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SCHOOL OF CHEMICAL AND BIO-ENGINEERING

Parametric Optimization for Adsorptive Removal of Lead Ions by Magnetic Activated Carbon Prepared from Corn Cob

By

Yoktan Seifu

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ABSTRACT

Water pollution has been a major challenge to environmental engineers today due to the release of toxic heavy metals from various industries. Among various heavy metals, Lead ion (Pb^{2+}) is considered as highly toxic, and causes various health disorders. Different sources of Lead ion (Pb^{2+}) pollution include effluents from mining, electroplating, painting, and electroplating industries. Among various technologies, adsorptive removal of Lead ion (Pb^{2+}) by using different adsorbents is more promising and economical. Among various adsorbents used, Magnetic activated carbon (MAC) is well known for its high adsorption capacity due to its large surface area, and pore volume. Corn Cob is lingo-cellulosic material that was selected as the precursor for the preparation of Magnetic Activated Carbon. Activated carbon was prepared through prior chemical activation using phosphoric acid following embedding of the prepared Activated Carbon by Iron oxide. The effect of various process parameters such as carbonization temperature, and Carbonization time were investigated on Lead ion (Pb^{2+}) removal efficiency. The results indicated that BET surface area of 504 m^2/ g. at approximately 610°C carbonization temperature, and 3hr. of carbonization time was measured. Effect of adsorbent dosage, pH, and initial Pb^{2+} concentration were studied. Optimum removal of Lead ion was recorded at 0.6 g. adsorbent dosage, pH of 5, and initial Lead ion concentration of 75 mg /l with Lead ion removal efficiency of 92.86% and desirability of 0.844 Kinetics and isotherm studies indicated that the adsorption mechanism of Corn Cob based Magnetic Activated Carbon follows pseudo second order (R^2=0.9902) while Freundlich isotherm model well fitted the adsorption data with R^2=0.9841. In terms of regeneration, adsorption efficiency of CCMAC for six cycles decreased from 89.34 to 34.68%. Corn Cob can be a good precursor for Magnetic Activated Carbon preparation and can be used to remove Pb^{2+} from wastewater.

Key words: Activated carbon, Magnetic Activated Carbon, Chemical activation, Surface area, Adsorption Isotherm/Kinetics

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List of Acronyms

AC	Activated carbon
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CCMAC	Corn Cob Magnetic Activated carbon
R^2	Correlation coefficient
CO_2	Carbon dioxide
℃	Degree Celsius
q_e	Equilibrium adsorbed Amount
C_e	Equilibrium concentration
K_F	Freundlich isotherm constant
g	Gram
HCl	Hydrochloric acid
hr	Hour
C_o	Initial concentration
K_L	Langmuir isotherm constant
MAC	Magnetic Activated carbon
mg	Milligram
Mg/l	Milligram per litter
min	Minute
pH	Negative logarithm of concentration of hydrogen ion
K_1	Pseudo-first order rate constant
K_2	Pseudo-second order rate constant
H_3PO_4	Phosphoric acid
NaOH	Sodium hydroxide
H_2SO_4	Sulphuric acid
SEM	Scanning electron microscope
t	Time

1. Introduction

1.1. Background

Heavy metals exist in immobilized manner in deposits and rocks in Mother Nature. However, due to human actions these metals become mobilized into the normal bio-geo-chemical cycles, which disrupted nature by increasing deposition of heavy metals in both land, and water environment (Dimpe et al., 2017). As of their non-biodegradability, heavy metals contamination brings about a disastrous threat to humans face (Virgen et al., 2018). The occurrence of heavy metals in both surface waters, and waste water, they can accumulate in the food chain, poses severe environmental concern. Furthermore, because of their non-degradability, these metals bring danger to human health (Y. di Chen et al., 2018; Nejadshafiee & Islami, 2019).

Lead is one of dense and ductile heavy metals used in the many industries. It is used in the manufacture of batteries, pipes, fuel, cable sheaths, electric light, paints, and machineries. Lead plates are valuable to resist corrosion, and radiation that cemented the path for ship-building, and medicines (Noor et al., 2017; Zhang et al., 2018). Despite its wide usage, Lead is toxic heavy metal, which bring a severe health hazard, because it has wider effects on the hormonal, respiratory, nervous, blood circulation, and reproductive health’s up to kidney failure, cancer, and anaemia (Sedighi et al., 2012; Waji, 2018).

Reaction of lead with other substances could yield lead compounds that is more hazardously soluble than pure lead. Moreover, rains can have negative effect on bodies of water via the “flushing-effect” due to the flushed lead which is present in run-off areas and coastlines. Studies show that during wet season, the levels of lead are relatively high (Emenike et al., 2016).

Various investigations of lead analyses were done in Ethiopia. In Ethiopia (particularly Addis Ababa), around 390 hectares of land for vegetable farming was irrigated with the polluted *Akaki* river, reported to have high quantities of toxic Pb, and Pb^{2+} (Sime, 2018; Waji, 2018). The reports also found this element in the tissues of vegetables (lettuce, cauliflower, cabbage, and kale). This illustrates that industrial wastewater required to be treated before being used for irrigation.

The sustainability of the environment has become a critical global issue, and the protection of fresh water bodies from various contaminants has become a major challenge facing the planet earth. Adsorption is one of the physical processes in treating heavy metal contaminants in water such as lead for protect natural water bodies. This process is more efficient, and economical in treatment of water as compared to oxidation, coagulation, filtration, flocculation, and ionization (Shrestha, 2016; Yin et al., 2018).

As with other developed countries, Ethiopia cannot meet the expense to use advanced technologies (like Reverse osmosis (RO), Molecular Sieving etc.) for the treatment of contaminated water. Accordingly, it is crucial to explore locally available materials for the treatment of industrials wastewater. The Magnetic Activated Carbon based adsorption principles are cost-effective, simple to design and operate locally available materials Magnetic Corn Cob Activated Carbon (CCMAC) will be investigated for removal of Pb^{2+} from synthetic Lead ion containing wastewater under batch experiments (Emenike et al., 2016). The use of magnetic Nano-composite will be loaded in the adsorbent particles which will ease the separation of the adsorbent from the effluent, which is the resulting treated water (Malekzadeh et al., 2015).

1.2. Statement of Problem

The increasing usage of heavy metals over the preceding few decades unquestionably led to an increased change of metallic substances in ground, drinking, and surface water, and came up with severe ecological, and health risks. Lead (Pb^{2+}) is extremely toxic metal without any known biological function, toxic whenever they are not metabolized (catabolized or anabolized) by the human body, and stored in soft tissues. They can enter the bodies of humans via the food chain (Scientifically, the threshold level of Lead is 10μg/decilitre). The presence of lead pollution in paint industry, battery industry, and glass industries are the most common ones. So, these risky metallic ions are required to be removed. The removal of Lead (Pb^{2+}) is not a simple task, since it needs advanced technologies and cost. In Ethiopia, light industries like paint uses heavy metal for to increase the durability and ability of binding on the surface of the wall, the leftover heavy metal are then released without being treated these situation gets our surrounding became complicated and leads to severe problem.

An incentive of this study is that the magnetic activated carbon applied in the adsorption process could be regenerated, since it’s too costly to only use once, and dispose it without recycling. The Magnetic Activated Carbon (MAC) is magnetic composite by which separation from the aqueous solution after adsorbing the Pb^{2+} is easily done by a simple magnetic process. However, according to the readings, and knowledge of the researcher, there no particular research were undertaken to investigate these issues particularly in Ethiopia Corncobs activated carbon as potential Magnetic Activated Carbon adsorbent to get rid of heavy metal lead ion (Pb^{2+}) from synthetic wastewater. Therefore, this research was conducted to treat the lead contaminant on the synthetically prepared Lead solution using a locally available Corn Cobs based Magnetic Activated Carbon (CCMAC).

1.3. Objectives of Research

1.3.1. General Objective

The general objective of this research is to prepare, regenerate, and characterize magnetically recyclable activated carbon from Corn Cob, and investigate its adsorption application for Pb^{2+} remediation.

1.3.2. Specific Objectives

The specific objectives of the research include:-

- ✓ To synthesize and characterize magnetic activated carbon (Activated carbon/Fe_3O_4 composite) from Corn Cob.
- ✓ To optimize adsorption parameters of pH, CCMAC dose, and Initial Pb^{2+} Concentration.
- ✓ To investigate the regeneration capability of CCMAC.

1.4. Significance of the study

A major challenge of many industries is obtaining solutions that troubleshoot the possible environmental and economic impacts regarding the treatment of their effluents. Solution to this challenge is of extreme importance to facilitate improvement of water quality. Since the magnetic activated carbons used in this study are prepared from natural resources and also an agricultural waste (Corn Cob), they can bring financial and environmental friendly alternatives to conventional adsorbent (commercial activated carbon). And also the specific raw material (being used) corn cob is suitable for preparing micro porous activated carbon due to its excellent natural structure and low ash content. Some significance include:

- ✓ The regeneration capabilities of these magnetic activated carbons after used is another promising quality (D. Chen et al., 2016).

- ✓ To work for the industry to practise agricultural wastes for other value important projects such as waste water treatment.
- ✓ To enhance to extra knowledge on heavy metal waste eradication process by magnetically recyclable activated carbon adsorbent.
- ✓ It provides an alternative way for researchers, and scientists on heavy metal removal, and material recycling methods in wastewater treatment.

1.5. Thesis structure

This thesis is structured in different parts. The first part is a wide introduction about the research, statement of the problem, objectives of the study, and its significance. The second part includes a literature review about precursor sources for AC, toxic effects, conventional metal ions removal methods, Magnetic AC adsorbents, metal ions uptake mechanism, factors affect the sorption pattern, and recycling study of magnetic activated carbon adsorbent. The third part is all about the methodologies applied during the research. Part four discusses the result as best as it could to get more of the topic. Finally, the research was concluded, and recommended for further investigating areas.

2. Literature Review

2.1. Waste water

Wastewater is water generated from agricultural, industrial, domestic and industrial sources. Billions of gallons of liquid waste from purpose and non-point sources discharged into contemporary surface water bodies a day (Sime, 2018). Worldwide, three hundred to four hundred million tons of liquid, venturous wastes to living organisms are discharged yearly into close surface water bodies from industries (Moosavi et al., 2020). Approximately, two million tons of liquid waste is discharged day after day from non-point sources like agricultural areas and from purpose sources like industries to surface water bodies across the world. The discharge of untreated waste matter into the surroundings will result in the contamination of rivers, streams and alternative surface water bodies. Industrial waste matter contains harmful suspended and dissolved matter, like serious metals, and inorganic matters, that once discharged untreated greatly affects the surroundings and causes serious health issues to living organisms (Benedetti et al., 2017; Gottipati, 2012).

According to World Health Organization, heavy metals like Lead (Pb), Mercury (Hg), Iron (Fe), Copper (Cu), Chromium (Cr), Zinc (Zn), and Cadmium (Cd) environmentally concerning. The industrialization drive of Ethiopia attracted foreign investments. However, it led to discharge of untreated industrial wastewater. This pollution has been concern to governments, and various stakeholders (Gottipati 2012). As a result, discovering inexpensive and effective treatment techniques is the focus of the many researchers across the globe.

2.2. Heavy Metals

Heavy metal pollution is an inorganic chemical hazard, which is mainly caused by lead (Pb), chromium (Cr), arsenic (As), cadmium (Cd), mercury (Hg), zinc (Zn), copper (Cu), cobalt (Co), and nickel (Ni). These heavy metals are classified as strong carcinogens by the International Agency for Research on Cancer (Nejadshafiee & Islami, 2019). Speedy enlargement of industries such as batteries, steel, mining operations, paper, casting, electroplating, fertilizer, tanneries, and pesticides industries enhanced the increment of heavy metals wastewaters. (Feng et al., 2020; Sedighi et al., 2012).

For this reason, decreasing the heavy metallic concentrations under the allowable limits is vital to protect the health of people and all other organisms. By affecting key microbial processes, heavy metals exhibit toxic effects on soil biota, decrease the number, and activity of soil microorganisms (Y. di Chen et al., 2018; Malekzadeh et al., 2015).

Even low levels of heavy metals can hinder plant metabolism. Animals and humans are likely to be affected by heavy metals absorbed by plants and accumulated throughout the food chain (Baghdadi et al., 2016; Saleh et al., 2017). Unlike other metals, heavy metals found in waste water don't have the ability to degrade naturally and are harmful/ dangerous to terrestrial and aquatic environmental lives regardless of the concentration, making its removal imperative. Lead is one of popularly used for manufacturing of paints, mining and pigments, as well as other industrial applications (Seyoum & Asso, 2015).

2.2.1. Lead

It is a heavy metal that is denser than most common materials. Lead is soft and malleable, and also has a relatively low melting point. When freshly cut, lead is silvery with a hint of blue; it tarnishes to a dull grey colour when exposed to air. Lead has the highest atomic number of any stable element and three of its isotopes are endpoints of major nuclear decay chains of heavier elements (Kim et al., 2017; Waji, 2018).

Lead is a relatively unreactive post-transition metal. Its weak metallic character is illustrated by its amphoteric nature; lead and lead oxides react with acids and bases, and it tends to form covalent bonds. Compounds of lead are usually found in the +2 oxidation state rather than the +4 state common with lighter members of the carbon group. Exceptions are mostly limited to organo-lead compounds. Like the lighter members of the group, lead tends to bond with itself; it can form chains and polyhedral structures (Noor et al., 2017).

There are two major categories of production: primary from mined ores, and secondary from scrap. The primary and secondary lead production processes are similar. Some primary production plants now supplement their operations with scrap lead, and this trend is likely to increase in the future. Given adequate techniques, lead obtained via secondary processes is indistinguishable from lead obtained via primary processes. Scrap lead from the building trade is usually fairly clean and is re-melted without the need for smelting, though refining is sometimes needed. Secondary lead production is therefore cheaper, in terms of energy requirements, than is primary production, often by 50% or more (Amalia et al., 2017; Waji, 2018).

2.2.2. Toxicity of Lead

Throughout the world, lead has caused extensive environmental contamination/ pollution, human exposure, and significant public health problems due to its widespread use. Mining, smelting, manufacturing, and recycling activities are important sources of lead contamination in the environment. Hazardous substances or chemicals just like leaded paint, gasoline, and aviation fuel add to these sources (Amalia et al., 2017).

Lead (Pb^{2+}) consumption. Lead is also used in many other products, such as pigments, paints, solder, stained glass, lead crystal glassware, ammunition, and ceramic glazes. Children and infants are more susceptible to lead poisoning as a result of they absorb four up to five times more lead from ingested sources from a given source (Zhang et al. 2018).

Lead enters the body and is distributed throughout organs such as the brain, kidneys, liver, and bones. As lead accumulates in teeth and bones over time, it will be remobilized into the blood during pregnancy time, and be absorbed by the foetus inside of the body. Furthermore, lead exposure affects the immune system and the reproductive system and the neurological and behavioural effects are irreversible. As lead exposure increases, the range and severity of symptoms and effects also increases (Sedighi et al., 2012; Sime, 2018; Waji, 2018).

Table 2.1:- source and impact of heavy metals with their WHO limit in ppm.

Heavy Metal	**Impact**	**Source into the environment**	**WHO Limit in ppm**
Lead (Pb)	Causes damage to kidneys, nervous system, learning ability, to synthesize protein, nerve and red blood cells.	Paint, water from lead pipes, mining wastes, solder, automobile exhaust, incinerator ash	0.01
Chromium (Cr)	Pulmonary, fibrosis, lung cancer.	Cement industry, chemical plants, tobacco smoke, and land fill.	0.05
Mercury (Hg)	Damage to nervous system, kidneys and vision.	Leaching of soil by acid rain, coal burning (from industrial, and household)	0.001

Cadmium (Cd)	Causes kidney disease.	Electroplating, mining and plastic industries, sewage.	0.003
Nickel	Headache, dizziness, chest pain, tightness of the chest, dry cough and shortness of breath,	Porcelain enameling, nonferrous metal, paint formulation, electroplating	0.05
Arsenic (As)	Cause damage to skin, eyes, and liver, cancer	Enters the environment through Herbicides, wood preservatives, and mining industry.	0.01

2.3. Advanced Wastewater Treatment

Water treatment processes designed to produce effluent of higher quality than that produced by secondary treatment are considered advanced wastewater treatment processes. This advanced wastewater treatment method removes organic matter, suspended solids, nitrogenous oxygen and toxic matter from the wastewater (Llopis, n.d.). There are several methods for removing polluting materials from industrial effluents, such as chemical precipitation, electrochemical (Yang & Zhang, 2018), membrane filtration (Homaeigohar, 2020), flocculation and coagulation (Farhaoui & Derraz, 2016), reverse osmosis, and adsorption (Ping et al., 2016).

2.3.1. Chemical Precipitation

Among the most effective and basic methods for removing heavy metals from inorganic effluent is chemical precipitation. The most common precipitant agents are lime and lime stone due to their availability and low cost in most countries. Utilization of lime precipitation can be effective in treating inorganic effluents that have metal concentrations in excess of 1000 mg/L (Jain et al., 2018). Utilizing lime precipitation also comes with several advantages, including the simplicity of the process, the affordability of equipment, and the capability of handling the process in a safe and appropriate manner. Chemical precipitation, however, requires a large amount of chemicals to reduce metals to a level suitable for discharge. These methods have a number of drawbacks including the high production of sludge, excessive sludge treatment, metal precipitation, poor settling, metal precipitation aggregation, and long-term environmental impacts associated with sludge disposal (Dargo et al., 2014).

2.3.2. Coagulation and Flocculation

Coagulation-flocculation is a method for dealing with wastewater contaminated by heavy metals. Colloid particles are destabilized by adding a coagulant during coagulation and sedimentation results (Farhaoui & Derraz, 2016). As a result of coagulation, the particles become larger when they are flocculated together into bulky floccules. pH adjustments are generally required for this technique, and added ferric and alum salts act as coagulants to ensure smooth particle separation. As a general rule, coagulation-flocculation can treat inorganic effluent with a metal concentration of less than 100 mg/L or higher than 1000 mg/L the process of heavy metal removal (Emenike et al., 2016; Farhaoui & Derraz, 2016). Coagulation and flocculation are most commonly used to improve sludge settling, bacterial inactivation, dewatering, and sludge stability. The major disadvantage of coagulation-flocculation is its high operating costs due to chemical consumption. Coagulation-flocculation generates a greater volume of sludge, which may prevent it from being fully adopted as a global wastewater treatment strategy. Toxic sludge must be converted into a stabilized product to prevent heavy metals from leaking into the environment (Analytical, n.d.; Dhote & Ingole, 2012).

2.3.3. Membrane Filtration

Membrane filtration has attracted much interest for treating inorganic wastewater since it can remove both suspended solids and organic components, while also inorganic pollutants like heavy metals. Various forms of membrane filtration, such as ultra-filtration, reverse osmosis, and nano-filtration, can be used for heavy metal based on particle sizes that could be retained. Membranes offer a high water flux rate, high salt rejection, biological resistance, mechanical strength, chemical stability, and the capacity to sustain extreme temperatures, among other benefits (Emenike et al., 2016). Allows industrial users to comply with the effluent limit of discharge standards required by environmental legislation by reusing water from industrial processes. Membranes, despite their advantages, have problems such as fouling and irreversible pollution by effluent. Fouling has a number of negative consequences on the membrane system, including decreased flow, increased trans-membrane pressure, and membrane biodegradation. The other disadvantages of this method are expensiveness of membrane, replacement, increasing the operational costs, high energy consumption, and the need for experienced personnel to run the process (Homaeigohar, 2020).

2.3.4. Electrochemical methods

Electro chemical method is one of technology used to remove metals from wastewater streams. This process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Various types of electro chemical method such as electro-Dialysis (ED), Membrane electrolysis (ME) and electrochemical precipitation (EP) (Teklu, 2007). Electro-dialysis is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential (Emenike et al., 2016).

Membrane electrolysis, a chemical process driven by an electrolytic potential, can also be applied to remove metallic impurities from metal finishing wastewater. Unlike Electro-Dialysis. Membrane electrolysis can be employed to treat plating wastewater with a metal concentration of higher than 2000 mg/L or less than10 mg/L (Homaeigohar, 2020). The major drawback of membrane electrolysis is its high energy consumption. Electrochemical precipitation is the most common heavy metal precipitation method forming coagulants by electrolytic oxidation and destabilizing contaminants to form flock. The electro-coagulation processes the coagulant is generated in situ by electrolytic oxidation of an appropriate anode material. The major drawback of electrochemical precipitation (EP) are huge sludge production, slow metal precipitation, poor settling, the aggregation of metal precipitates and the long-term environmental impacts of sludge disposal (Warhurst et al., 1996).

2.3.5. Ion Exchange

Ion exchange is also one of the most frequently applied treatments worldwide for wastewater laden with heavy metals. In ion exchange, a reversible interchange of ions between the solid and liquid phases occurs, where an insoluble substance (resin) removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent amount without any structural change of the resin (Jia et al., 2018; Levan et al., n.d.). Ion exchange can also be used to recover valuable heavy metals from inorganic effluent. After separating the loaded resin, the metal is recovered in a more concentrated form by elution with suitable reagents. The disadvantage of this method is that it is not all ion exchange resin is suitable for metal removal and high capital cost. Therefore, the use of other method such as adsorption, adsorption appears to be an attractive process due to its simplicity, effectiveness and economical in the removal of pollutant from wastewater (Gottipati, 2012).

2.3.6. Phyto-remediation

Phytoremediation is the use of certain plants to clean up soil, sediment, and water contaminated with toxic metals. Advantages include: aesthetically pleasing, the effectiveness in contaminant reduction, low cost, applicable for wide range of contaminants and environmentally friendly method. The disadvantages include that it takes a long time for removal of metals and the regeneration of the plant for further bio-sorption is difficult. Due to the disadvantages mentioned above, like incomplete metal removal, high reagent and high energy requirements, generation of toxic sludge or other waste products that require cost effective alternative technologies or adsorbents for the treatment of metal containing wastewaters are needed (Dhote & Ingole, 2012; Noor et al., 2017; Saleh et al., 2017).

2.3.7. Adsorption

The Adsorption method is a method that uses solid adsorption materials with good porosity and high specific surface area as a sorbent to adsorb heavy metal from wastewater (Herrera-Barros et al., 2018). Adsorption is a widely used method for the treatment of industrial wastewater having heavy metals, colour and other inorganic and organic impurities. The benefits of adsorption process are for its simplicity in operation, inexpensive, easily available. Adsorption refers to the attachment of substances from a liquid or gaseous phase to solids. The solid is referred to as the adsorbent (Li et al., 2010; Nejadshafiee & Islami, 2019). The substance taken up is called the adsorbate. Adsorption has important for industries which use for removal of metal from industrial wastewater. In general, there are three main steps involved in pollutant sorption onto solid sorbent. The transport of the pollutant from the bulk solution to the sorbent surface, adsorption on the particle surface, and transport within the sorbent particle

Removal of hexavalent chromium from industrial wastewater, recovery adsorbent, gas masks containing adsorbents to purify the air from poisonous gases and vapours, removal of impurities from petroleum oils, Inactivation of bacteria toxin, hormone or a mineral or as antidote in cast of poisoning, removal of impurities from motor spirits, purification of enzymes, clarification of sugar liquid, separation of gas mixture, in chromatographic analysis, In softening of hard water, in drying gases, de-colorization and purification (Crini et al., 2019; *Principles of Adsorption and Adsorption Processes (PDFDrive.Com).Pdf*, n.d.).

2.4. Activated carbon

Activated carbon is one of the most commonly used adsorbents due to its high specific surface area, porosity, chemical resilient and thermal stability. However, the used activated carbon often suffers from serious problems of separation in liquid solid phase processes. Among many adsorbents, activated carbon (AC) is a kind of black porous solid adsorption material with unique properties (Gottipati, 2012). During the process of activation of activated carbon, a large number of interspaces are produced, forming a large surface area and many functional groups, including carboxyl, hydroxyl, and other functional groups. Due to its large surface area, surface chemistry, and porous structure, AC has shown excellent efficiency for contaminants' removal in the liquid phase. In recent years, many studies have been reported for the production of activated carbon from wastes, such as (Shell, 2011) shell, acorn shell (Saleh & Danmaliki, 2017), cotton stalks (Ameen et al., n.d.), pine cone (Ahnemark et al., n.d.), almond shell (Mohan et al., 2011), bamboo (Waji, 2018), mangos teen peel (Amirza et al., 2017), palm (Zhi & Zaini, 2020), coconut shell ("Properties of Activated Carbon Prepared from Coconut Shells in Ghana," 2012), coal (Rafsanjani et al., 2013), mangrove (Patil, 2015), sewage sludge activated carbon, corncob char (From et al., 2016), and paper mill sludge (Feng et al., 2020) etc.

(Liu et al., 2020) Prepared, and characterized activated carbon from Corn Cob by KOH activation for removal of Hg^{2+} from aqueous solution by firstly soaking the corn cob in 10% sulphuric acid and heated at 170 °C for 48 h in FCF reactor kettle. Secondly, mixing the intermediate product with potassium hydroxide at a mass ratio of 1:2 was done. In the study, the adsorption of Hg^{2+} by CCAC conforms to the Langmuir adsorption isotherm and pseudo-second-order kinetic model. When 20 mg L^{-1} CCAC was used and the initial concentration of Hg^{2+} was 60 μg L^{-1}, the Hg^{2+} adsorption rate reaches 97.2% at 120 min. On the other hand, (Seyoum & Asso, 2015) investigated on Heavy Metals Removal from Electroplating Waste Water Using Activated Carbon from Coffee Husk. Chemical activation was done by weighing a known amount of coffee husk, and treat it with 0.1M sulphuric acid and activated at 150℃ for 5h. The thermal activation was at 550℃ for 60min. The sorption efficiency at equilibrium adsorption of chromium was found to be 99.65%, nickel 99.84% and Zinc 96.24%. The highest adsorption capacity occurred at distinct pH=7 values for each metal ion. Langmuir providing the best fit for Ni (R^2=0.987) and Freundlich sorption isotherm model best fit for Cr (R^2= 0.987), and Zn (R^2=0.965). The sorption kinetics was better described by the pseudo-second-order model for Ni, Cr and Zn (R^2 = 0.999), (R^2= 0.999), and (R^2=1), respectively.

(Y. di Chen et al., 2018)Studied on removal of lead ion from waste water using corn cob activated carbon as an adsorbent. The corn cob was carbonized in a horizontal cylindrical furnace with continuous Nitrogen flow in nitrogen atmosphere at a activation temperatures of 400,450, and 500℃, activation time of 2hr followed by impregnation of One hundred grams of the corn cob carbon 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 optimum conditions for corn cobs activated carbon preparation were determined as impregnation ratio of 1.5, carbonization temperature of 450℃, activation time of 120min, and acid concentration 60% by weigh. 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.

2.5. Magnetic activated carbon

Magnetic technology makes it possible to effectively separate and recover the spent activated carbon by a simple magnetic process. In recent years preparation and application of magnetic activated carbon (MAC) have been paid more and more attention. The term “magnetic adsorbent” is commonly used to describe the materials derived from iron (particles of γ-Fe_2O_3, Fe_3O_4 and $CoFe_2O_3$) or composites prepared from different types of matrix modified with iron compounds, which are used in the adsorption of water contaminants. Activated carbon (AC) is a novel adsorbent to remove various compounds from water due to its large available surface area, high pore volume and high surface reactivity (Y. di Chen et al., 2018; Saleh et al., 2017). However, AC powder is difficult to be separated and reused after adsorption treatments by using traditional methods such as filtration and centrifugation, resulting in loss of the adsorbents and secondary pollution, limiting application of AC powder in practice.

At present, MAC is mainly prepared by a two-step method, which combines activated carbon with magnetic material by mixing, adsorption, chemical co-precipitation and reactivation. At two-step method has several disadvantages of complicated and costly process and the loss of adsorption capacity (Baghdadi et al., 2016). In contrast, MAC made by a one-step method can maintain high specific surface area and stable magnetic properties because the magnetic additive is added to the raw material and involved in the whole process of preparing activated carbon. But few reports on the one step method focused on the preparation of magnetic coal based activated carbon.

(Zhang et al., 2017) Had efficiently prepared Magnetic Activated Carbon for Efficient Removal of Pb^{2+} from Aqueous Solution. In this work, magnetic based activated carbon

(MPSAC) was prepared via a simple one-step method in the presence of K_2CO_3 and Fe_3O_4 and further examined as an adsorbent for the removal of Pb^{2+}.MPSAC possessed a well-developed porosity structure with a high surface area of 1,219m^2/g and contained rich carboxylic functional groups on the surface. Negatively charged surface was largely distributed in the external area. (Benjedim et al., 2021) Used two alternative synthesis routes for magnetic adsorbents to remove Pb^{2+} and Cd^{2+} in an aqueous solution. First, activated carbon was prepared from *Argan shells* (C). One portion was doped with magnetite (Fe_3O_4+C) and the other with cobalt ferrite ($CoFe_2O_4$+C). Characterization studies showed that C has a high surface area (1635 m^{2}g^{-1}) due to the development of micro-porosity. For Fe_3O_4+C the magnetic particles were Nano-sized and penetrated the material's texture, saturating the micro-pores. In contrast, $CoFe_2O_4$+C conserves the meso-porosity developed because most of the cobalt ferrite particles adhered to the exposed surface of the material. (Herrera-garc et al., 2019) Had assessed Activated Carbon from Yam Peels Modified with Fe_3O_4. Potential reuse of a magnetic adsorbent prepared from agricultural wastes of yam peels *(Dioscorea rotundata)* was studied. The procedure was performed through carbonization and activation at 400, and 500℃, respectively. Then, the as-prepared activated carbon (AC) was chemically modified using magnetite (Fe_3O_4) nanoparticles. AC and MAC were showed to have micro-porous structures with surface areas of 715 and 325 m^2/g, respectively. Super-paramagnetic behaviour was observed for MAC with a saturation magnetization of 6 emu/g. (Faulconer, 2012) had prepared Magnetic AC from Commercially available bituminous coal-based powdered activated carbon. The adsorbent composites were synthesized at room temperature by heterogeneous nucleation. According to the equation:

$$2Fe(OH)_2^+ + Fe(OH)^+ + 3OH^- \rightarrow (Fe)_2^{3+}(Fe)^{2+}(OH)^-{}_8$$

$$(Fe)_2^{3+}(Fe)^{2+}(OH)^-{}_8 \rightarrow \mathrm{Fe_3O_4} + 4\mathrm{H_2O}$$

The amount of activated carbon was adjusted to obtain 1:1, 2:1, and 3:1 C: Fe mass ratios. the 1:1 C:Fe resulted in approximately a 50% reduction of surface area from 1020 m^2/g to 551 m^2/g while the 2:1 and 3:1 C:Fe showed surface areas reduced by the expected to be approximately 33% and 25% to 709 m^2/g and 790 m^2/g, respectively. XRD data (not presented here) indicated no significant difference in iron speciation between the 1:1, 2:1 and 3:1 C: Fe MPAC samples. XRD analysis was performed by the researchers to identify the iron oxides present on un-oxidized 3:1 C:Fe as well as 3:1 C:Fe samples subjected to oxidation for 6 hours at 250°C, 350°C, and 450°C, respectively. The prepared adsorbent was retrieved from aqueous solution via magnetic solid-phase extraction. The sorbent recovery was not significantly influenced by the C: Fe, oxidation temperature or duration with all adsorbents investigated reaching a sorbent recovery rate ranging from 75 -91%.

(Ma et al., 2015) Had widely investigated on Novel synthesis of a versatile magnetic adsorbent derived from corncob. According to this literature, Corncob agricultural waste was successfully converted into a novel magnetic adsorbent by a low- temperature hydrothermal method (453 K), including carbonization under saline conditions and magnetization using iron (III) salt. The resultant magnetic carbonaceous adsorbent (MCA) exhibited a porous structure with a higher specific surface area and more oxygen-containing functional groups than its carbonaceous precursor (CP), which can be attributed to the catalytic effect of Fe (III). In addition, similar effect of $ZnCl_2$ on carbon precursor could be observed by XRD patterns. In comparison to the raw corncob, the characteristic peaks of lignocellulose became more obvious indicating that single hydrothermal process only removed impurities but without destroying the ‘‘core’’ structure of corncob. When $ZnCl_2$ was added into the hydrothermal system, signals of lignocellulose were completely depleted while a broad diffraction peak (2ϴ= 15–30°) attributable to aromatic carbon became dominant in the XRD pattern.

(Zhang et al., 2015) Prepared peanut shell based magnetic activated carbon (MPSAC) via a simple one-step method in the existence of K_2CO_3, and Fe_3O_4. The effects of activation temperature and activation time on the structures and properties of the activated samples were analysed. Results show that the development of the porous structures can be facilitated by increasing the activation temperature of the activation time. Compared with the activation time, the activation temperature was found to play the key role in the formation of magnet Fe_3C. At 750℃ for 1.5h or 800℃ for 1h, Fe_3O_4 was almost converted into Fe_3C. The prepared MPSAC-750-1.5 and MPSAC-800-1 demonstrated the high surface area with a micro-,meso- pores and macro pores combination.

2.6. Batch Adsorption

For last few years, researches have been undertaken using Magnetic ACs from biomass materials to study the efficiency of some fundamental requirements (Adsorption Isotherm, Adsorption Kinetics, and equilibrium data) on adsorption process. Parameters like Initial metal ion concentration, Contact time, pH, adsorbent dosage, and agitation temperature were mostly studied together with Adsorption Isotherm, and Adsorption Kinetics. Lead and various metals were removed using MAC prepared from various biomasses.

(Zhang et al., 2017) Batch adsorption experiments were carried out by varying the initial pH, contact time, adsorbent dosage, initial Pb^{2+} concentration, and temperature of solution. Results show that adsorption of Pb^{2+} on magnetic peanut shell based activated carbon was dependent on contact time, solution pH, adsorbent dosage, initial Pb^{2+} concentration, and temperature, especially solution pH having strong effects at pH 2–4. The study demonstrated, adsorption kinetic and equilibrium data were well described by the pseudo-second-order model and Langmuir isotherm with the maximum monolayer adsorption amounts of 146.20, 152.67, and 158.73 mg/g at 293, 303, and 313 K, respectively. Intra-particle diffusion mechanism was partially responsible for the adsorption. The thermodynamic study indicated that the adsorption was a spontaneous and endothermic process. (Jain et al., 2018) On the article presented, the optimum conditions for the removal of ions were pH=2 for Cr^{5+} and 6 for Cu^{2+} and Cd^{2+}, initial metal ion concentration=50 mg L−1, nanoparticle dose=50 mg/10 mL, temperature=25 ± 1℃, shaking speed=180 rpm, and contact time=3h. The equilibrium data of ions sorption were well described by Langmuir, Freundlich, Redlich-Peterson and Intra-particle Diffusion model. The R2 values obtained by Langmuir model were highest by Fe3O4/AC for Cr^{5+}=0.9994, Cu^{2+}=0.9998, and Cd^{2+}= 0.9750. The temperature dependent study in the range of 288–328 K confirmed that the adsorption process was endothermic in nature. Desorption studies with 0.1M HCl stated that these nanoparticles can be regenerated effectively, and can be used after four adsorption-desorption cycles without any mass loss.

(Benjedim et al., 2021) On the study, the adsorption capacity for Pb^{2+} was 389 mg g^{-1}, and 249 mg g^{-1}; while for Cd^{2+} was 269 mg g^{-1}, and 264 mg g^{-1}, for the Fe_3O_4+C and $CoFe_2O_4$+C, respectively. On the investigation, the predominant adsorption mechanism was found to be the interaction between -FeOH groups with the cations in the solution, which are the main reason these adsorption capacities remain high in repeated adsorption cycles after regeneration with HNO_3. (Nethaji et al., 2013) On the article have presented maximum adsorption of Cr^{6+}at pH 2. Isotherm data were modelled using Langmuir, Freundlich, and Temkin isotherm. The prepared MCCAC had a heterogeneous surface. The maximum monolayer adsorption capacity was 57.37 mg/g. Kinetic studies were carried out and the data fitted the pseudo second-order equation.

(Yin et al., 2018) Activated magnetic bio-chars were successfully synthesized via one-step synthetic method with different temperature (300, 500 and 700℃). The adsorbent showed better adsorption performance for 17β-estradiol (E2) and copper (Cu^{2+}) in single/ binary-solute systems than unmodified pristine bio-char. AMBC-700 exhibited the highest capacity (153.2 mg/g) for E2, while the AMBC-300 showed the best adsorption capacity (85.93 mg/g) for Cu^{2+} in single-solute system. Adsorption of Cu^{2+} and E2 both followed by pseudo-second-order and Langmuir isothermal model. The initial pH of the solution had an effect on the adsorption of E2 and Cu^{2+} in single-solute system. Co-adsorption experiments indicated that there existed site competition and enhancement of E2 and Cu^{2+} on the sorption in binary solute system. Results from this study indicated that the E2 was adsorbed by hydrogen bonds, π-π interactions. Cu^{2+} was mainly adsorbed via chemical complexation between contained oxygen functional groups and Cu^{2+} ions.

3. Materials and Methods

3.1. Materials

3.1.1. Chemicals

All chemicals used were analytical grade and bought from chemical shops in *Cherkos* area of Addis Ababa. Iron (III) chloride, phosphoric acid, distilled water were used for preparation of the magnetic activated carbon adsorbent. For batch adsorption experiments, stock solutions of Pb were prepared by adding analytical grade of $Pb(NO_3)_2$ into distilled water. H_3PO_4 was used as an activating agent. 0.1M NaOH, and 0.1M HCl were used to adjust the pH of the solutions, and NaOH was used to adjust the Point Zero Charge (PZC) of the adsorbent.

3.1.2. Equipment

Atomic Absorption spectrophotometer (Perkin Elmer model 3110) was used for the measurement of the concentration of elemental Lead. pH meter (Precisa model 900), Hot plate, filter papers (Advantech, 45µm), flasks, beakers (Borosilicate), analytical balance (PB 602-S), crucible, vacuum filter, magnetic stirrer, oven, and furnace (Muffle) were major equipment’s in Addis Ababa institute of Technology laboratory used in the preparation of the adsorbent.

3.2. Methods

3.2.1. Magnetic Activated Carbon Preparation

At first 1.5kg of corn cob sample was collected, washed by distilled water, and oven dried (105^0C for 24hr.). The corn cob sample was milled to 750 micrometre (Zhang et al., 2015) of sieve size. Soak 120g of powdered corn cobs by H_3PO_4 for 24hr at an impregnation ratio of 1:4, and H_3PO_4 concentration of 60%. Repeatedly wash the modified corn cobs, and then dry it again for 24hr at 105^0C. For the remaining 90g of impregnated corn cob, 45g of Iron (III) chloride was added, based on the ratio obtained from (Zhang et al., 2015). The mixture was stirred for 4hr by mechanical stirrer at 600rpm (Wang et al., 2017), then kept for overnight. The liquid part was filtered out, and the treated cobs kept. One Variable at a Time experimentations were made for temperature, and carbonization time in terms of response variables of Yield (%), and Pb^{2+} Removal (%). Those maximum values from the Pb^{2+} removal were used for further adsorption conditions.

Besides on the Carbonization process, carbonized materials after furnace were directly taken into a desiccator to inhibit the contact with oxygen (moisture absorption), and permitted to be cooled to room temperature. Then, weight losses while carbonization were calculated and recorded as yield. After the H_3PO_4 impregnation, and carbonization, the produced Corn Cob Magnetic Activated Carbons (CCMAC) found were washed by distilled water until neutral (desired) pH was achieved to eradicate contaminants, and residual Iron chloride ions, and Phosphoric acid from the pores and surfaces of the CCMAC. Lastly, activated carbons were dried in an oven at 105^0C for 24hr, milled, and packed by Aluminium foil for further analysis.

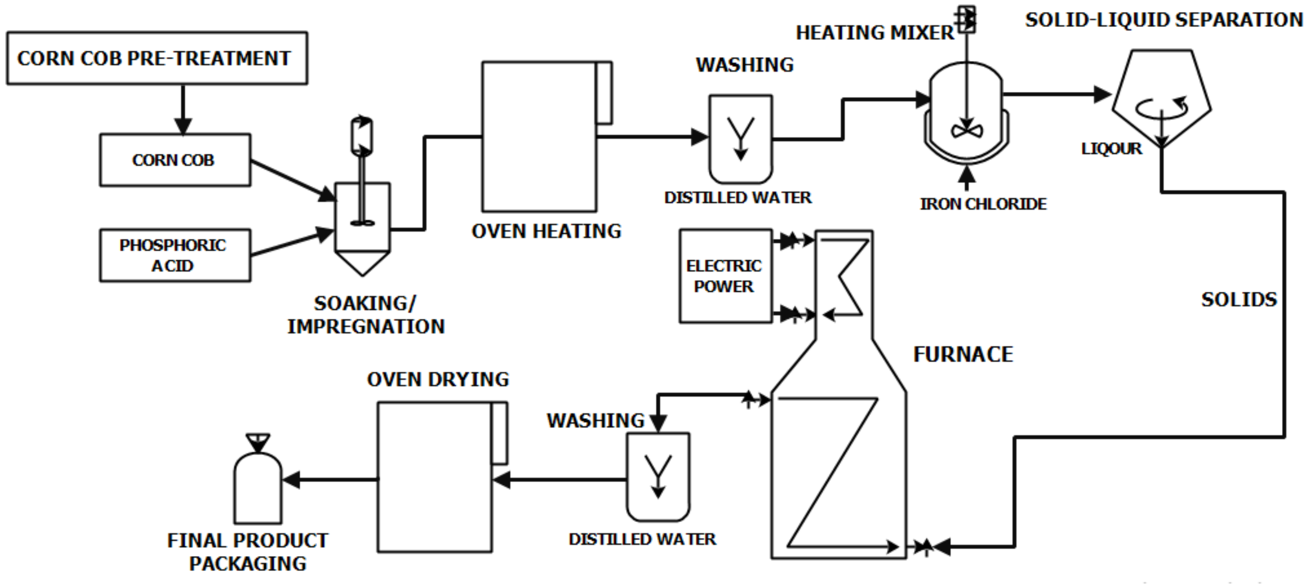


Figure 3.1:- Process flow diagram of Corn Cob Magnetic activated carbon (CCMAC)

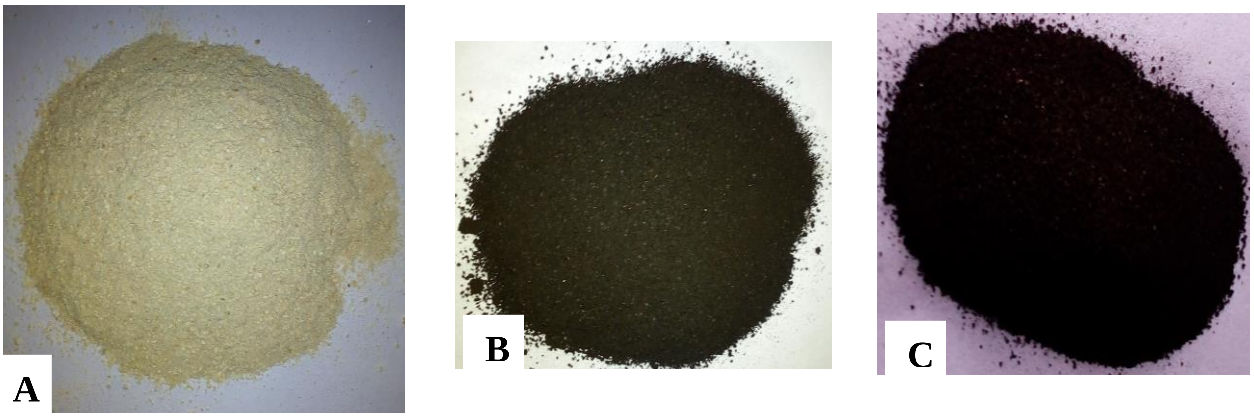


Figure 3.2;- A shows the Corn cob precursor, B shows the Phosphoric Acid impregnated and Iron Chloride treated Corncob, C is sample B after furnace (CCMAC).

3.2.2. Adsorbent Characterization

I. BET Surface Area Analysis

Surface areas of the produced Magnetic activated carbon were calculated using BET (Horiba, SA-9600) surface area analysis method through N_2 gas adsorption at a uniform temperature. The method was established by Stephen Brunauer, Paul Emmett and Edward Teller. This method determines the surface area according to gas adsorption on the solid porous material. It provides the surface area by applying the adsorption desorption data. From the output data the amount of gas required to create a monolayer on the surface of the material could be determined.

II. SEM Analysis

The SEM (INSPECT-F50) image of CCMAC was generated using scanning electron microscope to record the exterior surface morphology of the CCMAC. For the SEM image the carbon tape was cut into small pieces and fixed on the disc. Then the upper layer of the disc was detached and very small amount of carbon was positioned on the black carbon tape, well fixed just pressing on a clean silicon wafer (Miguel et al., 2001). The result was recorded as an image.

III. Determination of point of zero charge

Fifty millilitres of 0.1 M NaCl solution were transferred to 7 100 ml calibrated beakers and capped. The initial pH of the solutions was aset in the range of 3-9 by using 0.1 M HCl and 0.1 M NaOH solutions. The total volume of the solution in each bottle was adjusted exactly to 80ml by inserting the NaOH solution. 0.5g of dry CCMAC was added into each beaker and the suspensions were then equilibrated for 48hr. After equilibration time, the solutions were filtered and the final pH value of the filtrate was measured. The difference between initial and final pH values (ΔpH= pHi-pHf) was plotted against pHi. The intersection point of the resulting curve with X-axis, at which ΔpH=0, was the indication of the point of zero charge.

IV. X-ray diffraction (XRD)

X-ray diffraction is required to investigate the deposition of Fe containing ions on the surface of CCMAC. It is used to provide details which will help to realize the structures of minerals and other crystalline matter on an atomic scale. It creates associations between the crystal structure, physical and chemical properties of the CCMAC

X–ray diffraction (XRD) patterns was recorded with Cu-Kα (λ=1.540593-1.544414 Å, 40 KV and 15 mA) radiation having a continuous scanning mode with speed of 10 deg/min. X-ray diffractograms of the samples were obtained for the 2θ angles.

3.2.3. Batch Adsorption Experiments

I. Solution preparation for the experiment

The wastewater (contaminant) containing Pb^{2+} ions were artificially prepared in a laboratory. This was to investigate effect of Pb^{2+} ions particularly. A lead stock solution with 1000 mg/L (1000 ppm) of was prepared by dissolving 1.599g of lead nitrate, $Pb((NO_3)_2$ in one litre of distilled water, and was used to prepare the other working solutions with various initial lead concentrations by series of dilutions. 1g of standard solution of Pb^{2+} could be made based on the calculation of division of the total Molecular Weight of lead nitrate (331.2g/mol.) to total Molecular Weight of lead (Pb = 207.2 g/mol.). Therefore, the result will be 1.599g of lead nitrate to be inserted in 1000ml volumetric flask.

II. Effect of Adsorbent Dosage

The effect of adsorbent dosage for the removal of Pb^{2+} was assessed by performing a batch adsorption study using CCMAC sample with optimum Pb^{2+} removal efficiency. 150 ml of Pb^{2+} solution with concentration of 75 mg/l were added in to series of seven 250 ml beakers each of them containing various masses of CCMAC sample (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4g). The mixture was agitated by magnetic stirrer at room temperature till constant efficiency was attained. Once filtered using *beimu* filter paper, the Supernatant were taken in to Atomic Absorption Spectrophotometer to determine the final Pb^{2+} concentration (C_f) of the supernatant. The removal efficiency of the adsorbent was calculated by the equation (1).

$$Lead\ Pb^{2+}\ Removal = \frac{C_o - C_f}{C_o} * 100 \qquad (1)$$

Where: Co = initial conc. of Pb^{2+}*, and Ct = finial concentration of the* Pb^{2+} *after time*

III. Effect of Contact Time

To analyse the effect of contact time on the adsorption process, various experiments were performed by varying the stirring (30, 60, 90, 120, 150, 180, and 210 min). 1g of CCMAC sample were taken in to five different beakers of 250 ml, and 150ml of prepared Pb^{2+} containing solution having initial Pb^{2+} concentration of 75mg/l, and pH of 5. The mixture was stirred at atmospheric temperature. At the end of adsorption of each time periods, samples filtered and final concentration checked by AAS. Finally, the percentage removal was calculated accordingly to equation (1) presented above.

IV. Effect of pH

Determination of the effect pH value for removal of the Pb^{2+}, the batch type adsorption experiments were performed at various solution pH of 3.5, 4, 6, 8, and 9 by addition of required volumes of either 0.5M HCl or 0.5M NaOH solution to adjust the pH. 1g of CCMAC was stirred with 150 ml solution of Pb^{2+} in each beaker at room temperature. Adsorption experiments were carried out, and the Pb^{2+} ion removal percentage was calculated using the formula as stated earlier.

V. Effect of Initial Concentration of Pb^{2+}

The effect of initial concentration of Pb^{2+}, 150 ml of Pb^{2+} solution at a concentration of (75, 100, 125, 150, 175, 200, 225, 250, and 275 mg/l) were added in series of 250 ml beakers each having 1g of CCMAC. The mixture was stirred at room temperature till constant efficiency was attained. At the end of the appropriate time, the solution filtered, and the supernatant kept to know the final concentration by AAS. Finally, percentage removal of the Pb^{2+} was determined from the relationship mentioned by equation (1), as a result the sample with highest adsorption efficiency could be taken as the best condition for optimization process.

3.2.4. Optimization of Adsorption

The optimization of the adsorption process was planned to be performed based on the pre-made OVAT experimentations higher, and lower parameters for further optimization. For the ease of optimization well use of time, and budget, holding time was fixed to the optimum value of effect of contact time. This is because increasing time more than this time would be waste of time, without getting any change in the lead ion removal efficiency. Full factorial experiment is an experiment whose design consists of two or more factors, each with discrete possible values or "levels", and whose experimental units take on all possible combinations of these levels across all such factors. A full factorial design may also be called a fully crossed design.

3.2.5. Adsorption Isotherms

The adsorption isotherm is significant to define how the Pb^{2+} interacts with the CCMAC. The adsorption capability of the CCMAC is a vital factor for designing an adsorption system. Adsorption equilibrium isotherm forms the relationship between Pb^{2+}, and CCMAC at a fixed Temperature. Adsorption isotherm is an empirical relationship applied to calculate how much Pb^{2+} can be adsorbed by CCMAC. Adsorption isotherms provide information about the effects of the solution concentration on the adsorption capacities of the Pb^{2+}, and interaction of adsorbate molecules with CCMAC. Distribution of Pb^{2+} between the liquid phase and the solid phase can be described by the two well-known isotherms such as Freundlich, and Langmuir, adsorption isotherm.

In this investigation, Adsorption isotherm were accompanied by addition 1g of CCMAC to 150 ml of various initial concentrations (50, 100, 150, 200, and 250 mg/l) of the Pb^{2+} to be adsorbed, and the adsorption process was done by magnetic stirrer 25^0C. After the adsorption was over, the CCMAC was filtered out, and equilibrium concentrations (C_e) were determined.

The Langmuir isotherm model assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform surface. The Langmuir isotherm equation could be expressed by:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_L} + \frac{C_e}{q_L} \qquad (2)$$

K_L (l/mg) is an adsorption constant that reflect the affinity between the CCMAC, and Pb^{2+}. q_L, and K_L could be determined from the slope, and intercept of the plots of C_e/q_e versus C_e. q_e represents the amount adsorbed per amount of adsorbent at the equilibrium (mg/g), C_e represents the equilibrium concentration (mg/L), and K_L is an adsorption constant.

The Freundlich isotherm is introduced as an empirical model. This model describes systems, where the adsorption done on heterogeneous surfaces with interactions between the adsorbed molecules; the form was given by Equation (3): The constant K_F is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. C_e represents the equilibrium concentration (mg/L).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (3)$$

Temkin isotherm based on the ions sorption heat, which is due to the adsorbate and adsorbent interactions, is given by the following equation:

$$qe = \beta ln K_T + \beta ln C_E$$

3.3. Adsorption kinetic

Kinetics of an adsorption process is a basic procedure that offers an information about mechanism, and characteristics of the adsorption process following that have an impact on the rate controlling step. In the investigation of kinetic experiments for Pb^{2+} uptake were approved by addition 1g of CCMAC to a 150 mL of Pb^{2+} containing solution (75 mg/l) in a stirrer at atmospheric temperature for varying contact time (20,40,60, 80, and 100 min).

Various kinetic models have been useful to inspect the controlling mechanism of Pb^{2+} ion adsorption from synthetic solution. Kinetic models like pseudo first order, and pseudo second order kinetic models were applied for the fitting of the experimental data, to distinguish the rate, and type of adsorption on adsorbents. The pseudo first-order model detects the adsorption based on the adsorption capacity of CCMAC. The pseudo first-order model could be expressed by the equation (4) below:

$$\log(q_e - q_t) = log\ q_e - \left(\frac{K_1 * t}{2.303}\right) \qquad (4)$$

Where: K_1 is pseudo first order rate constant, q_e, and q_t denotes the quantity of metal ions adsorbed at equilibrium, and at time (t), respectively.

A second order model for the adsorption of Pb^{2+} onto CCMAC particles based on the adsorption capacity of the CCMAC with the aim of differentiating the kinetics of a second-order rate expression based on the CCMAC adsorbent concentration from models, which are based on the solute concentration, and signify pseudo-second-order rate expression. The pseudo-second-order model is expressed by Equation (5).

$$\frac{t}{q} = \frac{1}{K_2} q_e^2 + \frac{t}{q_e} \qquad (5)$$

Where: q_e(mg/g) is the quantity of Pb^{2+} adsorbed on the CCMAC at equilibrium, K_2 ($g.mg^{-1}min^{-1}$) is the rate constant of the pseudo-second-order adsorption, and q_t(mg/g) is the amount of Pb^{2+} adsorbed on the CCMAC at any time (t).

3.4. Regeneration Studies

Regeneration and reusability of Magnetic adsorbent material was studied by employing 1M of HNO_3 as a desorbing solution. The experiments were performed by employing 1 g of saturated adsorbent in 100 mL of HNO_3, and were stirred at 200 rpm, at 25°C by mechanical stirrer for 2hr. 200mL of 10mg/L of Lead ion concentration was prepared (at pH of 8 and rpm of 200) and the regenerated sample was put in it. After well mixing for 2.5hr, the concentration of Pb^{2+} in the solution was checked by atomic absorption spectrophotometer, and the CCMAC was washed by ethanol then dried out at room temperature. Finally, the adsorbent material was recycled for cations adsorption in six consecutive cycles at pH = 5.

4. Result and discussion

4.1. Preparation of Magnetic Activated Carbon

4.1.1. The effect of Carbonization Temperature

The carbonization temperature is significant parameter in the preparation of CCMAC by having prominent effect on the yield, and Pb^{2+} removal efficiency. Figure 4.1 denotes the effect of temperature on yield of CCMAC, and Pb^{2+} removal efficiency. The percentage yield found decreased with the enhancement of temperature, meaning that the conversion of lingo-cellulosic matter to elemental carbon continued. The yield had lost from around 65% at 300 to 30% at 700^0C. Beyond 700^0C, the yield became almost constant. This is due to; the carbon materials were being lost with volatile components. For the case of Pb^{2+} removal, increasing temperature from 300-600^0C leads to an increment of Pb^{2+} removal efficiency from 33 to 91%. The lowest removal of Pb^{2+} beyond these maxima was found at 800^0C (around 73%). The decrease was due to the extreme thermal treatment that caused the collapse of cross-links in the carbon matrix, together with a rearrangement of carbonaceous aggregates, and the breakdown of pores. These either narrowed or widen the pores to accept the Pb^{2+} ions. Similar results were reported by many authors for various kinds of precursor (Zhang et al., 2018).

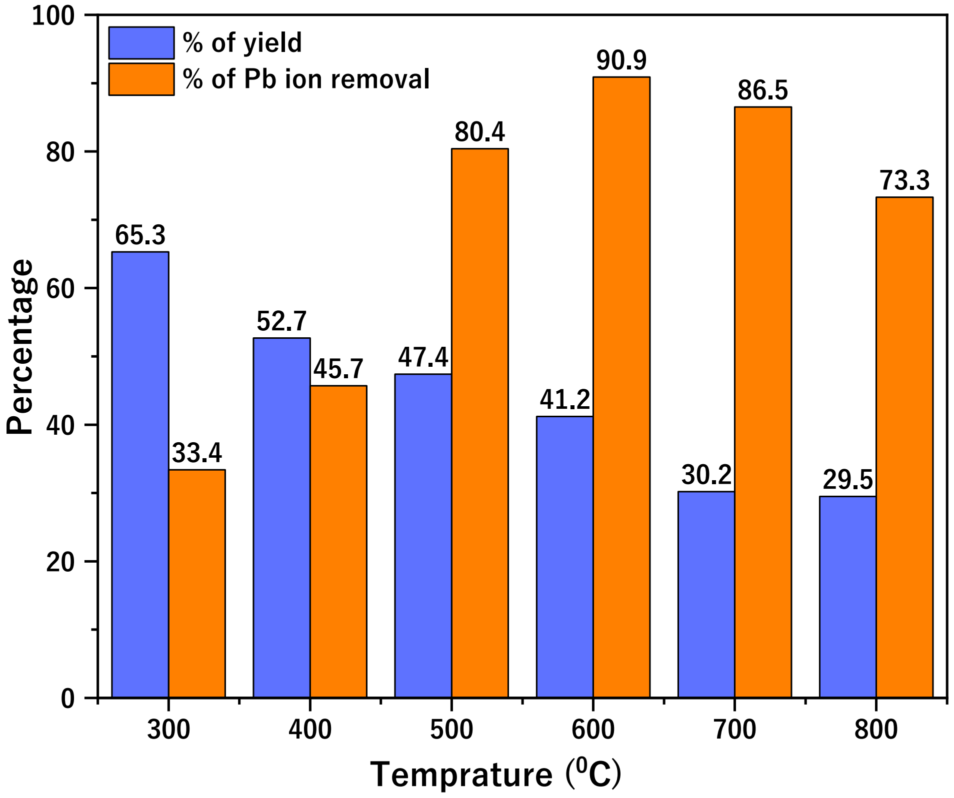


Figure 4.1:- The effect of Temperature on yield (%), and Pb^{2+} Removal (%) at constant parameters: Iron Chloride to Activated corncob ratio of 1:2, Corncob precursor to Phosphoric acid ratio of 1:4, adsorption time of 1Hr, Initial Pb^{2+} concentration of 75mg/l, adsorbent dose of 1g, Carbonizing time of 1.5hr, and stirring speed of 200rpm.

4.1.2. The effect of carbonization time

Figure 4.2 represents the effect of carbonization time on yield of CCMAC. The percentage of yield obtained decreased with the increase of holding time. With the increase of holding time from 0 to 6 hr, the yield of prepared CCMACs was decreased from 100 to around 38 %. According to [Zhi L.L, 2020], it could be attributed to the release of more volatiles by keeping the sample for longer duration in the furnace, because of the higher carbon burn-off. As the carbonization time increases, the pores of the CCMAC decreases due to damaging caused by excessive heating for long period of time. This diminishes both surface area of the CCMAC which lead to decrement of Lead (II) ion adsorption efficiency. In other words, the decrease in BET surface area of CCMAC for the carbonization time period was responsible for the decrement of Lead ion up taking efficiency due to the extended activation of the product, resulting in shrinkage of char structure, widening, and combining of some micro pores into meso pores.

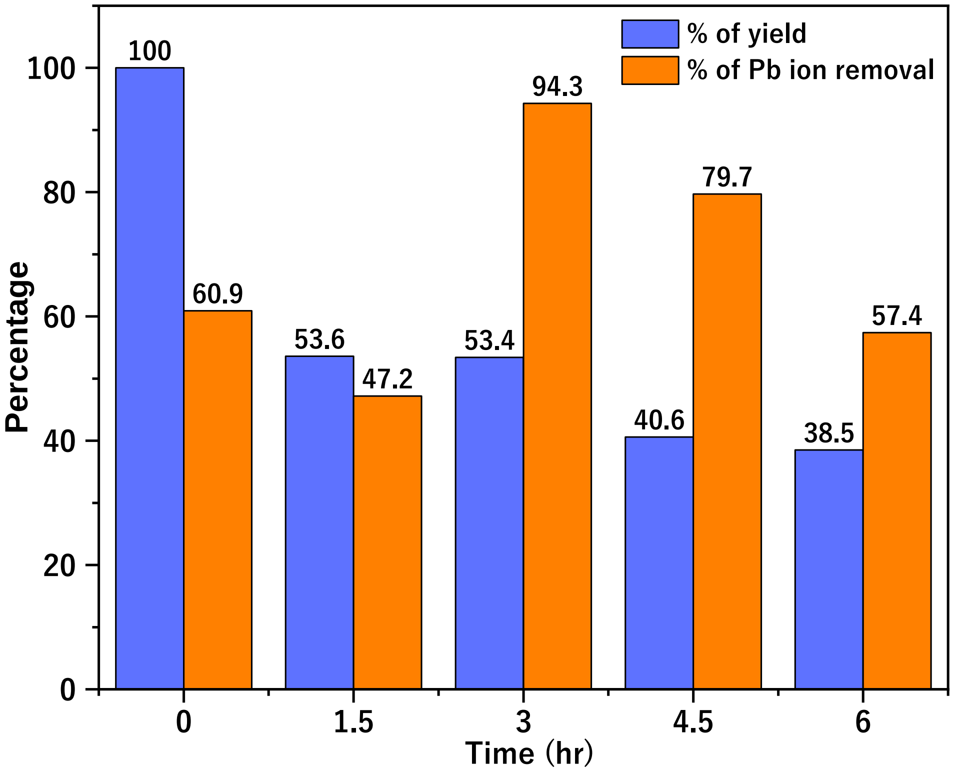


Figure 4.2:- The effect of Time on yield (%), and Pb^{2+} Removal (%) at constant parameters: Iron Chloride to Activated corncob ratio of 1:2, Corncob precursor to Phosphoric acid ratio of 1:4, adsorption time of 1Hr, Initial Pb^{2+} concentration of 75mg/l, adsorbent dose of 1g, Carbonization Temperature of 400^0C, and stirring speed of 200rpm.

4.2. Characterization of CCMAC

4.2.1. Physio-Chemical/ Proximate Characterization

This section of the work is presented to address specific objective to which is intended to describe physico- chemical and surface characteristics of Corn cob magnetic activated carbon produced and predicted to optimum production parameters. The optimum conditions according to the OVAT result show parameters of 3hr and 600℃ for respective carbonization time and temperature.

Table 4.1:-Experimental data on the Characterization of CCMAC prepared at optimum point (3hr and 600℃).

Characteristics	**Unit**	**Value at optimum point**
Moisture Content	%	1.26
Volatile Content	%	15.39
Ash Content	%	20.43
Fixed Carbon Content	%	62.92
Conductivity	ms/cm	0.91
Bulk Density	g/ml	1.09
pH	-	6.2

4.2.2. Point Zero Charge (PZC)

The electro-static properties of CCMAC surface were confirmed by drawing its pH_{PZC} graph as shown in Figure 4.3. It can be seen that the pH_{PZC} at, which the adsorbent surface of CCMAC acquires a neutral charge was around pH_{PZC} of 3.5. Consequently, the positively or negatively charged CCMAC exterior surfaces found by adjusting solution pH smaller or greater than pH_{PZC} of 3.5, respectively, is substantial to explain effects of pH on adsorption of Pb^{2+} ions. In other words, it can be expected that the solution pH greater than 3.5 is positive for adsorbing positively Pb^{2+} ions onto CCMAC adsorbent. This is acidic $pH_{PZC.}$ whereas (Zhang et al., 2018) shows a basic pH_{PZC} of approximately 8.1. Which show a good correlation between the pH_{PZC} and oxygen content of the prepared MAC.

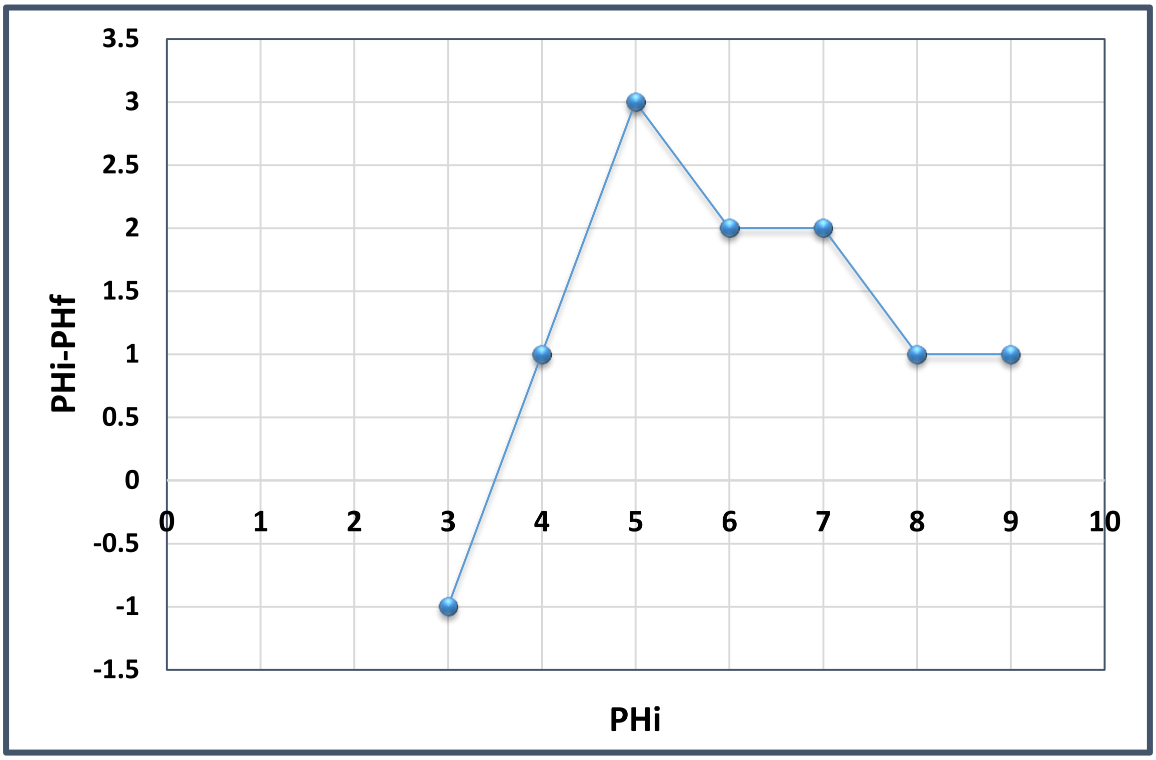


Figure 4.3:- Point Zero Charge plotting

4.2.3. Brunauer-Emmett-Teller Surface (BET) surface Area Analysis

BET, which is Nitrogen adsorption surface area measurement mechanism, is a highly convenient tool in the characterization of amorphous materials. It helps to know the exact surface area with only 1% of error. The Activated Carbon (separately prepared for the purpose of comparison) sample had a total surface area of 711 m^2/g. These surface area decreases to 504 m^2/g, while Corn Cob based MAC was checked. The reason behind was the existence of Iron oxide and elemental Iron with in the pores. The MAC containing/adsorbing lead ions was found to have a surface area of 398.5 m^2/g surface area. This was due to chemical/ physical adsorptions and magnetic attracting nature of the prepared CCMAC. These results are consistent and even better than some of the literatures with former studies of (C. Chen et al., 2019) and (Yin et al., 2018), they reported 645 and 359m^2/g.

4.2.4. Scanning Electron Microscopy (SEM)

The surface morphological structure of Corn Cob based Magnetic Activated Carbons have shown in Figure 4.4 Based on this Figures (A), which represents the SEM images of CCMACs, the surface exhibits a well porous morphology structure with small pores of various shapes and sizes. Substantial morphological variation was demonstrated Compared to Figure (B), which adsorbed Pb^{2+} ions. The image of Figure (B) at increased magnification of 68,823X didn’t indicate a well-developed macrospore structure, because of the residual polymeric matrix, Pb^{2+} ions, and other organic substances filled within them. The internal structure of the coarse particles was irregular with many gullies and openings. The Figures (A), (B) and (C) showed the morphology of CCMAC different magnifications of 5,578X, 68,823X, and 5,578X respectively. In addition, Roughs, gullies, and frequent hills had been observed on the SEM images of both samples, and the effect of the Lead ions had been seen by the images. Comparing SEM images of similar magnification roughness, and frequent hilliness were found to a more extent on after adsorption (C) samples. On the Figure 4.4 (C), the pore openings could be observed clearly. For the magnetically modified adsorbents after adsorption of heavy metals, the almost homogenous surface suggests that virtually all cavities on the surface have been occupied by the nanoparticles or pollutants (Ighalo & Adeniyi, 2020).

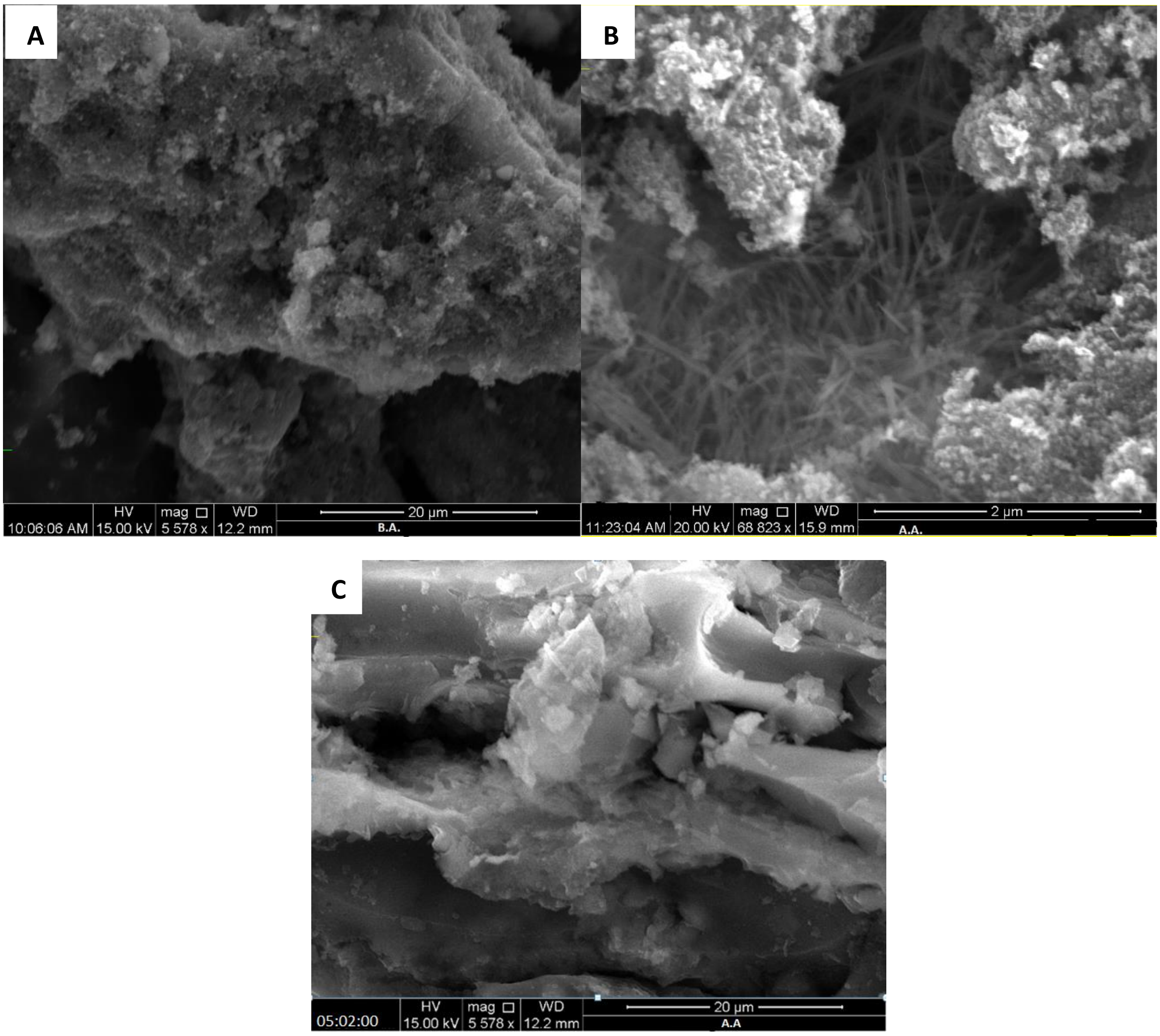


Figure 4.4:- SEM Imaging of CCMAC before Lead Ion Adsorption (A), After Lead Ion Adsorption (B), and (C) After Lead adsorption (B and C with different magnification).

4.2.5. XRD-Analysis

To discover which minerals are present in the samples XRD analysis were found important. In the first sample (Before Adsorption) the minerals like Carbon, Fe_2O_3, and Fe_3C, at degrees of 29.8, 44.8 and 65.7^0 respectively. The related XRD patterns are shown in Figure 4.5, which have the comparatively similar XRD profiles to (Jain et al., 2019). The dominant minerals were Carbon, Fe_2O_3, Fe_3C, and Lead Oxide at degrees of 24.8, 29.7, 44.6, and 75.5^0 respectively. Hence, it can be concluded that the Lead ions form oxide within the CCMACs that adsorbed Lead ions. In both samples elemental carbon, Iron Oxide and Iron Carbide were also been revealed.

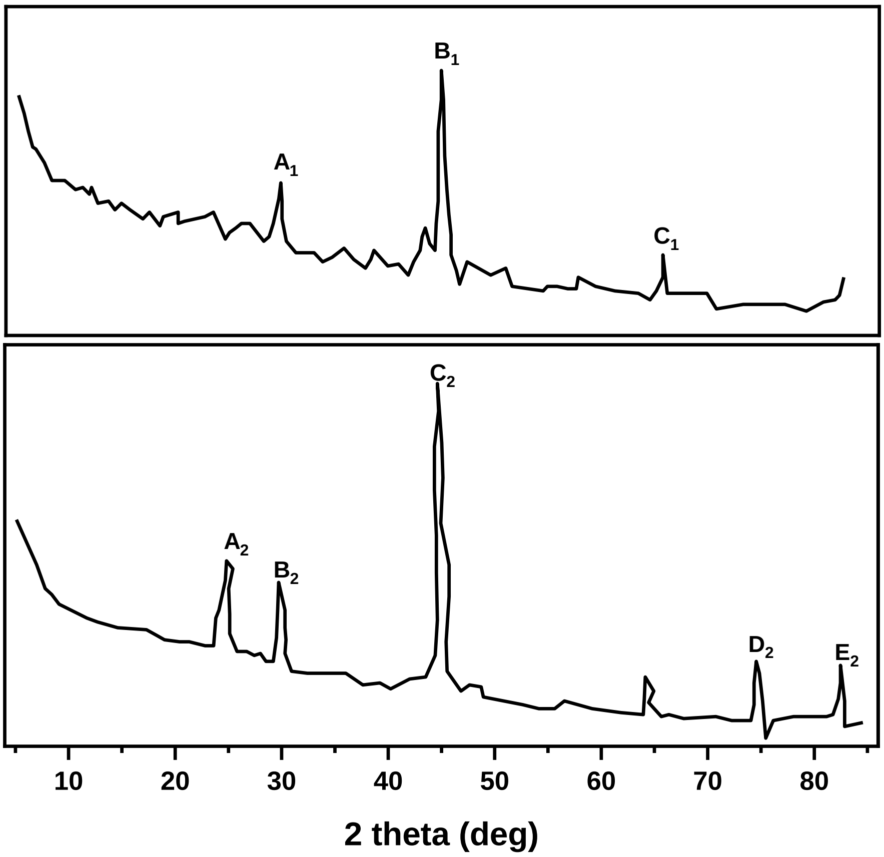


Figure 4.5:- Smoothed XRD analysis of CCMAC (Before adsorption of Lead ion (A_1= Carbon), (B_1 =Fe_2O_3), (C_1 =Fe_3C)) and CCMAC (After adsorption of Lead ion ((A_2= Carbon), (B_2 =Fe_2O_3), (C_2=Fe_3C), (C_2=Fe_3C), (D_2 = Lead Oxide)).

4.3. Batch Adsorption Experiments

All of the following adsorption processes had been carried out by using the CCMAC prepared at 3hr and 600℃.

4.3.1. The effect of Initial Pb^{2+} Concentration

The initial Pb^{2+} ion concentration offers driving force to exceed all mass transfer resistances of Pb^{2+} ion between aqueous and solid phases. In doing so, the amount of accessible adsorption sites in adsorbent is the same for all initial concentrations. As a result, the initial concentration increases with more number of ions, competes for similar adsorption sites. This causes Pb^{2+} ions to leave without being attached to the adsorbent, and to reduction of the adsorption efficiency of the removal of Pb^{2+}ions.

Solutions of various Pb^{2+} concentrations were organized from the stock solution at constant parameters: pH of 5, contact time of 2hr, CCMAC dosage of 1g, and temperature of 293K. As the initial concentration of Pb^{2+} in the solution increased, percentage removal efficiency of the Pb^{2+} decreases. The percentage removal efficiency of Pb^{2+} diminished from around 98% to 45% as the initial concentration is enhanced from 75 mg/l to 250 mg/l. The reason is that the total available adsorption sites of adsorbent with fixed dosage were insufficient when high Pb^{2+} concentrations were used. Similar results were reported by (Y. di Chen et al., 2018; Zhang et al., 2018). The removal efficiency at a stable adsorbent dose on the effect of initial concentration of Pb^{2+} ions is shown in figure 4.6.

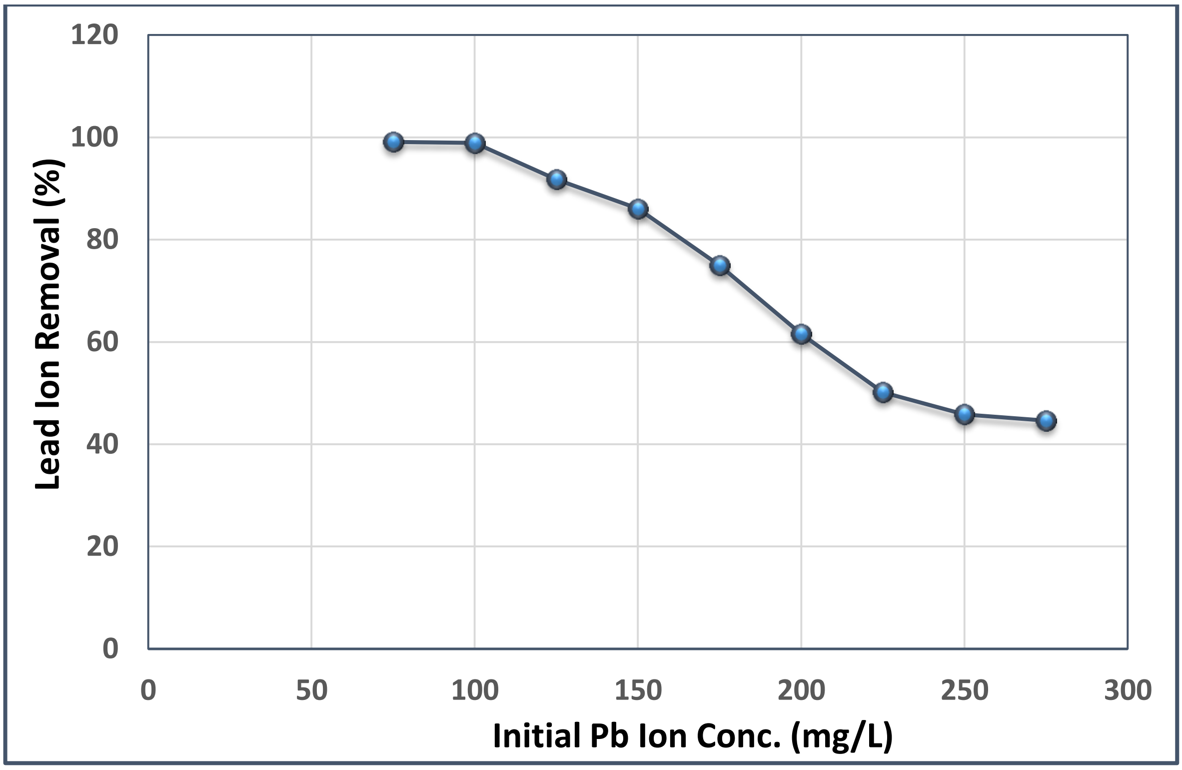


Figure 4.6:- The effect of Initial Pb^{2+} Concentration at constant parameters: pH of 5, contact time of 2hr, CCMAC dosage of 1g, 200rpm, and temperature of 293K.

4.3.2. The effect of Contacting time

As illustrated in figure 4.7. The removal of Pb^{2+} increased with contact time. The increment was rapid initially up to 150 minutes; afterwards it proceeded at sluggish rate in order to attain saturation/equilibrium. Numerically before equilibrium, time- removal efficiency varies directly as 30min (36%) to 180min (95%). This suggests that initially, adsorption took place quickly on the exterior surface of the adsorbent preceded by a slower internal diffusion, which may possibly be the rate defining step. Additionally, the variation was due to the plentiful surface sites available and the relatively high concentration gradient initially, which leads increased adsorption.

After 150min, it was challenging to occupy the existing vacant surface sites, due to the repulsion among the solute molecules in the solid, and bulk phases. A similar result was also reported by (Y. di Chen et al., 2018; Zhang et al., 2018). This situation was associated with the competitive diffusion process of Pb^{2+} through the micro channels, and pores. It could block the inlet of the micro channels/ pores, and stop the Pb^{2+} ions from passing entirely deep inside of the Magnetic activated carbon for the maximum initial Pb^{2+} concentrations, thus increasing the equilibrium time.

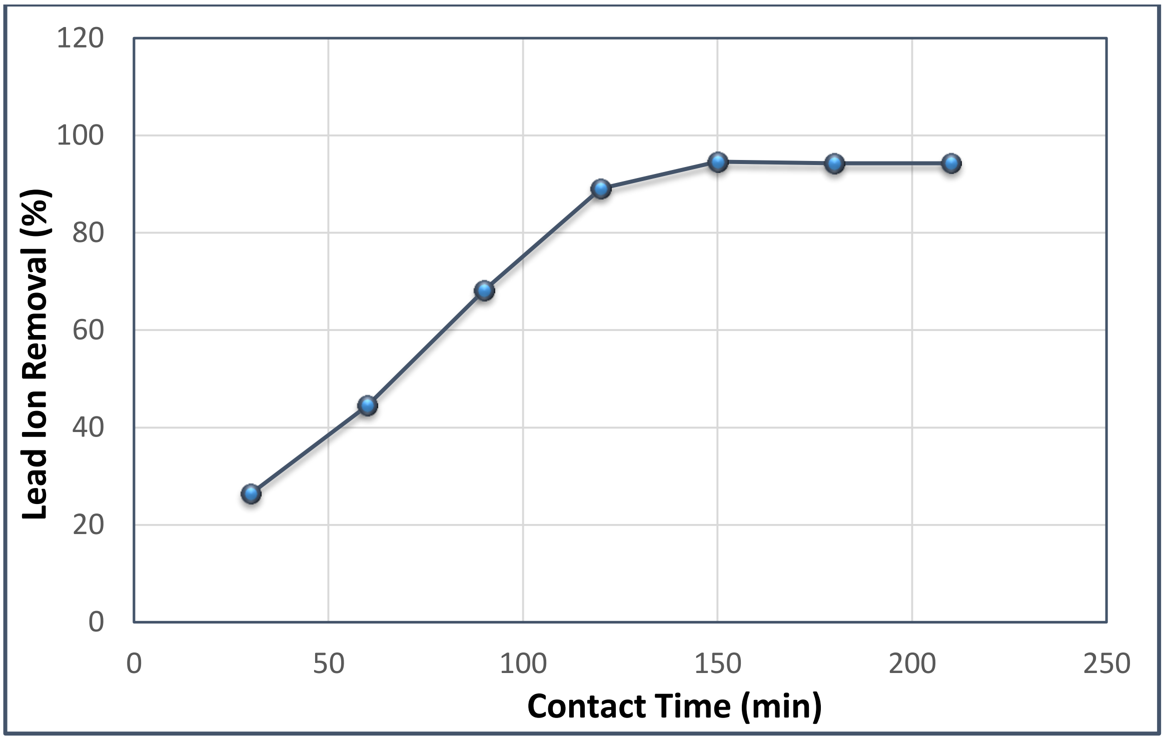


Figure 4.7:- The effect of Contacting time at constant parameters: pH of 5, initial Pb^{2+} concentration of 75mg/l, CCMAC dosage of 1g, 200rpm, and temperature of 293K.

4.3.3. The effect of Magnetic AC amount

The amount of CCMAC adsorbent added is important parameter to be studied in the adsorption process. As it can be understood from Figure 4.8, adsorption of Pb^{2+}increased from 48 to around 96% with addition of adsorbent dose from 0.2 to 0.8g, respectively. This can be explained due to the fact that the higher the dosage of adsorbent in the solution, the greater the availability of exchangeable sites for metal ions. The removal of Pb^{2+} 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, and loss of the initial Pb^{2+} concentration, which leads to the reduction of the mass transfer/ adsorption power. Therefore, 0.8g of adsorbent dose was taken as an optimum dose for further optimization experiments. According to (Zhang et al., 2018), it is suggested that the Pb^{2+} may transform into hydroxide precipitation of an extremely low solubility with the higher dosage of adsorbent. Larger dosage can provide more active sites which will improve the Pb^{2+} removal percentage, but not all adsorption active sites will be used to remove the Heavy Metal because of overlapping and aggregation. Comparable results were presented by (Emenike et al., 2016; Zhang et al., 2018).

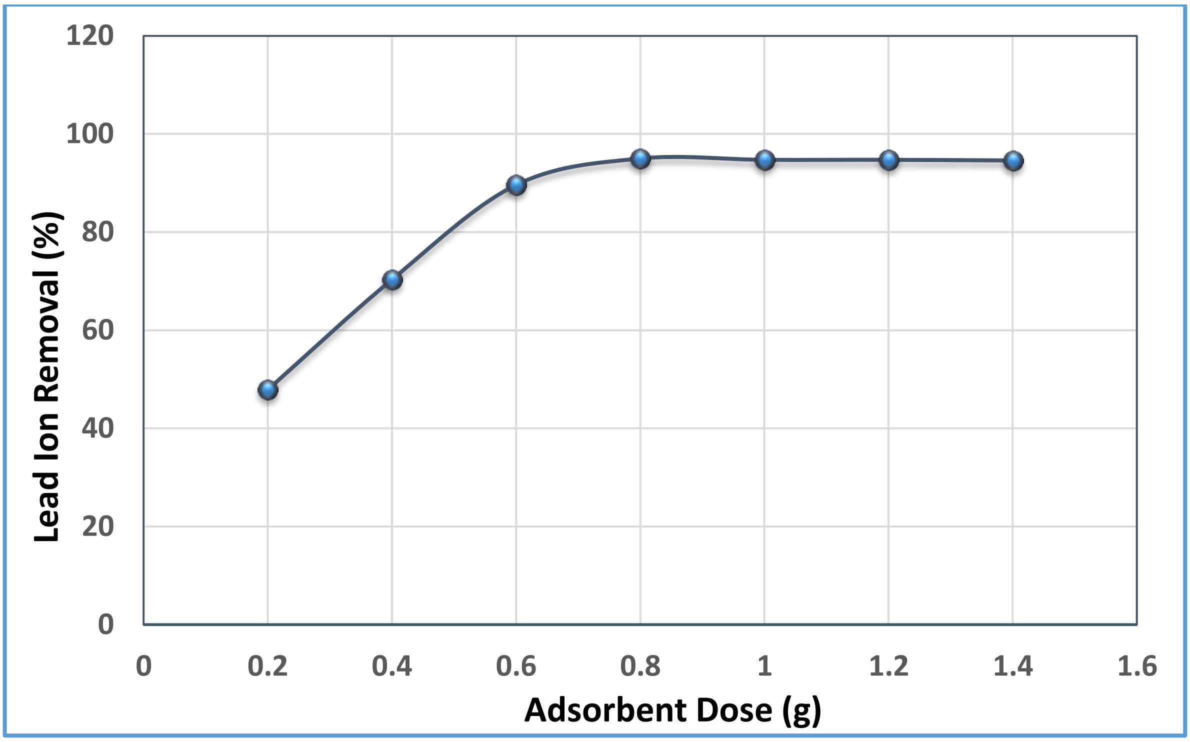


Figure 4.8:- The effect of adsorbent dose at constant parameters: pH of 5, initial Pb^{2+} concentration of 75mg/l, contact time of 2hr, 200rpm, and temperature of 293K.

4.3.4. The effect of pH

The pH of solution has a substantial impact on metal adsorption, since it defines the surface charge of CCMAC adsorbent, and the degree of ionization. On the study, it was exposed that the solution pH does directly affect the amount of lead adsorption. The effect of pH was tested by changing pH of solution in the range of 3.5-9, thereby found increment of the adsorption efficiency from 76 (pH=3.5) to 94% (around pH=5.2). This could be explained by the electrostatic interaction between the negative charge surface of CCMAC and Pb^{2+} ions. After this maxima pH of around 5.5, consistency of efficiency was attained for any increment of pH. At pH exceeding 6, as reported by (Sedighi et al., 2012; Zhang et al., 2018), species such as $Pb(OH)^{+}$, $Pb_3(OH)_4{}^{2+}$, and $Pb(OH)_2$ were produced. The interference of these ions results in the precipitation of lead, which no longer doesn't result in the increasing of the adsorption efficiency. This study demonstrated reason for the decreasing of removal efficiency of Pb^{2+} at low pH. More importantly, the higher pH would not influence the environmental water quality.

Additionally, the probable reason for the fact that acidic efficiency was lower than basic efficiency (overall), might be associated to the protonation of adsorbents exterior surface at relatively lower pH, inhibiting positive metal ions to reach adsorption sites due to the electrostatic repulsion. Besides, at relatively low pH, the adsorbent surface could be covered by a high concentration layer of positive charges of H^+, leading to a strong competition for occupying adsorption sites by metal ions, and ensuing in the reduced adsorption efficiency. The adsorption efficiency slightly increased to reach to saturation at pH values higher than 3.5. In general, the influence of relatively high pH on the removal efficiency of metal ions from aqueous solution can be attributed to not only the change of charge surface properties, but also the precipitation of metal hydroxides in solution as discussed above, and on the point zero charge (PZC) characterization section.

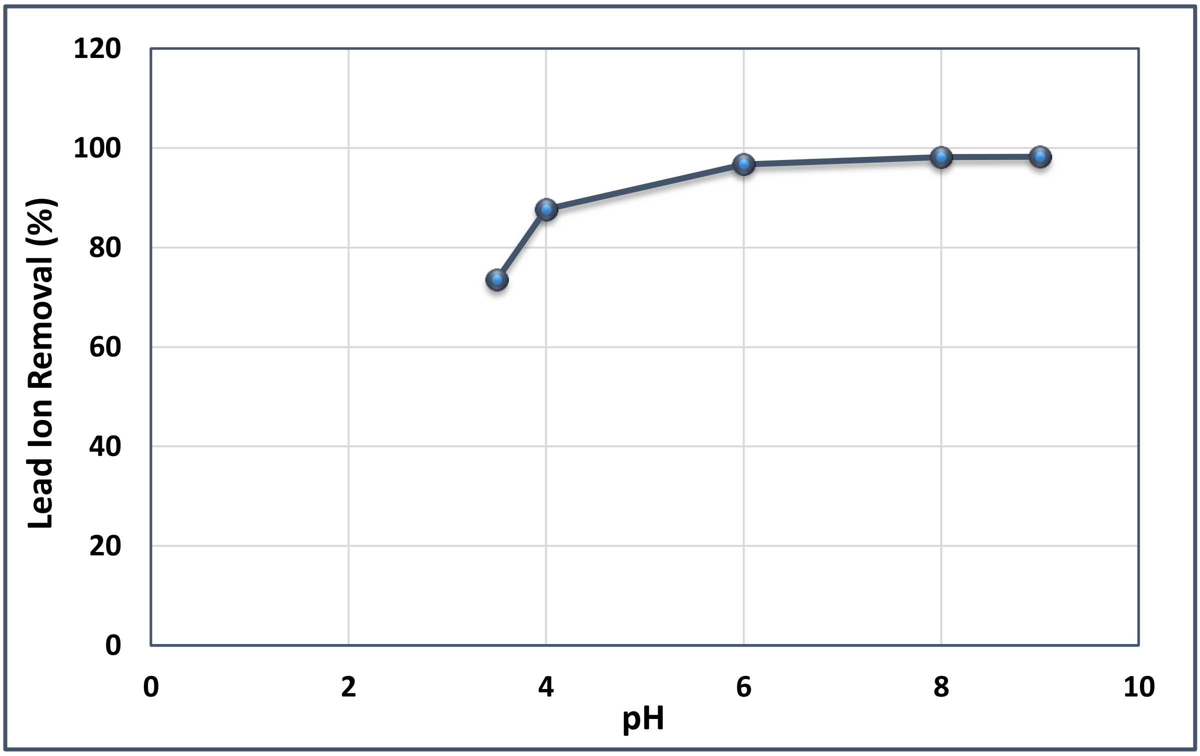


Figure 4.9:- The effect of pH at constant parameters: adsorbent dose of 1g, initial Pb^{2+} concentration of 75mg/l, contact time of 2hr, 200rpm, and temperature of 293K.

Based on these OVAT experiments, higher, and lower parameters for further optimization were determined, and depicted on the table below. Here with for the ease of optimization experimentation, well use of time, and budget. Holding time was fixed at 150min. This is because increasing time more than 150min is waste of time, without getting any change in the lead ion removal efficiency. The adsorbent used for optimization was the one prepared at 3hr and 600°C.

Table 4.2:- shows table of parameters and units with lower and higher values.

Parameter	**Unit**	**Lower value**	**Higher value**
Adsorbent dose	g	0.6	1
Initial Pb^{2+} concentration	mg/l	75	125
pH	-	4	6

4.4. Modelling of the Adsorption Process

Full Factorial Design was used to model, and optimize diverse processing parameters. Operational parameters with optimum adsorption removal efficiency of Lead ion were predicted using developed model. Consequently, first model development, and evaluation was presented. Second the effect of concentration of Pb^{2+} ion, pH, and adsorbent dose on adsorption removal efficiency of Lead ion (Pb^{2+}) was examined. Then finally via the model optimum points of operating parameters were projected.

4.4.1. Development and evolution of model prediction

Twenty Seven unique experimental runs were carried out. Each experiment conducted based on the procedure defined in methodology section. For each experimental runs, adsorption of Pb^{2+} removal was calculated using the methodology described. Experimental results of adsorption of Pb^{2+} removal were fed to Design Expert Software for full factorial design.

It was found that 2FI model was the most appropriate model to define effect of selected processing conditions in adsorption conditions of Pb^{2+}. The final obtained equation for prediction of response variable based on coded factors was tabulated as follows;

$$Rem\ eff = 88.93 - 3.74A + 2.41B - 7.48C + 0.3074\ A^2 + 0.3185\ B^2 + 5.28C^2$$

Where, A=Adsorbent dose, B=Initial Pb^{2+} ion concentration, and C=pH

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. CCMAC dosage, and pH have negative relationships towards the Pb^{2+} ion removal, whereas Initial concentration of Pb^{2+}, and all other interactions have positive effect towards the response variable.

Table 4.3:- Shows table of parameters for correlations, mean, standard deviation, and C.V.

Std. Dev.	2.29	**R^2**	0.9161
Mean	88.93	**Adjusted R^2**	0.8909
C.V. %	2.58	**Predicted R^2**	0.8471
		Adeq Precision	21.4337

The Predicted R^2 of 0.8471 is in reasonable agreement with the Adjusted R^2 of 0.8909; i.e. the difference is less than 0.2. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio found from Design expert 12 is 21.434 indicating an adequate signal. This model can be used to navigate the design space. To assess the adequacy of a model, the coefficient of determination (R^2), and the lack of fit test were commonly used. Coefficient of determination (R^2) refers to the changes described by the model to the overall changes. Therefore, whatever R^2 is closer to 1, the power of fitted model is greater to describe the response changes as a function of the independent variables. From the Model Summary Statistics, it can be observed that the coefficient of R^2 to be 0.9161. Generally, the coefficient of variance, and standard deviation were 2.58%, and 2.29 respectively.

The statistical significance of the model was investigated by analysis of variance (ANOVA). The significance of the models was determined by F-test, and p-test. The F and p-values show the significance of the model, and its terms. The larger the magnitude of F-test, and smaller the p value (<0.05), the more substantial is the corresponding model terms. The associated p value is used to estimate whether F is large enough to indicate statistical Significance. The values of $p > F$, less than 0.05 indicates that the model is considered to be statistically significant whereas values greater than 0.10 indicate the model terms are not Significant.

The ANOVA result also presented p- values of individual model terms. According to the result all three terms Adsorbent Dose, Initial Lead ion concentration, and pH are significant model terms together with the model. The **Model F-value** of 36.39 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.
Table 4.4:- shows ANOVA table of factorial design.

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**p-value**	
Model	1149.69	6	191.61	36.39	< 0.0001	Significant
A-Adsorbent Dose	232.40	2	116.20	22.07	< 0.0001	
B-Initial Lead Ion Conc.	119.95	2	59.97	11.39	0.0005	
C-pH	797.34	2	398.67	75.70	< 0.0001	
Residual	105.32	20	5.27			
Total	1255.01	26				

4.4.2. Diagnosis of the model

The normal probability plot compares the distribution of the residuals to a normal distribution (the straight line). Expect some scatter even with normal data. Look only for definite patterns like an "S-shaped" curve, which indicates that a transformation of the response may provide a better analysis. The points fit to the normal data as in this model case shown on Figure (4.10A) Predicted versus Actual graph show the predicted response values versus the actual response Values. It primarily used to detect a value, or group of values, that are not predicted well by the model. Each values indicate that they were perfectly predicted on the Graph (4.11B) depicted. Residuals versus Predicted plot checks for constant variance across the range of predictions. Non-constant variance is indicated by a pattern in the plot (upward or downward curves, etc.). If the plots are randomly scattered between the red lines then the assumption of constant variance is confirmed, likewise to our case.

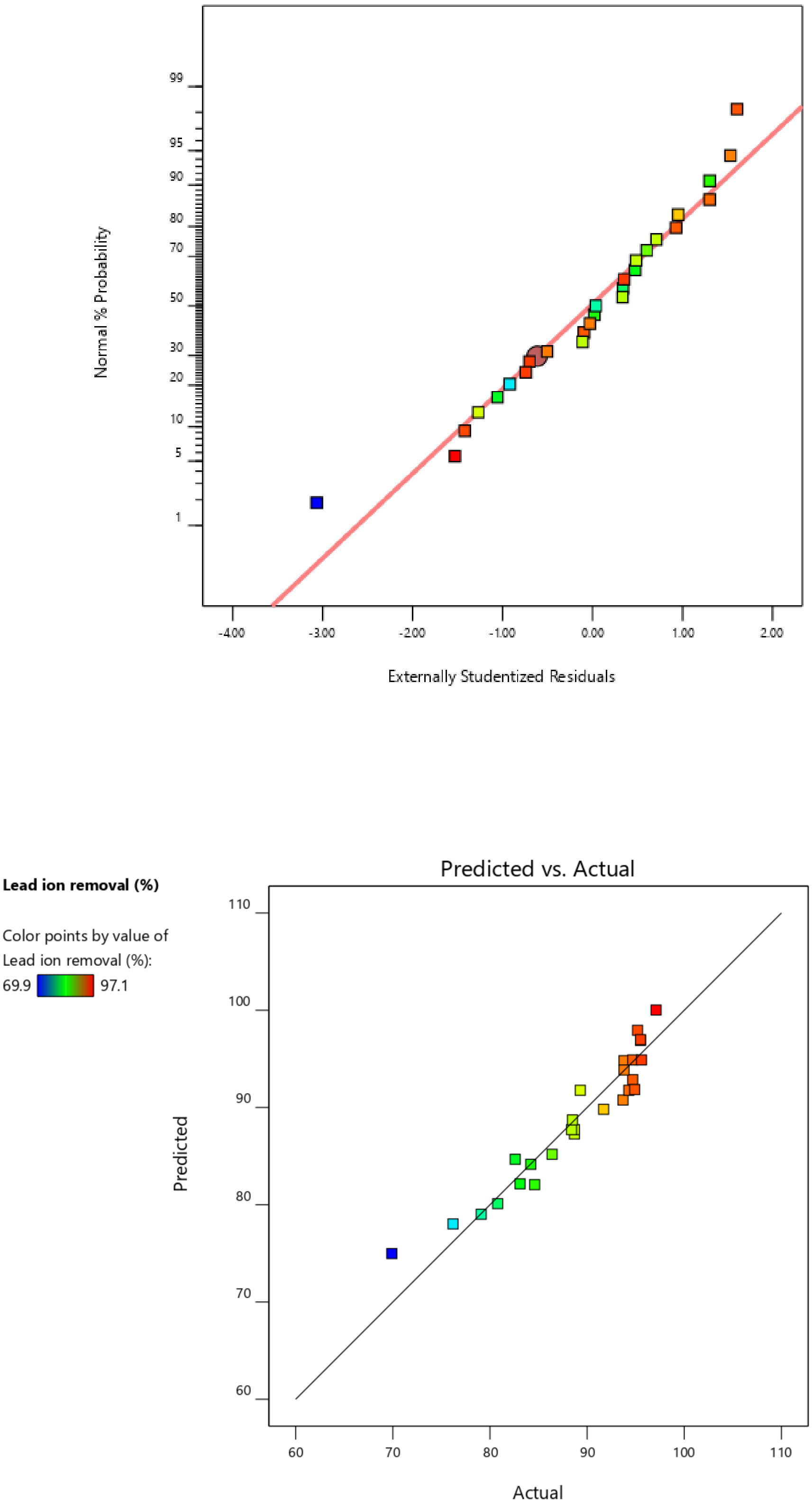
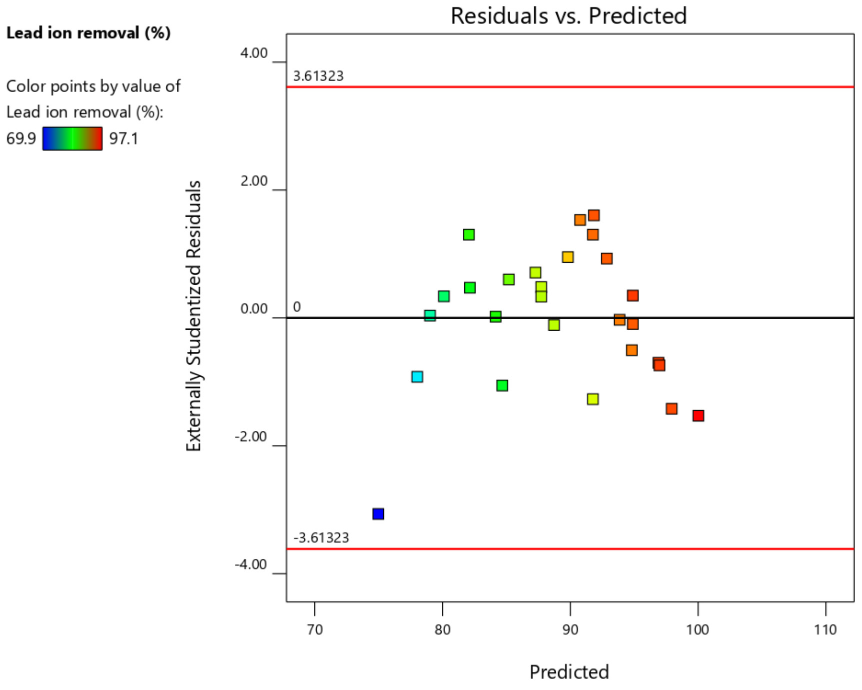


Figure 4.10:-Normal Probability Versus externally Studentized plot (A), Actual Versus Predicted plot (B).



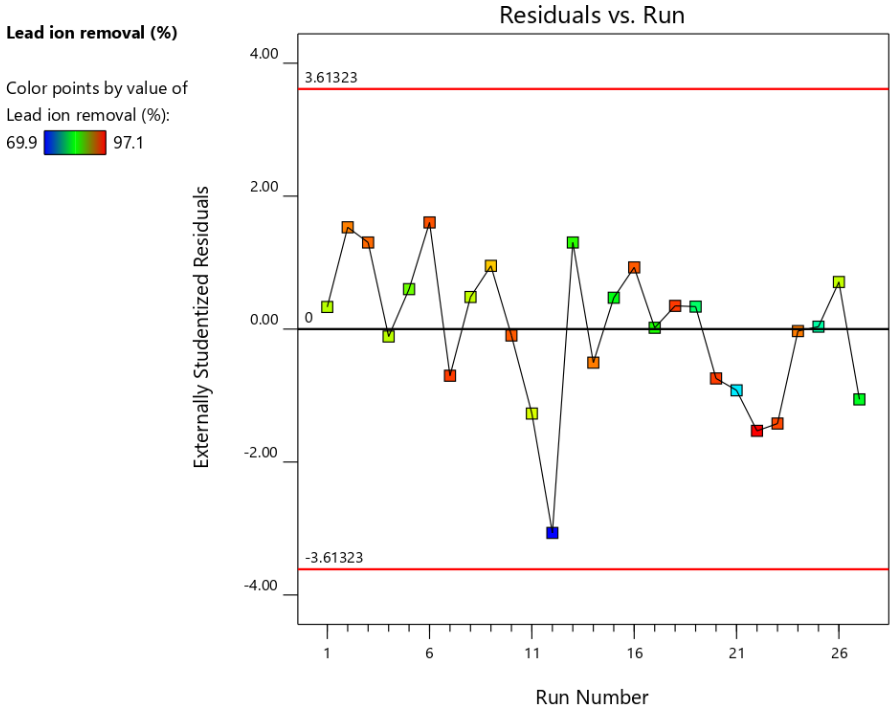


Figure 4.11:- Residual versus Run (B), and Residual versus Predicted plots (A).

4.4.3. Effect of Interaction factors

I. The interaction effect of solution pH and Adsorbent dose

The plot for combined effect of the solution pH and Adsorbent dose proposes that increasing Adsorbent dose results in a increasing of removal of the Pb^{2+}, and, it increases with increasing the pH value up to 5 then decreasing beyond. Ascending trend in Pb^{2+} uptake with increasing Adsorbent dose may be attributed to the increasing of surface area and magnetic agent to adsorb the lead ion. From figure it can be seen that at low pH value (pH=4) about 85% of initial lead in the solution was removed. While the increasing in the solution pH (pH = 5), with increase in the enhancement in the percentage removal of lead ion to about 98%. After this pH value there was a decrement in removal. The presence of positively charged functional groups will decrease the percentage removal due to the attraction of the positively charged lead ions and the positively charged surface functional groups.

II. The interaction effect of adsorbent dose and initial Pb^{2+} concentration

The combined effect of adsorbent dose and initial $\mathbf{Pb^{2+}}$ concentration on removal of $\mathbf{Pb^{2+}}$ in 3D surface plot is shown in Figure below. It may be noted that the $\mathbf{Pb^{2+}}$ removal decreased with increasing initial lead ion concentration. This is due to the fact that increasing in initial lead ion concentration at constant adsorbent dose (adsorption sites) surface area of the adsorbent was saturated, resulting in decrease in the adsorption efficiency. This behaviour can be understood as the increasing lead ion concentration with fixed adsorbent dose would result in saturation of the binding sites on the surface and subsequently declining of the adsorbate uptake with increasing concentration. Increasing adsorbent dose from 0.6-1g, the removal efficiency increases from around 81% to 87%. This increment was due to enhancement of adsorption sites with increment of adsorbent amount.

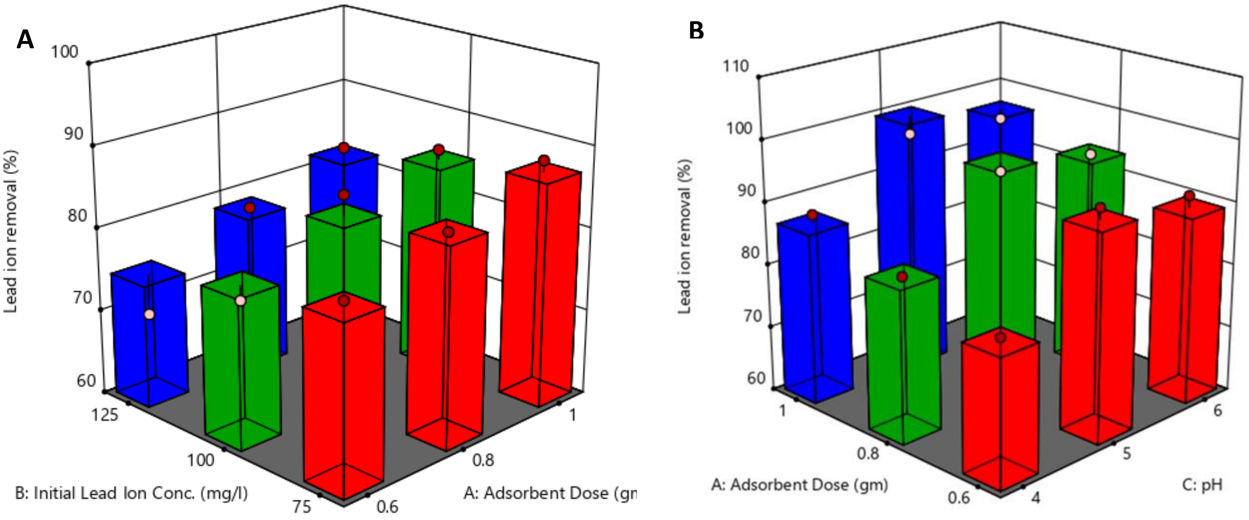


Figure 4.12:- The interaction effect of solution pH and Adsorbent dose plot (B), and The interaction effect of adsorbent dose and initial Pb^{2+} concentration plot (A).

4.4.4. Optimization of Pb^{2+} Ion Removal efficiency

One of the core aims of this study was to investigate the optimum processing parameters, which adsorption should have a high lead (Pb^{2+}) removal efficiency. In the optimization analysis, the target criterion was set in range values for adsorbent dose, and initial Pb^{2+} concentration. pH was set 5. It's because, this value was the maximum of the pH values investigated. The experiment conditions with the reasonable amount of desirability were selected to be verified. As shown below adsorbent dose of 0.6g, initial Pb^{2+} concentration of 75mg/l, and pH of 5 were optimum factors by giving Pb^{2+} removal efficiency of 92.86%. The desirability of the optimization process was 0.844.

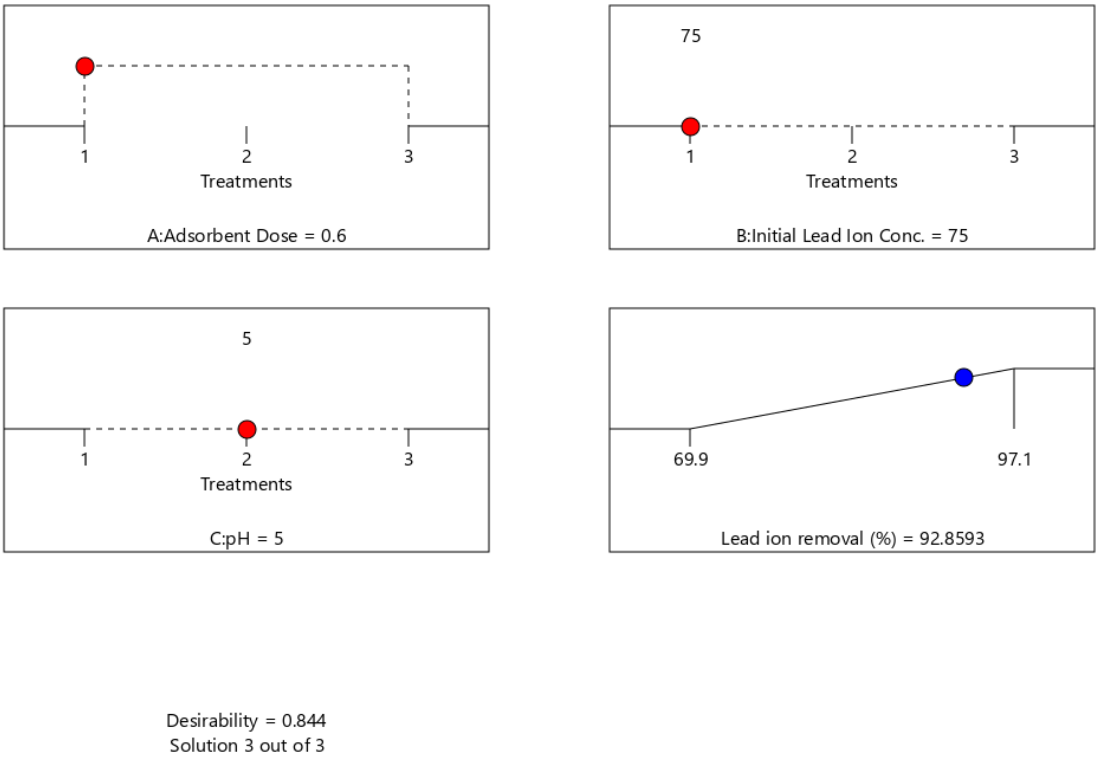


Figure 4.13:- graphical representation of Optimization process

Table 4.5:- optimization table representing the factors and response variables.

Factors	**Unit**	**Value**
pH	-	5
Initial Pb^{2+} ion Concentration	mg/l	75
Adsorbent Dose	g	0.6
Lead Ion removal	%	92.86

Desirability		0.844

4.4.5. Validation Experiments

An experiment with pH, adsorbent dose and initial Pb^{2+} concentration were conducted in order to study the outcome or effect of the design. Three experiments were carried out at the optimized conditions of pH=5, Initial Pb^{2+} concentration= 75mg/l, and dosage of 0.6g. The three experiments were 92.34%, 93.21%, and 92.78%. These showed the obtained value was in good agreement with the predicted one. Therefore the model is considered to be accurate and reliable for predicting the Pb^{2+} Removal efficiency.

4.4.6. Adsorption Isotherm Studies

I. Langmuir Isotherm

The Langmuir isotherm is a concept of the adsorption leading to a monolayer without interaction among the adsorbate molecules. The adsorption takes place at specific sites within the adsorbent. Each site holds one molecule of the given adsorbate. The adsorbent had a finite capacity for the adsorbate at equilibrium. Finally, a saturation point would have been reached, where, no further adsorption can occur. At this point, all sites were identical and energetically equal.

The values of Q_m and K_m were determined for the adsorbent from the intercept and slopes of the linear plots. The R^2 value was indicative of the actual deviation between the experimental points. As it could be indicated from figure 4.14, the plot had R^2 value of 0.9298 for Optimized sample of MAC, which were characterized with distinct, slope and intercept values. The values of the Langmuir constants were determined from the slope ($\frac{1}{Qm}$) and intercept ($\frac{1}{KL*Qm}$). Q_m and K_L were calculated to be 48.54, and 0.227 respectively.

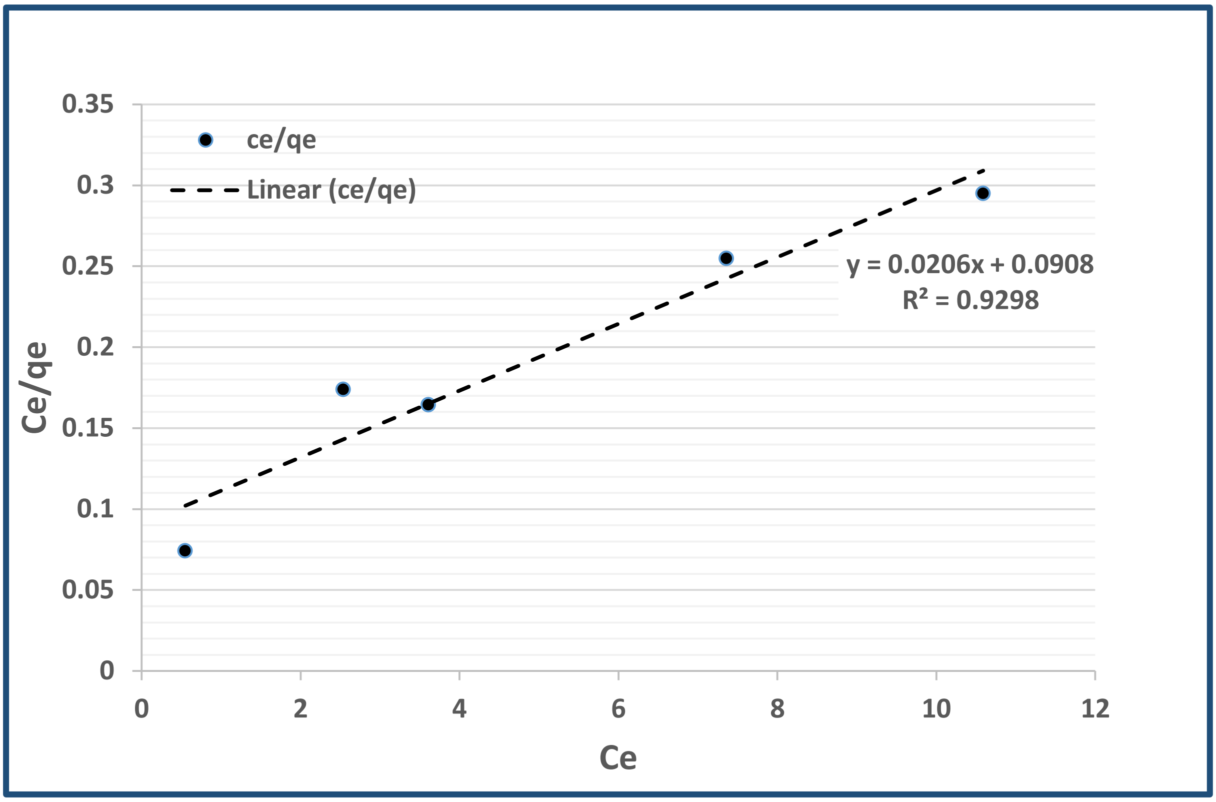


Figure 4.14:- Langmuir Isotherm model for adsorption of Pb^{2+} on Corn Cob based MAC at pH of 5, contact time of 150 min, and Adsorbent dosage of 1g.

II. Freundlich isotherm

Figure 4.15, shown that the linear plots of log Ce versus log qe for various samples of optimized samples of MAC. K_F is the Freundlich constant related to the adsorption capacity and 1/n is an indicator of adsorption intensity. If the value of 1/n is close to 1, it shows that just a little concentration change can relatively affect the adsorption. Value for 1/n below 1 indicates normal and favourable adsorption and the surface is more heterogeneous with more functional groups that favour the adsorption. Besides, high K_F values showed easier uptake of lead ions.

$$Qe = KfCe^{\frac{1}{n}} = 9.986Ce^{0.5379}$$

The plot had R^2 value of 0.9841 for CCMAC, which were characterized with distinct, slope and intercept values. The values of the Langmuir constants were determined from the slope $(\frac{1}{n})$ and intercept $(\log Kf)$. The value for 1/n for the MAC was 0.5379 which is less than 1 indicating normal and favourable adsorption and more heterogeneous surfaces with more functional groups that favour the adsorption. K_f was calculated to be 9.986.

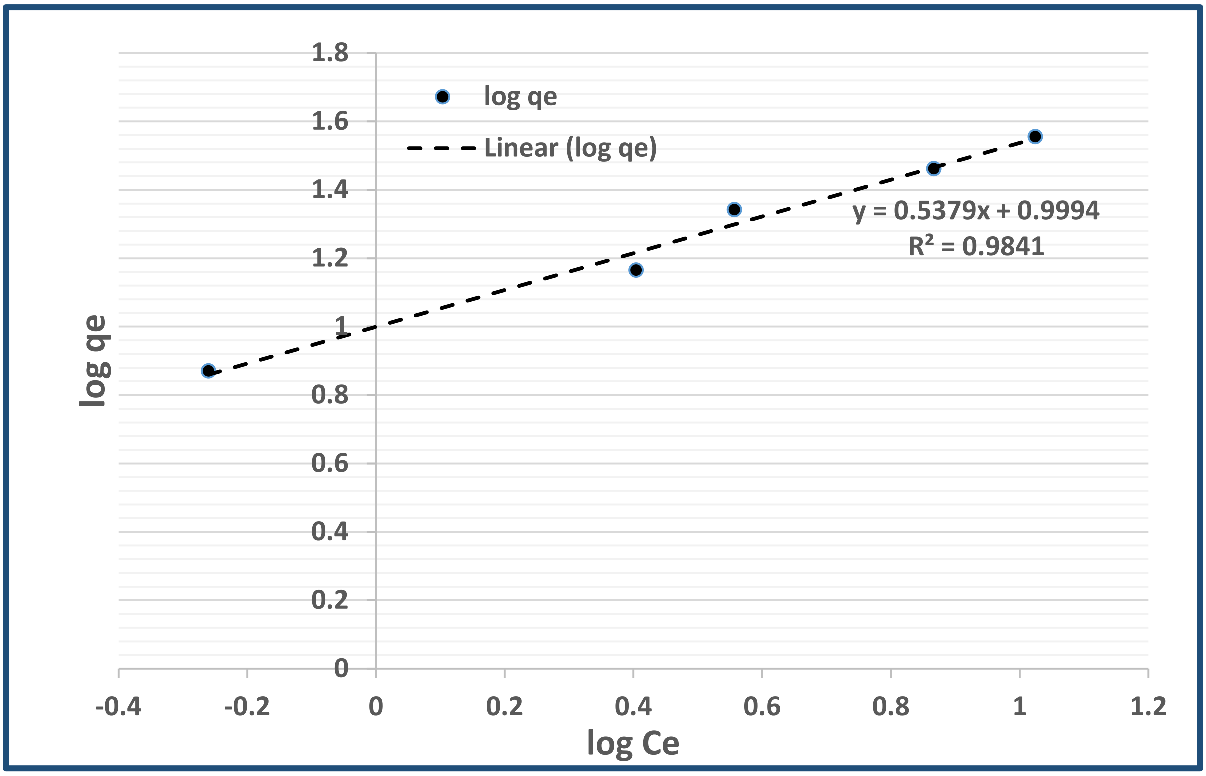


Figure 4.15:- Freundlich isotherm model for adsorption of Pb^{2+} on Corn Cob based MAC at pH of 5, contact time of 150 min, and Adsorbent dosage of 1g.

III. Temkin isotherm

Figure 4.16, presents the values calculated from slopes and intercepts of Temkin isotherms for different samples. Besides, the linear plots of $\ln Ce$ versus Q_e for MAC samples. Here, it is assumed that the heat of adsorption of all molecules in the layer reduces linearly with coverage. This was due to the interactions that exist between the Pb^{2+} ions and Corn Cob Magnetic Activated Carbon (CCMACs) adsorbents in this case.

The adsorption capacity of the CCMACs increases directly as with increasing equilibrium concentration of Pb^{2+} ions within the synthetic solution. This could be due to enhanced driving force, and concentration gradient which fast-tracked the diffusion of the Pb^{2+} ions towards the surface of CCMACs. The plot had R^2 value of 0.9234 for Optimized sample of MAC, which were characterized with distinct, slope and intercept values. The values of the Langmuir constants were determined from the slope (B_T) and intercept ($B_T \ln AT$). A_T was calculated to be 3.053. The value for B_T for the MAC was 9.416. To compare the different isotherms of CCMACs based on their R^2 values of the respective isotherm models, the adsorption process obeys Freundlich adsorption isotherm (by having R^2 value of 0.9841).

Ci (mg/L)	Ce (mg/L)	Qe (mg/ g)	Ce/qe	log Ce	log qe	ln Ce
50	0.55	7.42	0.074	-0.259	0.870	-0.599

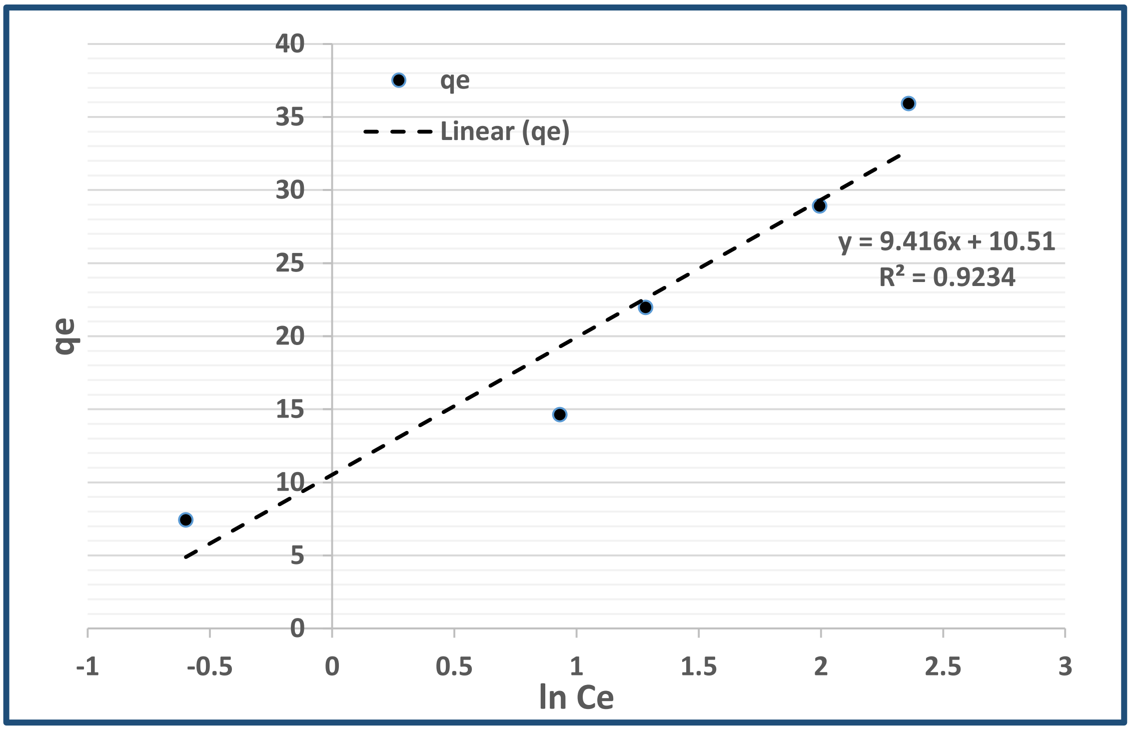


Figure 4.16:- Timken Isotherm model for adsorption of Pb^{2+} on Corn Cob based MAC at pH of 5, contact time of 150 min, and Adsorbent dosage of 1g.

Table 4.6. Adsorption isotherm data

100	2.54	14.62	0.174	0.405	1.165	0.932
150	3.61	21.96	0.164	0.557	1.342	1.284
200	7.36	28.89	0.255	0.867	1.461	1.996
250	10.59	35.91	0.295	1.025	1.555	2.359

4.4.7. Adsorption Kinetics

I. Pseudo-First and Second-Order Kinetics

Kinetic studies evaluated the details of the process whereby a system moves from an initial state to the final state and the time required for this transition. In this study, the relative slopes and intercepts of a plot of log (q_e-q_t) and t/q_t versus t have been used to compute q_e, the first-order rate constant K_1, second-order rate constant K_2. It is likely to forecast the behaviours over the range of adsorption and is in line with the chemisorption mechanism being the rate-controlling step. Table 4.7 lists the results of the constant rate studies for different samples of CCMAC by the pseudo-first-order and second-order models.

Generally, according to the values of correlation coefficient R^2, the pseudo-second-order adsorption mechanism has been found the preferred kinetic model, and that the overall rate of the Lead ion adsorption process appeared to be controlled by the chemical reaction. The linear Fitting of adsorption experimental data of the pseudo-first-order and second-order models showed values of 0.9902 and 0.951 for samples of CCMAC, respectively. Therefore, was selected. Similar phenomena have also been seen in the adsorption of Methylene blue on Magnetic activated carbons prepared from various precursors. Table of constants were presented below.

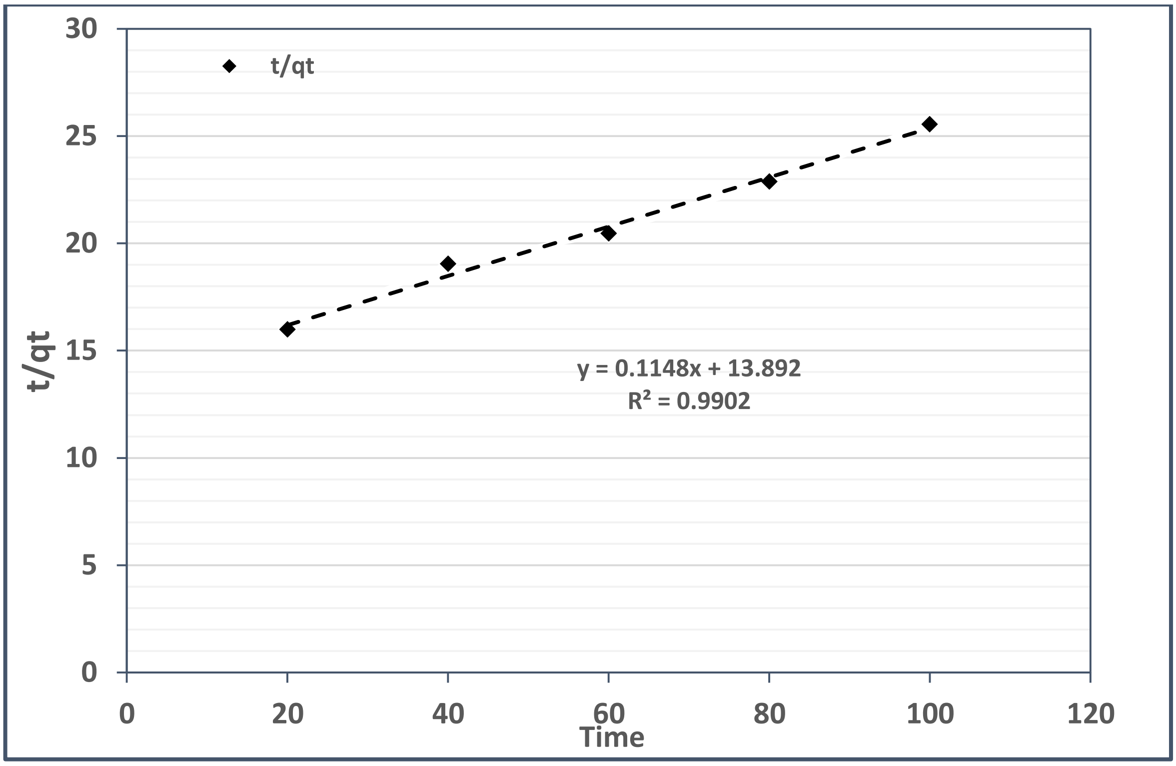


Figure 4.17:- Second-Order Kinetics model for adsorption of Pb^{2+} on Corn Cob based MAC at pH of 5, and Adsorbent dosage of 1g.

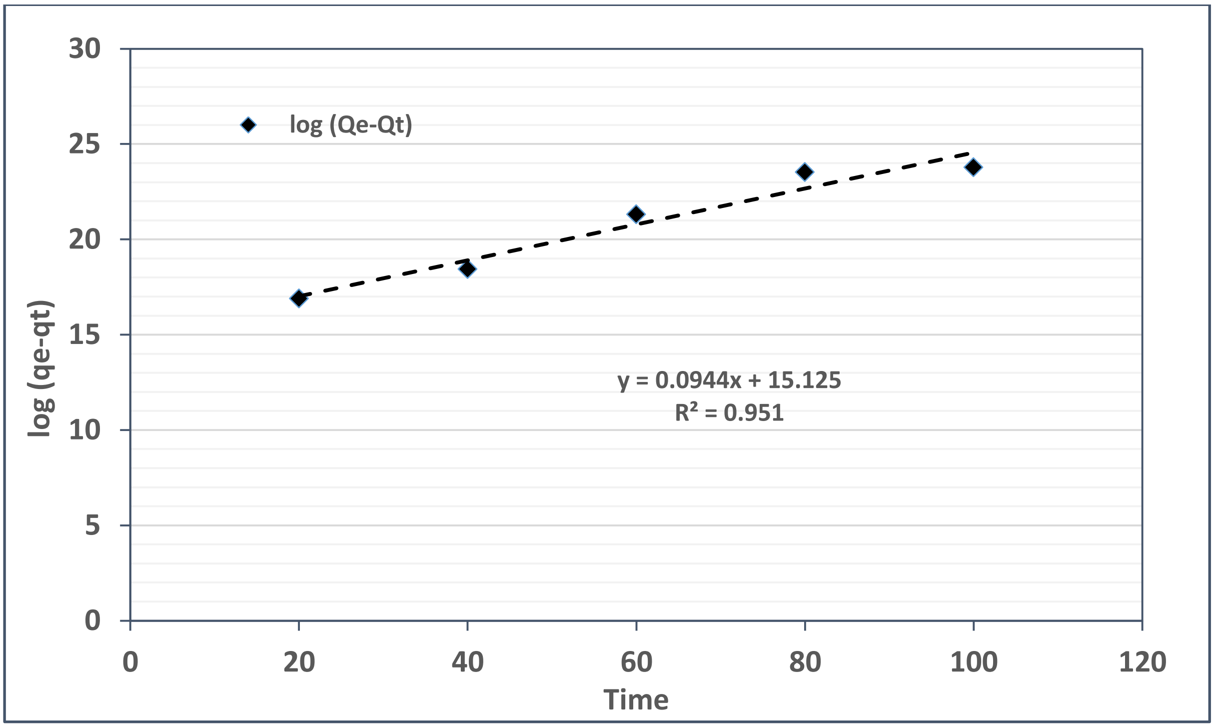


Figure 4.18:- First-Order Kinetics model for adsorption of Pb^{2+} on Corn Cob based MAC at pH of 5, and Adsorbent dosage of 1g.

Table 4.7:- Table of values for First order kinetics, and Second order kinetics.

	First order kinetics			**Second order kinetics**		
Samples	**R^2**	**q_e**	**K_1**	**R^2**	**q_e**	**K_2**
	0.951	10^{125}	0.2174	0.9902	8.711	$9.51*10^{-4}$

4.5. Regeneration Study

According to Figure 4.19, the adsorption efficiency of CCMAC for six cycles decreased from 89.34 to 34.68%. The adsorption efficiency of reused CCMAC dropped to about 11% in the first cycle. The reason could be the regeneration of the adsorbent was possible through the incorporation of HNO_3 which exchanges a proton with the cation adsorbed in the material in repeated adsorption-desorption cycles. Thus, the good low-temperature regeneration and high removal percentage showed that the magnetic AC could offer a much higher regeneration efficiency than the AC alone (Sun et al., 2020). The CCMAC adsorbent showed good reusability performance especially up to the sixth cycle with no significant reduction of removal percentage.

In most cases, including this research, the Lead ion removal percentage decreases slightly. This decrement can be due to two reasons. First, during the recovery step of magnetic adsorbents, loss of materials (such as carbon) may exist, which reduce the adsorbent dose and materials needed to adsorb dyes for the next cycle. Hence, the adsorbent recovery will not complete. Second, during recovery steps, magnetic adsorbents might have changes in their properties, such as fouling and aggregation. Reducing surface area and active site surface can also occur because of the irreversible particle aggregation in the high gradient region during reusing cycles. Therefore, the magnetic adsorbents should be removed from the cycles after reaching their maximum lifetime to avoid material leaching into treated water (Benjedim et al., 2021).

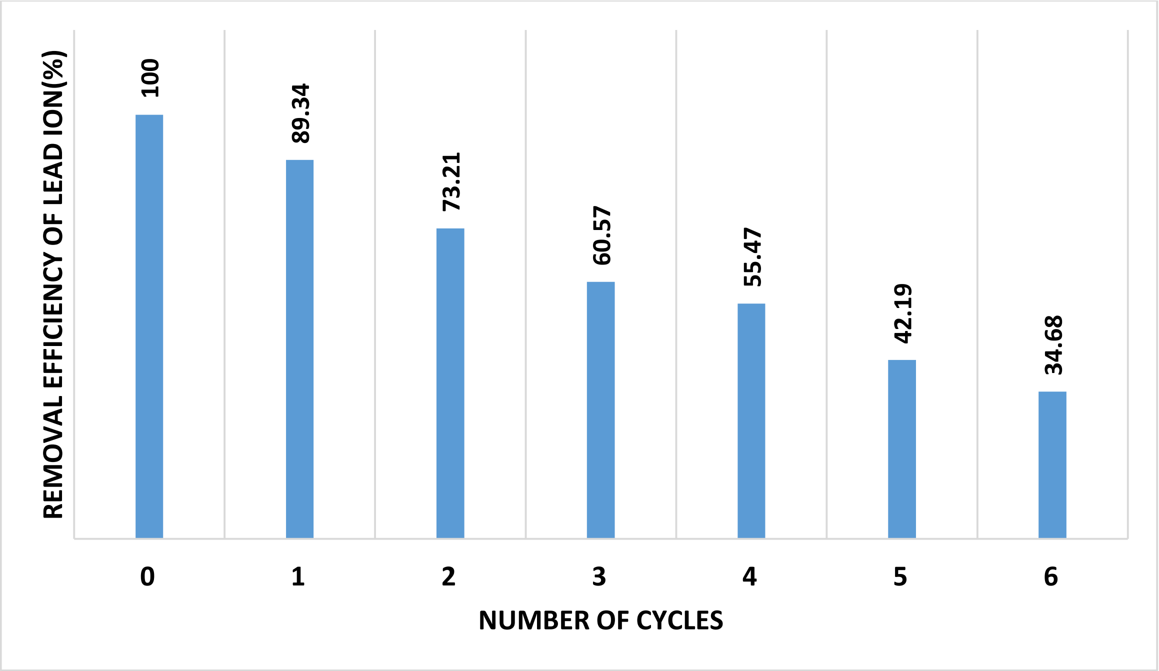


Figure 4.19. Regeneration study of the prepared magnetic activated carbon for six consecutive cycles.

5. Conclusion and Recommendations

5.1. Conclusion

The key conclusions that can be accessed from current investigation are presented below. The phyiso-chemical nature of the CCMACs, were studied. The moisture, yield, volatile matter, the ash, SEM, and XRD, the results observed were highly associated with formerly studied literature. The effect of carbonization time, and carbonization Temperature were studied for the preparation of CCMAC and then the adsorption of Pb^{2+} ion from aqueous solution (laboratory prepared wastewater) by CCMACs was explored.

Surface morphology of the CCMAC was analysed by SEM. SEM image of the corn cob magnetic activated carbon showed irregular and rough surface morphology with slit crack structures formed which support the formation well developed pores on the CCMAC surface. BET Surface area of the magnetic activated carbons was determined by N_2 adsorption - desorption. BET surface area of the activated carbon and MAC were 711 and 504m^2/g respectively. In adsorption, the effect of pH, contact time, initial Pb^{2+} ion concentration, and adsorbent dose on Pb^{2+} ion removal was studied. The maximum conditions for adsorption of Pb^{2+} on to CCMACs were found to be pH of 5, contact time of 150 min, Initial Pb^{2+} ion Concentration of 75mg/l, and Adsorbent dosage of 0.6g by giving 92.86% removal of Lead (II) Ion**.**

The adsorption equilibrium data were analysed by Langmuir, Freundlich, and Temkin adsorption isotherms. Plus, adsorption kinetics data were assessed by the first-order, and second-order kinetics. Hence, the isotherm samples best fitted with Freundlich adsorption isotherm. On the other hand, the kinetics of the adsorption obeys the second-order kinetic model. Adsorption study indicated that Corn Cob based MAC can be effectively applied for the removal of Lead ions from water streams due to the adsorption and magnetic capabilities. The adsorption efficiency of CCMAC for six cycles decreased from 89.34 to 34.68%. The CCMAC adsorbent showed good reusability performance especially up to the sixth cycle with no significant reduction of removal percentage. Thus, using CCMAC precursor could potentially reduce waste corn cob biomass disposal to the environment and also had a good regeneration capability.

5.2. Recommendations

Based on the results gained from the study, the following suggestions have been made further research needs

- ✓ Batch kinetic studies at various temperatures; various particle size of MAC and agitation speed may be conducted to determine thermodynamic parameter for lead adsorption on CCMAC.
- ✓ 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.
- ✓ Comparative analysis of Corn Cob based Magnetic Activated Carbon with commercial activated carbon.
- ✓ Regeneration/recovery of heavy metal from the adsorbent surface for other application.
- ✓ Further research works should be done to evaluate the economic feasibility of a corn cob based magnetic activated carbon production process.

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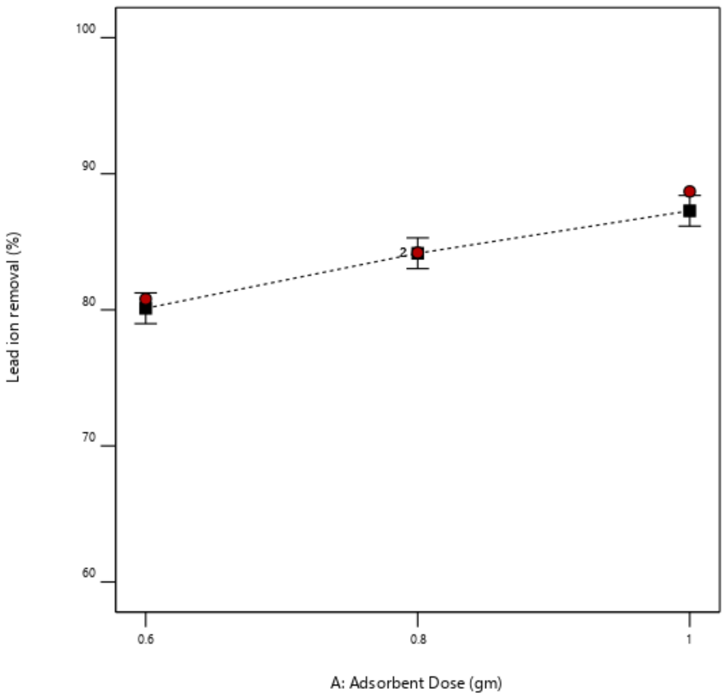
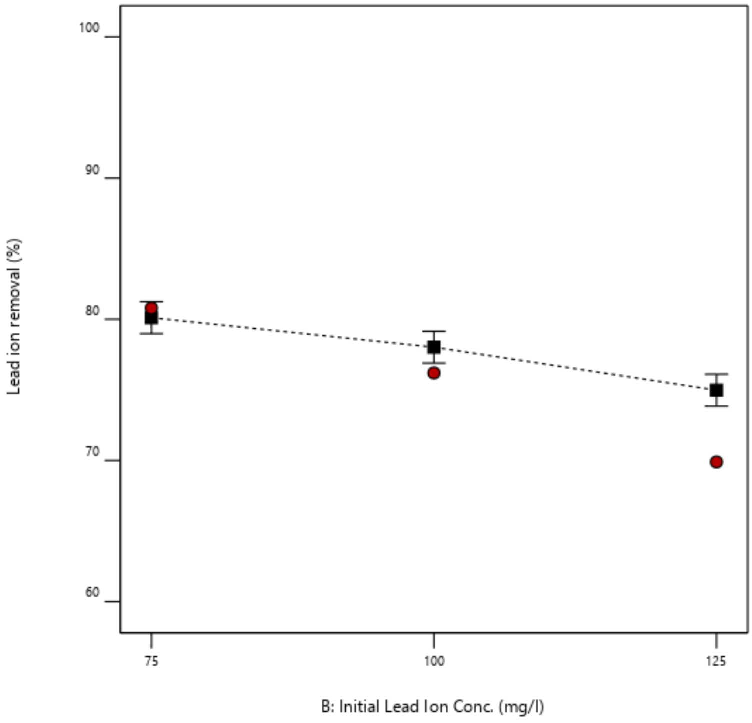
Appendix

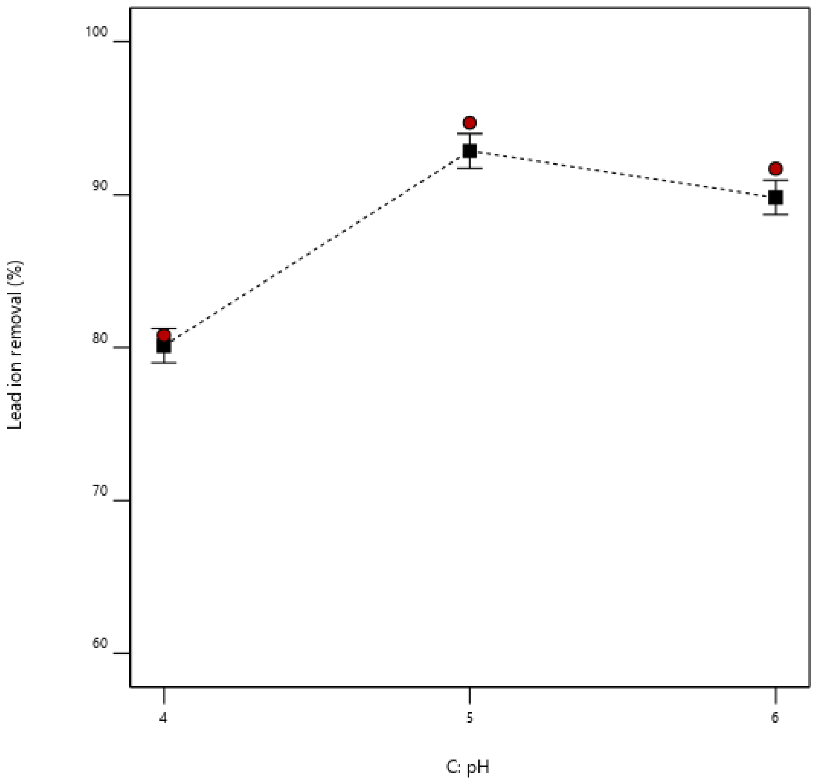
Appendix 1

Run	Adsorbent Dose (g)	Initial Pb^{2+} Concentration (mg/l)	pH	Pb^{2+} Removal
1	0.6	100	6	88.4
2	0.6	100	5	93.7
3	0.8	125	5	94.3
4	0.8	125	6	88.5
5	1	100	4	86.4
6	1	125	6	94.9
7	0.8	75	5	95.5
8	0.6	125	5	88.7
9	0.6	75	6	91.7
10	1	125	5	94.7
11	0.8	100	6	89.3
12	0.6	125	4	69.9
13	0.8	100	4	84.6
14	0.8	100	5	93.8
15	1	125	4	83.1
16	0.6	75	5	94.7
17	0.8	75	4	84.2
18	1	100	6	95.6
19	0.6	75	4	80.8
20	1	75	6	95.5
21	0.6	100	4	76.2
22	1	75	5	97.1
23	1	100	5	95.2
24	0.8	75	6	93.8
25	0.8	125	4	79.1
26	1	75	4	88.7
27	0.6	125	6	82.6

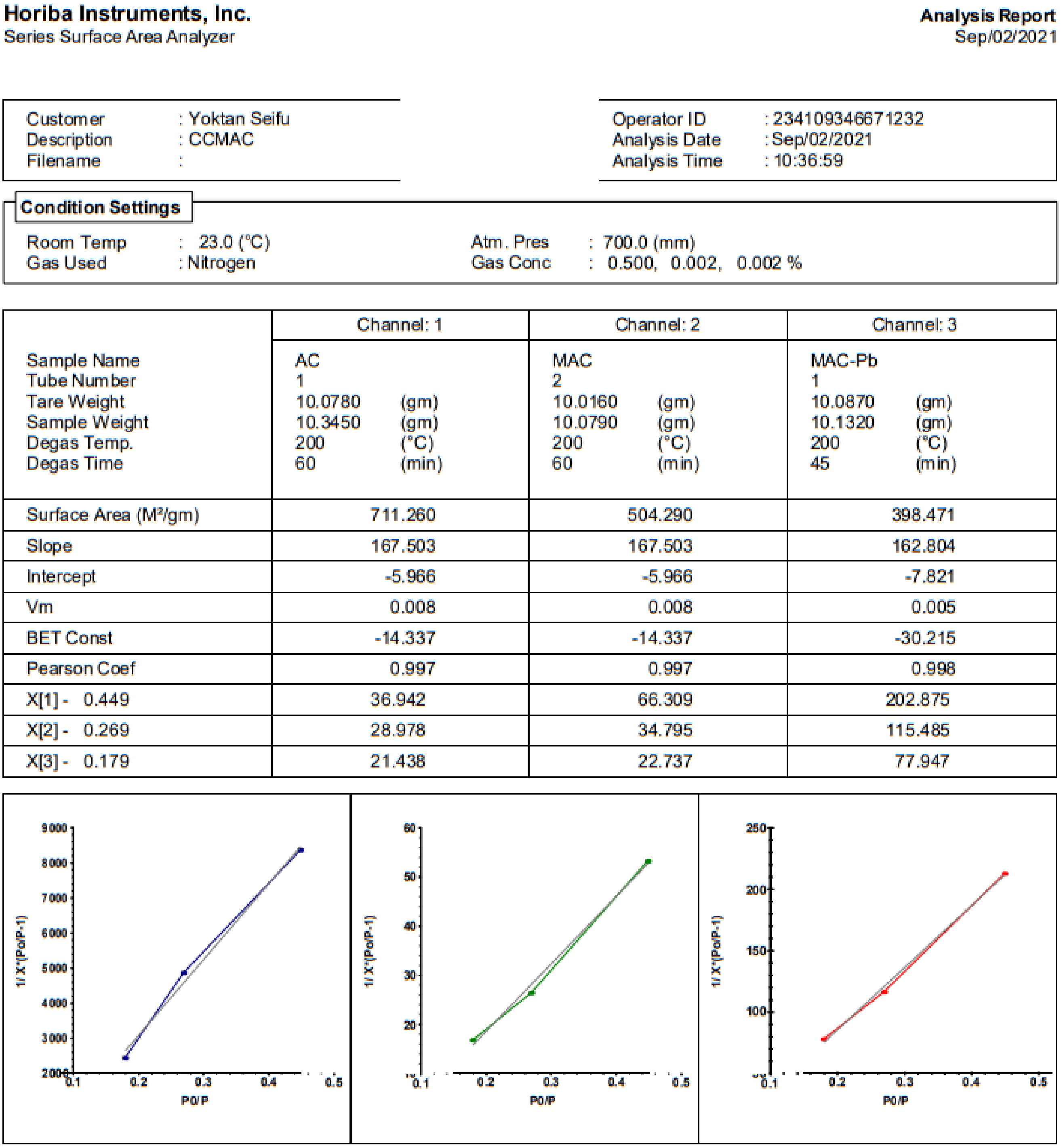
Appendix 2: The effect of individual factors






Lead ion removal (%)
100
90
80
70
60
4
5
6
C: pH

Appendix 3: BET Surface Area



Horiba Instruments, Inc.
Series Surface Area Analyzer

Analysis Report
Sep/02/2021

Customer : Yoktan Seifu
Description : CCMAC
Filename :

Operator ID : 234109346671232
Analysis Date : Sep/02/2021
Analysis Time : 10:36:59

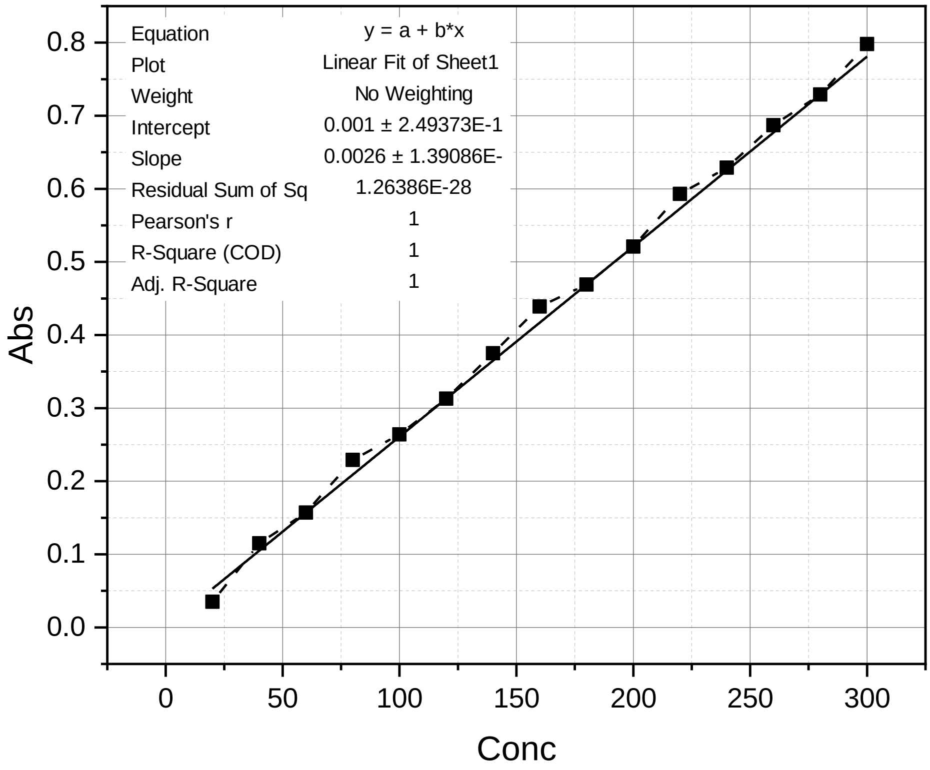
Condition Settings

Room Temp : 23.0 (°C)
Gas Used : Nitrogen
Atm. Pres : 700.0 (mm)
Gas Conc : 0.500, 0.002, 0.002 %

	Channel: 1	Channel: 2	Channel: 3
Sample Name	AC	MAC	MAC-Pb
Tube Number	1	2	1
Tare Weight	10.0780 (gm)	10.0160 (gm)	10.0870 (gm)
Sample Weight	10.3450 (gm)	10.0790 (gm)	10.1320 (gm)
Degas Temp.	200 (°C)	200 (°C)	200 (°C)
Degas Time	60 (min)	60 (min)	45 (min)
Surface Area (M²/gm)	711.260	504.290	398.471
Slope	167.503	167.503	162.804
Intercept	-5.966	-5.966	-7.821
Vm	0.008	0.008	0.005
BET Const	-14.337	-14.337	-30.215
Pearson Coef	0.997	0.997	0.998
X[1] - 0.449	36.942	66.309	202.875
X[2] - 0.269	28.978	34.795	115.485
X[3] - 0.179	21.438	22.737	77.947

Appendix 3: Calibration curves

A) For the adsorption



B) For the preparation