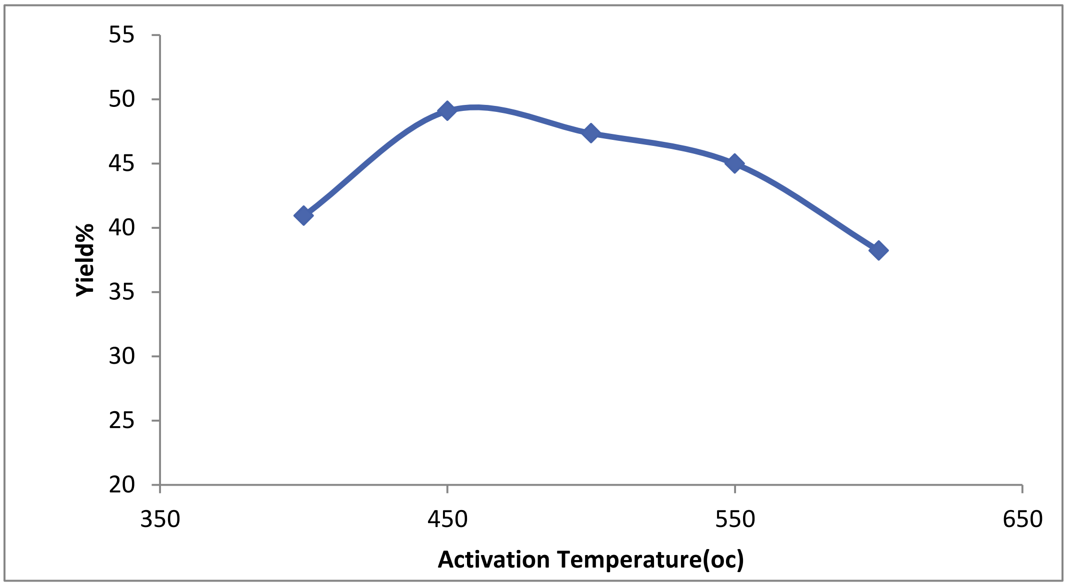


Figure 4-2; Effect of activation temperature on the yield of corn cob activated carbon

Figure 4.2; Effect of activation temperature on the yield of corn cob activated carbon:

The effect of iodine number adsorption on corn cob activated carbon result showed that increase in iodine values is due to development of pores and increased porosity in the carbons, which reached a maximum value at activation temperature of 450°C for corncobs activated carbon. The reduction in adsorptive capacity of the carbons after the maximum values is an indication of the beginning of structural deformation of the already formed activated carbons. It is evident that the activation temperature had a significant influence on the iodine number. The iodine number was observed to increase at higher activation temperatures. However, at activation temperature around 500°C and above the iodine number practically decreases. Thus it is deduced that the optimum activation temperature is around 450 -500°C for H_3PO_4 activation which is also considerable in terms energy saving. The iodine values were significantly affected by activation temperature, activation time and impregnation ratio. The results indicated that acid is the best activating agent for corncob activated carbon. The iodine values obtained in this study is in ranges of 211 to528mg/g .The corn cob activated carbon produced chemically using phosphoric acid has the highest iodine number of 528 mg/g. This indicates highly active surfaces present on the activated carbon, with high porosity and surface area. The optimum conditions were similar to those suitable for corn cob. (Yahya et al., 2015),The observed analytical differences in iodine values could be attributed to differing adsorptive characteristics, which is derived from the specific surface area, pore size and pore volume of the carbon.(Renge et al., 2012)

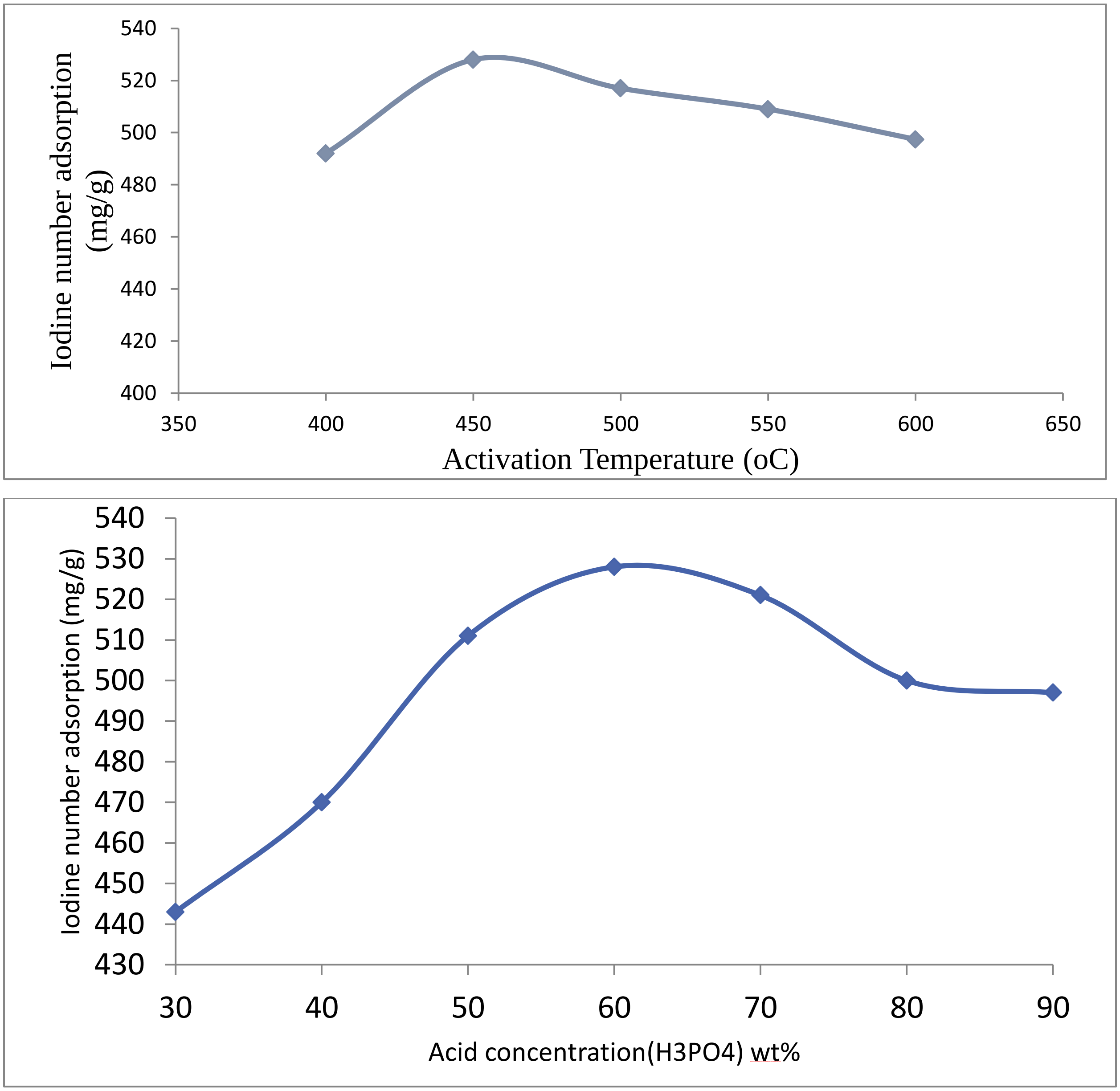


Figure 4-3; Effect of activation temperature and acid concentration on iodine number adsorption

The effect of the impregnation ratio on the iodine number illustrated in figure 4.4. The highest iodine number was obtained at an impregnation ratio of 1.5. At a value more or less than 1.5 the iodine numbers decrease. Therefore, 1.5 is the suitable impregnation ratio value leading to the best iodine number and consequently, to the best development of micro porous structure**.**

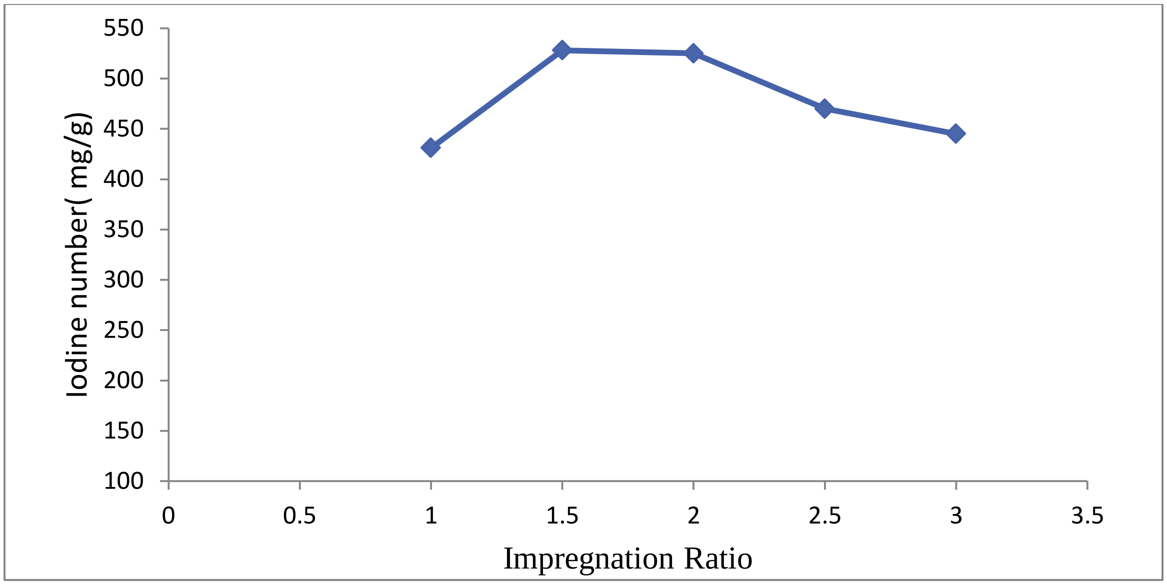


Figure 4-4; Effect of impregnation ratio on iodine number adsorption

Figure 4.4; Effect of impregnation ratio on iodine number adsorption:

The above results shows that the most efficient corn cobs activated carbon is that obtained under the following optimal conditions: an acid concentration equal to 60% in weight, an impregnation ratio of 1.5 and activation temperature of450 ℃. It is to note that the results obtained when studying the effect of each parameters on the whole considered response variables namely carbon yield and iodine number the optimum conditions were similar to those suitable adsorbent for preparation of activated carbon conducted by most of the researchers.

4.2. Characterization of Corn Cobs Activated Carbon

Characteristics of the activated carbon prepared under the optimal conditions mentioned above, are presented in Table4.2. Results showed good agreement with the earlier reported literatures to work with the other precursors of CCAC for removal of Pb^{2+} from its own aqueous solution. .(Rohaizar, Nurul, Hadi, 2013) ; For the sake of comparison, we have shown in the same table the value of some activated carbon characteristics available in literature. As it can be seen, the characteristics of the carbon obtained in this work compare well and it might be more favourable than other sorbents. The yield of the CCAC which defined as the weight ratio on a dry basis, of the resulting activated carbon to that of the original corn cob waste in our case 55.7. This value is significantly higher than those observed for other lignocellulose materials such as wood ash, tea waste and bamboo waste.

The CCAC of this present investigation was found to have lower volatile content and higher carbon content, indicating the suitability of CCAC for results were shown in good agreement with the reported literatures.(Hiremath M.N. & Shivayogimath C.B., 2012)

The increased in weight loss is as a result of increase volatilization (loss of volatile matter) of heat labile substances which reached a maximum value at a carbonization time of 2hr for corn cobs activated carbon. The reduction in weight loss after the maximum values is an indication of the beginning of activation of the already formed carbon. Similar observations were reported for other materials. According to these authors, during carbonization, a primary pore structure is developed followed by development of porosity and reduction in weight losses (Agbozu & Emoruwa, 2014). The ash results show that activation reduces the ash levels of carbon. The reduction in ash could be attributed to volatilization of some inorganic constituents at higher temperature during activation that could lead to a reduction in ash and also acid could react with the mineral constituents of carbon and thereby reducing the ash during activation. Acid treatment was reported to have been used to reduce high ash levels of sub-bituminous and lignite carbon. The corn cob activated carbon had lower ash (1.5%) was observed in this study. The lower ash content of corn cob carbon could be attributed to low inorganic component of corn cobs activated carbon.

The bulk densities observed in this work are in close agreement with values of 0.3876 g/m^3 reported for other agricultural raw materials.(Khan et al., 2015)

The moisture contents of 10.5% for acid corn cob activated carbon. This observation is in agreement with studies by who reported the moisture content of corn cob$10 \pm 2\%$.(Zhang et al., 2012)

The porosity analysis presented in work 48.8% shows that the surface area for the activated carbons fall within the range of 400 to 900m2/g. The high surface area of the carbons is important since it limits the amount of adsorb ate which can be adsorbed. The surface areas were higher for acid activated carbons and this is expected because chemical activation normally develops more porosity and gives high surface area when compared with thermal activation (Ajayi and Olawale, 200`)

The results show that agricultural waste corn cob can be used as a promising precursor material for the production of low cost activated carbon.

Table 4-2; Compared characteristics of the optimal activated carbon

	Activating agent	Adsorbent characteristics									Reference
		PH	Porosity (%)	MC (%)	AC (%)	VC (%)	FC (%)	Yield (%)	IN(mg/g)	BD (kg/m3)	
Corn cobs	Chemical (H_3PO_4)	6.2	48.8	10.5	1.5	78.2	24.8	55.7	528	287.6	This work
Bamboo stem	Chemical (H_3PO_4)	6.4	-	7.6	5.55	24.4	62.4		-	650	(Khan et al., 2015)
Coffee husk	Chemical (H_3PO_4)	5.4	57.3	6.3	9.4	13.2	71.1	57.09	396	690	Awugachew (2015)

4.2.1. FTIR-characterization of the corn cob activated carbon

Pore structure of activated carbon is very important in determine adsorption properties of the adsorbent .However; the importance of surface chemistry of activated carbon should not be ignored. In this work, spectrum 65 FT-IR (Perkinelmer) model in rang of 4000-400 cm^{-1} using KBr pellets was used in order to gain better insight into the surface functional groups available on the surface of the investigated adsorbent, their IR spectra were recorded as shown in Fig.4.5.

The band at 3000- 2800 cm^{-1} corresponds to the C-H vibrations in Alifatic, olefinic, and aromatic hydrocarbons groups and 1770-1650cm^{-1} corresponds to vibration in C=O Carbonyl causes the emergence of the bands while 1700-1600 cm^{-1} corresponds to C=C Olefinic structures band s , 1480-1420 cm^{-1} to C-H Alifatic structure bands , 1430-1360cm^{-1} Bending O-H and C-H Hydroxyl, carboxylic acid Olefins, methyl, 1120-1070cm^{-1} to Stretching C-O Secondary Hydroxyl and 1060-1000 cm^{-1} Stretching C-O Primary Hydroxyl. (Awugchew.T, 2015).It can be seen that the IR-spectra indicated the presence of ionisable functional groups; their ionization leaves vacant sites which can be replaced by metal ions. This gives an indication that those materials could be used as adsorbents for heavy metals removal.

Considering the spectrum of the carbon, we can essentially notice there is no a dramatic decrease in intensity of the bands showed in figure 4.5. this suggests that the activated carbon preparation parameters and raw materials are in proportional amount but decrease of carbonyl groups may be due to the hydrolysis effect of phosphoric acid , resulting in decomposition of these groups and subsequently release of their by- products as volatile matters. The apprеance of strong absorption (1640 and 111.5 cm-1) corresponds to aromatic C=C groups. This translates the fact that the activated carbon structure is richer in aromatic. Taking into account the whole observations can conclude that acid impregnation of the raw material followed by the pyrolysis step lead to more carbonaceous and aromatic structure due to the dehydration effect of phosphoric acid and evolution of volatiles during pyrolysis. In other respect, impregnation ratio and chemical analysis suggest that phosphoric acid chemical activation leads to the incorporation of phosphorous element in the structure of the obtained carbon.

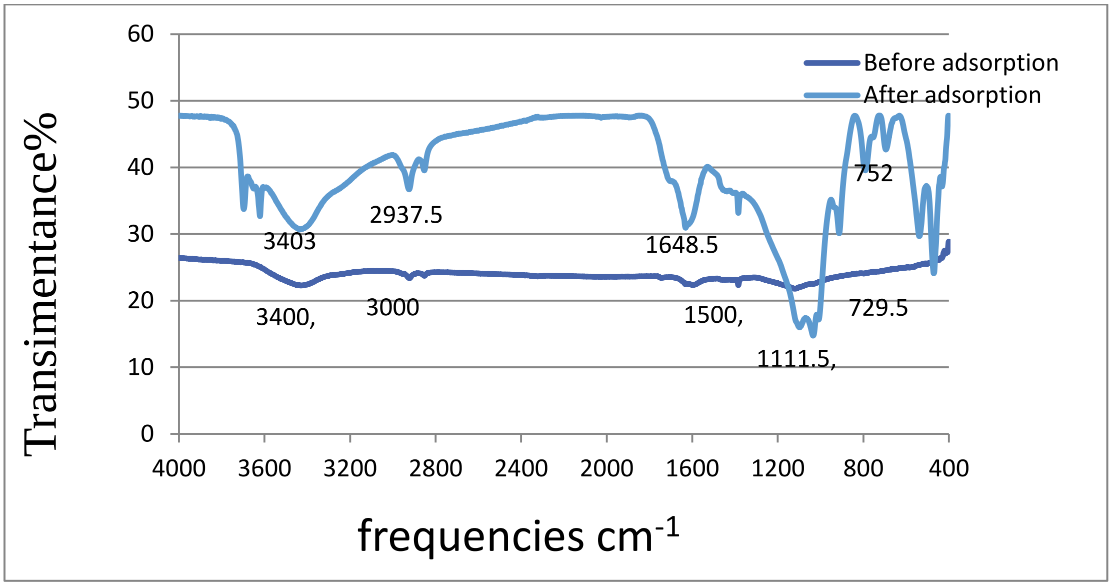


Figure 4-5;FTIR (Fourier transform infrared spectrophotometer) spectra of activated corn cob

4.3. Development and evolution of prediction model

In a characterization experiment, we are usually interested in determining which process Variables affect the response. A logical next step is to optimize, that is, to determine the region in the important factors that leads to the best possible response.

4.3.1. Full factorial design for corn cobs activated carbon production

In the full factorial design considered, twenty seven runs were conducted for production of corn cobs activated carbon (CCAC) where three factors each at three levels (high and low) were studied. The response variables considered which are iodine number and carbon yield.

The three factors considered were: activation temperature (x_1), acid concentration (x_2), and impregnation ratio (x_3), The levels of each factors are for activation temperature (A) were: 400 ,450 and 500℃.the three levels of acid concentration are 30, 60 and 90 % and the three levels for impregnation ratio were 1,1.5, and 2 w/w.

Tables 4.3 and 4.4 represent the design matrix, main effects, and interactions between factors, the generated regression models and the ANOVA analysis. Results in Table 4.3 show a significant (positive) effect activation temperature (factor (x_1),), acid concentration (factorx_2) and a moderate (positive) effect of the IR (factorx_3), on the carbon yield and iodine number. These results prove that the all three factors used is still of major importance in selecting the optimum operating conditions for the production of corn cobs activated carbon.

The ANOVA analysis shown in the lower part of Table 4.3 proves the results discussed above at a confidence level of 95%. The regression model generated for the full factorial designs using the twenty seven runs conducted using each factors. As we observe the agreement between the experimental and the predicted values is excellent. This indicates that there is a linear relationship between the calculated carbon yield and the three factors considered.

3-D surface plots and contour plots for the response variable were also generated and are shown in Figures 4.3 for carbon yield. These graphs prove the validity of conclusions presented earlier regarding the interactions between the three factors.

Table 4-3; ANOVA for yield of corn cobs activated carbon (CCAC):

	Sum of		Mean	F	p-value
Source	Squares	Df	Square	Value	Prob > F
Model	578.5111	6	96.41852	3.621385	0.0135
Activation temperature(x_1)	30.70667	1	30.70667	1.153313	0.0029
Acid concentration(x_2)	29.85069	1	29.85069	1.121163	0.0302
Impregnation ratio(x_3)	159.0733	1	159.0733	5.974639	0.0239

X_1X_2	5.3067	1	5.3067	0.199314	0.66
X_1X_3	104.9617	1	104.9617	3.942258	0.061
X_2X_3	248.612	1	248.612	9.337625	0.0062

The significance and adequacy of the models were further justified through analysis o f variance (ANOVA). In the ANOVA, the mean squares were obtained by dividing the sum of the squares of each of the variation sources the mode and the error variance, by the respective degrees of freedom. The fishers variance ratio, F-value is the ratio of the mean square owing to regression to the mean square owing to error. The higher the F-value, the greater is the significance of the corresponding variable to cause effect. In addition if Prob.>F less than 0.05, the model terms are considered as significant.(Azmier et al., 2011)

Referring to F-value shown in Table 4.3 the interaction effects between the acid concentrations IR were considered high.

The ANOVA for the 2F model for carbon yield of CCAC is listed in Table 4.3. The model F-value of 3.62 and Prob.>F of 0.0135 implied that this model was significant.

4.3.2. Effect of of independent variables on the yield of CCAC

Applying a factorial design analysis helped in identifying the most significant factors affecting the yield corncobs activated carbon . A set of experimental data on the Carbon yield was analyzed using full factorial designs. For the factorial designs, results show that the absolute effect of the activation temperature (x_1) and acid concentration(x_2) are negative effect and IR (x_3), are positive effect on the response variable considered. Furthermore, results show that significant interactions between the acid concentration(x_2) and IR (x_3), factors were found moderate positive effect for the response variable yield . The interaction between the factors was between the amount of activation temperature and the activation time,ipregnation ratio ($x_{1*}x_{2*}x_3$),), highly dependent on the each other for production of corn cobs activated carbon at optimum condition as we observe from the design of experiment.(Azmier et al., 2011)

Acid concentration and impregnation ratio are the important factors that govern the development of porosity of the prepared carbon. The interaction effect of these two parameters on the carbon yield of the adsorbent is shown in figure4.6. As it can be showed the carbon yield increase rapidly with an increase of acid concentration from 30% to 60% H_3PO_4 and until an impregnation ratio of 1.5. Beyond this impregnation ratio, the yield decreases while it increases slightly with acid concentration higher than 60%. Taking into account this slight increase of the carbon yield occurring in the acid concentration range 60-90% H_3PO_4. A concentration of 60%H3PO4 and an impregnation ratio of 1.5 seems to be the most suitable values for the development of the best carbon yield and consequently, to the best development of porosity.

In order to observe the effect of activation temperature on the yield of CCAC, the activation temperature was changed from 400℃ to 500℃.while all other activation parameters such as activation time and activation ratio were kept constant at 2h and 1.5 w/w (CCAC to H2SO4 ratio) respectively. As the activation temperature is increased from 400℃ to 500℃ the carbon yield also increases from 25 to 55.7%. However beyond 450℃ the yield of corn cob activated carbon showed decrease. Initially as the activation temperature is increased, rate of reaction between activating agent H_3PO_4 and CCAC is also increased which results in the enhancement of the carbon yield. Figure 4.6, showed that at 450℃, maximum the yield of 52.51% was obtained and this it might be the optimum activation temperature. The increase in the yield is due formation of porous structure which results in the attainment of high surface area. Also, at lower temperature, the rate of reaction between CCAC and H_3PO_4 will be slow and thus the yield is less as compared to yield obtained beyond 450℃ . The effect of CCAC to H_3PO_4 activation ratio for CCAC is presented in figure 4 6. Activation time, acid concentration and activation temperature were kept constant at 2h, 60% and 450℃, respectively. In figure 4.6 it is shown that as the CCAC to H_3PO_4 activation ratio is increased from 1 to 1:5 the yield of CCAC increases from 25% to 55.7%. Thus it is evident that CCAC to H_3PO_4 activation ratio significantly affects the yield of CCAC. The optimum CCAC to H_3PO_4 activation ratio it might be 1:5 at the activation temperature of 450℃, acid concentration of 60% and activation time of 2h.

Thus all the activation parameters such as activation temperature, activation time, acid concentration and impregnation ratio have notable effect on the adsorption yield of CCAC .(Buxton, 2007), Figure 4.6 shows the effect of the main process parameters(H_3PO_4 acid concentration, impregnation ratio and activation temperature) their mutual interaction on the performance of the prepared corn cobs activated carbon expressed in terms of yield.

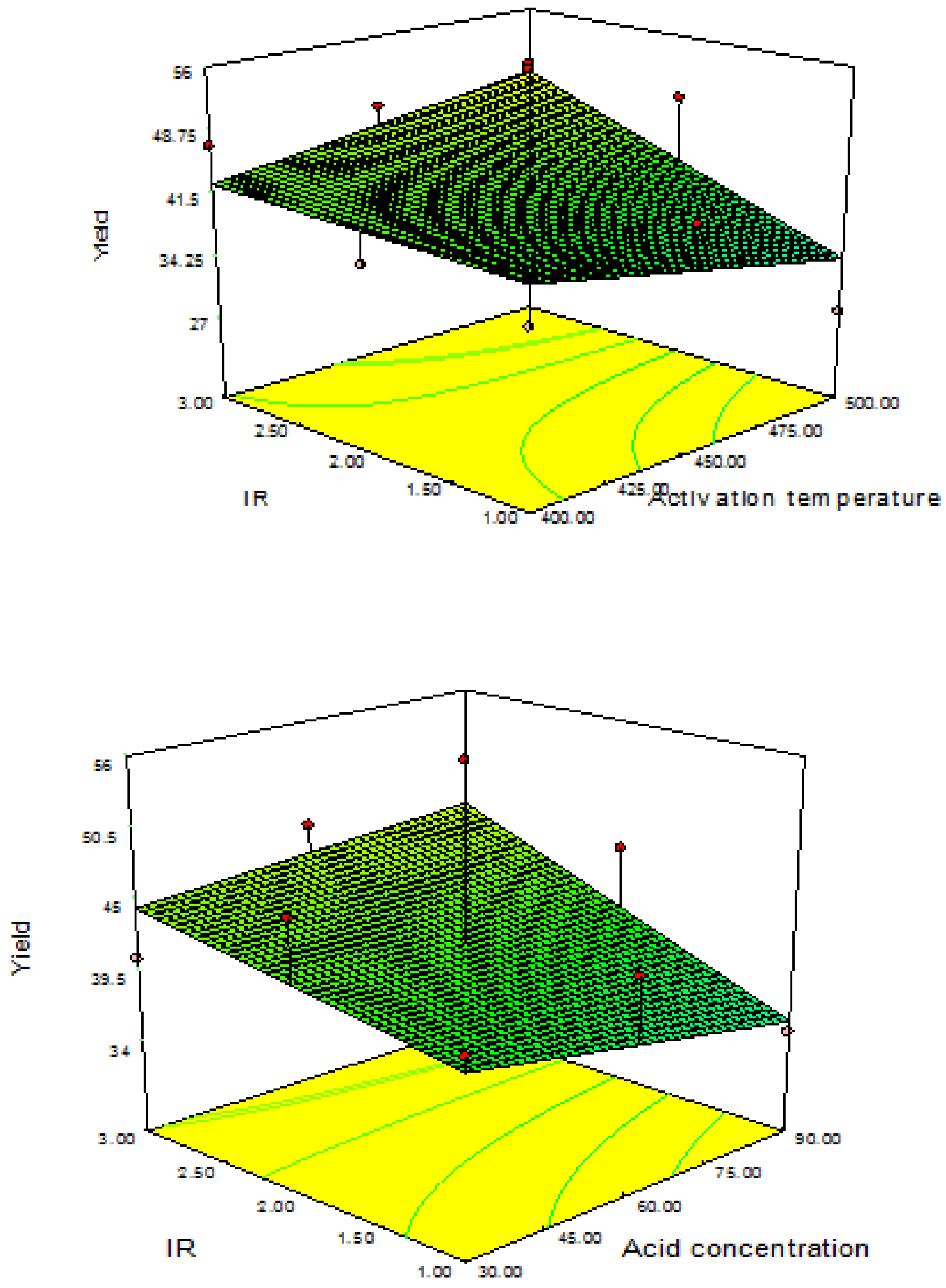


Figure 4-6; Effect of acid concentration and impregnation ratio on the CCAC yield

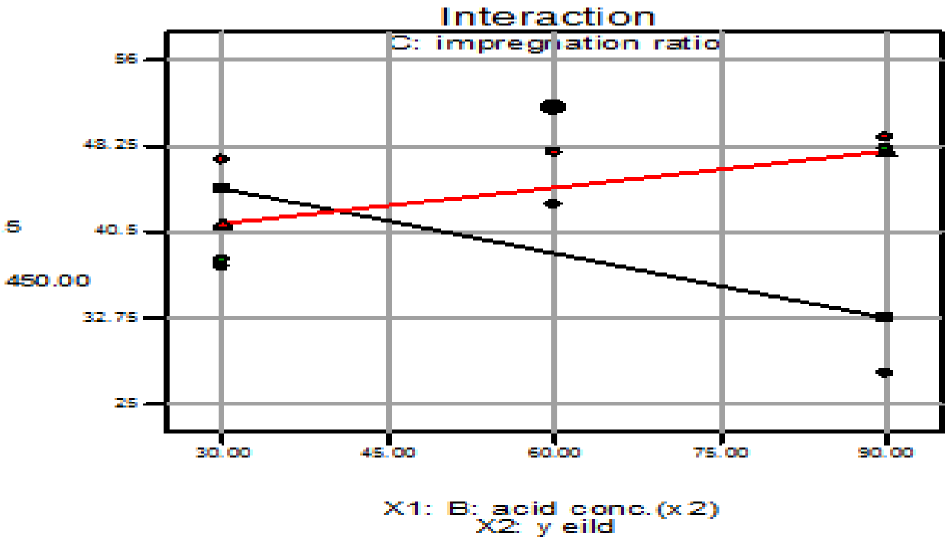


Figure 4-7; Interaction effect acid concentration and IR on the CCAC yield

From this graph you can see that all three factors work very well at the high acid concentratoin 60% and impregnation ratio of 1.5. None of the factors perform very well at the lowest temperature 400°C.

4.3.3. Effect of of independent variables on the iodine number adsorption of CCAC

The ANOVA analysis shown in the lower part of Table 4.4 proves the results discussed above at a confidence level of 95%. The regression model generated for the full factorial designs using the twenty seven runs conducted using each factors. As we observe the agreement between the experimental and the predicted values is excellent. This indicates that there is a linear relationship between the calculated iodine number adsorption and the three factors considered.

3-D surface plots and contour plots for the response variable were also generated and are shown in Figures 4.8 for iodine number. These graphs prove the validity of conclusions presented earlier regarding the interactions between the three factors.

Referring to F-value shown in Table 4.4 the main effect between the activation temperature and impregnation ratio were considered high.

The ANOVA for the 2F model for carbon yield of CCAC is listed in Table 4.4. The model F-value of 2.99 and Prob.>F of 0.0298 implied that this model was significant.

Table 4-4; ANOVA for iodine number adsorption of corn cobs activated carbon (CCAC):

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
Model	82337.64	6	13722.94	2.992851	0.0298
Activation temperature(x_1)	22840.97	1	22840.97	4.981412	0.0372
Acid concentration.(x_2)	8192	1	8192	1.786602	0.1963
Impregnation ratio(x_3)	45300.5	1	45300.5	9.879635	0.0049
x_1 x_2	752.0833	1	752.0833	0.164023	0.6898
x_1 x_3	5166.75	1	5166.75	1.126822	0.3011
x_2 x_3	85.33333	1	85.33333	0.01861	0.8929

The effects of activation temperature and impregnation ratio are the important factors that govern the development of micro porous of the prepared carbon. The effect of these two parameters on the iodine number illustrated in figure 4.7. As it can be seen the quantity of iodine number adsorbed increase with an increase of the activation temperature from $400\ to\ 450℃$ and an impregnation ratio from 1 to 1.5. Thus keeping the activation temperature around its optimal value $450℃$ leads to better development of the corn cobs activated carbon microporousity. Several investigation has established that in the case of H_3PO_4 activation of other agricultural wastes (woods, coconut shell, coffee husk, grain sorgum), temperatures neighboring 450 ℃ were also suitable to obtain optimal properties of the activated carbon.(Pradhan, 2011)

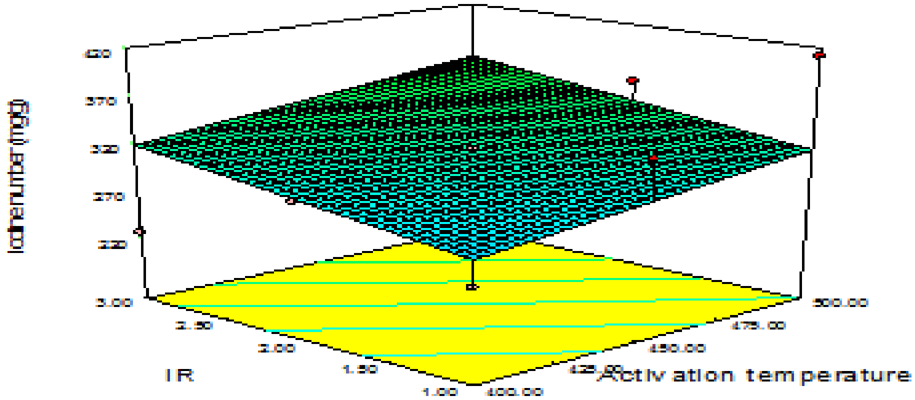


Figure 4-8; Effect of activation temperature and impregnation ratio on the iodine number

One of the main aims of this study was to find the optimum process parameters which CCAC produced should have a high carbon yield for heavy metal adsorption from waste water therefore, in order to do this the function of desirability was applied using Design-Expert software version 7.0. 0. In the optimization analysis the target criteria were set as maximum values for the responses of variable iodine number and CCAC yield while the values of the three variables were set in the ranges being studied. The above results show that the most efficient corn cob activated carbon is that obtained under the following optimal conditions: an acid concentration of 60% in weight, an impregnation ratio of 1.5 and activation temperature of 450℃ and the predicted and experimental results for corn cobs activated carbon response variables such as iodine number adsorption and carbon yield obtained from design of experiment was 528mg/g and 55.7% respectively. It was observed that the experimental values obtained were in good agreement with the values predicted from the models, with relatively small errors between the predicted and the actual values.

4.4. Batch Adsorption studies

The equilibrium adsorption capacity and removal efficiency were determined by using:

$$q_e = \frac{(c_o - c_e)}{m_{ac}} * V \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 4.1$$

$$E(\%) = \frac{(c_o - c_e)}{c_o} * 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.4.2$$

Where q_e (mg/L) is the equilibrium adsorption capacity, c_o (mg/L) is the initial concentration of lead ions in the solution, c_e (mg/L) is the equilibrium concentration of the lead ions in the solution, c_t is the concentration of lead ions in the solution at time t, V (L) is the volume of the lead solution, m_{ac} (g) is weight of activated carbon or the adsorbent. E(%) ;Removal efficiency.

The average of three repluction batch tests obtained results is tabulated in Table4.5 and the discussion of the result obtained from bath study is discribed below the table in detail.

Table 4-5;The average experimental design matrix for CCAC Pb+2 removal efficiency and adsorption amount from three replication data:

	Variables			Responses	
Run	Initial concentration(mg/l)	pH	Adsorbent dosage (g)	Average removal efficiency (%)	Average Adsorption amount (mg/g)
1	10	4	1	91.1	1.822
2	55	4	1	72.72	7.9992
3	100	4	1	43	8.6
4	10	5	1	91.8	1.836
5	55	5	1	78.2	8.602
6	100	5	1	53.5	10.7
7	10	6	1	87.5	1.75
8	55	6	1	71.22	7.8342
9	100	6	1	41.7	8.34
10	10	4	2	92.6	0.926
11	55	4	2	75.4	4.147
12	100	4	2	67.85	6.785
13	10	5	2	94.31	0.9431
14	55	5	2	81.74	4.4957
15	100	5	2	55.9	5.59
16	10	6	2	73.6	0.736
17	55	6	2	72.57	3.99135
18	100	6	2	43.8	4.38

19	10	4	3	93.82	0.625467
20	55	4	3	78.3	2.871
21	100	4	3	69.11	4.607333
22	10	5	3	96.8	0.645333
23	55	5	3	84.78	3.1086
24	100	5	3	57.9	3.86
25	10	6	3	74.6	0.497333
26	55	6	3	73.18	2.683267
27	100	6	3	48.11	3.207333

4.4.1. Effect of initial lead concentration on CCAC

The initial metal ion concentration provides an important driving force to overcome all mass transfer resistances of metal ion between aqueous and solid phases.

The capacity of the adsorbent increased significantly even though there is slight decrease in the adsorption efficiency with the increment of initial concentration. The increase of capacity can be due to increment of driving force that is concentration gradient, which causes an increase in the number of metal ions coming in contact with the adsorbent. On the other hand, the number of available adsorption sites in adsorbent is the same for all initial concentrations; thus, the initial concentration increases with more number of ions and the same change to be adsorbed and competes the same adsorption sites. This may cause to left many ions without being adsorbed and to decrease the efficiency of the removal upon increases the concentration of Pb^{2+}ions. (Khan et al., 2015)

Solutions of different lead (II) concentrations were prepared (10 mg/L,55mg/L, and 100 mg/L) from stock solution of 1000 mg/L. Parameters like contact time (2h), shaker rpm (150) and temperature ($25\pm2\ ^0C$) were kept constant for all the solutions of different concentrations. The effect of initial concentration was also considered to observe the trend of adsorption. The initial concentration of lead (II) in the solution is increased, percentage removal efficiency of the lead (II) decreases. The percentage removal efficiency of lead (II) decreases from 96.8% to 41% as the initial concentration is increased from 10 mg/L to 100 mg/L. The removal efficiency at a fixed adsorbent dose on the effect of initial concentration of Pb^{2+} ions is depicted in figure 4.9.

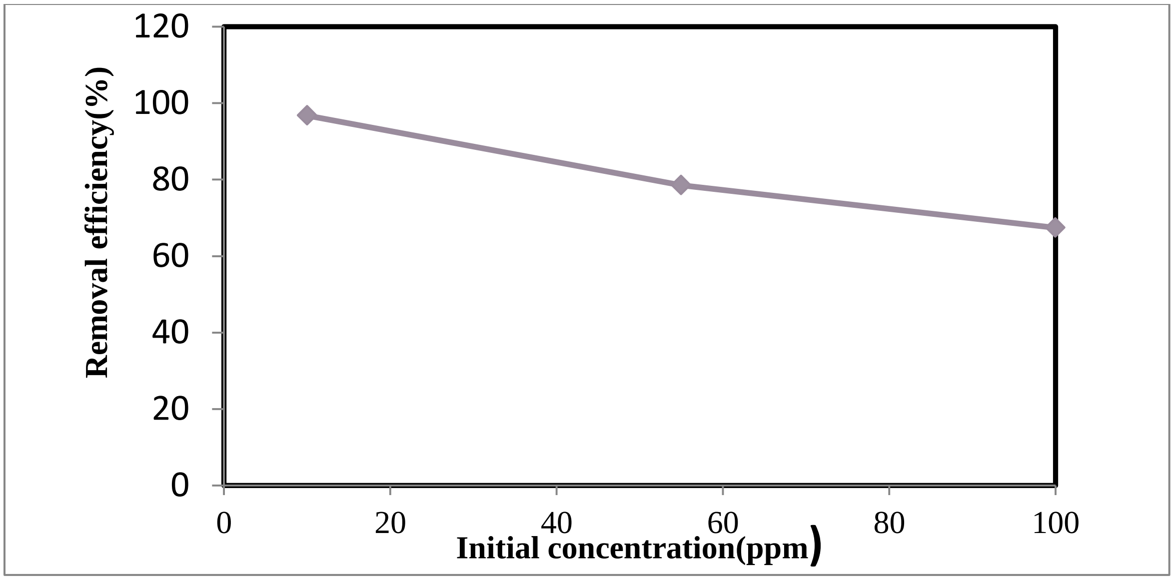


Figure 4-9; percent removal efficiency of Pb+2 as function of initial concentration of metal

4.4.2. Effects of contact time of Pb^{2+} adsorption on CCAC

Effect of contact time on the removal of lead is illustrated in figure 4.10 . It shows that the removal of lead increased with contact time and it was rapid at initial up to 30 minutes, and then it proceeds at slower rate of increases and finally attained saturation. This behavior suggests that at the initial stage adsorption was takes place rapidly on the external surface of the adsorbent followed by a slower internal diffusion process, which may be the rate determining step. The trend in adsorption of Pb^{2+}suggests that the binding may be through the interactions with the functional groups located on the surface of the carbon. Equilibrium adsorption was established at 60 minutes (for 30 mg/L) and 120 minutes for other studied concentrations of $^{Pb2+}$ion solutions respectively. It is clearly shows that the maximum contact time is required for greater uptake of metal ions by CCAC is depends on the initial concentrations of metal ion. It is evident that the contact time was fixed at 120 min for the batch experiments to make sure that equilibrium was attained. Thus, the % removal for 30, 55 and 100 mg/L of lead ions upon contact time 120 min. were 96.8 %, 95.2 % and 94.7 %, respectively. The results were demonstrated that at a fixed adsorbent dosage, the amount of adsorbate increased with increasing concentration of Pb^{2+}solution, but the percentage of adsorption was decreased. This is due to at lower concentrations, the ratio of number of metal ions to the available adsorption sites is almost fulfilled and subsequently the adsorption becomes greater. But, at higher concentrations of metal ions, however, the available sites on CCAC for adsorption become fewer and subsequently the removal of lead depends on the concentrations of $Pb^{2+}$and decreases with increase in initial Pb^{2+}concentration was good agreement with reported.(Farooq, 2013)

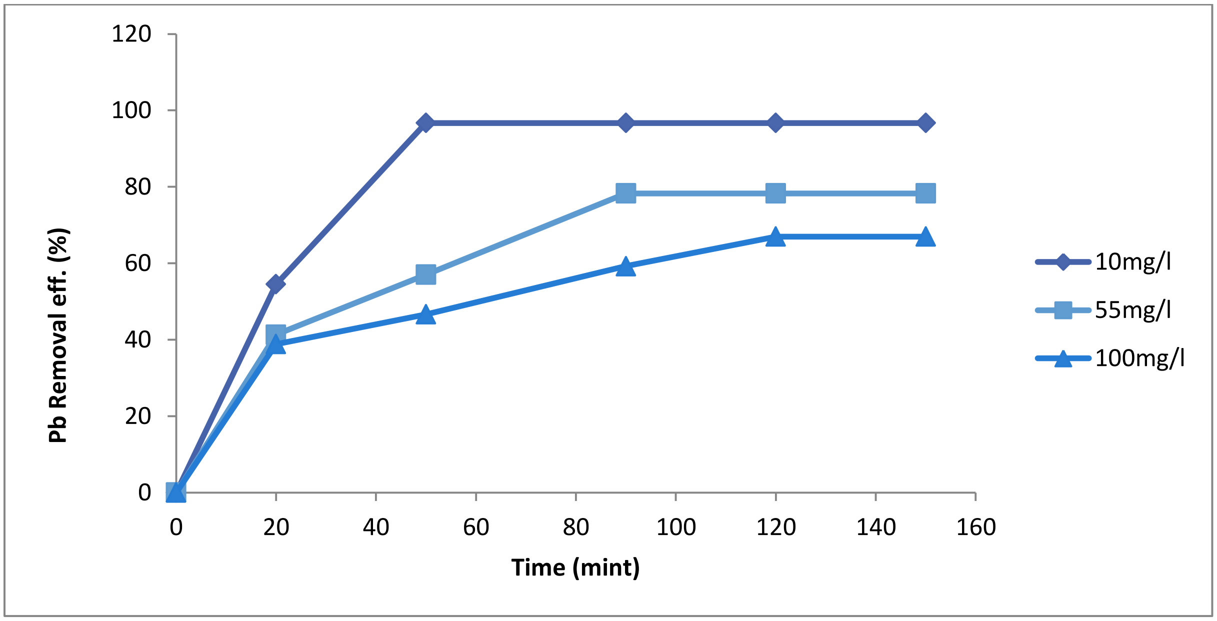


Figure 4-10; Effect of contact time on the removal efficiency of lead (II) by CCAC. Initial concentrations: 10mg/L, 55mg/l and 100mg/L; adsorbent dose: 3g and pH; 5:

4.4.3. Effect of pH on percentage adsorption

pH is an important parameter in the adsorption process. The pH of solution has a significant impact on metal uptake since it determines the surface charge of adsorbent and the degree of ionization and speciation of adsorbate.(Franca et al., 2013)

The effect of pH on the removal of lead was studied, and it is revealed that the solution pH does affect the amount of lead adsorption. The lead uptake was found to be increase with increasing pH. In this study the effect of pH was tested by changing pH of solution in the range of 4-6 in concentration of(10 -100 mg/L) as (shown in fig.4.11). Three different solutions (10 - 100 mg/L) of Pb^{2+}were studied, the maximum removal of lead appeared at pH 5 in all three solutions. Therefore, pH 5 was selected as optimum pH for further studies for the removal of Pb2+from it aqueous solution. In most of the studies, best pH for removal heavy metals was between 5-7. Increasing solution pH increases the rate of adsorption because of electrostatic forces. This process continued until pH reached to equilibrium pH after that, increasing pH did not show positive effect on increasing absorption. This is because of reduced mobility of ions resulting from changing the properties and its load . Lead (Pb) ion occupies the adsorption places soon due to its larger ionic radius. Enhanced adsorption with increasing pH from 4 to 6 suggests that adsorbents' surfaces become more negatively charged. This resulted in a more favourable electrostatic attraction forces and so, enhanced cationic metal ion adsorption as pH increased (Cho et al., 2005; Krishnani et al., 2008). In contrast, decreases in Pb2+adsorption at low pH values is due to an increase incompetition for adsorption sites by H+. This may be due to decrease in competition between hydronium ions and metal ions for the surface sites. This is also by the decrease in positive surface charge on the adsorbent, which resulted in a lower electrostatic repulsion between the surface and the metal ions and hence uptake of metal ions get increased. A similar theory was proposed earlier for metal adsorption on different adsorbent. It is also supported in an alkaline medium lead ions tend to hydrolyze and precipitate instead of adsorption on adsorbent. It was deteriorated with accumulation of metal ions, and making impossible true adsorption(Zayat & Smith, 2006)

Percentage adsorption was highest for the adsorbents at the acid pH and but equilibrium was attained at pH 6 as previously reported. (Length, 2009)

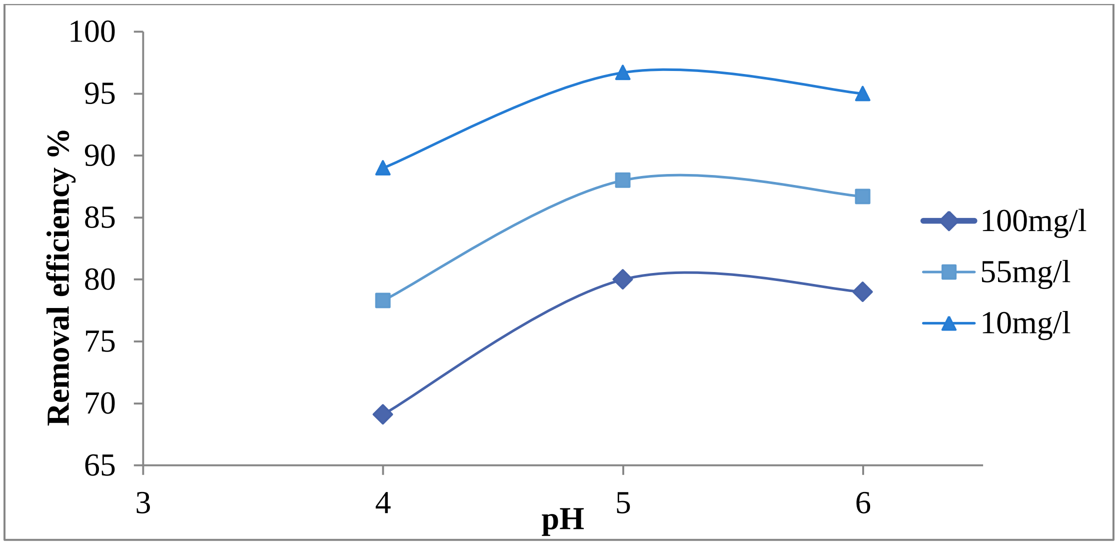


Figure 4-11; Effect of the pH on sorption of Pb+2 onto CCAC

4.4.4. The effect of adsorbent dosage on P_b^{+2} ions.

The dose of adsorbent is another important parameter in the adsorption process. As it can be seen from Figure 3, adsorption of Pb2+increased from 41 % to 96.8 % with increasing adsorbent dose from 1 g/L to 3 g/L, respectively. This is because for a fixed initial metal concentration, while increasing the adsorbent dose provides a greater adsorption sites. On the other hand, the plot of capacity (metal uptake per adsorbent unit) versus adsorbent dose revealed that the capacity was high at low doses and low at greater dose of adsorbent, which shows increase in adsorption with the growth of adsorbent. Similar results were reported (Khan et al., 2015) in adsorption of Pb^{2+}using bambo as adsorbent This result can be attributed to the fact that some of the adsorption sites remain unsaturated after the adsorption process. It might be because of formation of particle aggregation, resulting in a decrease in the total surface area and an increase in diffusion path length, which contribute to decrease in amount adsorbed per unit mass. Studies were indicating that the efficiency of (hydroxide) oxides to adsorb heavy metal ions is due to their high surface/mass ratio . (Ademiluyi & Nze, 2016), Even if the up-take of the metal increased by increasing the adsorbent dose, beyond a dose of 3 g/L of CCAC, and the rise of the adsorption efficiency is insignificant and the capacity of adsorbent is very low. The removal of lead (II) increased with an increase in the adsorbent dosage up to a certain level and then it remains almost constant. This is expected because of the increase in the adsorbent surface. Therefore,3g/L of adsorbent dose was taken as an optimum dose for further experiments.

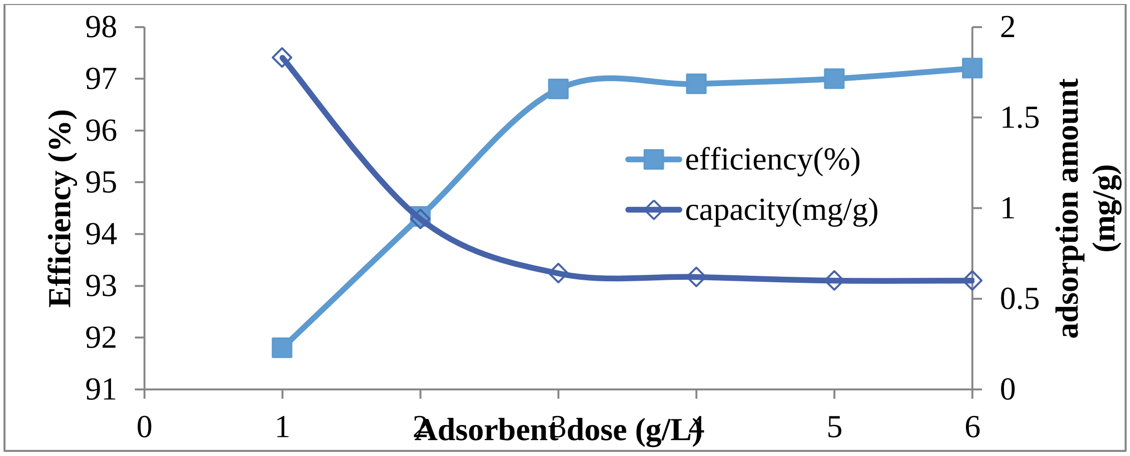


Figure 4-12; Adsorption amount and removal efficiency of Pb2+ at different adsorbent dose

4.4.5. Development of Regression Model Equation for Batch Adsorption Study

The effect of the CCAC removal efficiency and adsorption amount were analyzed regarding the different conditions was optimized using design of experiment in this section and operational parameters with optimum removal efficiency and adsorption amount were predicted using developed model. Accordingly, first model development and evaluation was discussed. Second the effect of independent variables on response variables was examined. Then finally using the model optimum points of operational parameters were predicted. Full factorial design used to develop a polynomial regression equation in order to analyze the correlation between corn cob activated carbon (CCAC) to the lead removal efficiency and adsorption amount.

For response corn cobs activated carbon Pb^{+2} removal efficiency and adsorption capacity the two -factor interaction (2FI) model was selected as suggested by the software.

The coefficient with one factor represents the effect of the particular factor, while the coefficients with two factors and those with second-order terms represent the interaction between two factors . The quality of the models developed was evaluated based on the correlation coefficients, R^2 statistics which is closer to unity as it will give predicted value closer to the actual value for the responses.(Dowlatshahi, Torbati, & Loloei, 2014)

4.4.5.1. Analysis of variance

The significance and adequacy of the models were further justified through analysis of variance (ANOVA).

Table 4-6; ANOVA for corn cobs activated carbon removal efficiency Pb+2 ions:

ANOVA for Response Surface 2FI Model					
	Sum of		Mean	F	
Source	Squares	DF	Square	Value	Prob > F
Model	6443.64	6	1073.94	24.94	0.0001
A	5521.6	1	5521.6	128.24	0.0001
B	529.43	1	529.43	12.3	0.0022
C	116.84	1	116.84	2.71	0.0151
AB	1.71	1	1.71	0.04	0.044
AC	147.7	1	147.7	3.43	0.0388
BC	126.36	1	126.36	2.93	0.1022

The ANOVA for the two -factor interaction (2FI) mod el for lead removal efficiency of CCAC is listed in Table 4.7 above.

This study has also demonstrated a statistically significant difference between PH, initial concentration of lead ions and adsorbent dosage .Considering factor interactions, the three factors of removal efficiency were analysed for developing a model equation that can be used in order to develop the laboratory scale finding to an application scale. The ANOVA for the data entered proved the model to be significant In relation to this factor interactions were points of interest and the factors coded showed significant effect. The model F-value of 24.94 and Prob.>F of 0.0001 implied that this model was significant. In this case, A, B, C. AB, and AC., were the model terms that showed significant effect. Whereas BC were insignificant to the response. A related parameter called "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Here ratio of 15.256 indicates an adequate signal. Therefore, this model can be used to navigate the design space .Furthermore; in this experiment, the R^2value was 0.88 which, in another check, implied the model to be significant.

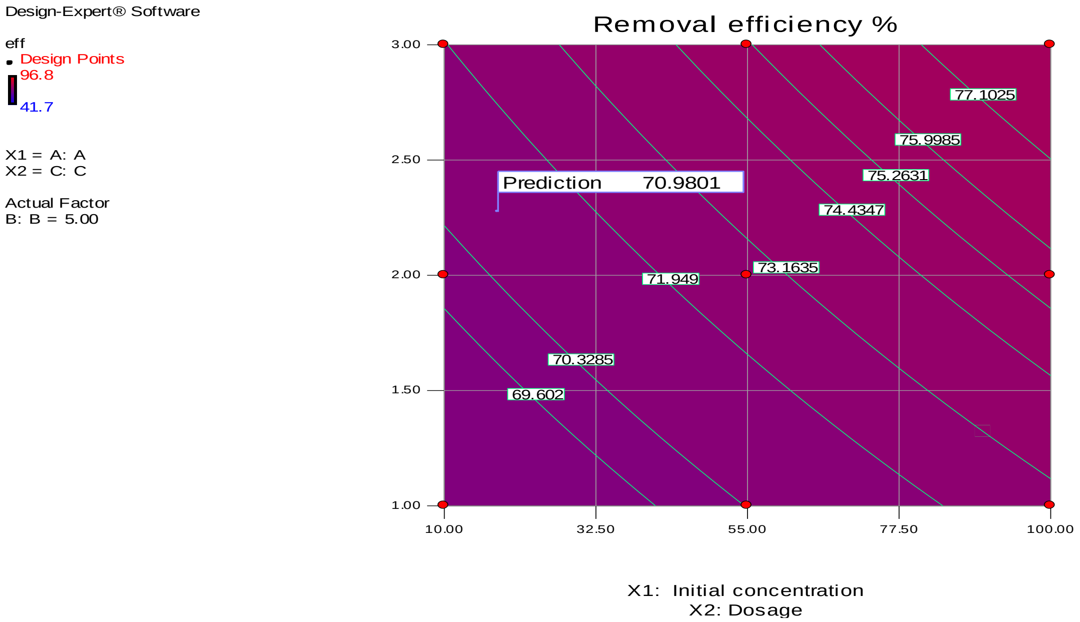
Table 4-7;ANOVA for corn cob activated carbon adsorption amount of Pb+2 ions:

Response	2	Adsorption amount			
ANOVA for Response Surface 2FI Model					
Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
Model	611.509459	6	101.918243	25.35	< 0.0001
A-Initial conc,	357.0322	1	357.0322	88.8	< 0.0001
B-PH	4.09005048	1	4.09005048	1.02	0.0362
C- dosage	208.656299	1	208.656299	51.89	< 0.0001
AB	3.35775023	1	3.35775023	84	0.0429
AC	38.0076381	1	38.0076381	9.45	< 0.0001
BC	0.36552121	1	0.36552121	92	0.036

From the ANOVA for adsorption amount of CCAC as shown in Table4.7 the model F-value of 25.35 and Prob.>F of 0.0001 revealed that the model was also significant. In this case A, B,C, AB ,AC and BC are significant to the response.

4.4.6. Effect of Independent Variables on Lead removal efficiency

Based on the F-value as shown in Table 4.7,the main effects; initial concentration, adsorbent dosage and p^H was found to has significant effect compared to interaction effects on the Lead removal. In addition, the quadratic effect of adsorbent dosage was considered high. Figure4.13(a) shows the interaction effects between initial concentration and activation pH, whereas Figure 4.13(b) shows the three -dimension response surfaces which was constructed to show the interaction effects of the initial concentration and adsorbent dosage on the lead (Pb^{+2}) removal efficiency. The contour plot was constructed to show the interaction effect of the response for selected factors in two dimensions.



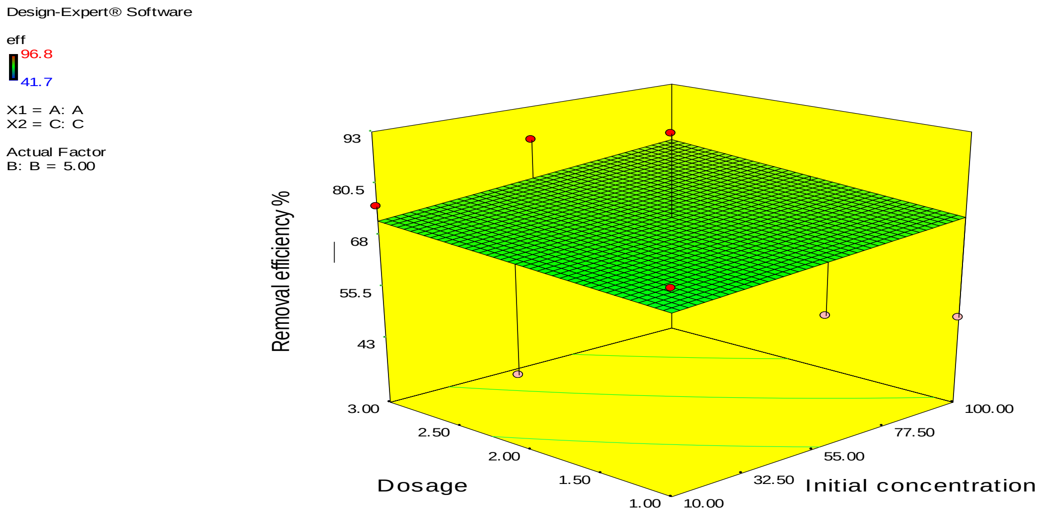


Figure 4-13; Contour and 3D plots showing the effect of initial concentration, and adsorbent dosage on removal efficiency

From fig 4.13 the highest lead removal was predicted when the initial concentration 10mg/l, adsorbent dose 3g and p^H 5 respectively.

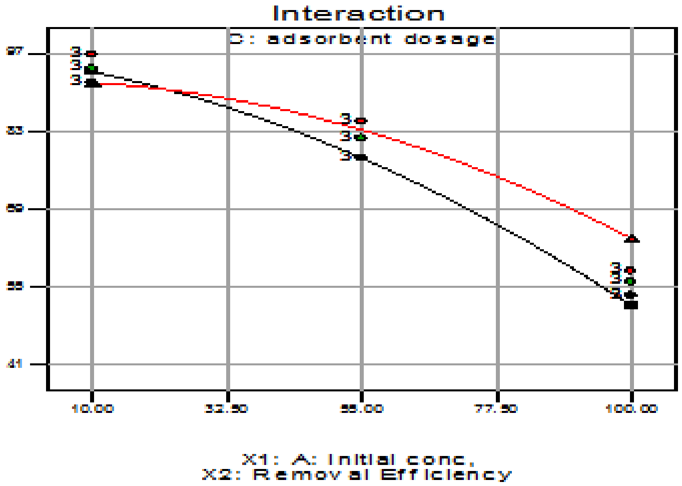


Figure 4-14; Interaction effects of initial concentration and adsorbent dosage for removal efficiency of Pb+2 ions

From the interaction graph observed that as initial concentration increase and adsorbent dose decrease the removal efficiency also decrease.

4.4.7. Effect of independent variables on adsorption capacity

Referring to F-value shown in Table 4.5 , initial concentration and adsorbent dose imposes the greatest effect on adsorption capacity. The interaction effects between the initial concentration and adsorbent dose were considered high.

Figure 4.15 showed that the adsorption amount decrease with increasing adsorbent dose from 1g to 3 g and increase with increasing initial Pb^{+2} concentration from 10 to 100mg/l and the maximum adsorption amount obtained at 1g corn cob activated carbon dosage ,p^H 5 and initial Pb^{+2} ions concentration from 100mg/l in present study. It might be conclude that the adsorption amount increase with increase of initial concentration and with decrease of adsorbent dosage due to fact that the adsorbent has a limit number of active sites.

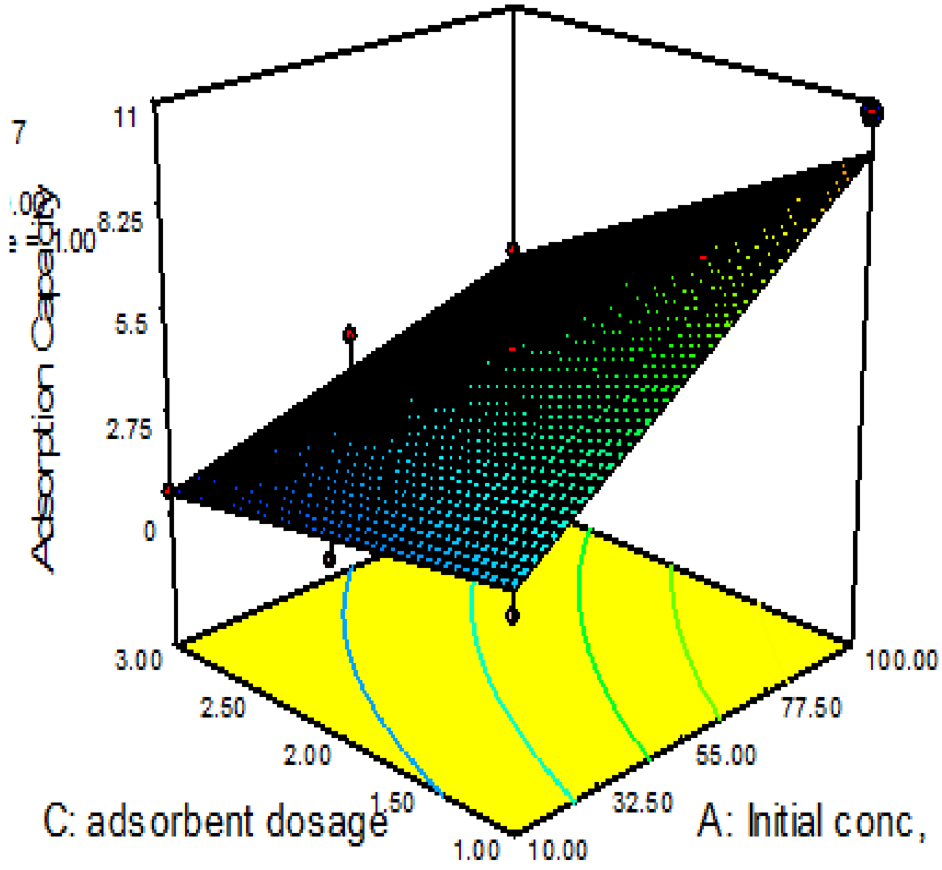


Figure 4-15; Plots showing the effect of initial concentration, and adsorbent dosage on adsorption amount:

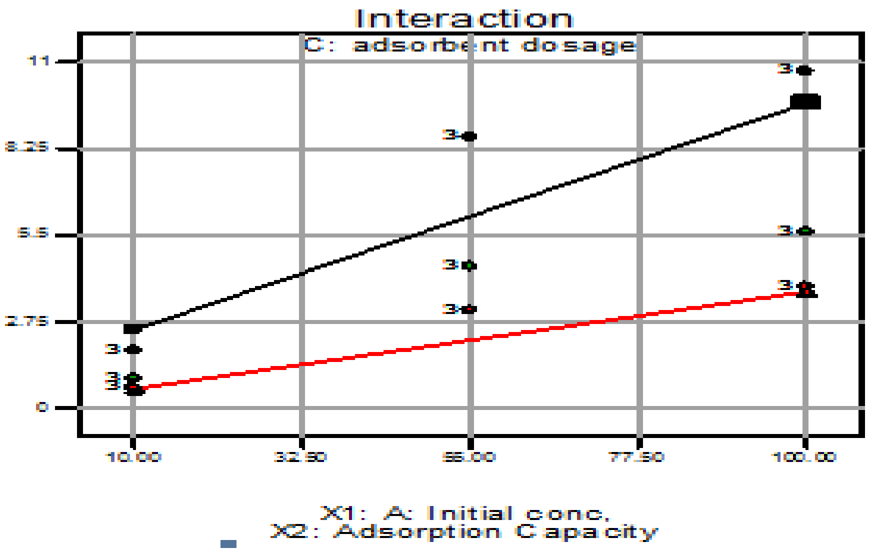


Figure 4-16; Interaction effects of initial concentration and adsorbent dosage for adsorption capacity:

4.4.8. Process optimization by design of experiment for batch adsorption tests

One of the main aims of this study was to find the optimum process parameters which CCAC produced should have a high lead (Pb^{2+}) removal efficiency and adsorption amount. However, it is difficult to optimize both responses under the same condition because the interest region of factors is different. When removal efficiency increases, adsorption capacity of CCAC will decrease and vice versa. Therefore, the function of desirability was applied using Design-Expert software version 7.0.0, in order to compromise between these two responses. In the optimization analysis, the target criteria was set as maximum values for the two responses of lead removal efficiency and CCAC adsorption amount while the values of the three variables were set in the ranges being studied. The experiment conditions with the highest desirability were selected to be verified. The predicted and experimental results of lead removal efficiency and CCAC adsorption capacity obtained at optimum conditions are listed in Table.4.8.

In order to estimate the confidence interval for the metal removal in this experiment, I tested the lead removal five times under the same conditions (initial concentration of $Pb^{2+}$and CCAC were 10mg/l and 1g, respectively.

The results are shown as follow: Lead removal: {96.8%, 97.94%, 98.52%, 96.87%, 99.42%} for illustration, I used t-distribution to find a 95% confidence interval for the lead removal using CCAC as an adsorbent.

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} xi = 97.91 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.3$$

$$S^2 = \sum_{i=1}^{n} \frac{(xi-\bar{x})^2}{n-1} = \frac{1}{n-1}\left\{\sum_{i=1}^{n} xi^2 - \frac{1}{n}\left(\sum_{i=1}^{n} xi\right)^2\right\} = 0.01914875\% \ldots\ldots\ldots\ldots 4.4$$

$$1-\alpha = 95\% \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.5$$

$$t_{\alpha/2}, n-1 = t_{0.025,4} = 2.774$$

$$\bar{x} \pm t_{\alpha/2}, n-1 * \sqrt{\frac{S^2}{n}} = 97.91\% \pm 2.774 * \sqrt{\frac{0.01914875}{5}} = 97.91\% \pm 0.172\%$$

So we have a 95% confidence that the true lead removal in this experiment will locate in the interval [97.74%; 98.082%].

In this experiment, the main source of error comes from the batch to batch difference

Table 4-8 predicted optimum conditions for selected parameters using design of experiment

Predicted optimum conditions	
Variables	optimum value
Initial concentration	10.13mg/g
p^H	5.08
Adsorbent dosage	1.002g
Lead removal efficiency	97.911%
Adsorption amount	9.62mg/g

The optimum lead removal efficiency of 96.8% by corn cobs activated carbon was obtained by using initial concentration , pH and adsorbent dosage ; 10mg/l , 5 and 3g respectively. The optimum adsorption amount showed 10.7 mg/g by corn cobs activated carbon obtained by using initial concentration, p^H and adsorbent dose ; 10mg/l, 5 and 3g respectively.

It was observed that the experimental values obtained were in good agreement with the values predicted from the models, with relatively small errors between the predicted and the actual values, which was less than 5% for both response.

4.5. Adsorption isotherm

The results obtained on the adsorption of Pb^{2+} ions with different adsorbent dose and fixed initial concentrations and p^H were analysed by using the models given by Langmuir and Freundlich which correspond to homogenous and heterogeneous adsorbent surfaces, respectively.

4.5.1. Langmuir's isotherm

Langmuir's isotherm calculated using equation 3.18 stated in methodology section and the result is tabulated in table 4.9 below.

Table 4.9; Langmuir Isotherm for Adsorption of Pb^{2+} ions using corn cobs activated carbon:

Table 4-9; Langmuir Isotherm for Adsorption of Pb2+ ions using corn cobs activated carbon:

Ce	Qe	1/qe	ce/qe
0.32	0.645	1.55	0.496124
8.371	3.1086	0.32	2.692852
42.1	3.86	0.26	10.90674

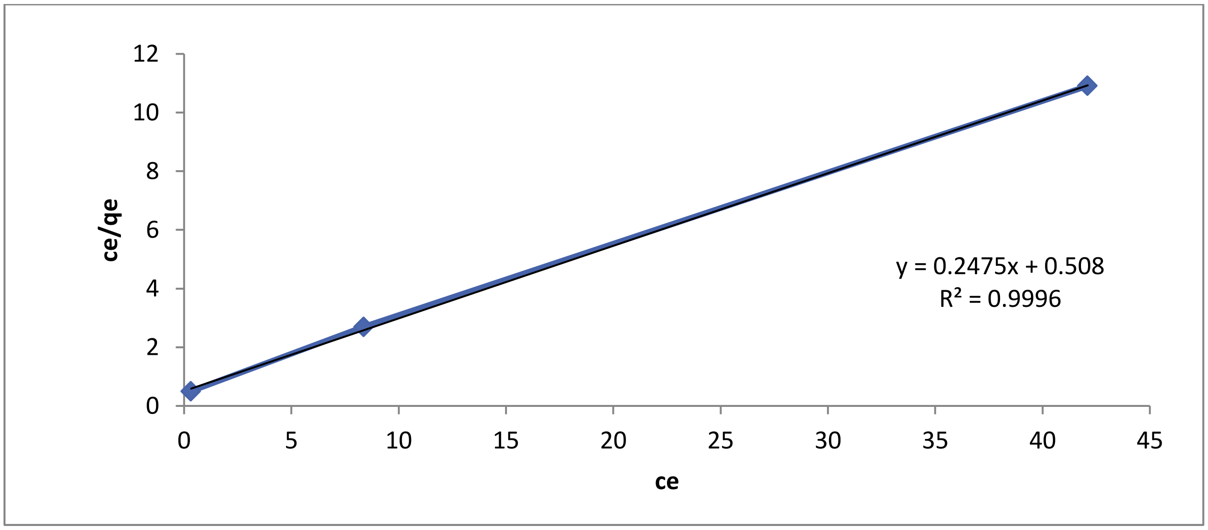


Figure 4-17;Langmuir adsorption isotherm for adsorption of Pb2+ on CCAC pH: 5 temperature: 250C; adsorbent dose: 3g; contact time: 2h

Fig 4.17 gives the linear plot of the ratio of equilibrium concentration to mass of the adsorbent versus equilibrium concentration.

The plot has R^2 value of 0.9996 with a slope and intercept values of 0.2475 and 0.508 respectively. The values of the Langmuir constants (b, and Q_o) for the adsorption of Pb^{2+} ion using corn cob activated carbon were determined from the slope and intercept values are shown in Table 4.11.

4.5.2. Freundlich isotherm

Freundlich isotherms are displayed in a logarithmic scale. By taking the logarithmic equation 3.19 and result is tabulated in Table 4.10. Figure 4.19 shows plot of $\boldsymbol{log\ q_{eq}}$versus $\boldsymbol{log\ C_{eq}}$in order to determine the Freundlich isotherm constants.

Table 4-10;Freundlich Isotherm for Adsorption of Pb2+ ions using corn cob activated carbon:

ce	qe	1/qe	ce/qe	logqe	logce
0.32	0.645	1.55	0.496124	-0.19	-0.495
8.371	3.1086	0.32	2.693	0.493	0.923
42.1	3.86	0.26	10.90674	0.587	1.63

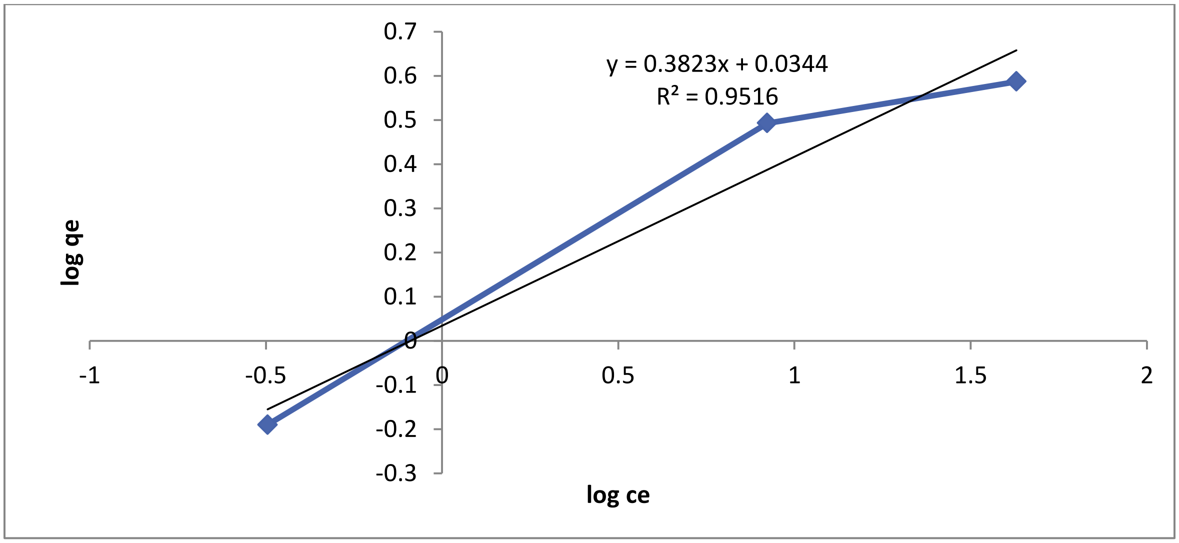


Figure 4-18;Freundlich adsorption isotherm for adsorption of Pb+2 on CCAC. Initial pH: 5; temperature: 250C; adsorbent dose: 3g/ and contact time 2hr

Table 4.11 gave the values of the equilibrium concentration, c_e the amount adsorbed q_e and the logarithm of c_e and q_e at the various initial concentrations of the Pb^{+2}ion. These values were achieved by keeping other parameters (pH, time, temperature and dose) constant and varying the concentration from 10 to 100 mg/L. Fig. 4.18 shows the linear plot of log q_e versus logc_e with R^2value of 0.9516, with values of slope and intercept of 0.3823 and 0.0.0344 respectively. The Freundlich parameters (K_F and n) for the adsorption of Pb(II) ion onto corn cob activated carbon are determined from the slope and intercept values of the equilibrium data well fitted in this isotherm as compared to Langmuir isotherm this plots were tabulated in Table 4.11

Table 4-11;Values of Langmuir and Freundlich adsorption Isotherm Parameters and Coefficient of Regression, R2 for Lead ion adsorbed by Activated Carbons from corn cob.

Isotherm model	Parameters	Values
Langmuir	q_o (mg/g)	4.04
	b(L/mg)	0.49
	R^2	0.9996
Freundlich	K_f(mg/g)	1.08
	n_f	2.6
	R^2	0.9516

The table displays the adsorption parameters of Langmuir and freundlich for lead adsorption onto corncobs activated carbons derived from the linear plots of the two isotherms it might be seen from the table that high value for q_o(mg/g) and b((L/mg), (related to energy/rate of adsorption) was obtained from Langmuir isotherm plot . From the high values of coefficient of regression $R^2 = 0.9996$ obtained for the adsorption of the metal ions (Pb^{+2} it was clear that adsorption of lead onto activated carbons derived from these adsorbents obey Langmuir isotherm model. Therefore, the isotherm parameters together with the correlation coefficients (R^2) of the Langmuir equation for the adsorption of Pb^{+2} ions on the adsorbent showed that the Langmuir equation gives a better fit to the adsorption Isotherm than the Freundlich. Th Freundlich parameters. n gives an indication of the favourability and capacity of the adsorbent/ adsorbate system. In Table 4.11, the values of n for lead adsorption were 2.6, for corn cobs activated carbon. According to (Renge et al., 2012) values of n (which reflects the intensity of adsorption) ranging between 2 and 10 represents favourable adsorption. Therefore, the results obtained are consistent with the requirement for favourable adsorption since they were within the range of 2 to 10. However, the higher values of R^2 obtained from Langmuir Isotherm plots compared to Freundlich plot suggests that Freundlich model gave a poorer fit to the experimental data than the Langmuir isotherm model

Form this study we obtain behavior of the adsorbent, Langmuir and Freundlich adsorption isotherms were plotted, and On the basis of the obtained correlation coefficients, it can be concluded that the adsorption of ions studied on prepared adsorbent given to the correlation coefficient higher than 0.9996 follows Langmuir isotherm.

4.6. Adsorption kinetic

The kinetic data was obtained from the adsorption of Pb^{2+}ions on CCAC. This was studied by includes the common kinetics such as pseudo-first order, and pseudo-second order models.

The best fit model was selected based on the linear regression correlation coefficient (R^2).

The pseudo-first and second order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The pseudo-first and second order results was calculated mathematically according to equation 3.20 and 3.21 as described in methodology section and tabulated in table 4.12 below. The pseudo first and second order kinetics of $Pb^{2+}$was studied for different concentrations of Pb^{2+}, results were obtained and presented in figure 4.19 and 4.20 below.

4.6.1. Pseudo-first order kinetic model

Table 4.23 reveals the values of, experimental and calculated values of q_e as well as the R^2values for the pseudo-first order kinetic plots. As can be seen, also the R^2 values obtained from the plots were high. The calculated values of q_e were far lower than the corresponding experimental data obtained. This suggested that a poor fit between the kinetics data and the pseudo-first order model. These results were confirmed that this adsorption system is not follows a pseudo first order reaction.

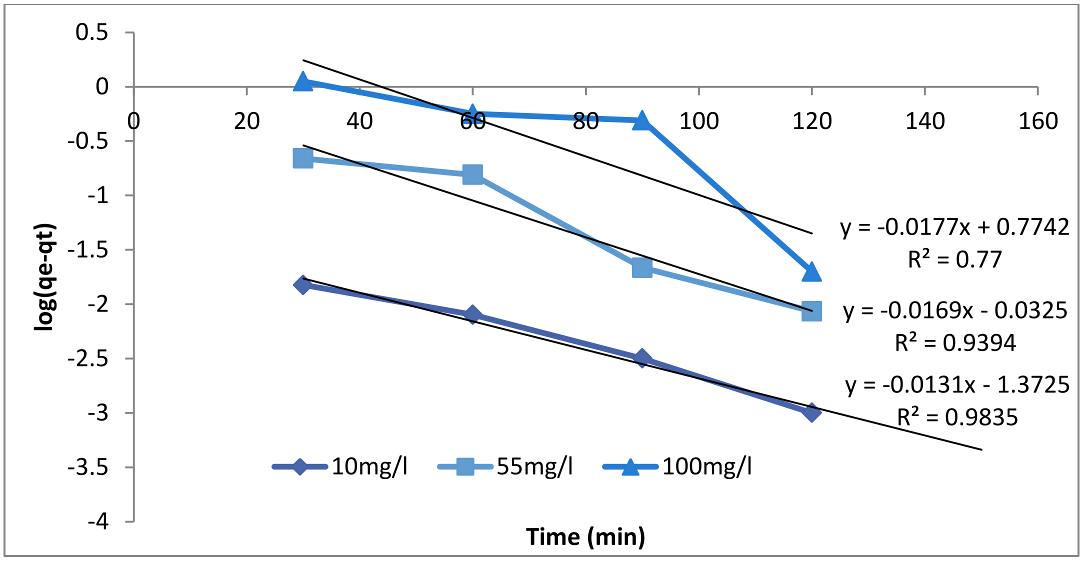


Figure 4-19Shows the linear plots of log(qe-qt) against t at initial metal ion concentration of 10 mg/L, 55 mg/L and 100 mg/L.

The k1 and qe values were determined from the slope and intercept of the linear plots respectively and given in table 4.12.

4.6.2. Pseudo-second order kinetic model

The adsorption kinetics may also be described by a pseudo second order. The pseudo second order is based on the assumption that the rate limiting step may be chemical sorption involving valence forces through sharing or exchange of electrons between heavy metal ions and adsorbent

The pseudo second order kinetic model was studied with different concentrations and the results were described in figure 4.20. The figure does give the linear plots of $\frac{t}{q_e}$ against t at all studied concentrations of Pb^{2+}solutions. The values of q_e and $k_2$were calculated from the slope and intercept of the respective plots, and also calculated the k_2 for each plots are presented in table.4.12.

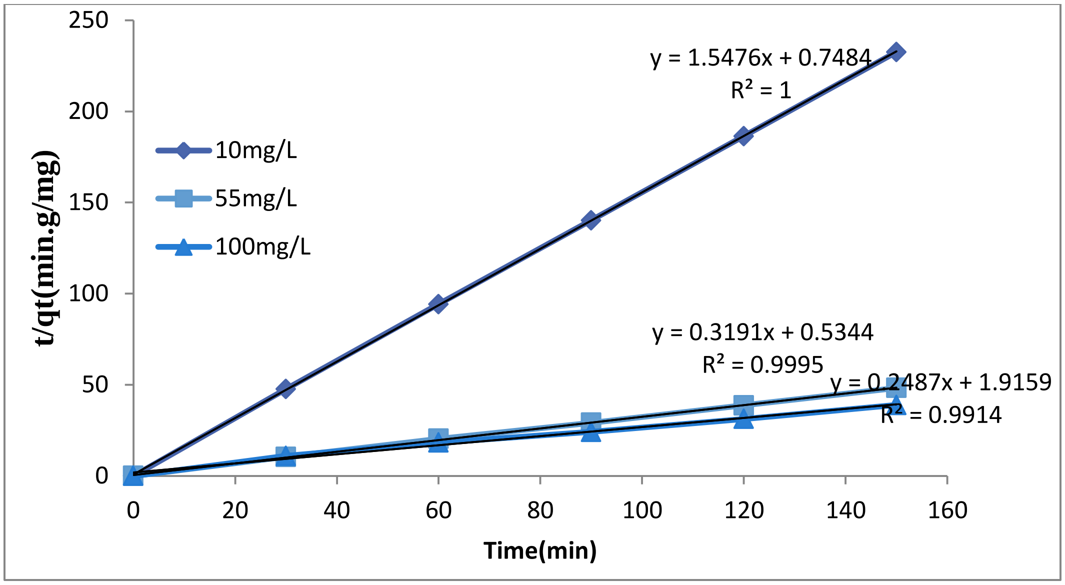


Figure 4-20; Showed the linear plots of t/qt against t at initial metal ion concentration of 10 mg/L, 55 mg/L and 100 mg/L

The k_2 and q_e values were determined from the slope and intercept of the linear plots respectively and given in table 4.12

Table 4.12; reveals that all three linear plots with different initial concentrations of Pb^{2+}(shown in fig.4.20) have R^2values of 1. This indicates that the kinetics data fitted perfectly well with the pseudo second order model. In addition to the high values of R^2, the calculated q_e values also almost agreed well with the experimental data obtained from the pseudo second order kinetics. From table 4.12 also observed that the values of $'h'$ increased from 0.68 to 6.15 when the initial concentration of Pb^{2+}ions increased from 10 mg/L to 100 mg/L respectively. This was because the higher the initial concentration of Pb^{2+}ions, the greater chances of collision with the binding sites of adsorbent and hence leads to a higher initial sorption rate. The values of k2 was observed as higher than the corresponding values of k1. So, the pseudo second order kinetic model assumed as the best fit for this adsorption studies and also the sorption rate is proportional to the square of number of unoccupied sites.(Khan et al., 2015) In addition, the values of k_2 get decreases from 2.068 g/mg min to 0.413 g/mg min with increasing the initial concentration of Pb^{2+}. This is occurred because at higher concentration of metal ions, the competition for surface active sites was high and consequently lower sorption rates are obtained. The similar result was reported earlier.(Farooq, 2013).The pseudo-second order kinetic model was also reported to fit well with the kinetics data from studies of a number of authors, including the adsorption of Cd^{2}+ions on jatropha peel , (Mohammad, Yaakob, Rozaimah, & Abdullah, 2013), adsorption of Cu^{2+} ions on Tectona grandis leaves (Kyzas & Kostoglou, 2014) , adsorption of Pb^{2+} ions on pump kin seed shell activated carbon , adsorption of Ni^{2+}ions on potato peel, and adsorption of Cr6+ ions on cooked tea dust.(Kundu, Redzwan, & Sahu, 2014)

Table 4-12; Pseudo first and second order kinetics and constant value at different metal concentration and at constant pH- 5, and 3 g/l of adsorbent dose at 25℃:

	Pseudo first order				Pseudo second order				
	$K1^{min-1}$	$q_e(\frac{mg}{g})$		R^2	$K_2(\frac{g}{mg})$	$q_e(\frac{mg}{g})$		h (mg/mg)	R^2
		Exp.	Calc.			Exp.	Calc.		
10	0.04	0.645	5.94	0.77	2.068	0.645	0.6462	0.863	1
55	0.0389	3.1086	0.93	0.9394	0.597	3.086	3.314	5.864	0.9995
100	0.03	3.86	0.0424	0.9835	0.413	3.86	4.02	6.15	0.994

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Based on the result obtained within the frame work of this study it appears that the activated carbon prepared from corn cobs constitutes a good adsorbent for removing of heavy metal Pb^{2+}ions from it aqueous solution. The main conclusions that can be drawn from current investigation are given below: The optimum pH for lead removal was found to be 5. The percentage uptake was found to be highly dependent on the initial concentration of the adsorbate and sorbent fractional adsorption becomes dependent on initial concentration. For fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of sorbate thus resulting decrease in percentage removal of the adsorbate corresponding to an increase initial sorbate concentration.

Adsorption capacity of adsorbate had seen to decrease with increasing adsorbent dose while the efficiencies increased. In addition, a decrease in efficiency of adsorbent was observed with increasing initial metal ion concentration. This study indicated that lead ion could be removed by an inexpensive agricultural waste product—the CCAC with the minimum equilibrium time<2h.

This result is also confirmed in the ANOVA analysis given by the p-value. For the selected response variables studied using the regression models generated, good agreement between the experimental and predicted values was observed.

The adsorption process follows the Langmuir model isotherm provides the best correlation of (R^2) of 0.9996 .It indicates a monolayer formation over a surface of the material.

Kinetic data for the adsorbent follows a pseudo second-order model. Results indicated that Pb^{2+}ions adsorption kinetic study proved the applicability of the pseudo-second order model. This is confirmed by the calculated correlation coefficients.

It can therefore be concluded that agricultural by-products which are inexpensive, readily available are the effective adsorbents for the adsorption process is expected to be economically for wastewater treatment.

5.2. Recommendation

Further research needs

From the knowledge and insight gained during the course of this work, the following future work is recommended in the production and application of activated carbon from corn cob for removal of heavy metal from waste water.

- For future research, it is recommended Batch kinetic studies at various temperatures and agitation speed may be conducted to determine thermodynamic parameter for lead adsorption on corn cobs as they were kept constant in this work.
- Based on the current work, pilot studies should be considered for future research through column studies using industrial wastewater containing lead ions and other metals to investigate effect of competitive adsorption on lead and other metals.
- As Lead is not the only metals found in Battery industry wastewater, studying the adsorption efficiency of CCAC and other metals is also recommended.
- Some other characteristics of corn cobs ,useful in wastewater purification, should be investigated, such as for removal of suspended solids, dissolved solids, BOD,COD, free chlorine, and kjedahl nitrogen(TKN)
- More studies are needed to optimize the system from the regeneration point of view, to investigate the economic aspects and to confirm the applicability of this new sorbent under real conditions, such as in the industrial effluent treatment.

REFERENCE

Abas, SN, Ismail, MH, Kamal, ML and Izhar, S. 2013. Adsorption Process of Heavy Metals by Low-Cost Adsorbent: A Review. World Applied Sciences Journal, 28(11), 1518-1530.

Abdel-Ghani, N. T., Hefny, M., & El-Chaghaby, G. a. F. (2007). Removal of lead from aqueous solution using low cost abundantly available adsorbents. *International Journal of Environmental Science & Technology*, *4*(1), 67–73.

Abdualaziz, N., Hamza, E., Hammad, A. Y., & Eltayeb, M. A. (2013). Adsorption of Metals (Fe (II) , Cr (III) and Co (II)) from aqueous solution by using Activated carbon prepared from Mesquite tree, *1*(2), 12–20.

Ademiluyi, F. T., & Nze, J. C. (2016). Multiple Adsorption of Heavy Metal ions in Aqueous Solution Using Activated Carbon From Nigerian Bamboo.

Adie, D. B., Olarinoye, N. O., Oke, I. A., Ismail, A., Lukman, S., & Otun, J. A. (2010). Removal of lead ions from aqueous solutions using powdered corn cobs. *Canadian Journal of Chemical Engineering*, *88*(2), 241–255.

Aeisyah, A., Ismail, M. H. S., Lias, K., & Izhar, S. (2014). Adsorption process of heavy metals by low-cost adsorbent: A review. *Research Journal of Chemistry and Environment*, *18*(4), 91–102.

Agbozu, I. E., & Emoruwa, F. O. (2014). Batch adsorption of heavy metals (Cu , Pb , Fe , Cr and Cd) from aqueous solutions using coconut husk. *African Journal of Environmental Science and Technology*, *8*(April), 239–246.

Ahluwalia, SS and Goyal, D. 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. Bioresource technology, 98(12), 2243-2257.

Ahmaruzzaman, M. 2009. Role of fly ash in the removal of organic pollutants from wastewater. Energy and Fuels, 23(3), 1494-1511

Alfarra, RS, Ali, NE and Yusoff, MM. 2014. Removal of heavy metals by natural adsorbent International Journal of Biosciences (IJB), 4(7), 130-139.

Ali, S. M., Khalid, A. R., & Majid, R. M. (2014). The removal of Zinc , Chromium and Nickel from industrial waste water using Corn cobs , *55*(1), 123–131.

Aloko, D. F. & Adebayo, G. . (2007). Production And Characterization of Activated Carbon from Agricultural Waste (Rice-husk And Corn-cob). *J of Eng & Applied Science*.

Anagement, M. (2014). Adsorption Studies of Heavy Metals by Low-Cost Adsorbents. *J. Appl. Sci. Environ. Manage*.

Arunlertaree, C., Kaewsomboon, W., Kumsopa, A., Pokethitiyook, P., & Panyawathanakit, P. (2007). Removal of lead from battery manufacturing wastewater by egg shell. *Songklanakarin Journal of Science and Technology*, *29*(3), 857–868.

Asfaw, F. 2007. Modeling on Akaki rivers liquid waste disposal and base flow separation,AAU,

Ethiopia. Unpublished result, 6

Aziz, H. A., Adlan, M. N., Hui, C. S., Zahari, M. S. M., & Hameed, B. H. (2005). Removal of Ni, Cd, Pb, Zn and colour from aqueous solution using potential low cost adsorbent. *Indian Journal of Engineering and Materials Sciences*, *12*(3), 248–258.

Azmier, M., Tan, E., Yun, C., Abustan, I., Ahmad, N., & Kamal, S. (2011). Optimization of Preparation Conditions for Corn Cob Based Activated Carbons for the Removal of Remazol Brilliant Blue R dye.

Baccar, R., & Yangui, E. (2013). Removal of water pollutants by adsorption on activated carbon prepared from olive- waste cakes and by biological treatment using ligninolytic fungi,.

Barakat, MA. 2011. New trends in removing heavy metals from industrial wastewater. Arabian

Journal of Chemistry, 4(4), 361-377

Baysal, A., Ozbek, N., & Akman, S. (2013). Determination of Trace Metals in Waste Water and Their Removal Processes.

Belay, A and Sahile, S. 2013. The Effects of Dashen Brewery Wastewater Treatment Effluent on the Bacteriological and Physicochemical quality of Shinta River in Gondar, North West Ethiopia. World Environment, 3(1), 29-36.

Beyene, H and Banerjee, S. 2011. Assessment of the Pollution Status of the Solid Waste Disposal Site of Addis Ababa City with Some Selected Trace Elements, Ethiopia. World Applied Sciences Journal, 14(7), 1048-1057.

Biney, C and Ameyibor, E. 1992. Trace metal concentrations in the pink shrimp Penaeus notialis from the coast of Ghana. Water, Air, and Soil Pollution, 63(3-4), 273-279.

Binti, A. I. N., Thesis, J., & June, S. (2007). The Production And Characterization Of Activated Carbon Using Local Agricultural.

Birbas, D. (2011). Preparation of Activated Carbon : Forest residues activated with Phosphoric Acid and Zinc Sulfate Preparation of Activated Carbon : Forest residues activated with Phosphoric Acid and Zinc Sulfate.

Bocca, B, Pino, A, Alimonti, A and Forte, G. 2014. Toxic metals contained in cosmetics: A status report. Regulatory Toxicology and Pharmacology, 68(3), 447-467.

Buxton, R. (2007). Design Expert 7 : Mathematics Learning and support centre. *Response*, 1–10.

Chaturvedi, D and Sahu, O. 2014. Adsorption of Heavy Metal Ions from Wastewater. Global Journal of Environmental Science and Technology, 2(3), 020-028.

Cheenmatchaya, A., & Kungwankunakorn, S. (2014). Preparation of Activated Carbon Derived from Rice Husk by Simple Carbonization and Chemical Activation for Using as Gasoline Adsorbent. *International Journal of Environmental Science and Development*, *5*(2), 171–175.

Corcoran, E. 2010. Sick Water?: The Central Role of Wastewater Management in Sustainable

CROSTAT. 2012. Public sewage system, 2011.

CSA. 2010. Central Stastics Agency, Ethiopia. Unpublished result.

Davis, A. P., & Gietka, P. M. (1994). Removing Heavy Metals from Wastewater, (August), 1–21.

Dowlatshahi, S., Torbati, A. R. H., & Loloei, M. (2014). Adsorption of copper , lead and cadmium from aqueous solutions by activated carbon prepared from saffron leaves, *1*(1), 37–44.

Duruibe, J, Ogwuegbu, M and Egwurugwu, J. 2007. Heavy metal pollution and human biotoxic effects. International Journal of Physical Sciences, 2(5), 112-118.

Ekengele, MC and Ombolo A, . 2008. Metal pollution in freshly deposited sediments from river Mingoa, main tributary to the Municipal lake of Yaounde, Cameroon. Geosciences Journal, 12, 337-347.

Ekpete, O. A., Harcourt, P., Chemistry, I., & Harcourt, P. (2011). Preparation and Characterization of Activated Carbon derived from Fluted Pumpkin Stem Waste (Telfairia occidentalis Hook F), *1*(3).

Awugchew , T. (2015). Addis abababuniversity, School Of Chemical And Bio Engineering Coffee Husk Based Activated Carbon Preparation , Characterization And Application For Adsorption Of Cr (Vi) From Aqua Solution.

Fasinu, PS and Orisakwe, OE. 2013. Heavy metal pollution in sub-saharan Africa and possible implications in cancer epidemiology. Asian Pacific J. Cancer Prev, 14(6), 3393-3402.

Fatoki, MS. 2001. An assessment of heavy metal pollution in the East London and Port Elizabeth habours. Water Sa, 27, 2

Farooq, M. U. (2013). Separation of Heavy Metals From Water Using Fibroin As Adsorbent.

FDRE-CRGE. 2011. Federal Democratic Republic of Ethiopia. Unpublished result.

Fianko, OS, Adomako, D, Adotey, DK and Serfor-Armah Y. 2007. Assessment of heavy metal pollution of the Iture Estuary in the Central region of Ghana. Environ Monit Assess, 131,467-473.

Franca, A. S., Alves, C. C. O., & Oliveira, L. S. (2013). Production of adsorbents based on food waste (corn cobs) for removal of phenylalanine and tyrosine from aqueous solutions.

Fufa, F, Alemayehu, E and Lennartz, B. 2014. Sorptive removal of arsenate using termite mound. Journal of Environmental Management, 132, 188-196.

Fianko, OS, Adomako, D, Adotey, DK and Serfor-Armah Y. 2007. Assessment of heavy metal

pollution of the Iture Estuary in the Central region of Ghana. Environ Monit Assess, 131, 467-473.

Gebre, G, Rooijen, DV and Shaw, R. 2009. Urban water pollution and irrigated vegetable farming in Addis Ababa. Paper presented at the Water, sanitation and hygiene: sustainable development and multisectoral approaches. Proceedings of the 34th WEDC nternational Conference, United Nations Conference Centre, Addis Ababa, Ethiopia, 18-22 May 2009.

Getachew, T. 2006. Industrial Waste Management Practices in Addis Ababa: A Case Study on

Akaki-Kality Industrial Zone, Ethiopia.

Geetha, K. S., & Belagali, S. L. (2013). Removal of Heavy Metals and Dyes Using Low Cost Adsorbents from Aqueous Medium- , A Review, *4*(3), 56–68.

Ghiloufi, I, Khezami, L and El Mir, L. 2014. Nanoporous activated carbon for fast uptake of heavy metals from aqueous solution. Desalination and Water Treatment(ahead-of-print), 1-10

Gupta, K, Gupta, M and Sharma, S. 2001. Process development for the removal of lead and chromium from aqueous solution using red mud: An aluminum industry waste. Water research, 35, 1125-1134.

Gupta, V. 2009. Application of low-cost adsorbents for dye removal–A review. Journal of Environmental Management, 90(8), 2313-2342.

Gupta, VK, Mohan and Sharma, S. 1998. Removal of lead from wastewater using bagasse flyash: A sugar industry waste material. Separation Science and Technology, 33, 1331-1343.

Gupta, VK, Jain, R, Saleh, T, Nayak, A, Malathi, S and Agarwal, S. 2011. Equilibrium and thermodynamic studies on the removal and recovery of safranine-T dye from industrial effluents. Separation Science and Technology, 46(5), 839-846.

Gupta, VK, Jain, CK, Ali, I, Sharma, M and Saini, SK. 2003. Removal of cadmium and nickel from wastewater using bagasse fly ash – a sugar industry waste. Water research, 37, 4038-4044.

Handa, GD and Kumar A 1983. Pollution of natural waters by industrial waste effluents in some parts of North and Northwestern India. Asian Environment(5), 13-19

Hiremath M.N., & Shivayogimath C.B., S. S. N. (2012). Preparation and Characterization of Granular Activated Carbon from Corn Cob by KOH Activation. *International Journal of Research in Chemistry and Environment*, *2*(3), 84–87.

Huang, Y. (2016). Applications of Polyvinylamine in Removal of Heavy Metals from Wastewater by Polymer-Enhanced.

International, O. K., & Affairs, E. (2012). Health & Environmental Impacts from Lead Battery Manufacturing & Recycling in China.

Itanna, F. 2002. Metals in leafy vegetables grown in Addis Ababa and toxicological implications.

Ethiopian Journal of Health Development, 16(3), 295-302. IWRG701. 2009. Sampling and analysis of waters, wastewaters, soils and wastes

Kaakani, M. W. (2012). *Heavy Metal Removal From Wastewater Using Novel Adsorbent*.

Kapanji, KK. 2009. The removal of heavy metals from wastewater using South African clinoptilolite. Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg.

Keng, PS, Lee, SL, Ha, ST, Hung, YT and Ong, ST. 2013. Cheap materials to clean heavy metal polluted waters Green Materials for Energy, Products and Depollution (pp. 335-414):

Khan, M. A., Alemayehu, A., Duraisamy, R., & Berekete, A. K. (2015). ISSN 2348 – 2710 Original Article Removal of Lead ion from aqueous solution by Bamboo activated Carbon, *5*(4), 33–46.

Krishna, KD. 2011. Environmental Impact Assessment: a study on liquid waste management in Addis Ababa, Ethiopia. Abhinav National Monthly Refereed Journal of Research in Science and Technologyy.

Kulkarni, S, and Kaware, J. 2014. Fixed bed removal of heavy metal,a review. International Journal of Research, 1(6), 861-871.

Kundu, A., Redzwan, G., & Sahu, J. (2014). Hexavalent Chromium Adsorption by a Novel Activated Carbon Prepared by Microwave Activation. *BioResources*, *9*(Vi), 1498–1518.

Kurniawan, TA, Chan, G, Lo, WH and Babel, S. 2006b. Physico–chemical treatment techniques for wastewater laden with heavy metals. Chemical Engineering Journal, 118(1), 83-98.

Kyzas, G. Z., & Kostoglou, M. (2014). Green adsorbents for wastewaters: A critical review. *Materials*, *7*(1), 333–364.

Leta, S. 2004. Developing and optimizing processes for biological nitrogen removal from tannery wastewaters in Ethiopia: Bioteknologi

Length, F. (2009). Utilization of maize (Zea mays) cob as an adsorbent for lead (II) removal from aqueous solutions and industrial effluents, *8*(8), 1567–1573.

Li, Q, Zhai, J, Zhang, W, Wang, M and Zhou, J. 2007. Kinetic studies of adsorption of Pb (II), Cr (III) and Cu (II) from aqueous solution by sawdust and modified peanut husk. Journal of Hazardous Materials, 141(1), 163-167.

Majeed, MR, Muhammed, AS and Rasheed, KA. 2014. The removal of Zinc, Chromium and Nickel from industrial waste water using Rice husk.

Mandal, NK. 2014. Performance of low-cost bio adsorbents for the removal of metal ions, a review. International Journal.

Masoud, M. S., El-saraf, W. M., Abdel, A. M., Ali, A. E., Mohamed, E. A., & Hasan, H. M. I. (2012). Rice husk and activated carbon for waste water treatment of El-Mex Bay , Alexandria Coast , Egypt. *ARABIAN JOURNAL OF CHEMISTRY*.

Mersha, Z. 2008. Water Quality Monitoring Design for Little Akaki River. Unpublished result.

Addis Ababa University. Addis Ababa.

Mohammad, M., Yaakob, Z., Rozaimah, S., & Abdullah, S. (2013). Carbon Derived from Jatropha Seed Hull as a Potential Green Adsorbent for Cadmium (II) Removal from Wastewater, 4462–4478.

Mombeshora, AS and Osibanjo, O. 1998. Pollution studies on Nigerian rivers: toxic heavy metal status of surface waters in Ibadan city. Environ Ins, 5, 49-53.

Mohod, CV and Dhote, J. 2013. Review of heavy metals in drinking water and their effect on

human health.

Narayanan, L. (2014). Use of Corn Cob as Low Cost Adsorbent for the Removal of Nickel (II) From Aqueous Solution, *5*(Ii), 325–330.

Palaniappan, M. 2010. Clearing the waters: a focus on water quality solutions: United Nations

Environment Programme, Division of Environmental Policy Implementation

Pawar, K, Wankhede, S, Kaul, H and Karda, S. 2014. Removal of heavy metal ions from synthetic wastewater using various low-cost natural adsorbents.

Pehlivan, E, Yanık, BH, Ahmetli, G and Pehlivan, M. 2008. Equilibrium isotherm studies for the

uptake of cadmium and lead ions onto sugar beet pulp. . Bioresour Technology, 99, 3520-3527.

Patrick, L. (2006). Lead Toxicity , A Review of the Literature . Part I : Exposure , Evaluation , and Treatment, *11*(1).

Pizano, M, Besri, M, Marcotte, M and Porter, I. 2010. United Nations Environment Programme

(UNEP) 2010 Report of the Methyl Bromide Technical Options Committee. UNEP/Ozone Secretariat, Nairobi.

Polytechnic, K. (2008). Production of Activated Carbon from Corncobs and its Utilization in Crude Oil Spillage Clean Up. *Methods*, 1–9.

Pradhan, S. (2011). Production and characterization of Activated Carbon produced from a suitable Industrial sludge,.

Qadir, M, Bahri, A, Sato, T and Al-Karadsheh, E. 2010. Wastewater production, treatment, and

irrigation in Middle East and North Africa. Irrigation and drainage systems, 24(1-2), 37-51.

Renge, V. C., Khedkar, S. V, & Pande, S. V. (2012). Removal of Heavy Metals From Wastewater Using Low Cost Adsorbents : a Review. *Sci. Revs. Chem. Commun, 2*(4), 580–584.

Rohaizar, Nurul, Hadi, N. &Wong C. (2013). Removal of Cu (II) from water by adsorption on chicken eggshell. *International Journal of Engineering and Technology*, *13*(01), 40–45.

Sampranpiboon, P., Charnkeitkong, P., & Feng, X. (2014). Equilibrium isotherm models for adsorption of zinc (II) ion from aqueous solution on pulp waste. *WSEAS Transactions on Environment and Development*, *10*(Ii), 35–47.

Sato, T, Qadir, M, Yamamoto, S, Endo, T and Zahoor, A. 2013. Global, regional, and country level need for data on wastewater generation, treatment, and use. Agricultural Water Management, 130, 1-13

Scholar, M. T. (2013). Removal Of Chromium (Vi) By Activated Carbon Derived From Mangifera Indica, (Vi), 2319–2322.

Shahmohammadi-Kalalagh, S, Babazadeh, H, Nazemi, A and Manshouri, M. 2011. Isotherm and kinetic studies on adsorption of Pb, Zn and Cu by kaolinite. Caspian J. Environ. Sci, 9, 243-255.

Srisa-ard, C. (2002). ◌๊Removal of Heavy Metals from Wastewater by Adsorption using Chitosan.

Sugumaran, P., Susan, V. P., Ravichandran, P., & Seshadri, S. (2012). Production and Characterization of Activated Carbon from Banana Empty Fruit Bunch and Delonix regia Fruit Pod. *Journal of Sustainable Energy & Environment*, *3*, 125–132.

Tajrishy, M. 2012. Wastewater production, treatment and use in Iran , Presented at the Second Regional Workshop of the Project ‘Safe Use of Wastewater in Agriculture’, 16–18 May 2012,)

Tegegn, FE. 2014. Physico-chemical pollution pattern in Akaki River basin, Addis Ababa, Ethiopia. Paper presented at the 2014 GSA Annual Meeting in Vancouver, British.

Tnbaraj, S., & Sulochana, N. (2002). Basic dye adsorption on a low cost carbonaceous sorbent-Kinetic and equilibrium studies, *9*(May), 201–208.

UNEP. 2010. United Nations Environment Programme

Van Rooijen, DJ, Biggs, TW, Smout, I and Drechsel, P. 2010. Urban growth, wastewater production and use in irrigated agriculture: a comparative study of Accra, Addis Ababa and Hyderabad. Irrigation and drainage systems, 24(1-2), 53-64.

Volesky, B. 2003. "Sorption and Biosorption" BV Sorbex, Inc., Montreal St. Labert, Quebec,Canada.

Yahya, M. A., Al-Qodah, Z., & Ngah, C. W. Z. (2015). Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review. *Renewable and Sustainable Energy Reviews*, *46*, 218–235.

Zahra, N. (2012). Lead Removal from Water by Low Cost Adsorbents : A Review, *13*(1), 1–8.

Zayat, M. El, & Smith, E. (2006). Removal of Heavy Metals by Using Activated Carbon Produced from Cotton Stalks Mohamed El Zayat and Edward Smith Environmental Engineering Program, the American University in Cairo, 1–9.

Zinabu, E. 2011. Assessment of the impact of industrial effluents on the quality of irrigation water and changes in soil characteristics: The case of Kombolcha town. Irrigation and Drainage, 60(5), 644-653.

Zhang, Y., Ghaly, A. E., & Li, B. (2012). *Physical properties of corn residues 1, 2 1* (Vol. 8).

Zwain, HM, Vakili, M and Dahlan, I. 2014. Waste Material Adsorbents for Zinc Removal from Wastewater: A Comprehensive Review. International Journal of Chemical Engineering,