

# Remediation of metal ions in aqueous solution using activated carbon from *Zea mays* stem

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**University of Fort Hare**  
*Together in Excellence*

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# **Remediation of metal ions in aqueous solution using activated carbon from *Zea may* stem**

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Master of Science in chemistry

Of the

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**January 2016**

## DECLARATION BY CANDIDATE ON PLAGIARISM

I Mzukisi Matandabuzo, declare that:

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Date

## CERTIFICATION

This is to certify that this research is a record of original work carried out by Mzukisi Matandabuzo under my supervision in the Inorganic Materials Research laboratory of the Department of Chemistry, University of Fort Hare in fulfilments of the requirements for the award of Master of Science degree in Chemistry.

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Date

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PhD (UniZul); MRSC (London)

## ***DEDICATION***

*With great joy, happiness, and appreciation, I would like to dedicate this work to my entire family for their encouragement and support towards my studies. My Father, Mr. S. Matandabuzo, Mom, Mrs. N. Matandabuzo for their unwavering love and support throughout. To everyone who has been so supportive and has shown interest in my work, more especially my Pastor (J. V. Zoko).*

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## ABBREVIATIONS AND SYMBOLS

AC – Activated carbon

PAC – Prepared activated carbon

FT-IR – Fourier Transform – Infrared spectroscopy

SEM – Scanning Electron Microscopy

EDS – Energy dispersive X-ray spectroscopy

XRD – X-ray Diffraction

AAS – Atomic absorption spectrometry

PC – Pin (*Pinus contorta*) cones

AS – *Abies cilicica* seeds

MS – Maple (*Acer ginnala*) seeds

PS – Peach (*Prunus perдика*) stones

## ABSTRACT

*Zea mays* stem and its activated carbon were prepared through chemical activation method using four different activating reagents (NaOH, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, KOH) and were used as adsorbents for the removal of Pb(II), Cu(II), Hg(II) and Cr(III) from aqueous solution. The results shows that activated carbon has high surface area and pore volume compared to the powdered raw *Zea mays* stem. Prepared activated carbon was characterized using physico-chemical properties such as carbon yield, iodine number, moisture content, percentage adsorption, and analytical instruments such as Fourier transform Infrared spectroscopy (FTIR), atomic absorption spectrometer (AAS), scanning electron microscopy (SEM), Energy Dispersive X-ray analysis (EDS), powder X-ray Diffraction (pXRD). The adsorption of Pb(II), Cu(II), and Cr(III) ions were pH, contact time, and concentration dependent. Based on the results obtained from the batch experiments, activated carbon prepared from *Zea mays* stem is not good enough for the removal of Hg(II) from aqueous solution. Adsorption ability was calculated and found to be 66.67% for activated carbon obtained from H<sub>2</sub>SO<sub>4</sub>, 21.21% for activated carbon obtained from KOH, and 20% for activated carbons obtained from NaOH and H<sub>3</sub>PO<sub>4</sub>. The pH 5-6 was chosen for all experiments, contact time was 2 hours, and adsorbent dosage was 2 g, initial concentration range from 200, 400, 600, 800, and 1000 ppm at room temperature. The metal ion removal trend was found in the order Pb(II)>Cu(II)>Cr(III)>>Hg(II). The Langmuir model fitted well in most of the cases with  $R^2 > 0.99$ . Consequently, the adsorption of Pb(II) and Cu(II) followed Langmuir isotherm model while that of Cr(III) best fitted the Freundlich isotherm model. The results indicated that the adsorption process followed two possible mechanisms. (I) Metal ion – adsorbent complex model and (II) Metal ion – ion-exchange adsorbent complex model.



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## CHAPTER ONE

### INTRODUCTION AND LITERATURE REVIEW

#### 1. Water as natural resource

Water is essential natural resource and without water, life would not have evolved on earth. Water exists naturally on earth in three physical states or forms namely liquid, solid, and gaseous [1]. Pure and adequate water is colourless, odourless, and tasteless. Groundwater and rivers are the main sources of water supply for human use in the entire world. It is used for cooking, drinking, cleaning, industrial and agricultural purposes [1]. However, water supports all living organisms above and below the earth's surface, although it is also exposed to numerous sources of pollution. As the world's population is rapidly increasing, so also the demand for clean, safe, and drinkable (non-contaminated) water is exponentially increasing. Due to the scarcity of clean and fresh potable water, over one billion people worldwide have inadequate water supply [2].

Though water covers almost two-thirds of the earth's surface, it is still the most scarce and in demand resource on earth. Environmental studies has shown that less than 1% of water on the planet is available for drinking and agricultural use. While 97% is salty water stored in oceans and only 3% is free water. Out the 3% that is free, only 0.3% is contained in surface water bodies such as dams, lakes and rivers [2]. The remaining 2.7% of free water is confined between rocks beneath the earth's surface. Most of available water on earth is not fit for human consumption because it is contaminated by indiscriminate discharges or effluents from industrial and agricultural activities.



Figure 1.1: Photograph showing the effluent discharged from metal industry Source: Nadeem *et al.*, 2006 [3]

### **1.3 Water pollution**

Water pollution can be defined as the release of pollutants and other materials that can degrade the quality of water. In other words, anything that is released to the water bodies, above and beyond its capacity to break it down, is pollution [2 - 5]. Water pollutants are those materials that cannot be broken down by water into less harmful substances such as pesticides, industrial discharge (metal ions), and oil spillage. Most of these water pollutants are very toxic in human and aquatic life through food cycle. For example, lead, mercury, cadmium, and chromium metal ions are at the top of the toxicity list (Volesky, 1994).



According to Safe Drinking Water Foundation (SDWF), there are two major sources of water pollution namely point source and non-point source [6]. Point sources include factories, wastewater treatment facilities, and septic systems. Whereas non-point sources are fairly difficult to identify as they cannot be traced back to a particular location or site. These generally includes surface runoff fertilizers, chemicals, animal waste from the farms, construction sites and mines [7]. As indicated above metal ions contained in discharged effluents from these water-pollution sources are very harmful and some can cause kidney failure, decrease mental capabilities, abdominal cramps, anaemia, and severe headaches [USEPA, 2004].

### **1.3 Treatment of polluted water**

#### **1.3.1 Conventional methods**

A wide range of physicochemical methods have been widely employed to remediate or clean-up metal ions from industrial wastewater. Examples of these conventional methods are chemical precipitation, chemical coagulation, reverse osmosis (Figure 1.2), ion-exchange, electrochemical methods, adsorption using activated carbon, membrane process and ultrafiltration [8, 9]. These conventional methods have several limitations in their use as remediation methods for cleaning-up wastewater. They are usually expensive to operate, have high chemical requirements, not efficient in concentrations lower than 50 mg/L, and large amount of sludge containing metals [10].

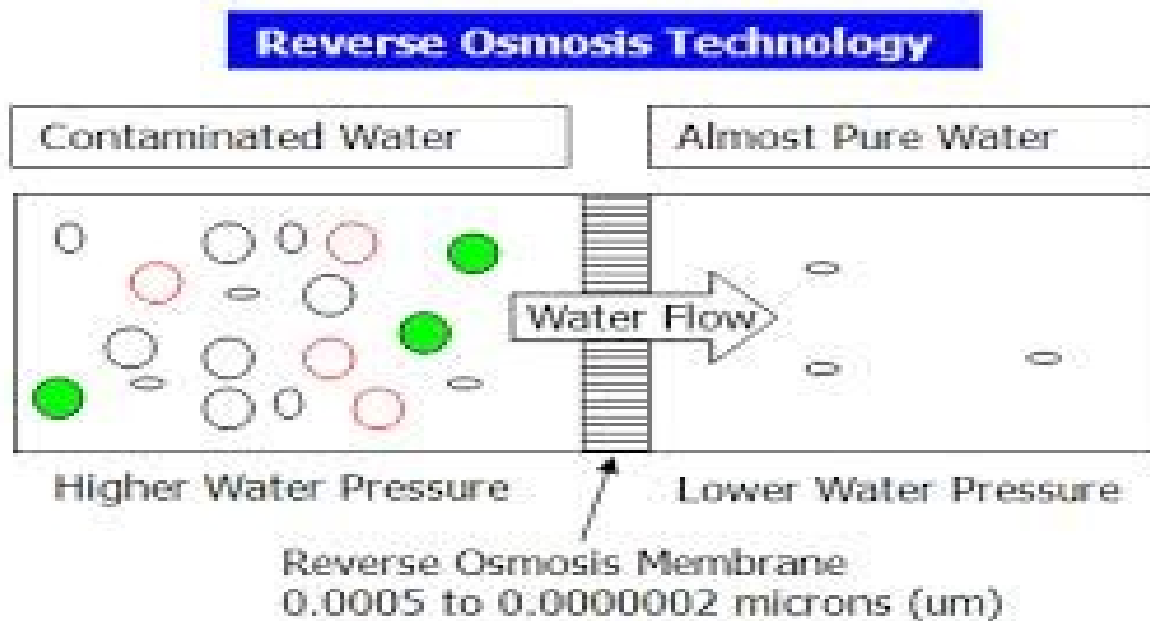


Figure 1.2: Diagram showing the Reverse Osmosis Principle source: Nadia *et al.*, 2009 [9].

Due to the above mentioned demerits, the industrial applications of these conventional methods has gradually reduced.

### 1.3.2 Bioremediation method

Recently, the use of biological methods such bioremediation and bioaccumulation provides a promising alternative in solving this worldwide water problem. Phytoremediation is the use of plants to partially remediate selected contaminants in contaminated soil, groundwater, surface water, and wastewater [10, 11]. Bioremediation has low operating cost, efficient at lower levels of concentration, eco-friendly, and low chemical requirements as compared to conventional methods [12]. The efficiency and effectiveness of the biosorbent ultimately rest upon the biochemical composition, particularly on the functional groups present in a cell wall polysaccharides [12]. Therefore, the choice of choosing the biosorbent plays a very important role with respect to the economic viability of the process. Abundance of biomaterial, stability

and cost are generally considered to be the most important parameters for the selection and consideration of biosorbents. The by-products obtained from biomaterials production are cheaper and their reactions are reversible. Many biological biosorbents such as rice hulls, corn cobs, coconut fiber, soya beans hulls, peat and others has been successfully used for effective metal ion removal [12, 13]. There are three mechanisms by which microorganisms remove metal ions from wastewater: these are bioremediation of metal ions on the cell surface, intracellular uptake of the metal ions, and finally the chemical transformation of metal ions by microorganism. Bioremediation has been declared to be largely effective than the bioaccumulation and phytoremediation [13 -15].

## **1.4 Literature review**

### **1.4.1 Biosorption studies**

Biosorption is the process in which agricultural biomass is employed to remediate metal ions from aqueous solution through the contact of the biosorbent and the solution containing the metal ions [14-15]. A significant number of biosorption studies on the removal of metal ions from aqueous solution have been conducted worldwide and all of them has been focusing on obtaining highest removal efficiency, though carried out using large quantities of agricultural waste or by product [16, 17].

The suitability of the green algae (*phornidium sp*), mango leaves and orange peels for the removal of Pb(II) and Cd(II) ions from aqueous solution in both batch and continuous process has been investigated [18]. Maranon and Sastre [19] investigated the ability of apple wastes in removal of metal ions in packed beds [19]. Senthikumaar *et al.* [20] studied the ability of bio-waste obtained from fruit juice industry for the removal of metal ions such as Hg(II),

Pb(II), Cd(II), Cu(II), Zn(II), and Ni(II). The results obtained from these studies conclude that bio-waste from fruit juice industry can be successfully used as potential biosorbents for the removal of metal ions and the order of metal ion removal by fruit residue was Cu(II)>Pb(II)>Ni(II)>Zn(II)>Hg(II) = Cd(II) [20]. Sobhanardakani *et al.* [21] studied the performance of rice husk on the removal of Cr(III) and Cu(II) ions from aqueous solution and evaluated the effect of various factors such as pH, initial concentration, reaction time and adsorbents doses. The results obtained indicated maximum removal of Cr(II) and Cu(II) occurred at pH around 5-6 by rice husk [21].

Biosorption characteristics of dried sugar beet pulp for the removal of Cu(II) metal ion from aqueous was reported [22]. Saeed *et al.* [23] studied the removal and recovery of Pb(II) from single and multi-metal (Cd, Cu, Ni, and Zn) solutions by crop milling waste (black gram husk) [23]. In this study, the removal ability order of the biosorbent was Pb>Cd>Zn>Cu>Ni.

Wang and Qin studied the possibility of using rice bran for sorption of Cu(II) ions from wastewater [24]. There are many other different agricultural waste materials that has been utilized as biosorbents in the literature. Some of them are wood, peat, pine bark, banana core, soybean, rice bran, saw dust, wool, orange peel and cotton hulls [25-28]. The most important benefit of these agricultural waste material biosorbents is that they are cheap, inexhaustible, harmless, and renewable materials.

#### **1.4.2 Activated carbon (AC)**

The use of activated carbon to remove metal ions from aqueous solution has received significant attention in recent years [29]. Activated carbon is a porous material with an

extremely large surface and intrinsic adsorption to many adsorbents [30, 31]. Reports in literature relating to the preparation of activated carbon from agricultural wastes such black gram husk, maize cob husk, apricot stone and peanut husks being applied to remove metal ions from wastewater [31].

Awoyale *et al.* [32] in their study showed that the adsorptive capacity of activated carbon from bamboo is comparable to the adsorption of capacities activated carbon from cocoa pod husk [32]. Activated carbon has been reported to have high and fast adsorption capacities due to its well-developed porous structure and surface area [33]. Gang and Wiexing [34], reported that activated carbon is only able to remove around 30-40 mg/g of Cd, Zn, and Cr in water and is non-regeneratable which is quiet costly for wastewater treatment [34].

The metal ions from the effluent are being attracted to or held on the surface of the carbon particles [35]. The efficiency of adsorption using activated carbon is influenced by the characteristics of the carbon material such as particle size, pore size, surface area, surface chemistry and hardness [35]. The most common method used with activated carbon is known as activated carbon filtration, which is based on the adsorption of the contaminants onto the surface of the filter. But this method is not effective for microbial contaminants, metal ions, and other inorganic contaminants [35]. Activated carbon is prepared in such a way that it exhibits a high degree of porosity and extended surface area as shown in Figure 1.3.

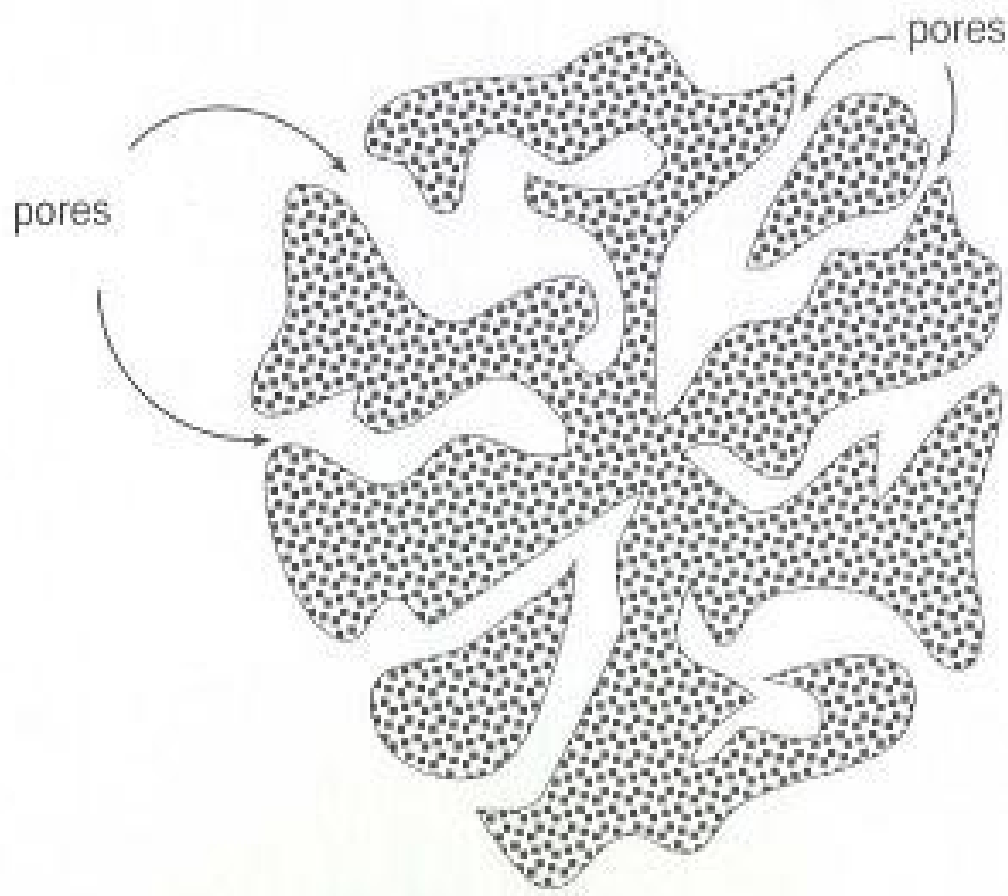


Figure 1.3: Activated carbon with high degree of porosity source: Lamley *et al.*, 2011 [36]

The adsorption capacity usually depends upon the properties on the activated carbon such as temperature, pH, ion strength, and adsorbate chemical properties [37]. Mustapha *et al.* [38] reported that activated carbon spines of *Bombax buonopozense* have been found to be economically viable and potential biosorbent for the removal of Cu(II) and Zn(II) metal ions [38]. The uptake of these metals was described by Dubinin-Radushkevick (D-R) [38]. The investigation conducted by Senthil *et al.* [39] indicates that nano-silversol-coated activated carbon (NSSCAC) is an effective adsorbent for the remediation of lead(II) from aqueous solution [39]. Maximum adsorption efficiency of 92.4% was obtained from the initial concentration of metal ion. The experimental results were in good agreement with both the

Langmuir and Freundlich adsorption isotherms. Ntuli *et al.* [40] studied the use of agroforestry waste in order to reduce environmental problems associated with it by using such waste in the production of activated carbons (A.Cs) using low-cost production technique, which effectively produce more reliable activated carbon as adsorbent for the treatment of effluent from wastewater [40]. Four different activated carbons from agroforestry materials-pin (*Pinus contorta*) cones (PC), abies (*Abies cilicica*) seeds (AS), maple (*Acer ginnala*) seeds (MS), and peach (*Prunus persica*) stones (PS). The four different activated carbon were prepared by single-step stem pyrolysis and were all characterized. Evaluation of the activated carbons was based on the iodine number, phenol specific area, ash content, pH, moisture content, and specific metal ion removal [40].

Sivakumar *et al.* [41] compared the effectiveness of activated carbon from *Balsamodendron caudatum* wood waste through various processes such as H<sub>2</sub>SO<sub>4</sub> impregnation, H<sub>3</sub>PO<sub>4</sub>, and CaCO<sub>3</sub> impregnation. According to Sivakumar *et al.* [41] activated carbon prepared from *Balsamodendron caudatum* showed excellent improvement in surface characteristics and the volume of pores varies based on the type of the activating agent used. They concluded that the activated carbon prepared from *Balsamodendron caudatum* wood waste using H<sub>2</sub>SO<sub>4</sub> impregnation produced activated carbon with high surface area and more developed pore spaces than others [41].

Pragya *et al.* [42] developed a modified method to produce activated carbon from almond shell and compare its physical and morphological characteristics with the activated carbon prepared from walnut shell using ortho-phosphoric acid impregnation. Based on the results from the SEM, FTIR, and the dye adsorption capacity for each activated carbon, the activated

carbon obtained from almond shell indicates heterogeneous carbonaceous structure compared to walnut shell based activated carbon. Methylene blue adsorption capacity of walnut shell activated carbon was 51% less compared to those obtained from almond shell [42]. Akpa and Nmegbu investigated the use of activated carbon prepared from three carbon rich agricultural materials; bamboo, coconut, and palm kernel shells for the adsorption of benzene. Benzene adsorption was proven to be minimal with activated carbon produced from bamboo as compared to the ones from coconut and palm kernel shells [43]. The percentage yield for activated carbon from coconut shell was high in comparison to bamboo (50%), palm shell (50.0%), and coconut shell (51%), respectively [43].

Yusufu *et al.* [44] indicated that efficient activated carbons can be obtained from bone, wood, and coconut shell by a controlled activation with phosphoric acid or heat for a number of industrial and residential applications. Surface areas for acid activated carbons were higher and this is always expected because chemical activation normally develops more pore spaces and high surface areas in carbon materials when compared with thermal activation [44].

Gumus and Okpeku [45] prepared activated carbon from snail shells by using  $ZnCl_2$  and  $CaCl_2$  salts as chemical reagent. Physico-chemical characteristics such pH, ash content, pore volume, porosity, and bulk density were conducted in order to determine the surface area and the effectiveness of the activated carbon produced. Physical and chemical properties shows that activated carbon prepared using  $ZnCl_2$  activation was better than the one prepared from  $CaCl_2$  [45].

Kumar *et al.* [46] prepared activated carbon from *Vitex negundo* stem waste using  $ZnCl_2$ ,  $H_3PO_4$ ,  $H_2SO_4$ , and KOH and the produced activated carbons were used to remove metal



ions from aqueous solution. The adsorption results showed out that the activated carbon prepared from *Vitex negundo* stem by  $H_2SO_4$  chemical activation was the best in removing metal ions [46]. Sugumaran *et al.* [47] reported the preparation of the activated carbon from banana empty fruit bunches (BEFP) and *Delonix regia* fruit pods (DRFP) by one step pyrolysis using  $H_3PO_4$  and KOH as chemical activation reagents. Highest yield of 41.09% was in DRFP chemical treated with  $H_3PO_4$  was recorded. Physicochemical characteristics studies are very important in assessing or determining the suitability and effectiveness of each active carbon prepared from various agricultural waste materials [48-51]. Based on literature report, surface area and pore volume are the most significant parameters to be fully considered in the preparation of activated carbon for adsorption applications [51, 52].

SEM images and IR results are among the most important characterization techniques used for preparation of activated carbon, they usually reveal the morphological structures for the active sites and functional groups present [53]. The preparation of activated carbon from melon seed husk by chemical activation using NaOH solution was reported by Madu and Lajide [54]. The work done by the two showed that powdered activated carbon from melon seed husk has good adsorptive capacity and can be used for both liquid and gaseous phase adsorption [54]. Bernard *et al.* [55] reported the removal of metal ions from industrial wastewater by zinc chloride treated activated carbon prepared from coconut shells. The effect of pH, contact time, stirring rate, and adsorbent dosage were carefully considered on adsorption of Cu(II), Fe(II), Zn(II), and Pb(II) from wastewater and the results obtained from literature concluded that the adsorption of metal ions was completely adsorbent dosage, pH, contact time, and stirring rate dependent [55,-60]. The pH, stirring speed, and adsorbent dosage were 6, 350 rpm, and 1 g respectively.

Activated carbon prepared from oil palm and coconut shells using sulphuric acid and phosphoric acid has shown significant high adsorption capacity in removing metal cations such as Ni(II) with 19.6 mg/g and Pb(II) with 74.6 mg/g removal respectively [58]. Rahman *et al.* [58] concluded that acid-treated activated carbons usually perform better in low concentration range. Raji *et al.* [59] reported the use of bicarbonate treated sawdust carbon in adsorbing metal ions such as Pb(II), Hg(II), and Cd(II) from aqueous solutions [59]. Maximum uptake were 98.6% for Pb(II), 97.2% for Hg(II), and 95.1% for Cd(II) at very low metal ion initial concentrations. Most of the activated carbon derived from agricultural waste materials by chemical treatment were experimentally found to be in agreement with Langmuir model, although some usually agreed with Freundlich model depending on the adsorptive behaviour of the metal ions and parameters such as pH, contact time, adsorbent dosage, and stirring rate [56-60].

#### **1. 4. 3 Zea mays stem**

*Zea mays* straw and corn cobs has been successfully utilized as potential biosorbents for the removal of Hg(II) and Cd(II) from aqueous solutions [61, 62]. Nadia *et al.* [62] reported a maximum uptake of about 89.9% for Hg(II) and 92% for Cd(II) around pH values of 9-10 using maize waste as biosorbent [62]. Igwe and Abia [63] reported the sorption kinetics and intraparticulate diffusivities of Cd, Pb, and Zn ions on maize cob [63]. Again, Igwe *et al.* [64] also reported sorption kinetics and intraparticulate diffusivities of Co, Fe, and Cu ions of EDTA-modified maize cob [64]. Competitive adsorption of Zn(II), Cd(II), and Pb(II) ions from aqueous and non-aqueous solution by maize cob and husk was reported [65].

Maize, that is, *Zea mays* from Spanish language, known as corn in some English-speaking countries, is a large grain plant domesticated by indigenous peoples in Mesoamerica [67]. It is one of the most sensitive plant to drought, hence it is usually cultivated during summer and spring seasons in the temperate regions of the world. It consists of leafy stalk which produces ears containing grain. The maize plant is usually about 2.4 to 2.5 m long with the stem having the appearance of a bamboo cane. Figure 1.4 shows the height of *Zea mays* plant taken from Fort Hare research farm in Alice.



Figure 1.4: *Zea mays* plant taken from Fort Hare research farm

The maize leaf usually begins (extends) from each node as shown in Figure 1.4. The longest *Zea mays* stem is usually composed of intercones of approximately 12 to 18 cm long. The

intercones and the structure of the *Zea mays* stem is similar to that of the sugarcane. Hence, in some local areas they use it for fruit consumption. Because of its shallow roots, maize is susceptible to droughts, intolerant of nutrient-deficient soils. It's also prone to being uprooted by severe winds. Immature maize shoots accumulate a powerful antibiotic substance, 2, 4-dihydroxy-7-methoxy-7-methoxy-1,4-benzoxazin-3-1-(DIMBOA)[47]. DIMBOA is a member of a group of hydroxamic acids (also known as *benzoxazinoids*) that serve as a natural defence against a wide range of pests, including insects, pathogenic fungi and bacteria [68]. *Zea mays* is widely cultivated all over the world for various purposes, mainly for food consumption [68].

Hence, a great quantity of maize is produced each year than any other popular grains such as wheat, rice, and soybean. Recently studies has revealed that United State of America is the leading producer of *Zea mays* followed by China, and South Africa is the tenth largest producer of maize [69]. Approximately 99% of *Zea mays* is used for food purposes throughout the world [70, 71]. The only commercially important part of the maize is the corn, which is used by many for food purposes after being harvested. Recently, maize has been getting attention to be used in bio-fuel and in some chemical preparations. It is used in production of ethanol fuel to be mixed with gasoline in order to decrease the amount of pollutants emitted from motor vehicles.

The use of maize to produce ethanol has led to high demand for maize production throughout the world. The entire part of the maize (stem and leaves) is usually thrown away as a waste by-product because of lack of usage and importance. Because of its high production advantage, maize has been successful utilized as the plant candidates for trace-element

phytoextraction and/or phytoremediation in soils contaminated by toxic metals. It is the fastest growing crop and exhibit the highest biomass production potential on moderately metal-contaminated land. But in this research, the by-product (stem) of the biomass will be used as potential biosorbent to clean-up water contaminated by toxic metal ions. This biomass is usually locally abundant and it is normally thrown to fire and burned in local and national farms.

#### 1. 4. 4 Adsorption kinetics

Adsorption isotherms commonly describe the phenomenon responsible for mobility of the adsorbent from the aqueous phase or medium to a solid-phase material at a given time and pH [72]. Equilibrium isotherms are determined to quantify the adsorption capacity of the biosorbent with respect to an adsorbate. The most common types of models describing this type of system are the Langmuir and Freundlich isotherms [73 - 75]. The Langmuir and Freundlich models are always selected to fit the equilibrium data obtained from the batch adsorption experiments [76].

Langmuir model is valid to adsorption onto a surface containing a limited number of identical adsorption sites which assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface, and that the adsorption of each molecule onto the surface has equal activation energy [76]. This model is presented in the form of the equation 1 below:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{C_e}{q_{max}} \dots \dots \dots Eq. 1 [77]$$

Where  $q_{max}$  is monolayer capacity of the biosorbent (mg/g),  $q_e$  is the amount of metal ion in unit mass of adsorbent at equilibrium,  $C_e$  is the equilibrium concentration of the metal ions, and b is the biosorption constant (L/mg).

Freundlich model is the earliest empirical model known for describing the non-ideal and reversible adsorption. This can be applied to multilayer adsorption with non-uniform distribution of adsorption over the heterogeneous surface [72, 76]. It has been observed for a wide range of heterogeneous surfaces which include activated carbon, silica, metals, polymers and clays [19- 20]. The Freundlich equation is expressed as follows [77]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots \dots \dots \text{Eq.2 [77]}$$

Where  $q_e$  is the retained metal ion at equilibrium,  $C_e$  is the non-retained metal ion at equilibrium,  $K_f$  and  $\frac{1}{n}$  are Freundlich isotherm constants related to biosorption capacity and intensity of biosorption, respectively. Freundlich isotherm is linear when  $\frac{1}{n} = 1$ , and as  $\frac{1}{n}$  increases, the isotherm becomes more non-linear [76].

Adsorption kinetics were investigated by using the saturation concentration of Pb(II), Cu(II), Hg(II), and Cr(III) in sorbent phase corresponding to their different initial concentrations at an adsorbent dosage of 2 g activated carbon, 20 mL of metal ion solution, at temperature of 25 °C and pH of 5-6.

### 1.5 Rationale and Motivation

The problem of water-contamination by industrial activities can be solved by the use of low-cost effective methods provided by the agricultural by-products. Bioremediation offers the

advantages of low-operating cost, and minimization of the volume of chemical and biological sludge to be disposed. Remediation is one of the simplest and effective method to solve the problem of high toxicity caused by effluents discharged from industrial activities such as mining and electroplating.

Remediation method is usually chosen over conventional methods, because it is eco-friendly, efficient, environmental friendly and is usually local abundant for use. Bioremediation method can be employed in aqueous solutions containing metal ion having concentration lower than 50 mg/L. Recent literature has reported that more attention has been given to activated carbon (AC) prepared from agricultural by-products, which have got sufficiently high metal binding capacity and selectivity metal ions [65-76]. Activated carbon prepared via chemical activation method has high yield and low- energy cost compared to physical activation method. High surface area and high pore volumes exhibited by activated carbon encourage its adsorption ability.

Equilibrium models and mechanisms behind the adsorption of metal ions are of importance in order to understand the full interaction or reaction between the adsorbent and adsorbate. The kinetic studies will reveal the adsorption/attraction forces involved.

## **1.6 Research statement**

The problem of water contamination is a world-wide problem and is continuously increasing as the world's population and urbanization increases daily. Therefore, cleaning-up of water using cheap, affordable, efficient and environmental friendly methods is desirable. Hence, using activated carbon, that is, the use of modified-biomass as the adsorbent of metal ions from aqueous solution is one of the promising solution to this global problem. According to



recent studies on the use of biomasses or agricultural by-product, potential agricultural biosorbents have shown possibilities to remediate some heavy metals from water. These includes *Tamarindus Indica* fruit nut testa [50], *Zea mays* cob [51], maize leaf [52], wheat corn [53], gelatin [54], *Moringa oleifera* seeds [10], orange waste [56, 57], bagasse fly ash from sugar industry waste [58], modified activated carbon [59], activated carbon from bagasse [60], hen feathers [61] . Although bioremediation is not 100 percent efficient, it does remove some percentage of heavy metals in water. Here, we will compare the ability of *Zea mays* stem and its activated carbon as the potential adsorbents to adsorb metal ions from dilute aqueous solutions containing metal ions.

### **1.7 Aims and objectives of this project**

The main aim of this work was to synthesis, characterize and use the activated carbon prepared from *Zea mays* stem to remediate metal ions from aqueous solution. In order to achieve this aim, the following specific objectives were formulated:

- 1) To synthesis and characterize activated carbon from *Zea mays* stem.
- 2) To investigate the adsorption ability of the prepared activated carbon and raw *Zea mays* stem.
- 3) To compare and evaluate the effect of pH, contact time, initial concentration, and adsorbent dosage on removal of metal ions.
- 4) To trace up the amount of metal ions that can be remediated by *Zea mays* stem and its activated carbon.
- 5) To determine the most suitable equilibrium adsorption isotherm for both biosorbents.

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## CHAPTER TWO

### 2. EXPERIMENTAL

#### 2.1 Chemicals and Reagents

All chemicals and reagents were obtained from Sigma-Aldrin/ Merck and were used as received. Sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), iodine solution, ammonia solution ( $\text{NH}_3$ ), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ), sodium hydroxide ( $\text{NaOH}$ ), potassium hydroxide ( $\text{KOH}$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), sodium sulphate solution ( $\text{Na}_2\text{SO}_4$ ), 35% hydrochloric acid ( $\text{HCl}$ ). Stock solutions of Pb(II), Cu(II), Cr(III), and Hg(II) 1000 mg/L were prepared by dissolving lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), chromium nitrate ( $\text{Cr}(\text{NO}_3)_2$ ), mercury chloride ( $\text{Hg}_2\text{Cl}_2$ ), and copper sulphate ( $\text{Cu}(\text{SO}_3)_2$ ) in de-ionized water and were used for further dilutions.

The pH of the solutions was adjusted using dilute solutions of 0.1 M HCl and 0.1 M NaOH. *Zea mays* stem waste material was collected from the University of Fort Hare research farm along the road to King Williams Town. Several portions of distilled water were applied to clean up this biomass material in order to remove any dirt and particulate materials attached to it. Washing the biomass with double-distilled water removes the surface impurities and expose the available binding sites for metal sorption. The biomass was then sun dried for almost 20 days. It was taken into the oven (Memmert oven Lasec SA) at 120 °C to be dried further. After being dried, it was chopped into smaller pieces suitable for grinding in AFRIMILL NO. 1 blender from Animal traction Centre to a powder-like form of about 0.85 – 0.1 mm internal diameter. The produced *Zea mays* stem material was stored in a desiccator for later use.

## **2.2 Physical measurements**

### **2.2.1 Fourier Transform- Infrared Spectroscopy (FTIR)**

The functional groups of *Zea mays* stem and its activated carbons were determined using Fourier transform- Infrared spectroscopy (PERKIN ELMER, SYSTEM 2000 FT-IR) in the range of 4000 -400  $\text{cm}^{-2}$ . Few grams of the sample were mixed with KBr pellets in a mortar. FTIR is an important tool to identify the characteristic functional groups of the material.

### **2.2.2 Scanning electron microscopy with Energy dispersive X-ray spectroscopy (SEM/EDS)**

SEM was used to identify the surface morphology and/or microstructure of the *Zea mays* stem and the prepared activated carbons. SEM images were obtained in a JEOL, JSM- 6390 LV (JEOL Ltd, Japan) instrument with a 3kV voltage at different magnifications x1000, x2000, x3000, x5000, and x10000.

### **2.2.3 Powder X-ray diffraction (pXRD)**

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition and physical properties of the sample without destroying it. X-ray diffraction produce the atomic structure of materials and is based on the elastic scattering of X-ray from the electron clouds of the individual atoms. Powder X-ray diffraction is a technique used to characterize the crystallographic structure and orientation of substrate –anchored thin films [1, 8]. Bruker-D8 advance powder X-ray diffractometer instrument operating at a voltage of 40 kV and a current of 30 mA with Cu  $\text{K}\alpha$  radiation was used in this study.

#### **2.2.4 Atomic absorption spectrometry (AAS)**

Atomic absorption spectrometry (Thermo Scientific, ice 3000 SERIES, AA Spectrometer) was used to determine the concentration of metal ions before and after adsorption.

### **2.3 Preparation of activated carbon from *Zea mays* stem**

Activated carbon was prepared from *Zea mays* stem using one step chemical activation method reported [9 - 10]. Chemical activation method was chosen over physical activation method because of a number of reasons such as; low temperature for pyrolysis, one step process, much high activated carbon yield, and very high surface area for chemical activated carbon than that produced through physical activation [11].

#### **2.3.1 Preparation of activated carbon from phosphoric acid**

About 10 g dried *Zea mays* stem was impregnated with 100 mL of phosphoric acid until an extensive swelling was observed. The mixture was then kept in an oven at 100 °C overnight. It was then removed from the oven and allowed to cool, colour changed to light brown as shown by beaker B in Figure 2.1 was observed



Figure 2.1: The impregnation mixture of *Zea mays* stem with  $\text{H}_2\text{SO}_4$  (A) and  $\text{H}_3\text{PO}_4$  (B)

The mixture was then taken into electric furnace for 1 hour 30 minutes at temperatures ranging from 400-600 °C. A deep black bubbles-like structure of activated carbon was produced and was allowed to cool down. After cooling, it was rinsed with hot distilled water to remove excess phosphoric acid from the activated carbon until the pH of the washings was neutral, that is,  $\text{pH} = 7$ . The obtained activated carbon was then dried further in an oven at 100 °C overnight. The activated carbon obtained from complete phosphoric acid treatment is presented in Figure 2.2.





Figure 2.2: Activated carbon synthesized from phosphoric acid.

### **2.3.2 Preparation of activated carbon from sulphuric acid**

The above procedure was followed, that is, 10 g of *Zea mays* stem material was mixed with 75 mL of  $\text{H}_2\text{SO}_4$  and the impregnation mixture turned to dark brown colour after it was kept overnight in an oven at 100 °C as shown in beaker A in Figure 2.1. The mixture was then taken into electric furnace for almost 1 hour, where it expanded and formed black carbon materials. It was then cooled and was neutralized with 80 mL of 1%  $\text{NaHCO}_3$  solution for 1 hour to remove the acid from the activated carbon. The activated carbon was filtered using Whatman filter paper and further dried in an oven at 100 °C overnight. Figure 2.3 shows the final product of activated carbon from sulphuric acid.

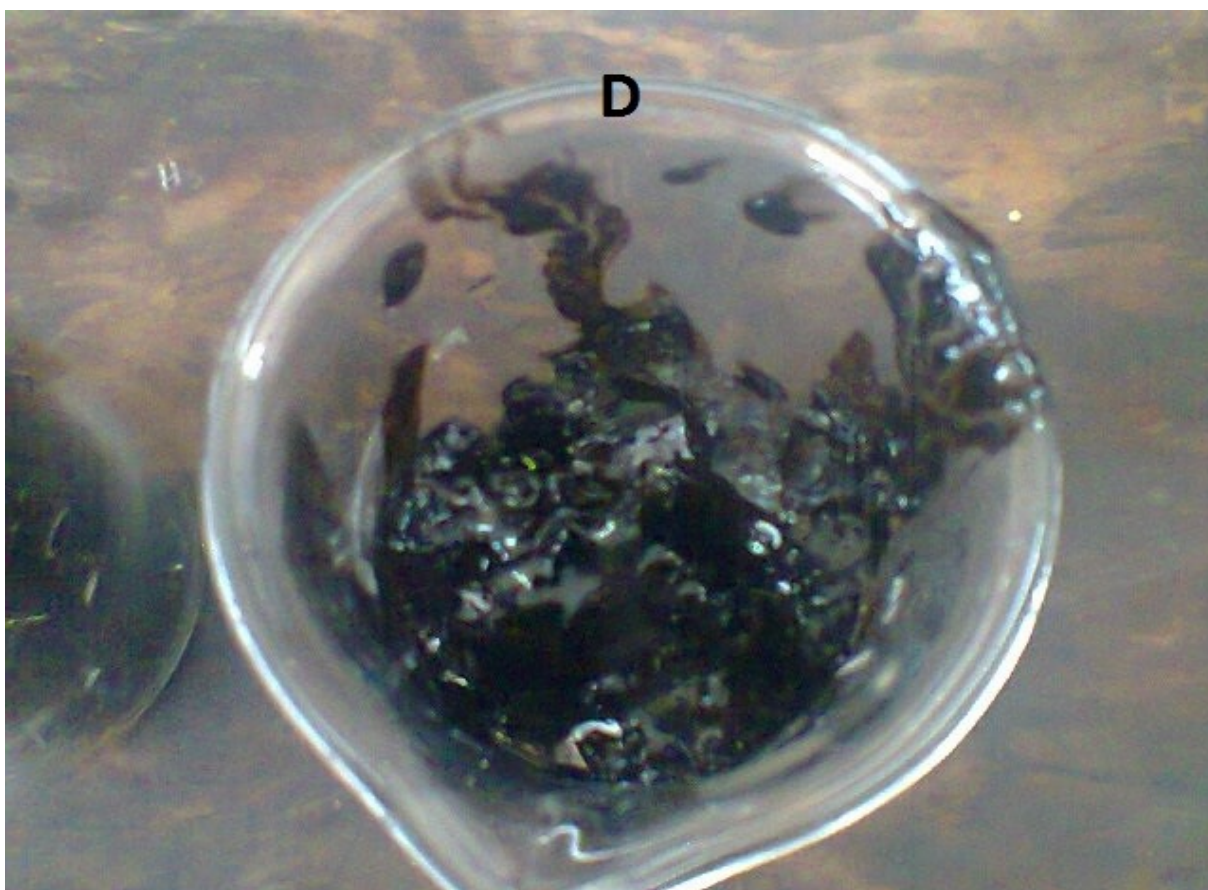


Figure 2.3: Activated carbon obtained from sulphuric acid

### **2.3.3 Preparation of activated carbon from sodium hydroxide**

10 g of *Zea mays* stem was impregnated with 100 mL NaOH solution and kept in an oven overnight. It was then introduced into electric furnace for 2 hours at temperatures ranging from 500-600 °C. After that duration it was cooled and neutralized for 1 hour with 35% HCl to remove NaOH in the activated carbon. It was then filtered and dried again overnight in an oven.

### **2.3.4 Preparation of activated carbon from potassium hydroxide**

To prepare of activated carbon from *Zea mays* stem using KOH, the same procedure used for NaOH in Section 2.3.3 was also applied, that is, 10 g of *Zea mays* stem material with 100 mL KOH solution and it produced large black activated carbon as shown in Figure 2.4 (E and D)

shows the mixtures of NaOH and KOH treated activated carbon after impregnation and kept in an oven at 100 °C overnight and Figure 2.4 (G and H) shows the NaOH and KOH treated activated carbon final products.



Figure 2.4: Impregnation mixture of *Zea mays* stem with NaOH (E), KOH (F), and resultant activated carbon from NaOH (G) and KOH (H).

## **2.4 Preparation of metal ion solutions**

Stock solutions of metal ion solutions were prepared by dissolving appropriate amounts of  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cr}(\text{NO}_3)_2$ ,  $\text{Hg}_2\text{Cl}_2$ , and  $\text{Cu}(\text{SO}_4)_2$  in de-ionized water in concentration of 1 g/L. Dilute solutions were prepared from the stock solutions in concentrations of 200 ppm, 400 ppm, 600 ppm, and 800 ppm respectively. For the assurance of the concentration of the metal ion solutions, the dilute solutions were measured with AAS in order to confirm the exact initial concentration of each metal ion in the solution before adsorption. These metal ion solutions were then stored in a hood to prevent them from reacting with atmospheric gases in the surroundings. Since the adsorption studies are mostly affected by the pH of the solution, shaking speed, and contact time, the experiment was therefore conducted under similar experimental conditions where the initial pH was set between 2-6, shaking speed was 110 rpm, and contact time was around 12 hours.

## **2.5 Adsorption experiments**

The effect of pH, contact time, stirring rate, and initial concentration of the metal ions in solution on biosorption and adsorption of  $\text{Pb}(\text{II})$ ,  $\text{Cr}(\text{III})$ ,  $\text{Cu}(\text{II})$ , and  $\text{Hg}(\text{II})$  on *Zea mays* stem and its activated carbon were studied. The concentration of each and every metal ion solution after adsorption/biosorption was determined using AAS. Characterization of *Zea mays* stem, activated carbon, and metal ion solutions after adsorption was done. The physical measurements FTIR, XRD, and SEM/EDS for activated carbon and *Zea mays* stem after adsorption were done.

### **2.5.1 Effect of pH**

The effect of pH on the biosorption and adsorption of Pb(II), Cr(III), Cu(II), and Hg(II) ions was investigated by adjusting the pH values to 2, 3, 4, 5, and 6 keeping the adsorbent dosage at 0.2 g in 20 mL of solution, biosorbent dosage at 2 g in 20 mL of solution and temperature constant at and 25 °C respectively. The initial concentration of all the metal ions solutions were kept at 200 ppm. The adjustment of pH was done by using 2.0 M of HCl and/or 2.0 M of NaOH solutions.

### **2.5.2 The effect of contact time**

The effect of contact time was studied or determined by dissolving 0.2 g of the adsorbent (activated carbon), or 2 g of biosorbent (*Zea mays* stem) in 20 mL of metal ion solution, keeping the pH constant for 6 hours.

### **2.5.3 The stirring rate**

The stirring rate was kept constant at 110 revolutions per minutes (rpm) for the whole experiment/study in making sure that similar results are obtained.

### **2.5.4 The effect of concentration**

The concentration of metal ion solutions were diluted to 200 ppm, 400 ppm, 600 ppm, and 800 ppm in order to investigate the ability of the biomass and its activated carbon to remediate metal ions from different lower concentrations of the aqueous solution.

### 2.5.5 The effect of biosorbent and adsorbent dosage

The effect of adsorbent and biosorbent dosage on removal of the metal ions from prepared aqueous solution was studied by adding 0.2 g, of the adsorbent and 2 g of biosorbent separately to glass flasks containing 20 mL of metal ion solutions having a concentration of 200 mg/L. The pH and the temperature were kept constant at 25 °C respectively. The flasks were constantly stirred continuous for 6 h at 110 rpm.

### 2.6 Determination of metal ion concentration, Percentage removal, and Sorption capacity

The following equation was used to determine the concentration of metal ions ( $M^{2+}$ ):

$$M_{Sorbent}^{2+(t)} = \frac{V_{solution} (M_{t=0}^{2+} - M_t^{2+})}{m_{sorbent}} \dots\dots\dots Eq. 3[10]$$

Percentage removal of the metal ions by activated carbons was calculated by the following equation:

$$R (\%) = \frac{C_i - C_f}{C_i} \cdot 100 \dots\dots\dots Eq. 4 [12]$$

Where:  $R$  – Removal percentage

$C_i$  – initial metal ion concentration

$C_f$  – final metal ion concentration (mg/L)

Sorption capacity was also calculated using the equation below:

$$Q_e = \frac{V(C_i - C_e)}{1000w} \dots\dots\dots Eq. 5[12]$$

Where:  $Q_e$  – adsorption capacity (mg/g)

$C_i$  – initial metal ion concentration (mg/L)

$C_e$  – equilibrium metal ion concentration (mg/L)

$W$  – Adsorbent dose (g)

$V$  – Solution volume (mL)

## 2.7 Physicochemical Characteristics

### 2.7.1 Activated carbon yield (%) determination

Carbon yields are desirable and vital in the preparation of activated carbon. On this work, carbon yield for four activated carbon prepared with different activating reagents will were calculated using equation 6 below and results are presented in chapter 3.

$$\text{Carbon yield (\%)} = \frac{\text{Activated carbon weight}}{\text{Raw material}} \cdot 100 \dots \text{Eq.6 [19]}$$

### 2.7.2 Adsorption capacity (%) using ammonia adsorption

The quality and effectiveness of the activated carbon as adsorbents was determined by its ability to adsorb gases such as  $\text{NH}_3$  [19]. Adsorption percentage was determined using the equation below:

$$\text{Adsorption (\%)} = \frac{W_a - W_b}{W_b} \cdot 100 \dots \text{Eq. 7 [19]}$$

Where  $W_a$  and  $W_b$  are weights of the activated carbon after and before ammonia adsorption, that is, after a particular amount of the activated carbon has been dissolved in the solution of ammonia and before that amount has been soaked in the solution of ammonia.

### 2.7.3 Iodine adsorption number method

Iodine adsorption number method is the most fundamental parameter used to characterize or test the activated carbon performance and credibility. It is the indication of the total surface area of the activated carbon produced through activation [19]. It is expressed in milligrams (mg) of iodine adsorbed by one gram of carbon when iodine concentration in the residual filtrate is 0.02 normal. Iodine adsorption number is given by the following equation:

$$\text{Iodine number} = \frac{V(T_i - T_f)C_i \cdot M_i}{(T_i - g)} \dots \dots \dots \text{Eq. 8 [19]}$$

Where:

V = 25 mL (mL iodine solution)

T<sub>i</sub> = 11.3 mL (mL NaSO<sub>4</sub> solution used for titration of 10 mL iodine solution)

T<sub>f</sub> = (mL NaSO<sub>4</sub> solution used for titration of 10 mL filtrate solution)

g = 0.1g (weight of the sample in grams)

M<sub>i</sub> = 126.90 g/mol (molar weight of iodine)

C<sub>i</sub> = 0.046 N (concentration of iodine)



## 2. 8 References

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## CHAPTER THREE

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Introduction

Adsorption of metal ions from aqueous and industrial solutions using agricultural biomass has received significant attention in recent years and research has been carried out in order to find out the best method for metal ion removal. For any biomass to be used, it has to be locally abundant and the production and operational cost must be low. In this work, *Zea mays* stem and its activated carbon were used as metal ion adsorbents. The results obtained using activated carbon and its precursor (*Zea mays* stem) for the removal of metal ions from aqueous solutions are presented in this chapter.

Activated carbon prepared from *Zea mays* stem was characterized using FT-IR, SEM, EDS, and XRD. The adsorption performance and credibility of the prepared adsorbent was determined using physico-chemical parameters such as carbon yield, adsorption capacity, moisture content and iodine number before the adsorption. The effect of pH, initial concentration, adsorbent dosage, and contact time were carefully studied during batch experiments and the results are described in this chapter. The best fitting equilibrium model between Langmuir and Freundlich isotherms were studied in order to deduce which model describe the adsorption of each metal ion more successfully. After the adsorption studies, FT-IR, SEM, EDS, and XRD were used to characterize the adsorbents (activated carbon and *Zea mays* stem) in order to determine whether the adsorbate adsorbed on the surface of the adsorbent. The results obtained from characterization were compared to literature findings [1-7].

## 3.2 Characterization of the prepared activated carbon

### 3.2.1 FTIR spectra studies of the activated carbon

FTIR spectra of the *Zea mays* stem and its activated carbon were obtained to examine the functional groups present that might be necessary for the adsorption of metal ions. The spectra are presented in Figures 3.1 (A) and 3.2 (B). It can be observed that the precursor (*Zea mays* stem) contained more vibration bands than the prepared activated carbons.

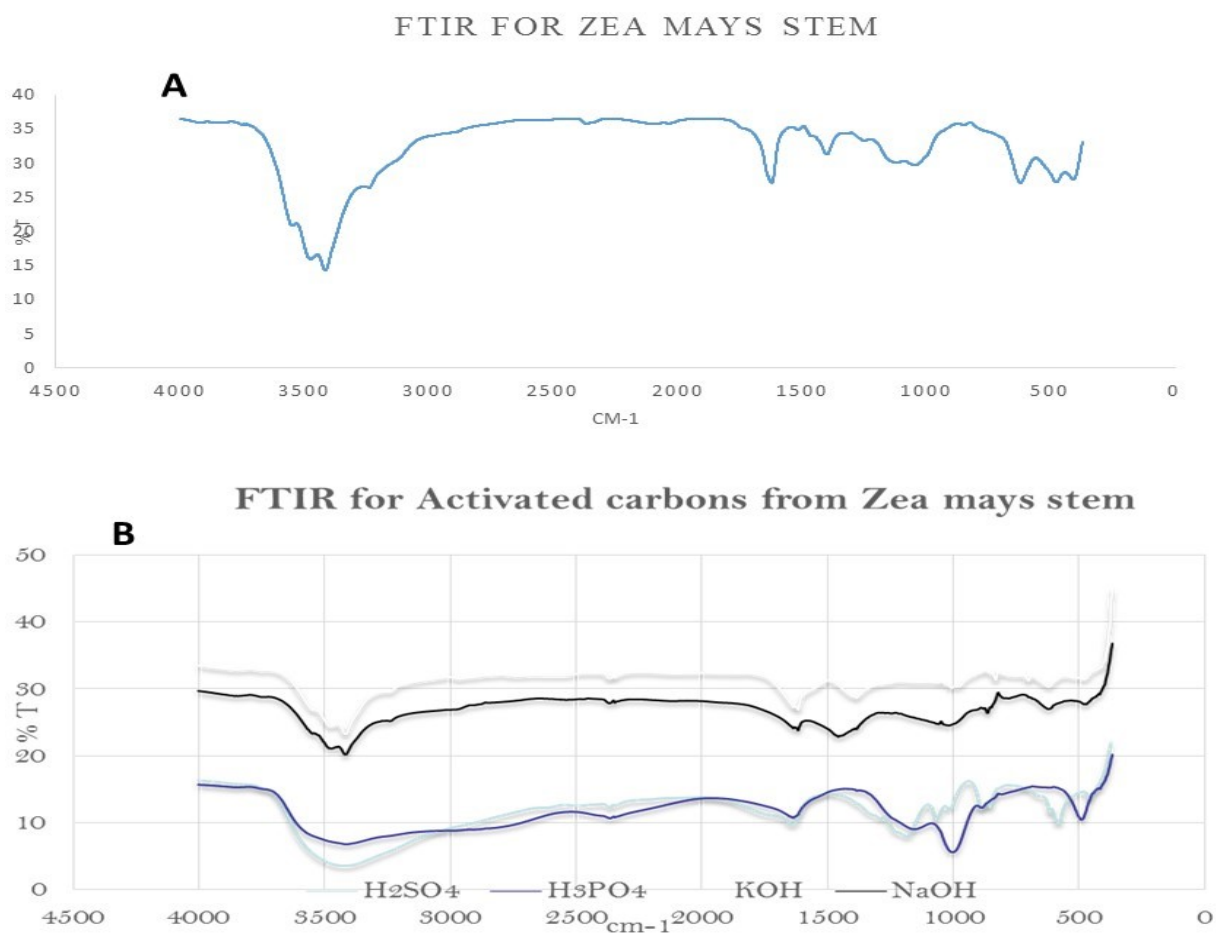


Figure 3.1-2: FTIR spectrum for *Zea mays* stem (A), FTIR spectra for activated carbons prepared from acids and bases (B)

Comparing the FTIR results for *Zea mays* stem and that of the four activated carbons prepared from *Zea mays* stem, a strong broad stretching vibration at  $3467\text{ cm}^{-1}$  is observed and can be assigned to O-H stretch for primary alcohol and phenols of the lignocellulosic *Zea mays* stem [8]. The other functional groups that can be observed in the FTIR of the pure *Zea mays* stem are two N-H vibrations stretch at  $3620\text{-}3500\text{ cm}^{-1}$  assigned to primary amide. The C=C stretching vibration of the lignocellulose aromatic ring appeared at  $1637\text{ cm}^{-1}$ , C-O-C stretching vibrations in ether, phenol and esters groups appeared between  $1041\text{ - }1248\text{ cm}^{-1}$ . For the activated carbons, the O-H stretching vibration is no longer intense and this O-H can be assigned to hydroxyl functional groups of the lignocellulose. The absence of N-H stretch and reduction of O-H stretch can be ascribed to degradation or dehydration of cellulosic material by the activating reagents used in the synthesis of the activated carbon [9]. The vibration stretch at  $1000\text{ cm}^{-1}$  for C-O group is more pronounced in the phosphoric acid activated carbon. This is so because activated carbon prepared from phosphoric acid has high carbon content and composed of well-developed carbonyl materials.

### **3.2.2 Morphology of the activated carbon**

SEM images for the activated carbons prepared from the *Zea mays* stem using  $\text{H}_3\text{PO}_4$  are presented in Figure 3.3.

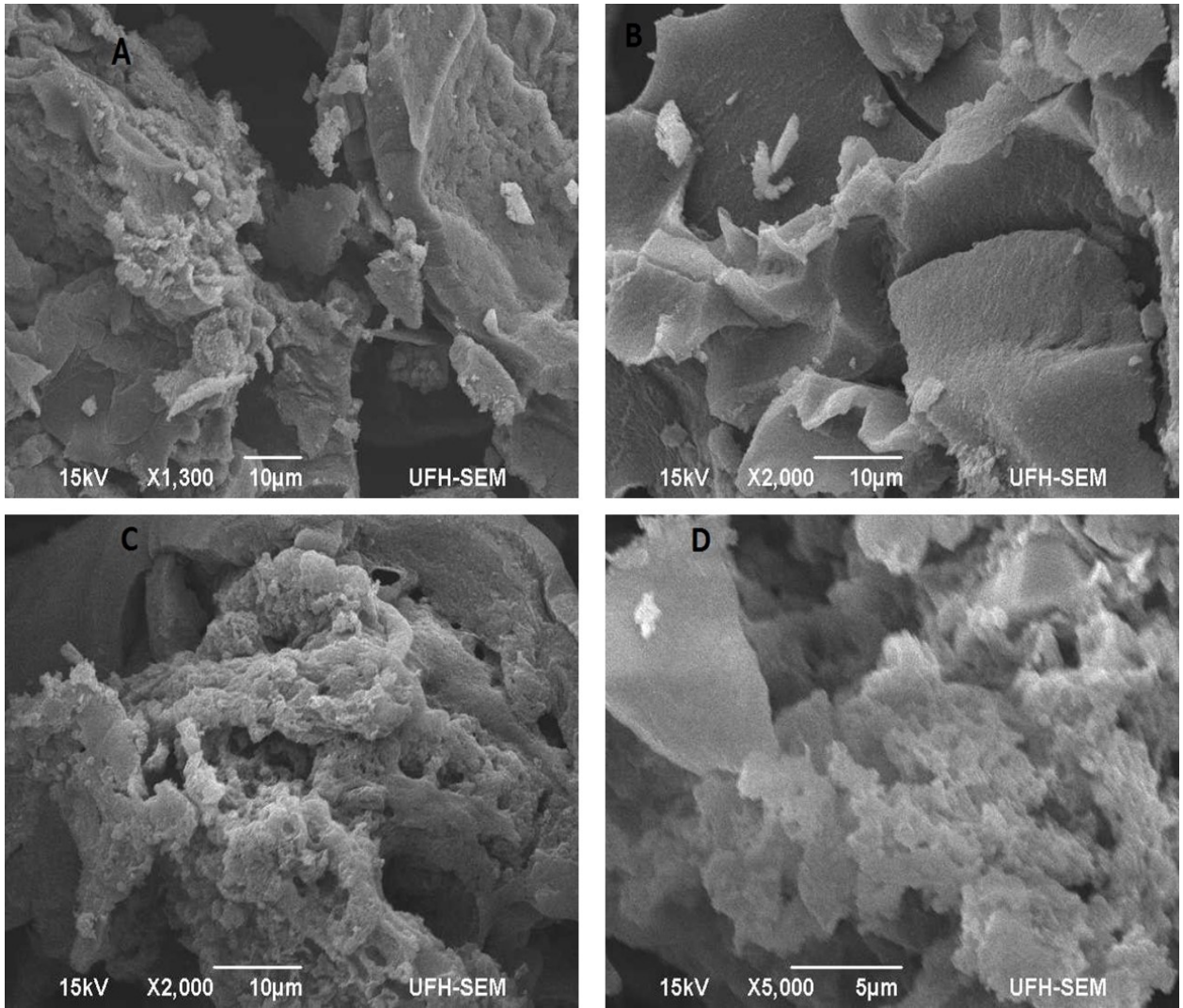


Figure 3.3: SEM images of the activated carbon prepared with  $H_3PO_4$  before adsorption

The SEM images in Figure 3.3 show that the phosphoric acid treated *Zea mays* stem activated carbon produced some external surfaces with irregular cavities and pores. Cavities and cracks on the surface of the activated carbons are believed to originate the evaporation of the activating agent such as phosphoric acid [10-13]. These irregular structures are responsible for entrapping metal ions during adsorption. The flaky morphologies shown by the SEM images have also been reported earlier [14].

Full scale counts: 768

H3PO4(1)\_pt1

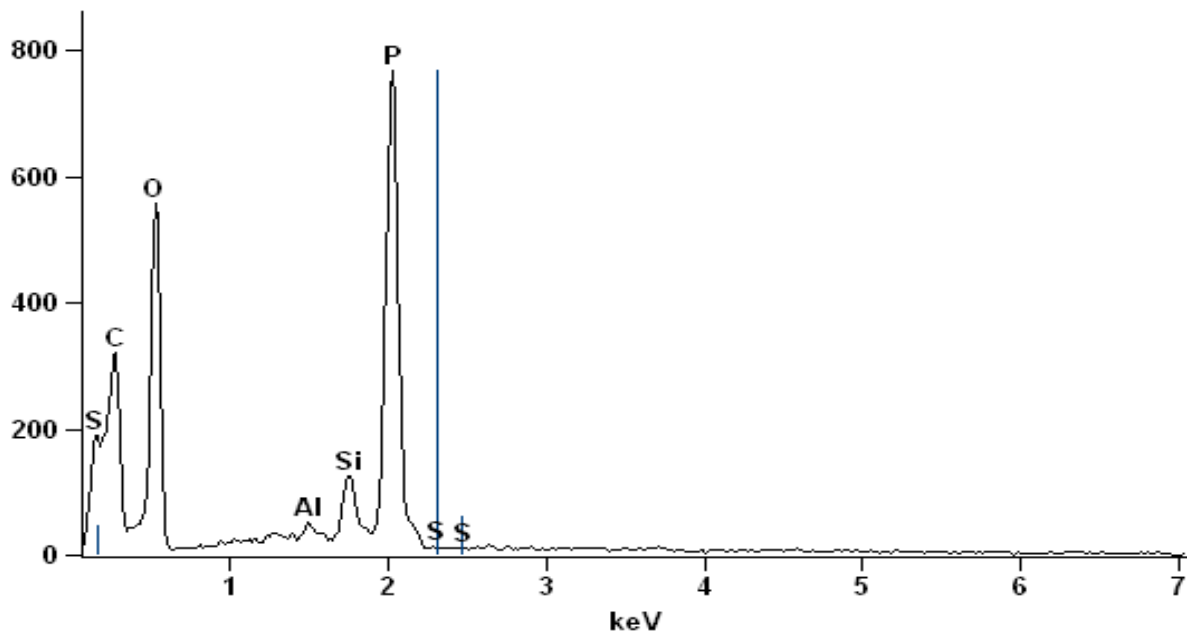


Figure 3.4: EDS spectrum for activated carbon prepared with H<sub>3</sub>PO<sub>4</sub> before adsorption

The high percentage of phosphorous (P), and oxygen (O) in the EDS of the prepared activated carbon might be due to phosphoric acid used as activating agent and that naturally present phosphorus. The presence of aluminium (Al) and silicon (Si) in the EDS spectrum might be due to the presence of some soil in the *Zea mays* stem.

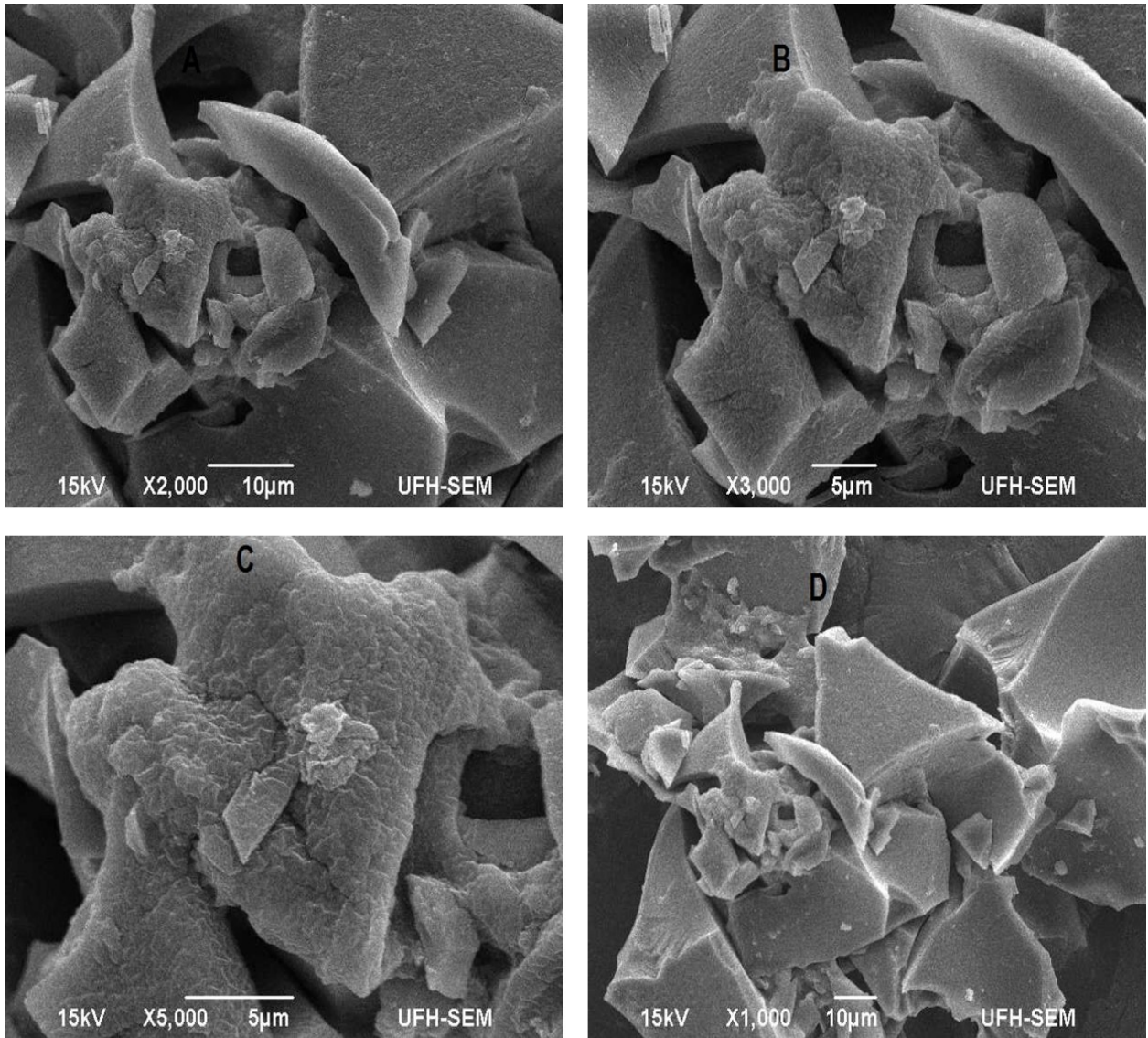


Figure 3.5: SEM images of activated carbon prepared with  $H_2SO_4$  before adsorption

SEM images of the activated carbon prepared with  $H_2SO_4$  in Figure 3.5 shows some fairly smooth surfaces, with very few cracks and voids external structures on the surface of the carbon. The asymmetrical linings on the activated carbon surface when magnification is 5000x of images C above could be the one responsible for attracting metal ions.



Full scale counts: 496

H2SO4(1)\_pt1

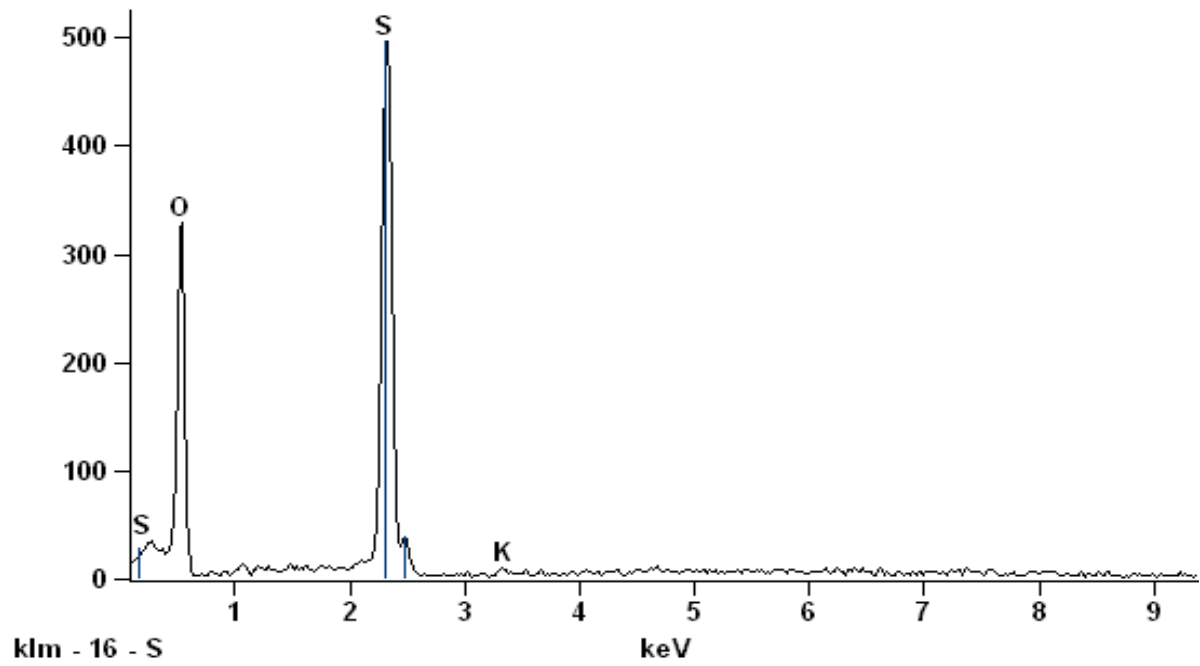


Figure 3.6: EDS spectrum for activated carbon prepared with sulphuric acid before adsorption

The high percentage of sulphur (S) and oxygen (O) in the prepared activated carbon are from the sulphuric acid used as activating agent used to prepare activated carbon from *Zea mays* stem.

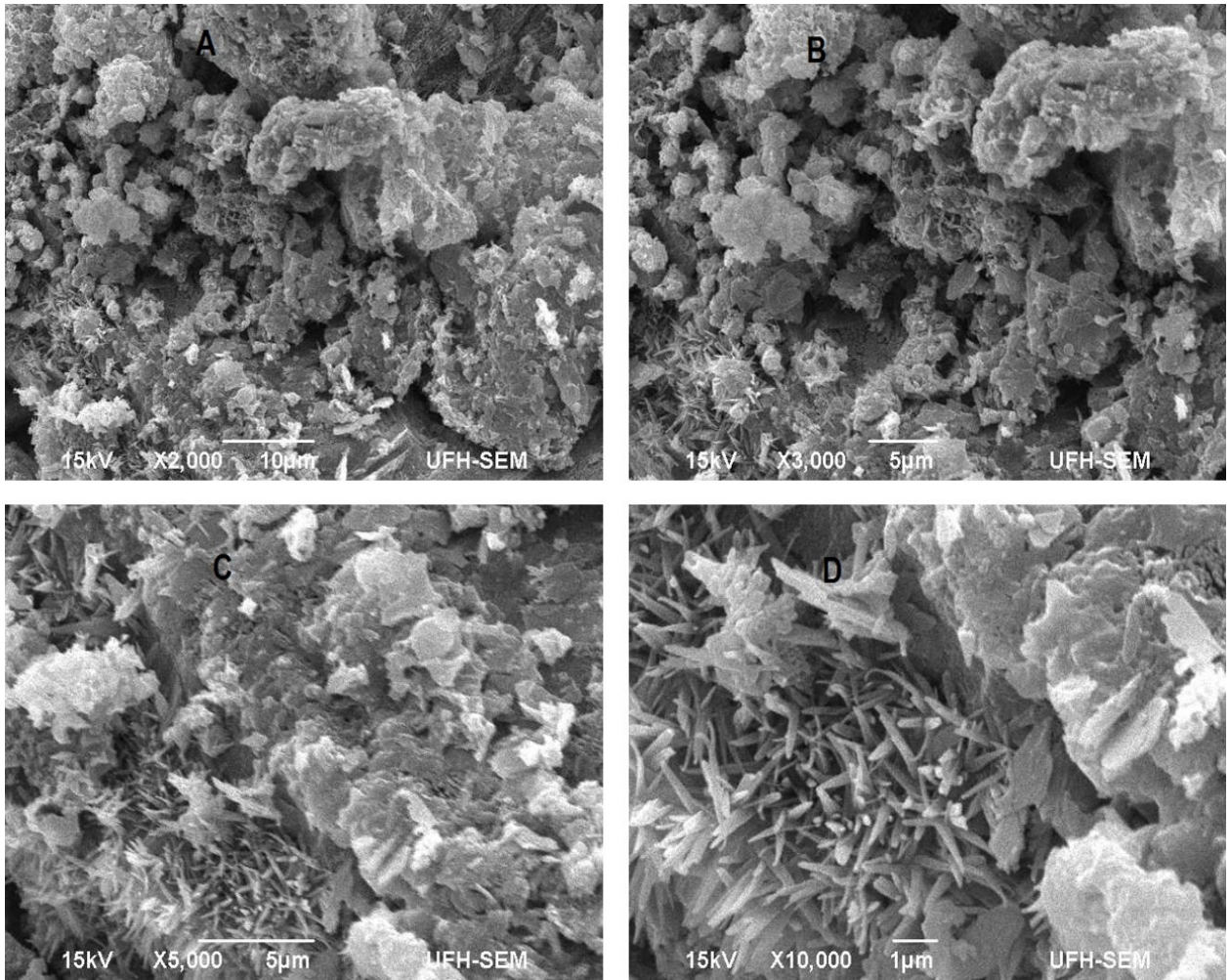


Figure 3.7: SEM images of activated carbon prepared with NaOH before adsorption

SEM images of activated carbon prepared with NaOH shown in Figure 3.7 have some fibrous (image D above) and uneven rough surfaces. The variety of open pores and cavities in the structures can also be observed in images A and B in Figure 3.7.

Full scale counts: 585

NaOH(1)\_pt1

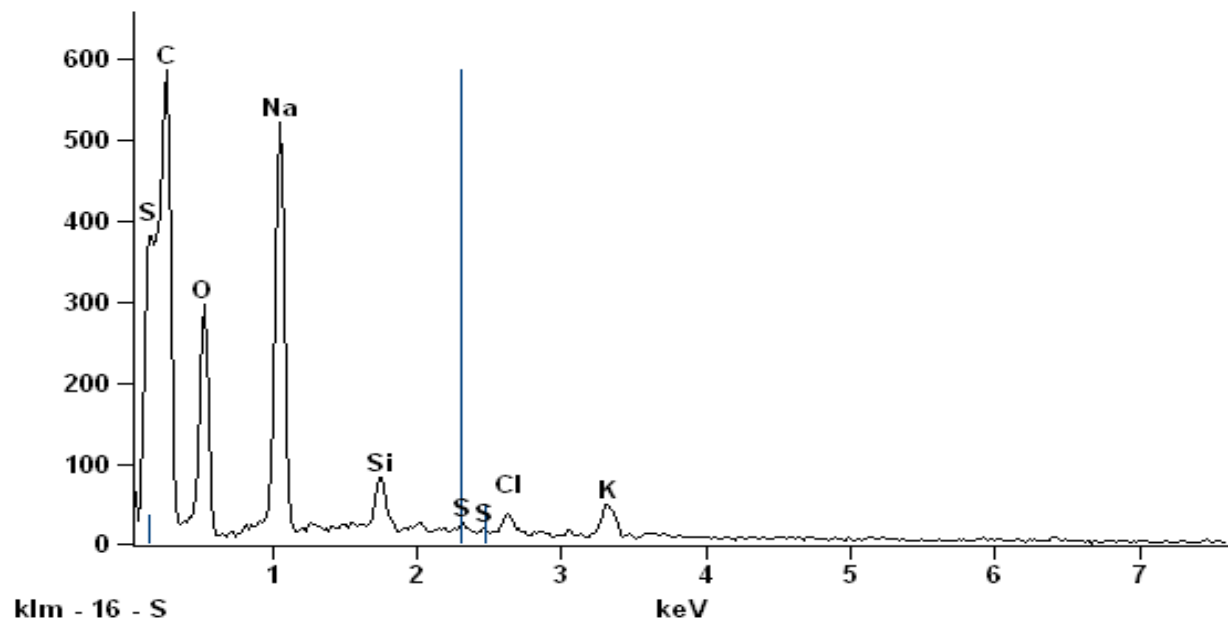


Figure 3.8: EDS spectrum of activated carbon prepared with sodium hydroxide before adsorption

EDS results for activated carbon prepared with NaOH indicates high values of sodium (Na), carbon (C), sulphur (S), and oxygen (O). The presence of elements such as Na and O can also be attributed to the use of sodium hydroxide in the synthesis of the activated carbon, while the presence of C can be credited to the high content of carbon in the prepared activated carbon.

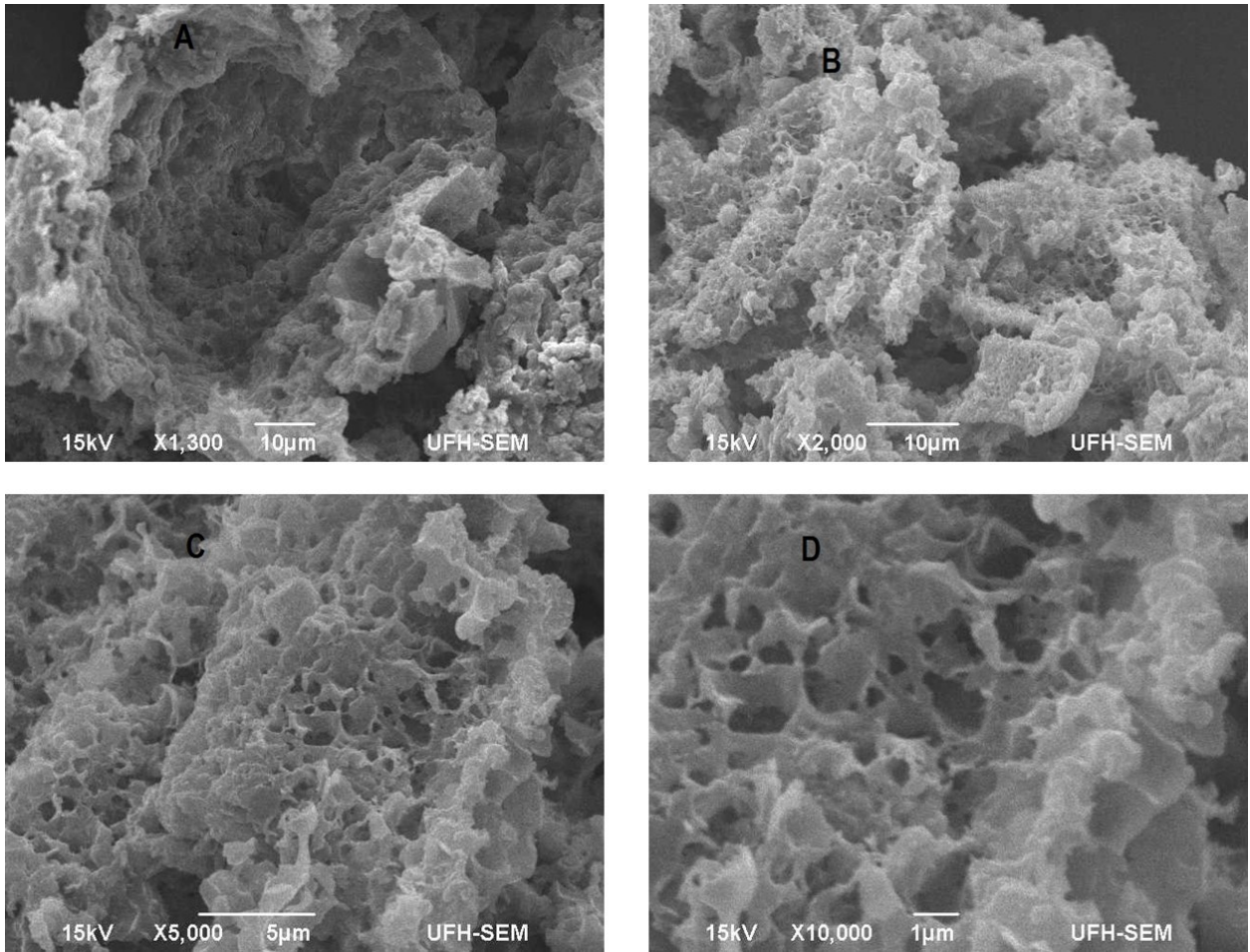


Figure 3.9: SEM images of activated carbon prepared with KOH before adsorption

Variety of pores along with fibrous structures, holes and cavity openings on the surface of the carbon can be clearly seen on the KOH treated activated carbon. The SEM images in (Figure 3.9, A –D) show some holes and cavities which are visible and available for metal ion adsorption [13]. The higher the magnification, the better the visibility of holes and cavities. According to Hesas *et al.* activated carbon prepared from agricultural biomass usually show wide variety of pores, holes and cavities with fibrous structures [15]. Therefore, the SEM results presented in this study are in good agreement with the findings of many previous studies [13, 15].

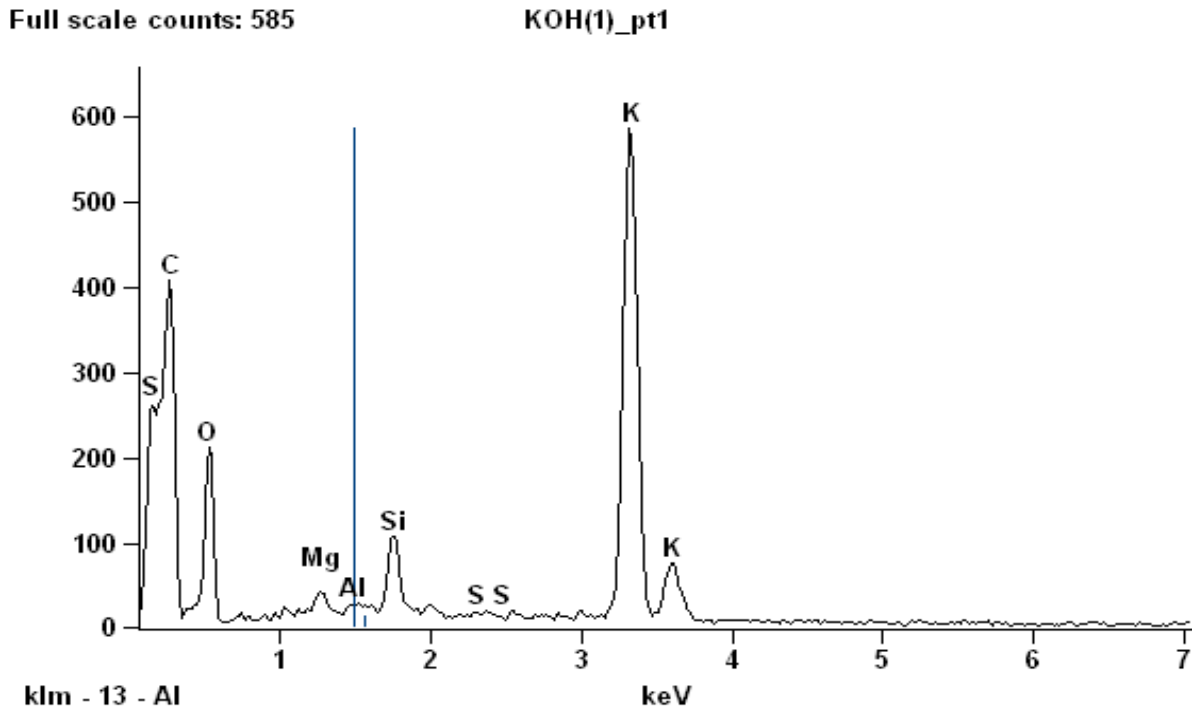


Figure 3.10: EDS spectrum of activated carbon prepared with KOH before adsorption

The EDS results in Figure 3.10 shows high values of carbon (C) which are due to the high carbon content in the activated carbon prepared. On the other hand, there are very high values of potassium (K), oxygen (O), and sulphur (S) present that could be attributed to fact that the cleaning of the activating reagents during the synthesis of the activated carbon was not complete or the recovering agent (HCl) used to neutralize the base was weak.

### 3.3 Physico-chemical characteristics of the activated carbon

Four physico-chemical properties of the activated carbon were determined in order to understand the adsorption ability of the activated carbon and reveal the volume of pores available for adsorbing metal ions. These properties were:

- ❖ Carbon yield (%)
- ❖ Adsorption capacity (%) using ammonia adsorption method
- ❖ Iodine number
- ❖ Moisture content

### **3.3.1 Carbon yield (%) determination**

Carbon yield percentage of activated carbons prepared with  $H_2SO_4$ , NaOH,  $H_3PO_4$ , and KOH from *Zea mays* stem were 77%, 50%, 34%, and 13% respectively. Activated carbon prepared with phosphoric acid had high percentage yield than the other three activated carbons. This indicates that sulphuric acid is one of the best chemical activating reagent to be used to prepared activated carbon from *Zea mays* stem, although other chemical activating reagents such sulphuric acid, sodium hydroxide, and potassium hydroxide are not that bad or low in producing activated carbon from *Zea mays* stem. The results obtained from carbon yield percentage indicates the amount of activated carbon produced from a specific amount of precursor (*Zea mays* stem) using a particular chemical reagent.

### **3.3.2 Adsorption capacity (%) using Ammonia adsorption**

Adsorption abilities were calculated and found to be 67% for the activated carbon prepared with  $H_2SO_4$ , 21% for activated carbon prepared with KOH, and 20% for both NaOH and  $H_3PO_4$  activated carbon. The differences in calculated adsorption ability using ammonia adsorption method signify that the adsorption ability of each activated carbon usually depends upon the amount of pore spaces and surface areas produced through the activation using a particular chemical reagent.

### **3.3.3 Iodine adsorption number method**

The calculated iodine number for activated carbon prepared with sulphuric acid was 348.71 mg/g, for phosphoric acid activated carbon was 142.07 mg/g, for sodium hydroxide activated carbon was 90.41 mg/g, and that activated carbon prepared with potassium hydroxide was 88.68 mg/g respectively. The results obtained from the determination of carbon yield,

adsorption ability, and iodine number of activated carbon prepared with sulphuric acid has shown to be better than that of activated carbons prepared with phosphoric acid, sodium hydroxide, and potassium hydroxide.

### **3.4 Adsorption experiments**

#### **3.4.1 Effect of pH on adsorption of metal ions**

In this study, the effect of pH of aqueous solution was studied from a range of 2 to 6 under fixed conditions of contact time of 120 minutes, 110 rpm shaking speed, initial concentration of 200 ppm 2 g of the adsorbent and that of biosorbent, and at room temperature. After careful study, the optimum pH 5-6 was chosen for all experiments. The maximum removal percentages that were obtained for metal ions at pH 5-6 are 97% for Pb(II), 98% for Cu(II), 89% for Cr(III) and there was no adsorption for mercury ions. Pb(II) and Cr(III) also showed a well-defined adsorption even at lower pH, of 98 % and 70 % respectively.

It was believed that the highest percentage removal of metal ions can be explained by the fact that at higher pH, the adsorbent surface is usually deprotonated and negatively charged, which causes more attraction between the positively charge metal cations and negatively charged adsorbent. While at lower pH, the competition between  $H^+$  and dissolved metal ions for ligands such as  $OH^-$ ,  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $Cl^-$ ,  $S^{2-}$  and phosphates become more and more significant. This usually decreases the adsorption of metal ions. The adsorption of Cr(III) has been reported at pH range of 6-7 [26]. Maximum adsorption of Pb(II) at lower pH of 2 has also been reported [27]. Figure 3.11 shows that the percentage removal of metal ions increases as pH of the solution increases except for Hg(II). It has been reported that the metal ion removal increases as pH values rises, reaching maximum around 5.0 [28 -29].

Table 3.1 shows the amount of metal ions adsorbed by the adsorbent ( $q_e$ ) at different pH levels.

Table 3.1: Effect of pH on adsorption of metal ions

Metal ions	Concentration (mg/L) at different pH levels				
	2	3	4	5	6
Pb(II)	196.25	195.35	196.61	194.88	193.27
Cu(II)	0.00	3.69	0.00	0.00	196.73
Cr(III)	139.84	161.99	135.55	178.74	178.05
Hg(II)	-	-	-	-	-



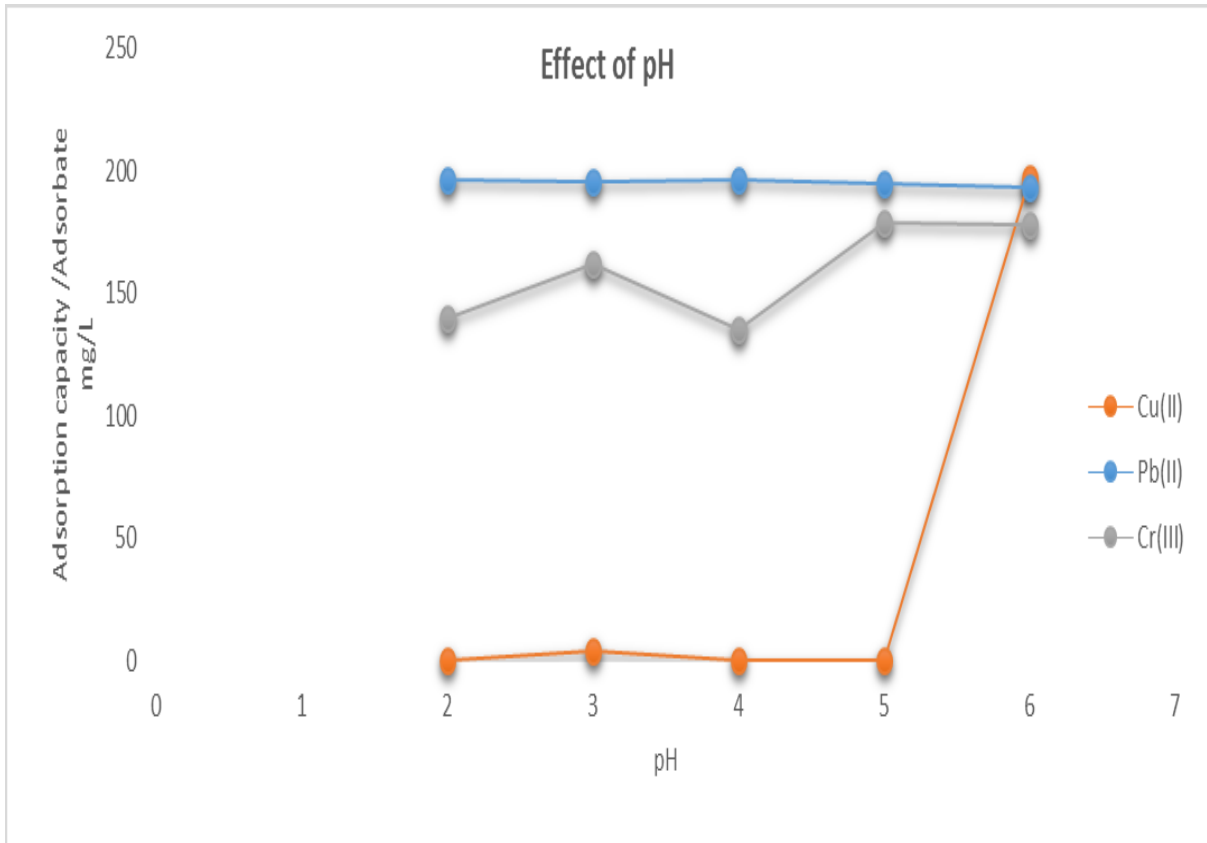


Figure 3.11: Effect of pH on the removal of Pb(II), Cu(II), and Cr(III) by activated carbons prepared from *Zea mays* stem

### 3.4.2 Effect of contact time on metal ion removal

The effect of contact time on the removal of Pb(II), Cu(II), Cr(III), and Hg(II) from aqueous solution with activated carbon prepared from *Zea mays* stem, at fixed pH 5-6, as presented in Figure 3.12.

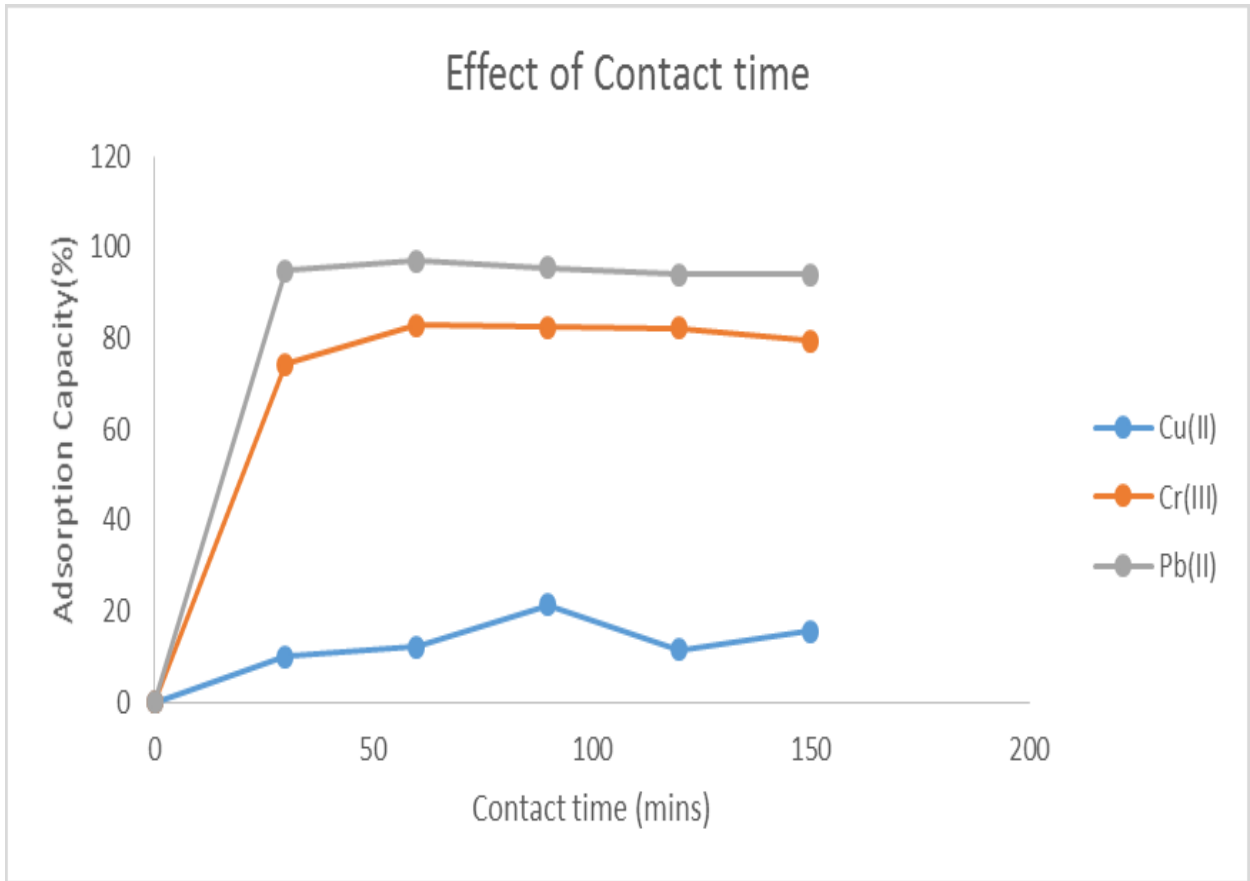


Figure 3.12: Effect of contact time on the removal of Pb(II), Cu(II), Cr(III), and Hg(II) by activated carbons from *Zea mays* stem

The result showed that the removal of Pb(II), Cu(II), Cr(III), and Hg(II) increased as the contact time between the adsorbent and metal ion solution increases. The percentage removal equilibrium was reached at different times, Pb(II) reached equilibrium at 35 min, Cu(II) at 80 min, Cr(III) at 60 min, and Hg(II) with a very slight adsorption shown after 120 minutes. The study was conducted at 25 °C and with a percent removal of 97% for Pb(II), 82% for Cr(III), and 21% for Cu(II) as shown in Table 3.2 (a-c). Therefore the metal ion removal trend was Pb(II) > Cu(II) > Cr(III) >>Hg(II). An increase in contact time after the metal ion removal equilibrium of each metal ion did not bring any improvement, that is, the metal ion removal was effective until it reached equilibrium where the  $C_e$  and  $q_e$  are at equilibrium.

Table 3.2 (a-c) shows the effect of contact time and adsorption capacity on the removal of Pb(II), Cu(II), Cr(III). Where  $C_e$  is the equilibrium concentration of metal ions in a solution and  $q_e$  is the Equilibrium concentration of metal ion in adsorbent.

Table 3.2 (a): Effect of contact time on removal of Pb(II)

Time (min)	$C_e$ (ppm)	$q_e$ (ppm)	$q_e$ (mg/g)	Adsorption capacity (%)
0	200	0	0	0
30	10.12	189.88	1.89	94.94
60	5.77	194.23	1.94	97
90	10.49	189.51	1.91	95.5
120	12.22	187.78	1.88	94
150	12.36	187.64	1.88	94
180	-	-	-	-

Table 3.2 (b): Effect of contact time on removal of Cu(II)

Time (min)	$C_e$ (ppm)	$q_e$ (ppm)	$q_e$ (mg/g)	Adsorption capacity (%)
0	200	0	0	0
30	179.99	20.01	0.200	10.01
60	175.81	24.19	0.242	12.15

90	157.30	42.70	0.427	21.35
120	176.75	23.25	0.233	11.63
150	168.89	31.11	0.311	15.56
180	-	-	-	-

Table 3.2 (c): Effect of contact time on removal of Cr(III)

Time (min)	$C_e$ (ppm)	$q_e$ (ppm)	$q_e$ (mg/g)	Adsorption capacity (%)
0	200	0	0	0
30	51.31	148.69	1.49	74.35
60	34.23	165.77	1.66	82.89
90	35.04	164.96	1.65	82.48
120	35.66	164.34	1.64	82.17
150	41.10	158.90	1.59	79.45
180	-	-	-	-

### **3.4.3 The effect of adsorbent dosage**

The optimum adsorbent and biosorbent dosage for the removal of Pb(II), Cu(II), Cr(III), and Hg(II) ions from aqueous solution was chosen to be 2 g for all experimental procedure. Although Pb(II) and Cu(II) produced maximum removal even at 1 g of adsorbent, for other metal ions, increase in adsorbent dosage above 2 g did not increase the adsorption. The study of the relationship between the adsorbent dosage and metal ion removal percentage was conducted under specific conditions where pH was 5-6, maximum contact time of 2 hours, shaking speed of 110 rpm, and at room temperature. The reason for less adsorption/metal ion removal for higher adsorbent dosage than 2 g can be due to overcrowding of adsorbent surface.

### **3.4.4 Effect of initial concentration on the uptake of metal ions**

The effect of initial concentration was studied under specific conditions where pH was 5-6, maximum contact time of 2 hours, adsorbent dosage of 2 g, shaking speed of 110 rpm with activated carbon from *Zea mays* stem as adsorbent. The initial concentration for metal ion solutions were 200 ppm, 400 ppm, 600 ppm, 800 ppm, and 1000 ppm respectively. The results obtained from the AAS Figure 3.13 shows that the metal ion removal increased as the metal ion concentration increases, except for Hg(II) in which there is no adsorption at all.

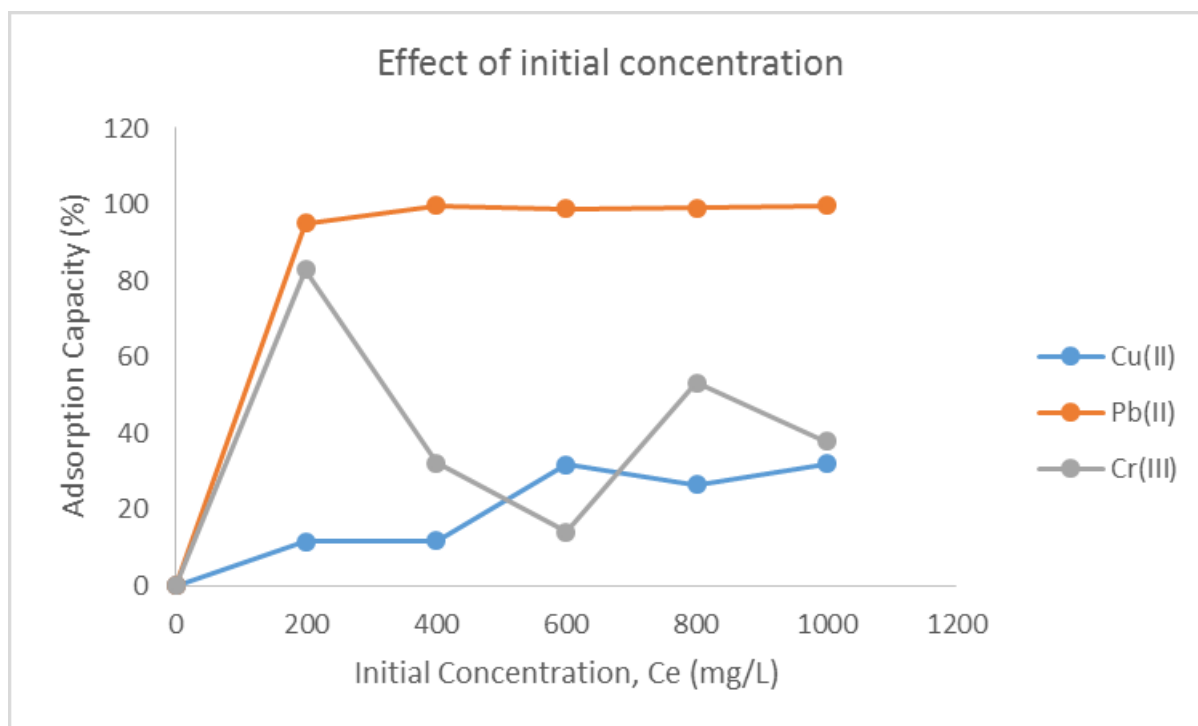


Figure 3.13: Effect of initial concentration on the removal of Pb(II), Cu(II), Cr(III), and Hg(II)

Figure 3.13 shows the effect of initial concentration of different metal ions on their uptake by the prepared activated carbon from *Zea mays* stem using sulphuric acid as activating agent. It is evident from Figure 3.13 that the use of prepared activated carbon for the removal of Pb(II) ion from aqueous solution shows promising results and can be used for the remediation of lead ion from the environmental water bodies to certain extent. Furthermore, the removal of Cr(III) ion from wastewater by prepared activated carbon can be achieved at concentrations around 200 ppm. Table 3.3 (a-c) shows the equilibrium concentration of metal ions in a solution ( $C_e$ ) and equilibrium concentration of metal ions in an adsorbent ( $q_e$ ) after adsorption for each metal ion Pb(II), Cu(II), Cr(III), and Hg(II). The mass of metal ion adsorbed,  $q_e$  in mg/g and the percentage removal is also shown in tables below.

Table 3.3 (a): Effect of initial concentration on the removal of Pb(II)

Initial Conc. (ppm)	$C_e$ (ppm)	$q_e$ (ppm)	$q_e$ (mg/g)	Adsorption capacity (%)
400	1.51	398.49	3.98	99.62
600	6.39	593.61	5.94	98.94
800	6.91	793.09	7.93	99.14
1000	2.93	997.07	9.97	99.71

Table 3.3 (b): Effect of initial concentration on the removal of Cu(II)

Initial Conc. (ppm)	$C_e$ (ppm)	$q_e$ (ppm)	$q_e$ (mg/g)	Adsorption capacity (%)
400	353.19	46.81	0.47	11.70
600	409.10	190.90	1.91	31.82
800	587.75	212.25	2.12	26.53
1000	680.73	319.27	3.19	31.93

Table 3.3 (c): Effect of initial concentration on the removal of Cr(III)

Initial Conc. (ppm)	$C_e$ (ppm)	$q_e$ (ppm)	$q_e$ (mg/g)	Adsorption capacity (%)
400	271.13	128.87	1.29	32.22
600	515.21	84.76	0.85	14.13
800	374.62	425.38	4.25	53.17
1000	622.11	377.89	3.78	37.79

Table 3.3 (a) shows the adsorption capacity (%) of Pb(II) ion by activated carbon at different concentrations. It is evident that the adsorption ability of the activated carbon on Pb(II) is greater than 99%. The amount of Pb(II) ion adsorbed by the adsorbent (activated carbon)  $q_e$  in mg/g and the adsorption capacity clearly indicates that activated carbon is one of the best methods for remediation of Pb(II) from aqueous solution and might be applicable for the remediation of Pb(II) from wastewater.

Table 3.3 (c) also indicate a better adsorption of Cr(III) which lies around 50%, then followed by that of Cu(II) metal ion which also lies around 30%. Although the amount of metal ion in the adsorbent increases as the concentration increase, there is no such difference. The amount of Pb(II), Cu(II), and Cr(III) ions adsorbed by adsorbent can also be confirmed on the SEM images produced after adsorption and the FTIR spectra after adsorption. The trend is Pb(II) > Cr(III) > Cu(II) >>Hg(II) respectively.



### 3.4.5 Effect of shaking speed on adsorption of metal ions

The effect of shaking speed on adsorption of metal ions Pb(II), Cu(II), Cr(III), Hg(II) with activated carbon prepared from *Zea mays* stem was studied under fixed conditions where maximum contact time was 2 hours, pH of the solutions was 5-6, 2 g of adsorbent, and at room temperature. Therefore the shaking speed was 110 rpm and all the experiments were conducted under this speed. The speed of the orbital shaker had no considerable effect on the adsorption of these metal ions, although the shaking speed is very important in making sure that the solution containing metal ion and the adsorbent get mixed as fast as possible. The sooner the contact time between the adsorbent and metal ion solution, the higher the adsorption efficiency.

Table 3.4 Effect of shaking speed on metal ion adsorption

Metal ions	Shaking speed (rpm)			
	90	100	110	120
Pb(II)	190.25	196.29	196.90	143.98
Cr(III)	130.25	130.70	149.90	110.99
Cu(II)	14.35	10.11	79.98	0.72
Hg(II)	-	-	-	-

### **3.5 Adsorption kinetics**

#### **3.5.1 Langmuir and Freundlich isotherms**

Biosorption isotherms describe how adsorbate interacts with biosorbents and equilibrium is established between adsorbed metal ions on the biosorbent and the residual metal ions in the solution during the surface adsorption. The most common types of models describing this type of system are the Langmuir and Freundlich isotherms [17-18]. In this study, Langmuir and Freundlich models were used to identify which model best fit each of the metal ions studied. For Langmuir model, the amount of metal ion adsorbed in unit of adsorbent mass ( $q_e$ ) was plotted against the equilibrium concentration of the metal ion ( $C_e$ ), whereas for Freundlich model, the logarithm of  $q_e$  (the amount of metal ion adsorbed in unit of adsorbent mass) was plotted against the logarithm of  $C_e$  (the equilibrium concentration of the metal ion). Trend-line was used to determine the equation and the correlation co-efficient.

Table 3.5: Langmuir isotherm results for the adsorption of Pb(II)

Initial Conc. (mg/L)	Mass of adsorbent (g)	Volume of solution (mL)	Final Conc. (mg/L)	Mass of ( $q_e$ ) adsorbate adsorbed (mg/g)	$x/m$ or $q_e$ (g/g)	$C_e$ (mg/g)
200	2	20	12.36	1.88	0.0019	12.36
400	2	20	1.51	3.98	0.0039	1.51
600	2	20	6.39	5.94	0.0059	6.39
800	2	20	6.91	7.93	0.0079	6.91
1000	2	20	2.93	9.97	0.0099	2.93

The values in Table 3.5 was used to plot Figure 3.14.

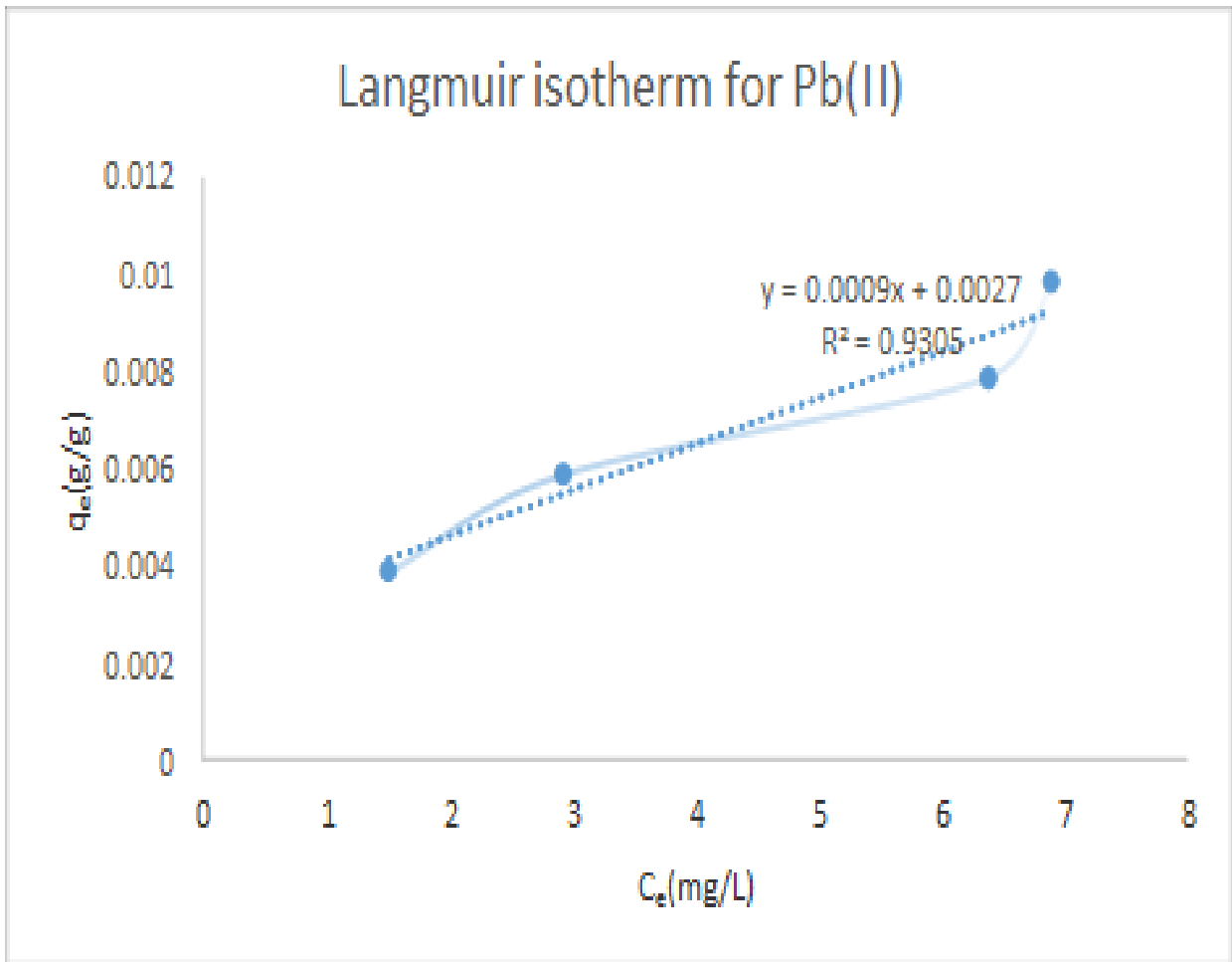


Figure 3.14: Langmuir isotherm for the adsorption of Pb(II) by activated carbon as adsorbent

The results obtained on Figure 3.14 correctly fit the Langmuir model and is confirmed by the correlation co-efficient of  $R^2=0.9305$ . The correlation co-efficient obtained above clearly indicates that the adsorption of Pb(II) ion was favourable and of monolayer process according to Langmuir model [36]. The high value of the correlation co-efficient indicates the better process of adsorption. Aqeel *et al.* [37] also report similar  $R^2$  values for the adsorption of

Pb(II) by banana peel (*Musa Sapientum*). The correlation co-efficient value usual indicates the relationship between the adsorbent and aqueous solution in equilibrium.

Table 3.6: Langmuir model values to plot  $\frac{1}{q_e}$  vs  $\frac{1}{C_e}$  for the adsorption of Pb(II)

Initial Conc. (ppm)	1/Ce	1/qe
200	0.081	526.32
400	0.662	256.41
600	0.156	169.49
800	0.145	126.58
1000	0.341	101.01

The results presented in Table 3.6 above were used to plot Figure 3.15

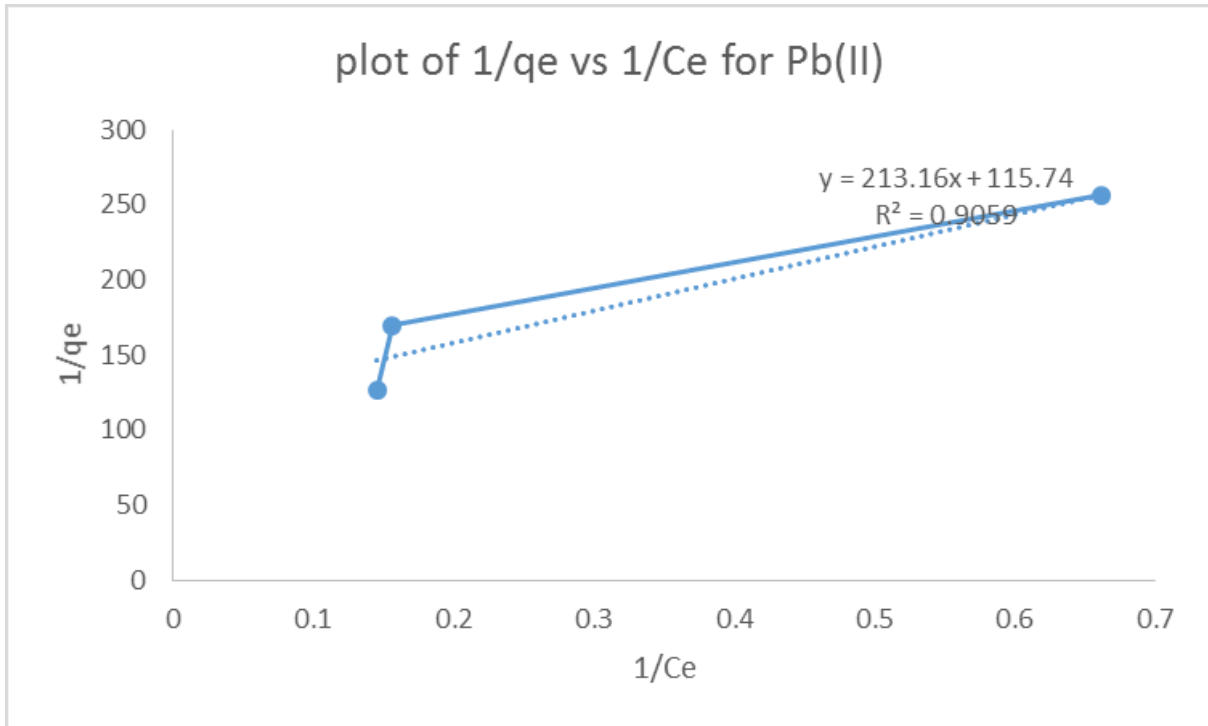


Figure 3.15: Langmuir model plot 1/qe vs 1/Ce for the adsorption of Pb(II)

$$\text{Slope} = \frac{Y_2 - Y_1}{X_2 - X_1} = \frac{256.41 - 169.49}{0.662 - 0.156} = 171.78$$

$$\text{Intercept} = \frac{1}{q_{max}} = 5$$

$$Q_{max} = 1/5 = 0.2$$

$$\text{Slope} = \frac{1}{k_A q_{max}} = \frac{1}{K_A \cdot 0.2} = 171.78$$

$$171.78 = \frac{1}{K_A \cdot 0.2}$$

$$k_A = 0.03$$

Therefore the Langmuir equation for Pb(II) is  $\frac{1}{q_e} = \frac{1}{K} + \frac{1}{KQ^0C_e}$

$$= \frac{1}{0.2} + \frac{1}{(0.2)(0.03)C_e}$$

$$\frac{1}{q_e} = 5 + 166.67 C_e$$

### Freundlich isotherm for Pb(II)

$$q_e = K_f C_e^{1/n}$$

Where  $K_f$  and  $1/n$  are the Freundlich isotherm constants related to the adsorption capacity and the intensity of adsorption.

Table 3.7: Freundlich model values to plot  $\log q_e$  vs  $\log C_e$  for the adsorption of Pb(II)

Initial Conc. (ppm)	$\log q_e$	$\log C_e$
200	1.09	-2.72
400	0.18	-2.41
600	0.81	-2.23
800	0.84	-2.10
1000	0.47	-2.00

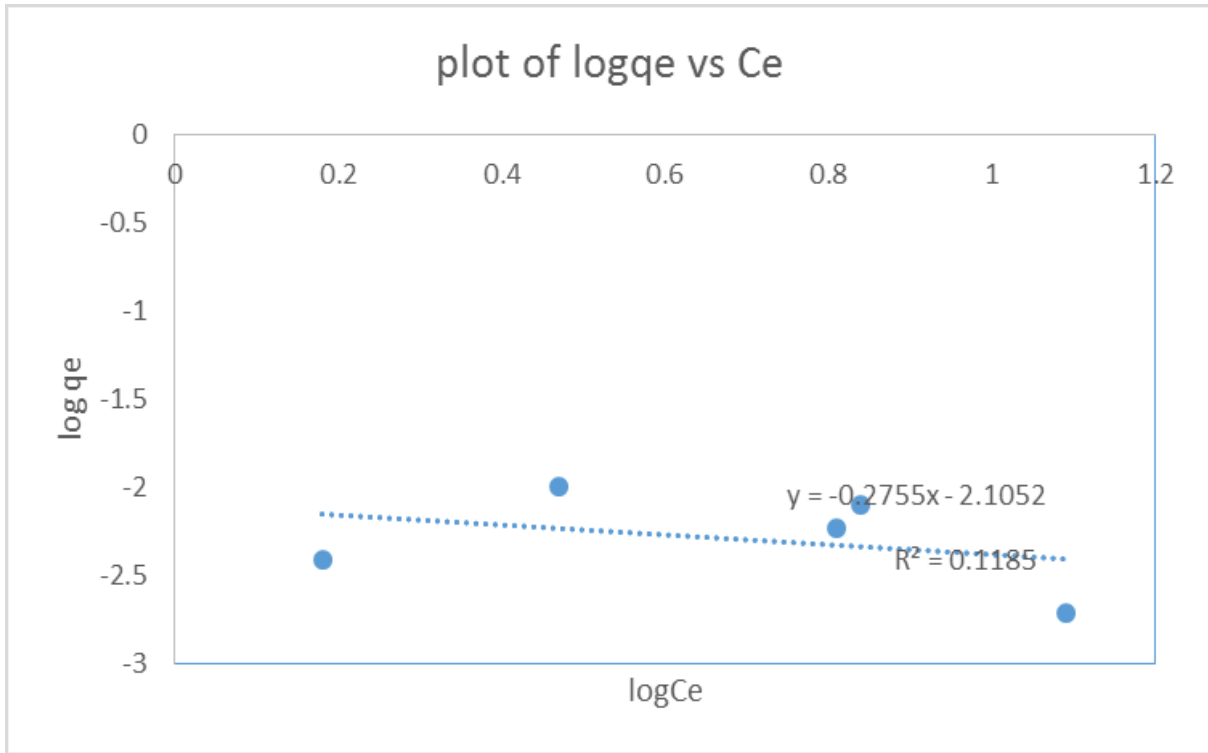


Figure 3.16: Freundlich isotherm for the adsorption of Pb(II)

Figure 3.16 shows the Freundlich model for the adsorption of Pb(II). The correction coefficient obtained was very low which indicates that the adsorption of Pb(II) was best defined by Langmuir model over the Freundlich model. The Freundlich constants were calculated by linear regression from the plot of  $\log q_e$  against  $\log C_e$ , where  $K_f$  was found to be  $4.7 \times 10^{-5}$ , while  $1/n$  was 4.33 as shown below.

$$\text{Slope} = \frac{1}{n} = \frac{\log q_{e1} - \log q_{e2}}{\log C_{e1} - \log C_{e2}} = \frac{-2.23 - 2.10}{0.81 - 0.84} = 4.33$$

Therefore,  $n = 0.23$

$$\text{Intercept} = \log K_f = -\left(\frac{1}{n}\right)$$

$$\text{Log } K_f = -\left(\frac{1}{n}\right)$$



$$K_f = 10^{\left(\frac{1}{n}\right)}$$

$$K_f = 10^{(-4.33)}$$

$$K_f = 4.7 \times 10^{-5}$$

Therefore, the Freundlich equation for Pb(II) adsorption is:

$$q_e = K_f C_e^{1/n}$$

$$q_e = 4.7 \times 10^{-5} C_e^{4.33}$$

Since  $K_f$  is the measure of the strength of absorption, the small value obtained in this study indicates that the adsorption did not fit Freundlich model, that is, the adsorption was not multilayer process. The value of  $1/n$  indicates that the adsorption was decreasing as the metal ion concentration increases.

Table 3.8: Langmuir isotherm values for the adsorption of Cu(II)

Initial Conc. (mg/L)	Mass of adsorbent (g)	Volume of solution (mL)	Final Conc. C <sub>e</sub> (mg/L)	Mass of adsorbate adsorbed q <sub>e</sub> (mg/g)	x/m or q <sub>e</sub> (g/g)
400	2	20	46.81	0.47	0.00047
600	2	20	190.90	1.91	0.0019
800	2	20	212.25	2.12	0.0021
1000	2	20	319.27	3.19	0.0032

The results in the Table 3.8 above were used to plot the Langmuir isotherm for Cu(II) below.

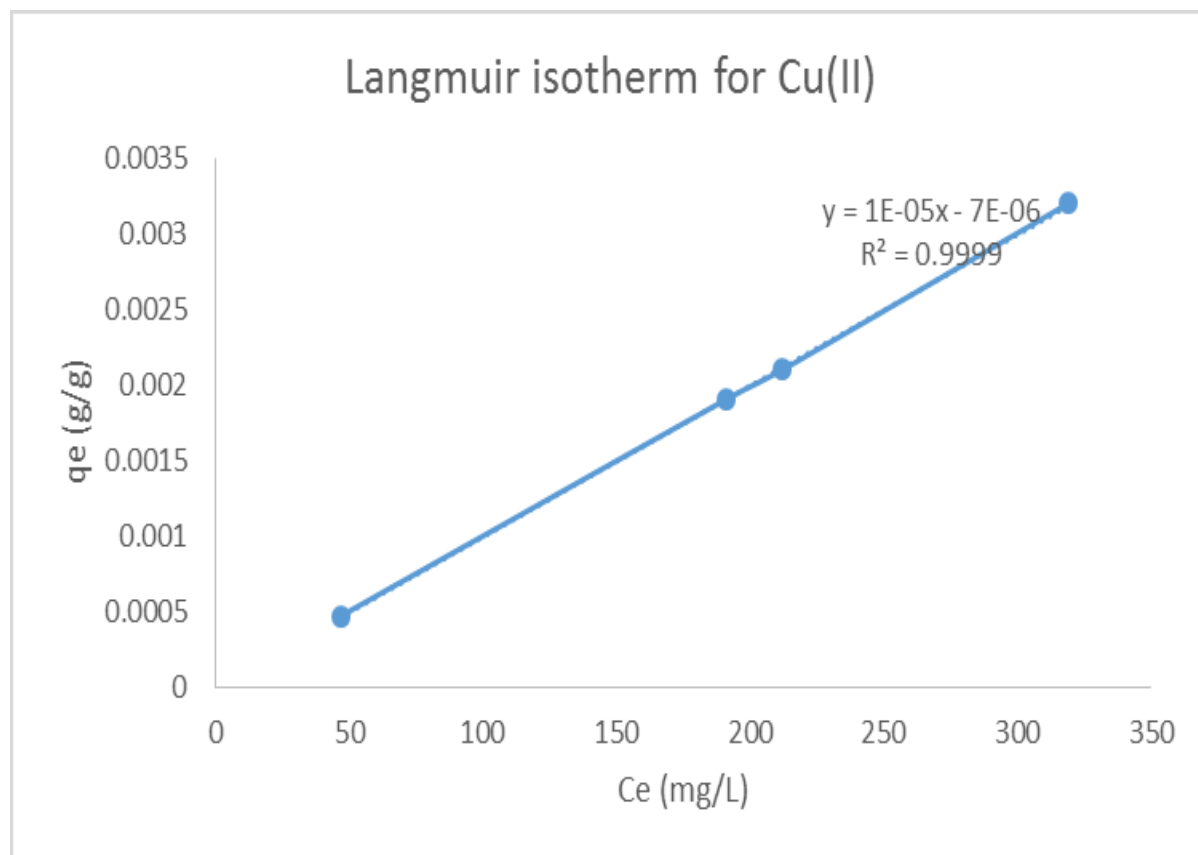


Figure 3.17: Langmuir isotherm curve for the adsorption of Cu(II)

The correlation co-efficient for Langmuir isotherm on the adsorption of Cu(II) also indicated better relationship between the activated carbon and aqueous solution in equilibrium and the high value of  $R^2$  shows out that the adsorption process was monolayer with homogeneous adsorbent. Aqeel *et al.* [20] report  $R^2 = 0.996$  on their study using banana peel (*Musa Sapientum*) as adsorbent.

Table 3.9: Langmuir values to plot 1/qe vs 1/Ce for the adsorption of Cu(II)

Initial Conc. (ppm)	$\frac{1}{C_e}$	$\frac{1}{q_e}$
400	0.021	2127.66
600	0.0052	526.32
800	0.0047	476.19
1000	0.0031	312.50

Langmuir model values in the Table 3.9 were applied to plot the curve on Figure 3.18 below:

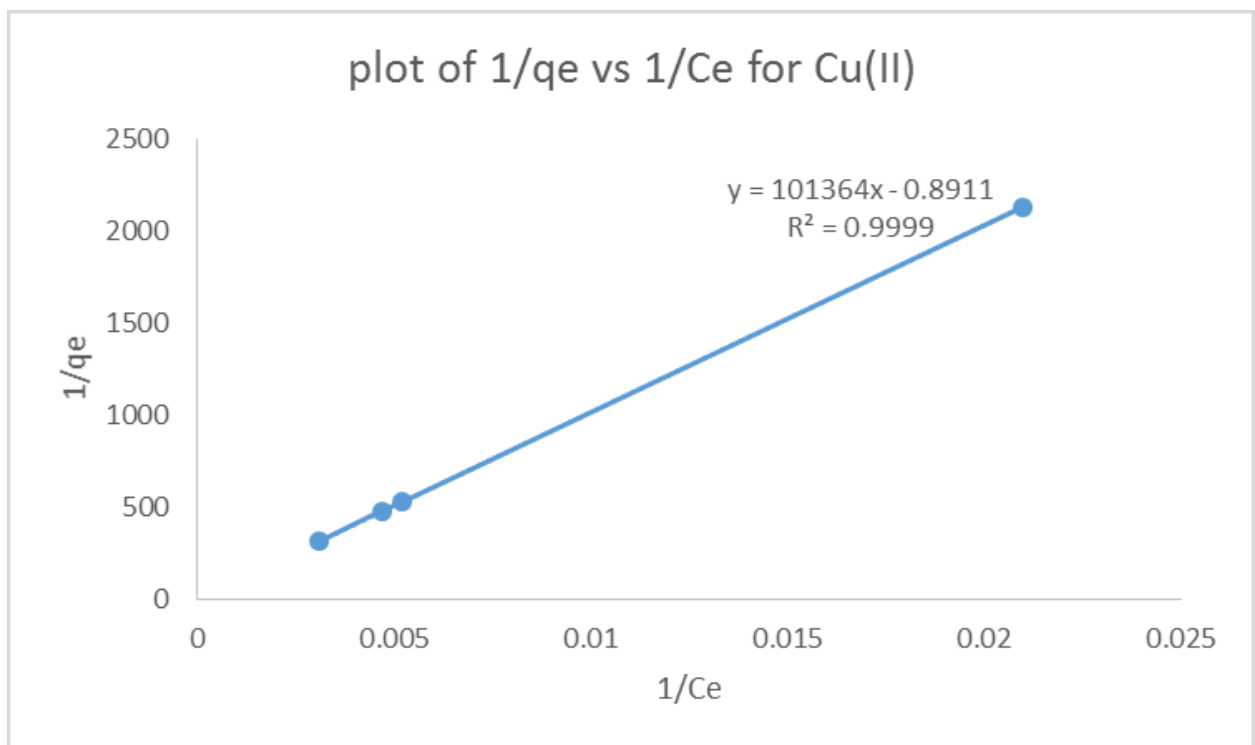


Figure 3.18: Langmuir model curve  $\frac{1}{C_e}$  vs  $\frac{1}{q_e}$  for the adsorption of Cu(II)

The correlation co-efficient,  $R^2 = 1$  in Figure 3.18 confirm the fact that the adsorption of Cu(II) ions was monolayer with homogeneous adsorbent and best fit on Langmuir model.

The Langmuir equation for Cu(II) is  $\frac{1}{q_e} = 4 + 10204082C_e$

### Freundlich isotherm for Cu(II)

Table 3.10: Freundlich isotherm values for the adsorption Cu(II)

Initial Conc. (ppm)	Log $C_e$	Log $q_e$
400	1.67	-3.33
600	2.28	-2.72
800	2.33	-2.68
1000	2.50	-2.49

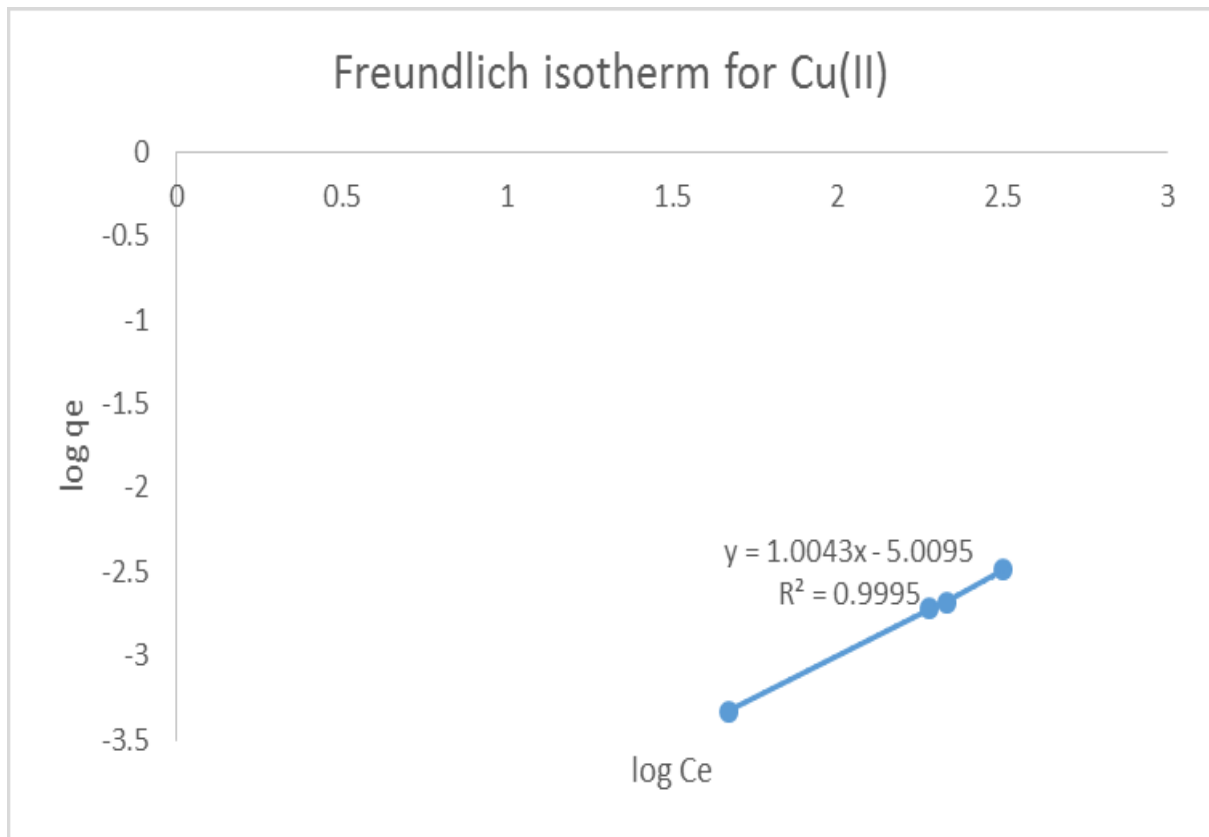


Figure 3.19: Freundlich isotherm curve for the adsorption of Cu(II)

The Freundlich isotherm curve in Figure 3.19 has produced a very high value of correlation co-efficient ( $R^2 = 0.999$ ), which indicates that although the adsorption of Cu(II) ions by activated carbon from *Zea mays* stem was well defined by Langmuir model according the small value of  $K_f$  obtained below, correlation co-efficient values obtained show best fitting for both models.

Therefore the Freundlich equation for Cu(II) is  $q_e = 0.158 C e^{0.8}$

Where  $K_f = 0.158$  and  $1/n = 0.8$  indicates a very minimal adsorption with heterogeneous material.

Table 3.11: Langmuir isotherm values for the adsorption of Cr(III)

Initial Conc. (ppm)	Mass of adsorbent (g)	Volume of solution (mL)	Final Conc. Ce(mg/L)	Mass of adsorbate adsorbed, qe(mg/g)	x/m or qe
400	2	20	271.13	1.29	0.0013
600	2	20	515.21	0.85	0.00085
800	2	20	374.62	4.25	0.0043
1000	2	20	622.11	3.78	0.0038

The values in Table 3.11 were applied to plot the Langmuir isotherm for the adsorption of Cr(III) on Figure 3.20.

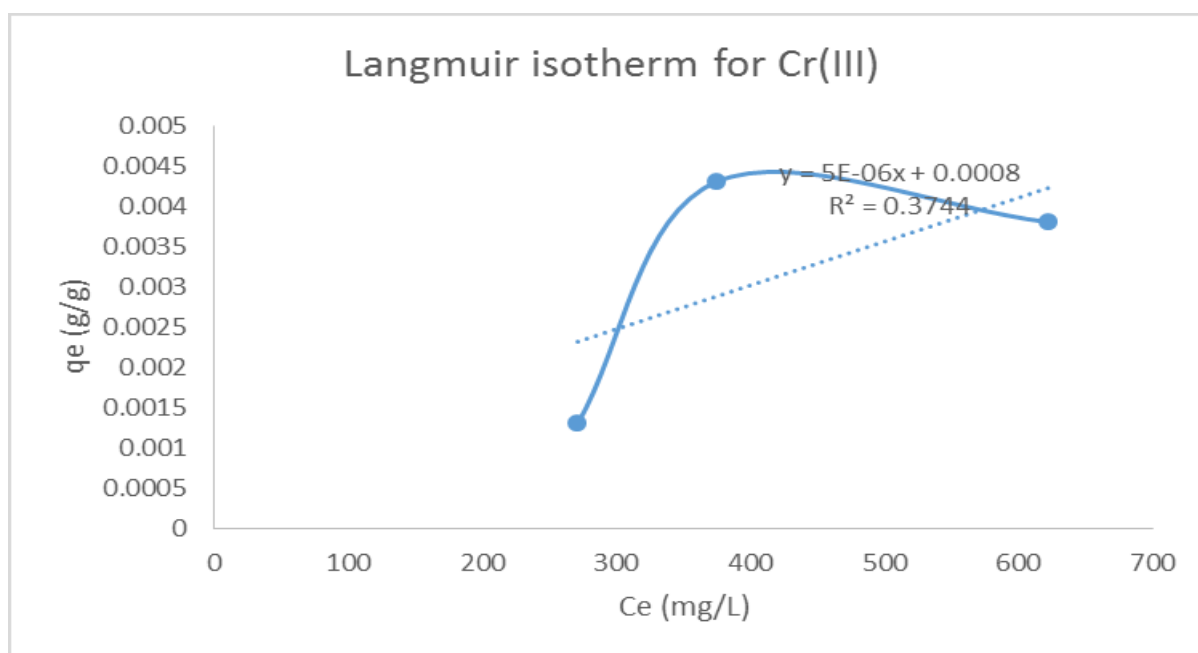


Figure 3.20: Langmuir isotherm curve for the adsorption of Cr(III)

Table 3.12: Langmuir model values to plot  $\frac{1}{C_e}$  vs  $\frac{1}{q_e}$  for adsorption Cr(III)

Initial Conc. (ppm)	$\frac{1}{C_e}$	$\frac{1}{q_e}$
400	0.0037	769.23
600	0.0019	1176.47
800	0.0027	232.56
1000	0.0016	263.16

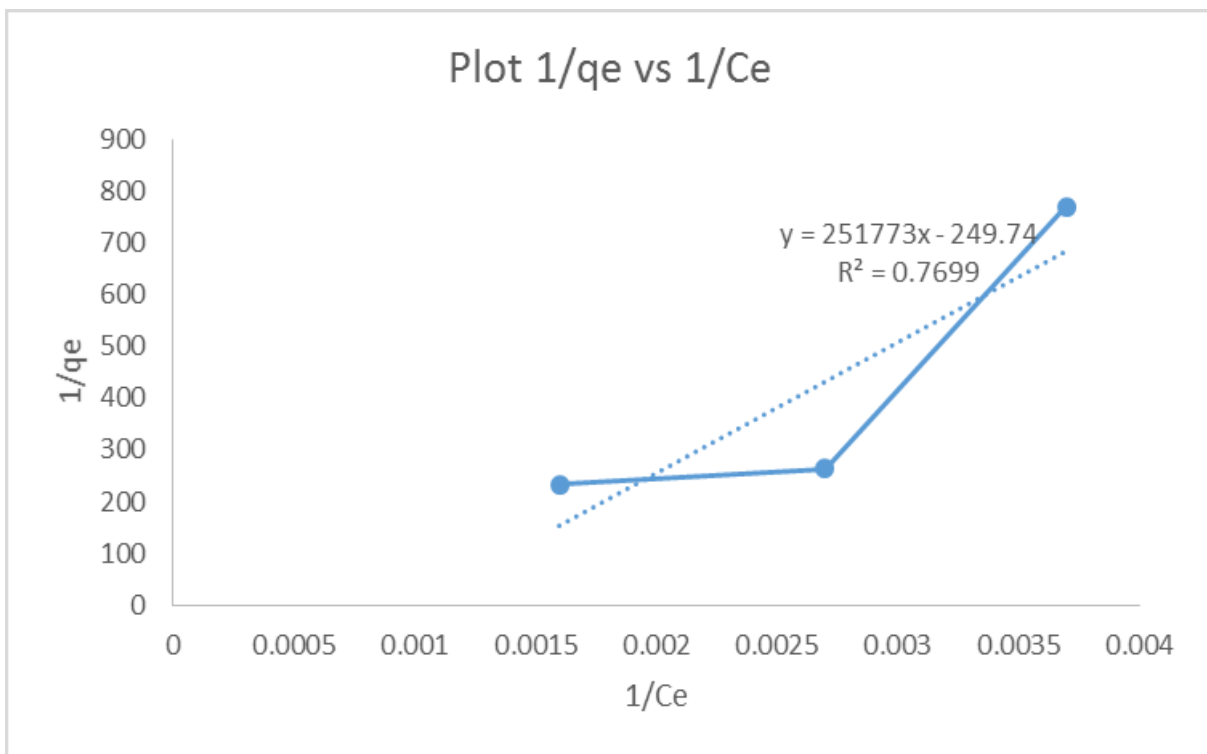


Figure 3.21: Langmuir model curve for  $\frac{1}{C_e}$  vs  $\frac{1}{q_e}$  on the adsorption Cr(III)

Therefore the Langmuir equation for Cr(III) is  $\frac{1}{q_e} = 4 + 526315.79 C_e$

Table 3.13: Freundlich isotherm values for the adsorption of Cr(III)

Initial Conc. (ppm)	Log Ce	Log qe
400	2.43	-2.89
600	2.71	-3.07
800	2.57	-2.37
1000	2.79	-2.42

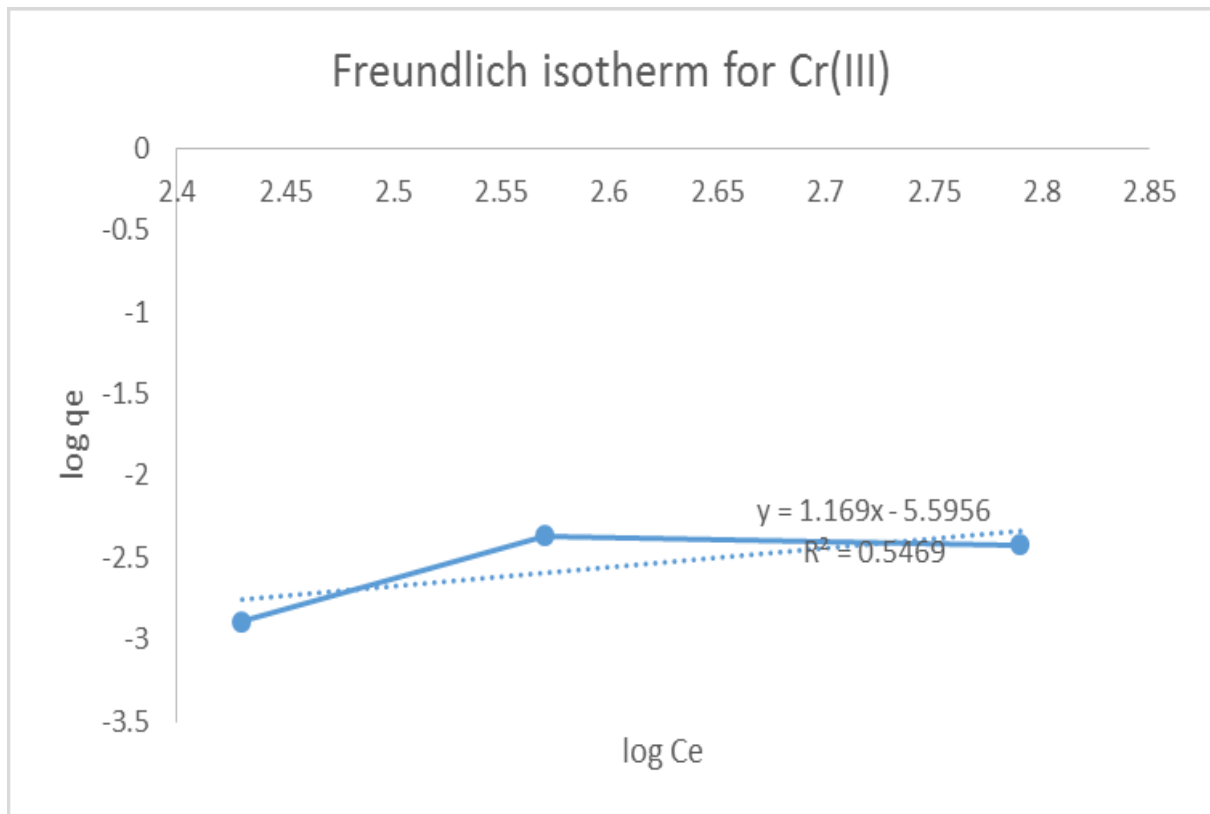


Figure 3.22: Freundlich isotherm curve for the adsorption of Cr(III)

Therefore the Freundlich equation for Cr(III) is  $q_e = 1.9 \times 10^{-4} C_e^{3.7}$ .



The correlation coefficient value obtained in Figures 3.20 is small and it clearly indicates that the adsorption of Cr(III) was unfavorable for monolayer adsorption. Figure 3.21 and 3.22 shows slightly better correlation coefficient values, which points out that activated carbon prepared from *Zea mays* stem was homogeneous material and was not good enough to remediate Cr(III). Pirajan and Giraldo [19] also reported similar correlation coefficient for Freundlich model of Cr(III) cations [19].

Table 3.14: Langmuir and Freundlich isotherm experimental constants for the adsorption Pb(II), Cu(II), and Cr(III) by activated carbon

Adsorption of metal ions	Langmuir isotherm			Freundlich isotherm constants		
	$q_{max}$	B	$R^2$	N	$K_f$	$R^2$
Adsorption of Pb(II)	0.2	0.3	0.9305	0.23	$4.7 \times 10^{-5}$	0.1185
Adsorption of Cu(II)	0.25	$3.9 \times 10^{-5}$	0.9999	1.25	0.158	0.9995
Adsorption of Cr(III)	0.25		0.3744	0.27	$1.9 \times 10^{-4}$	0.5469

### 3.6 Characterization of the activated carbon after adsorption

#### 3.6.1 Characterization of activated carbon after adsorption

Characterization of activated carbon after adsorption was performed using characterization instruments and physicochemical properties. The FTIR spectra after adsorption of the four metal ions namely Pb(II), Cu(II), Cr(III), and Hg(II) is shown in Figure 3.23 below.

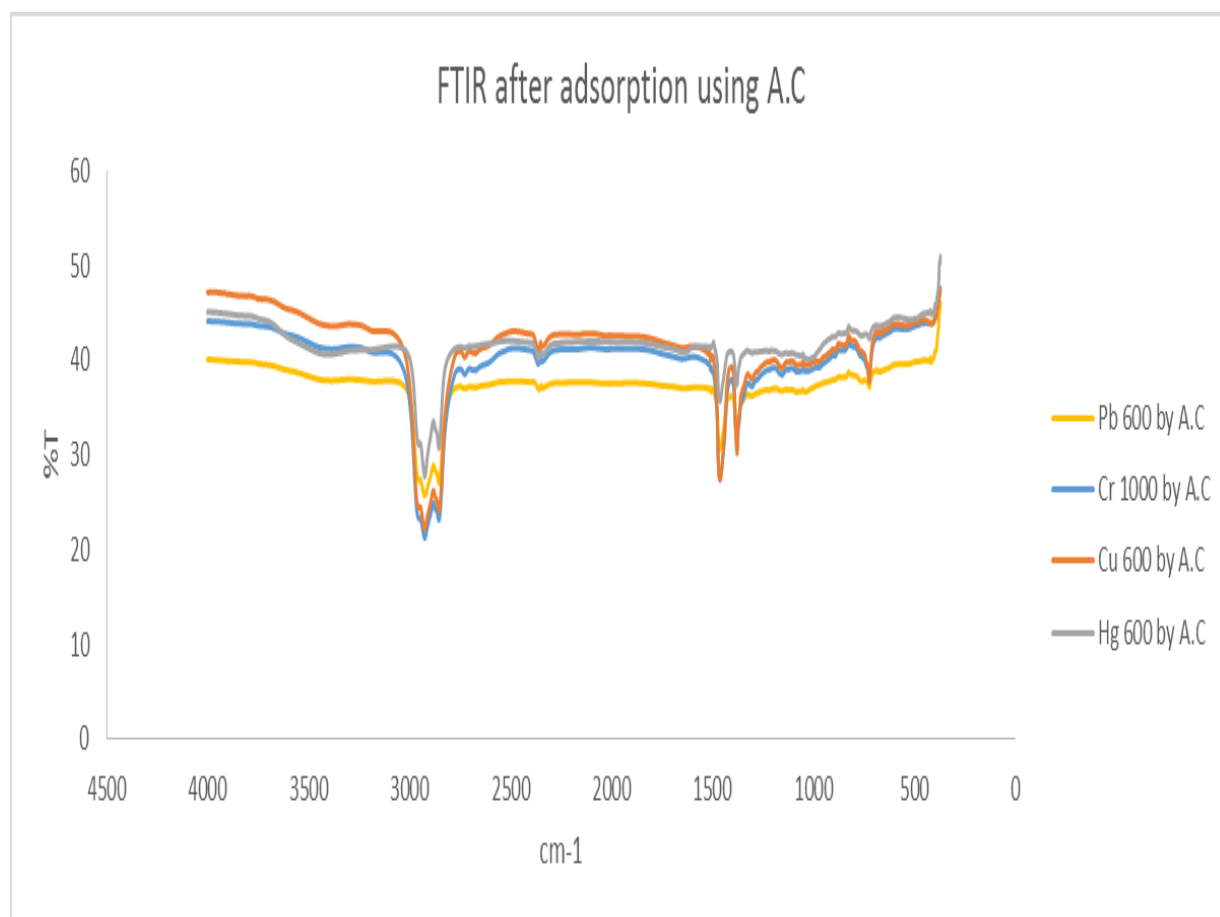


Figure 3.23: FTIR spectra after adsorption using activated carbon as adsorbent.

The IR spectra in Figure 3.23 shows a number of vibration peaks being shifted from original regions before adsorption, that is, the notable vibration bands are now located differently as before adsorption. The spectral shifting of these vibration peaks was a direct evidence that adsorption of metal ions has occurred on the surface of the adsorbent and that new bonds has

been formed between the functional groups and the adsorbate adsorbed on the surfaces of the adsorbents [29]. All the functional groups initially observed from the IR spectra of the activated carbons have completely changed or shifted by the interactions between metal ions and the functional groups. For example, on the IR spectra of the activated carbons in Figure 3.23, there were three important peaks: A strong stretching vibration at  $3467.76\text{ cm}^{-1}$  for O-H due to inter and intramolecular hydrogen bonding in alcohols, phenols, and acids group, another peak was also observed at  $1637.5\text{ cm}^{-1}$  for C=C, and the other one at  $1041.90 - 1248.14\text{ cm}^{-1}$  for C-O-C groups. After interaction and adsorption almost four new vibrational peaks were observed. The vibration peaks around  $2876.87 - 2945.90\text{ cm}^{-1}$  which can be attributed to symmetric and asymmetric C-H stretching vibration of aliphatic acids, new bond formation between the metal ion and adsorbent sites. The other vibration peaks around  $1350.65 - 1480.76\text{ cm}^{-1}$ . Similar observation of peak shifting have been reported [30].

Scanning Electron Microscopy (SEM) images after adsorption were also taken in order to examine the interactions of the adsorbate on the adsorbent sites. The different SEM images are shown from Figures 3.24 to 3.26.

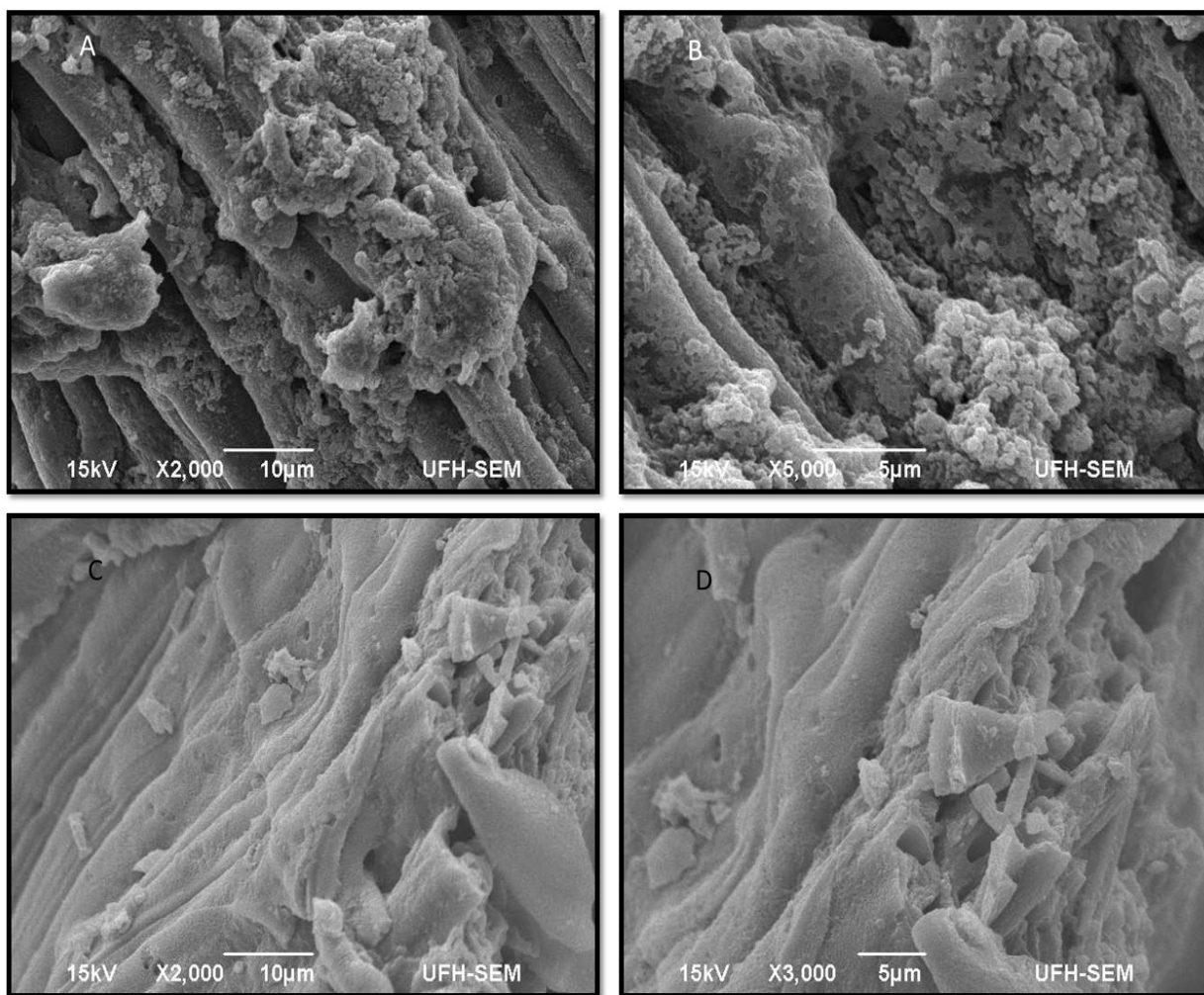


Figure 3.24: SEM images for activated carbon obtained after adsorption of Pb(II) and Cu(II)

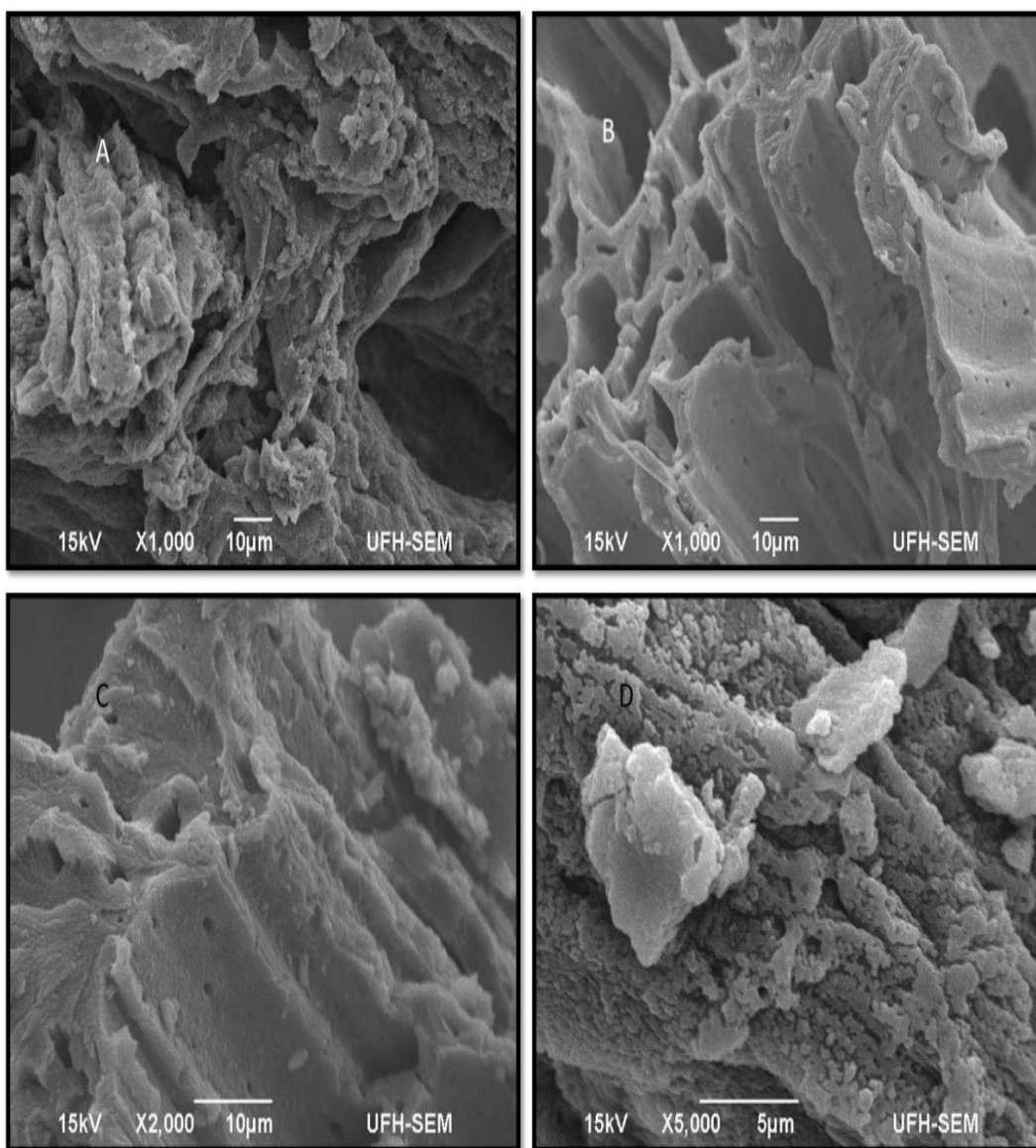


Figure 3.25: SEM images for activated carbon obtained after adsorption of Hg(II) and Cr(III)

Figures 3.24 and 3.25 shows the SEM images of activated carbon obtained after adsorption of Pb(II), Cu(II) and Hg(II), Cr(III) ions. These SEM images indicate some white irregular flakes or particles on the surface of the adsorbent. Some irregular flaky attachments on the surface of the adsorbent signify the adsorbate adsorbed by the adsorbent. Comparing the SEM images of the activated carbon before and after adsorption, it can be observed that there are morphological changes after adsorption. Pores and voids that were seen before adsorption

are occupied/filled with precipitates and complexes formed by metal ions with proton acceptors or binding site functional groups [14].

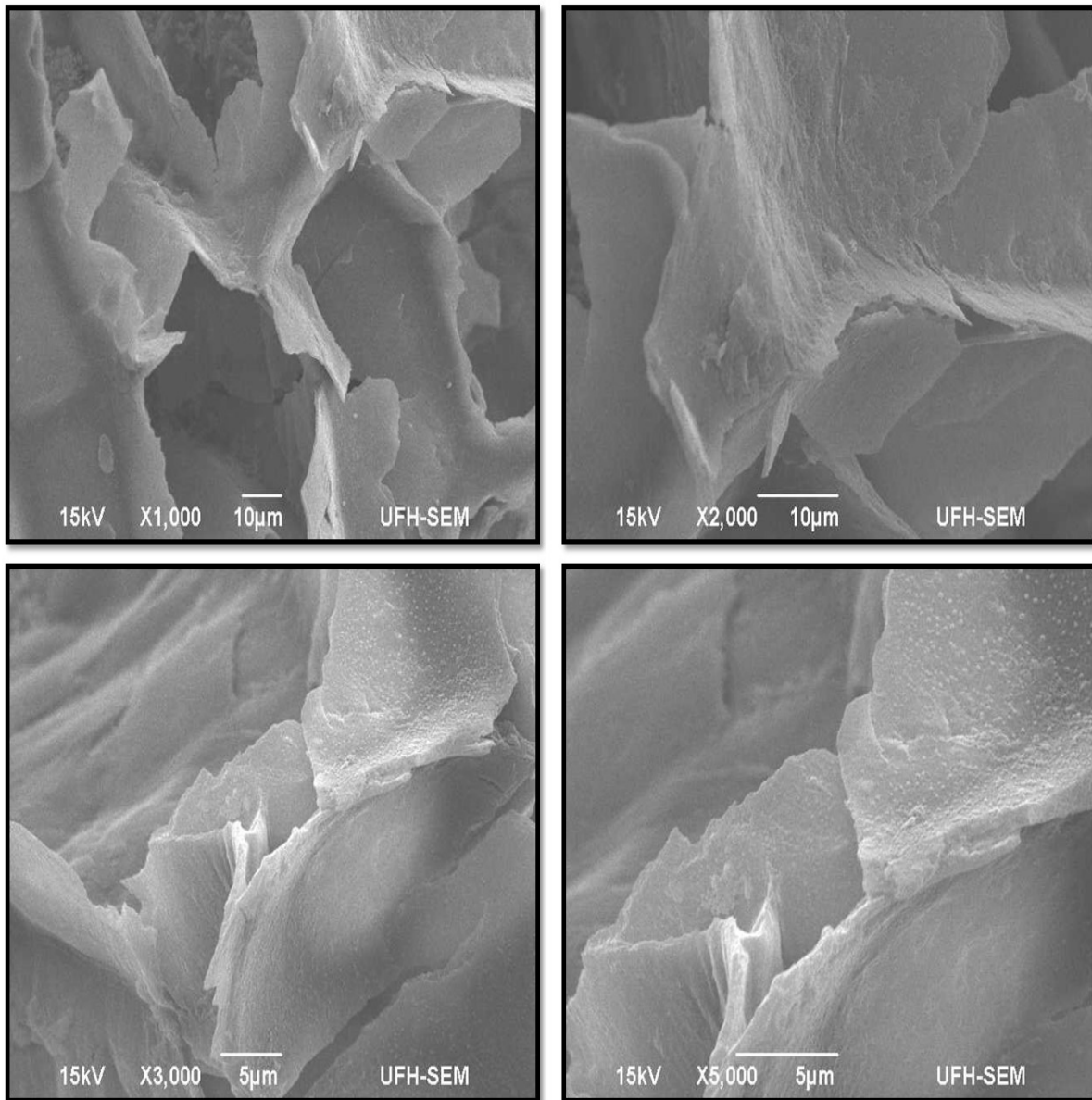


Figure 3.26: SEM images of *Zea mays* stem obtained after biosorption of Pb(II)

The biosorption of Pb(II) using *Zea mays* stem is not that much pronounced as compared to that of its activated carbon. Figure 3.26 above shows the SEM images of *Zea mays* stem after biosorption of Pb(II) and it can be seen from the images that biosorption of the metal ion by *Zea mays* stem is less efficient. This fully agrees with the conclusion in the literature that the

activated carbon is far better than its precursor in terms of remediating metal ions from wastewater.

Energy dispersive X-ray spectroscopy (EDS) results below revealed the composition of the adsorbent after adsorption. These results shows the elements which are essential in adsorption and those commonly found in plant cells such C, O, S, K, P, and Na. Kibomi *et al.* [21] also confirmed the presence of such elements from activated carbon prepared by phosphoric acid activation [31]. Activated carbon prepared from agricultural biomass are normally rich in carbon (C) and potassium (K) [31]. These elements are very important in evaluating the mechanisms of adsorption. In this study, elements such as K, Na, Ca are believed to be the ones which were involved in exchanging sites with metal cations Pb(II), Cu(II), Cr(III) during chemo sorption and acted as active sites of metal ions. On the other hand the other elements C, O, S, and P detected in the EDS spectrum are believed to be part of hydroxyl, carbonyl and other proton acceptor group such as  $-\text{SO}_3\text{H}$  which were also responsible for binding the positively charged metal cations during chemo sorption.

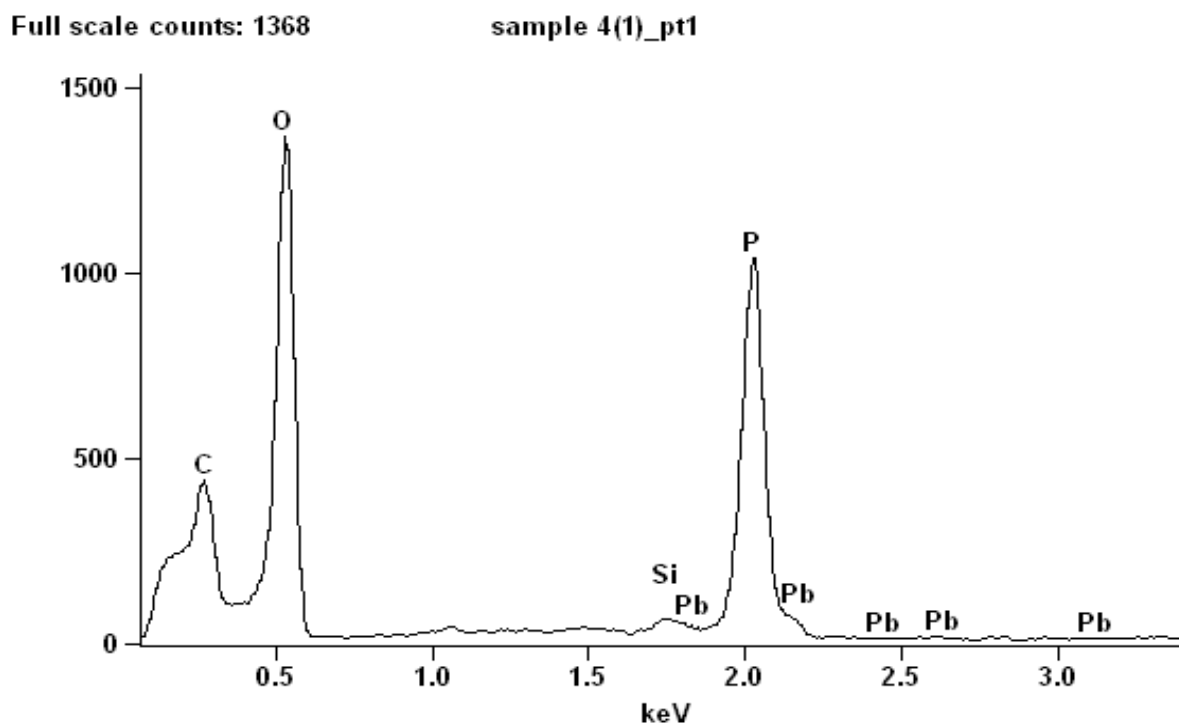


Figure 3.27: EDS results for the adsorption of Pb(II) by activated carbon.

The Pb peak in the EDS spectrum fully agreed with the results obtained from the SEM that the activated carbon prepared from *Zea mays* stem acted as adsorbent to remove the Pb(II) ions from aqueous solution.



Full scale counts: 1057

sample 5(1)\_pt1

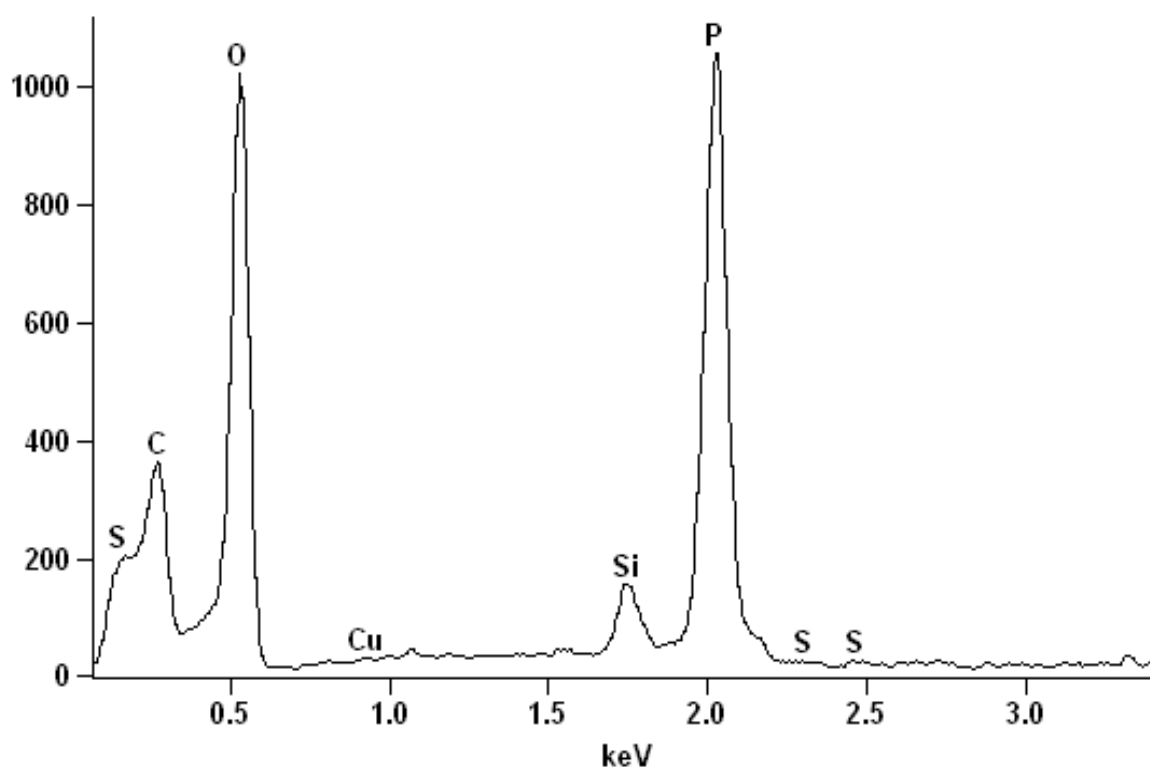


Figure 3.28: EDS spectrum for activated carbon after adsorption of Cu(II).

Figure 3.29 above shows that although the adsorption of Cu(II) was little, but activated carbon has adsorbed some Cu(II) ions and this is in agreement with the results from the FTIR and SEM conducted in this study.

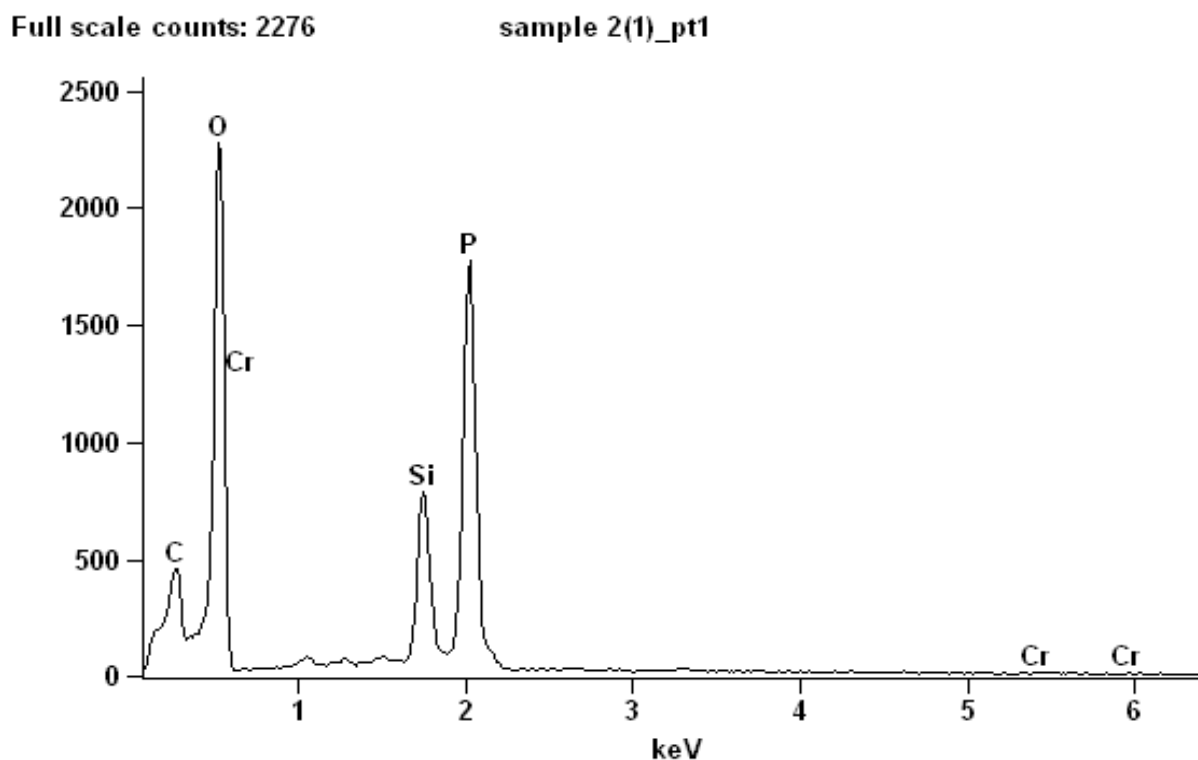


Figure 3.29: EDS spectrum after adsorption of Cr(III) by chemical activated carbon.

The presence of chromium in the EDS spectrum provided the evidence that activated carbon can adsorb such metal ion from wastewater and this is in agreement with the results on literature [19].

Full scale counts: 1407

sample 1(1)\_pt1

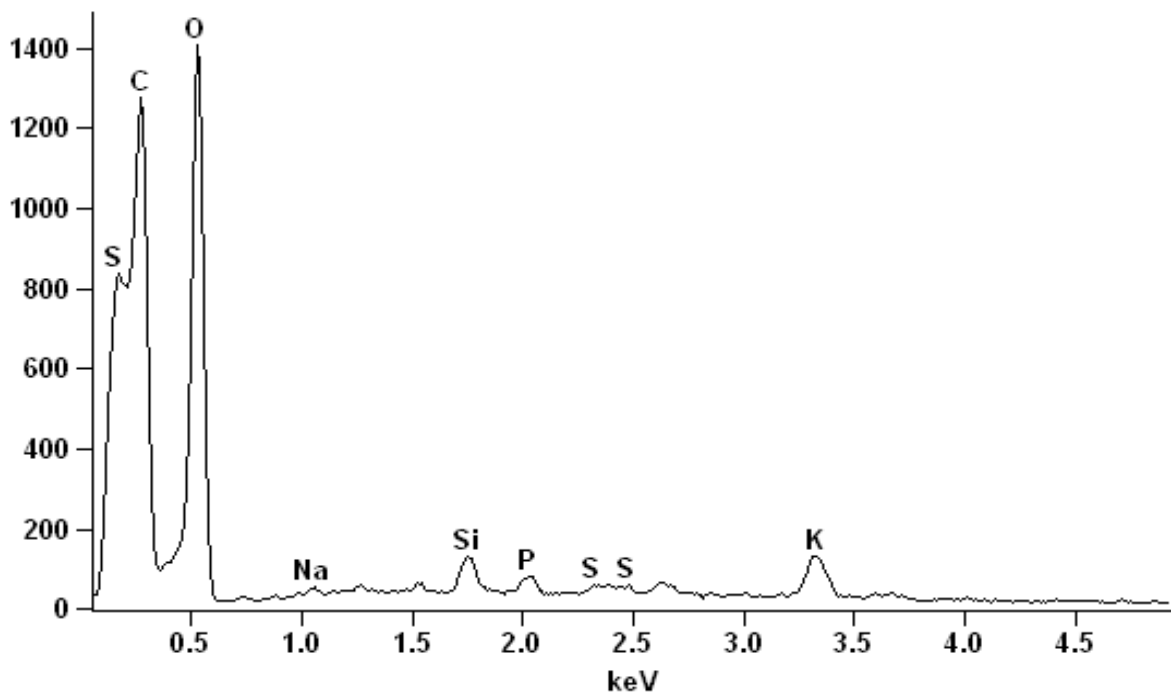


Figure 3.30: EDS spectrum of the activated carbon after adsorption of Hg(II) by chemical activated carbon.

Results obtained from the EDS in Figure 3.30 present the elements that are commonly found in plant cells such P, S, C, O, Na, and Si. No adsorption of Hg can be observed. This is in agreement with the observation that has been already described that activated carbon from *Zea mays* stem is not a good or potential adsorbent to adsorb mercury from aqueous solution. Figure 3.31 shows the EDS spectrum of the *Zea mays* stem after the adsorption of Pb(II) from aqueous solution using. When compared with the results obtained from the activated carbon, there is a very slightly adsorption of Pb(II) ions when using *Zea mays* stem as adsorbent than when using activated carbon. The adsorption advantage of activated carbon over its precursor (*Zea mays* stem) can be attributed to the fact that activated carbon possess high carbon porosity and surface area. Keane [23] and Ozdemir *et al.* [24] also evaluated the performance of activated carbon for pharmaceutical adsorption and in the EDS spectrum of the activated

carbon, they also observed the presence of elements such as S, O, C, Zr, and Ti[23 -24]. The amount of metal ions attached on the surface of the activated carbon as presented by the SEM images taken in this study, the presence of Pb(II), Cu(II), and Cr(III) ions in the activated carbon EDS spectra studied, and the vibrational peaks shifting observed in the IR spectra of the activated carbon after adsorption provide a full evidence that activated carbon material is far better than its precursor in terms of adsorbing metal ions from aqueous solution.

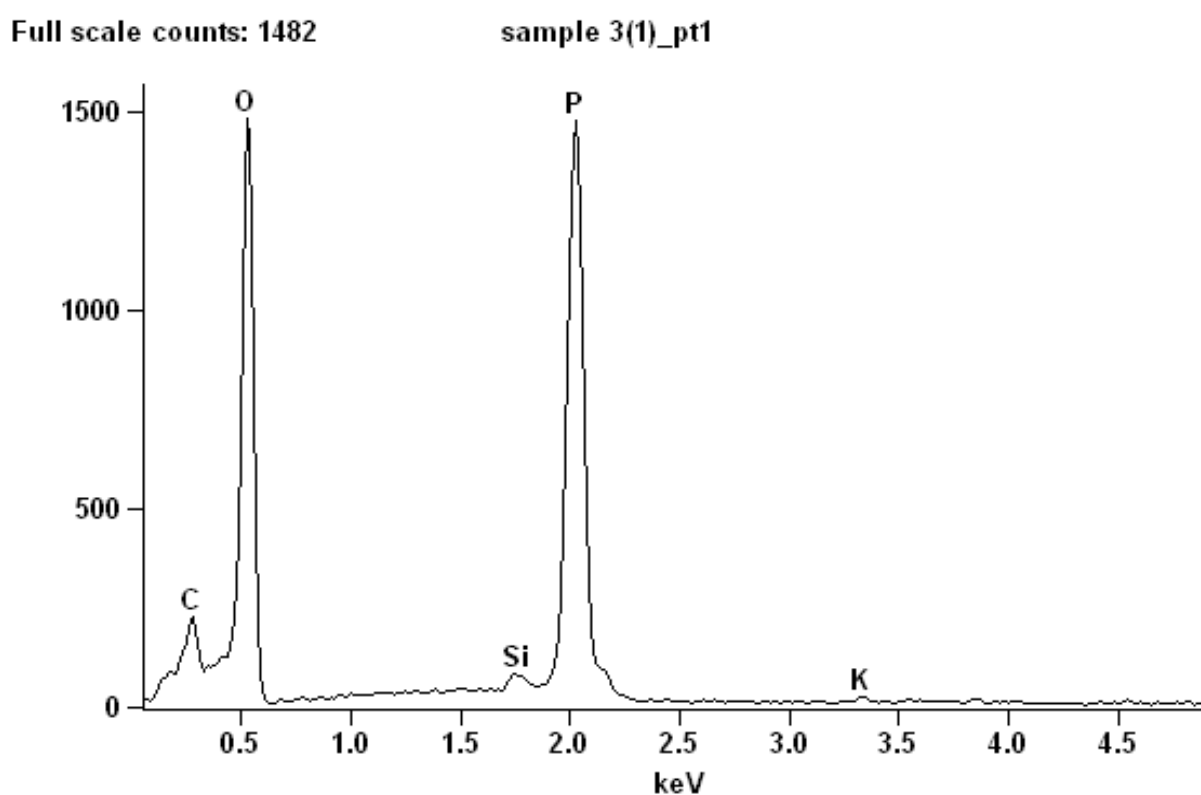


Figure 3.31: EDS results after biosorption of Pb(II) using *Zea mays* stem

The SEM and EDS results were consistent with the IR results and the texture and mineralogy of the adsorbent was determined using various number of techniques such as SEM, EDS, IR, and XRD.

X-ray powder Diffraction (XRD) patterns of the raw *Zea mays* stem and prepared activated carbon are shown Figure 3.32(a) The XRD patterns for *Zea mays* stem exhibit sharp peaks at  $2\theta = 23.5^\circ$  which can be assigned to the crystalline portion of the cellulose and  $2\theta = 16.2^\circ$  assigned to amorphous part of hemicellulose in the plant material. Similar sharp peaks at  $2\theta = 22.5^\circ$  and  $2\theta = 18.7^\circ$  which are mostly found in cellulosic materials were reported in literature [16, 19]. Figure 3.32(a) also shows the XRD patterns of the activated carbon after adsorption of metal ions from aqueous solution, with a very broad peak at  $2\theta = 12.6^\circ$ . Figure 3.32(b) shows the XRD pattern for prepared activated carbon before the adsorption of metal ions. As it was expected, the XRD patterns shows no peaks for the formation of carbonaceous crystalline material at  $2\theta = 24 - 26^\circ$  and  $2\theta = 42 - 45^\circ$ , although the sample was placed in the XRD crystallography for almost three days. The absence of these important peaks can be attributed to the presence of ion-exchangeable metals and elements such as C, K, Mg, Ca, S, P, O, and Cl which might affect the graphite crystalline peaks of the carbon materials.

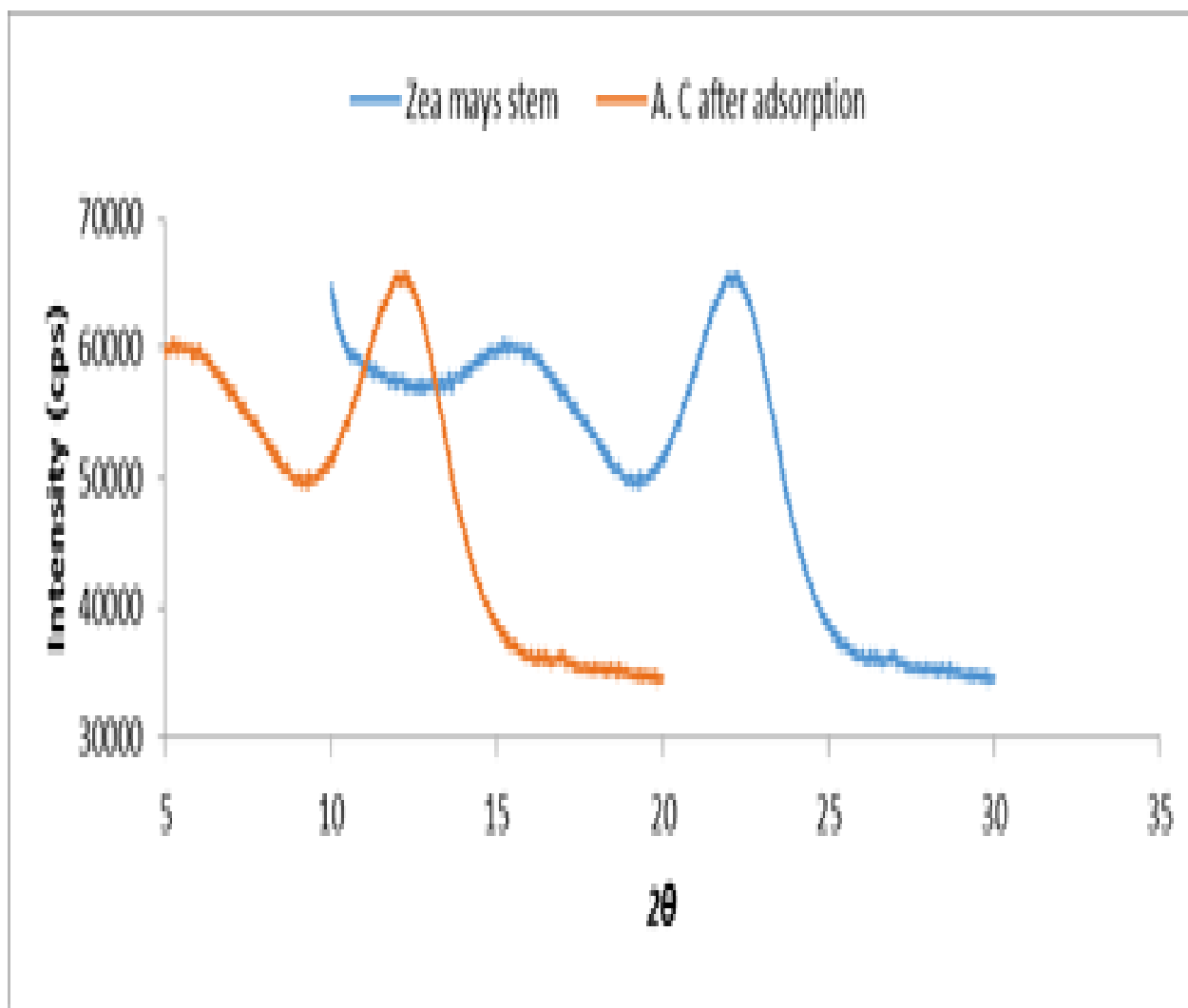


Figure 3.32(a): XRD patterns of the *Zea mays* stem and activated carbon after adsorption

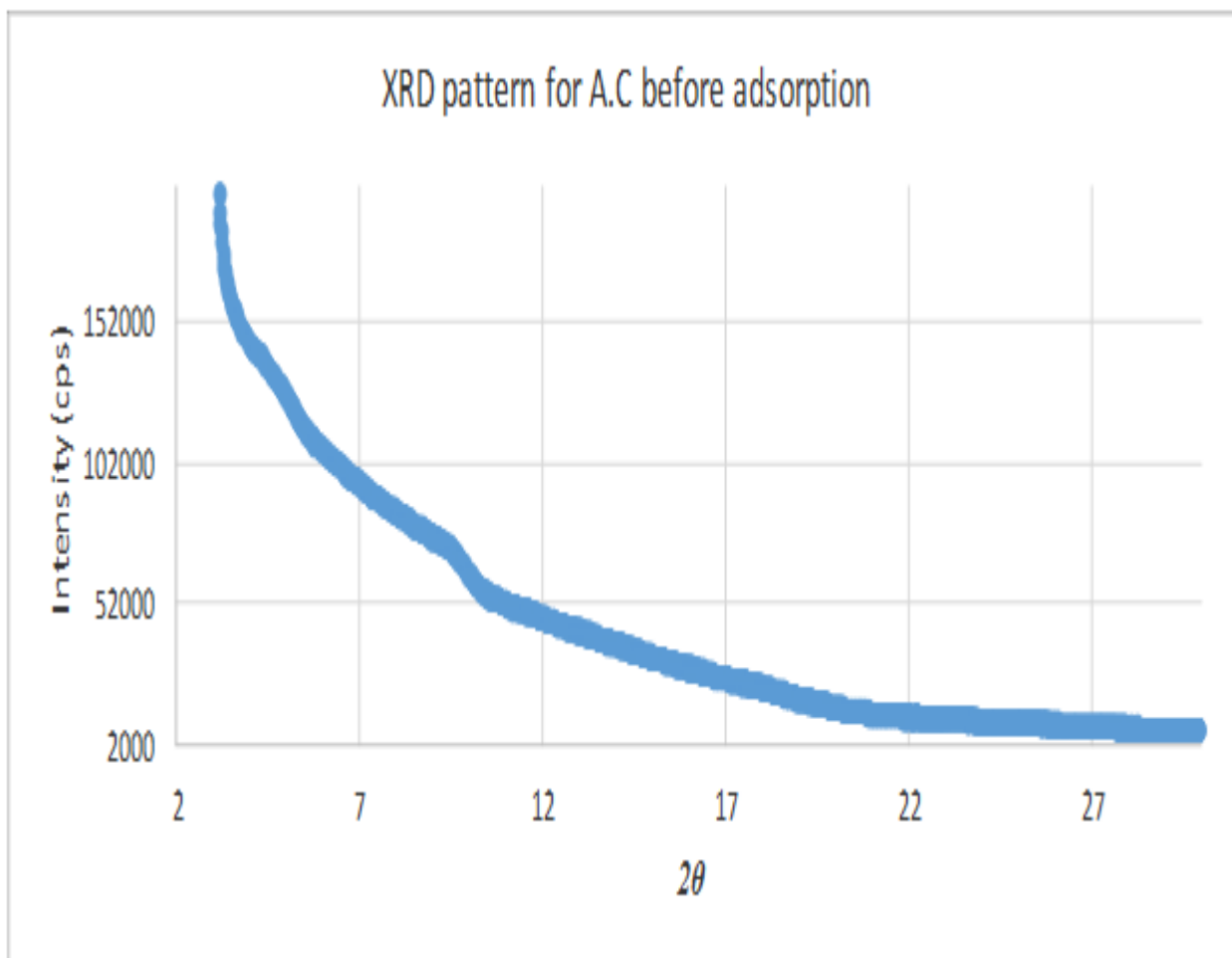


Figure 3.32(b): XRD pattern of the activated carbon before adsorption

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## CHAPTER FOUR

### 4. SUMMARY, CONCLUSION AND RECOMMENDATIONS FOR FURTHER STUDIES

#### 4.1 Summary of results

This work investigated the use of *Zea mays* stem and its activated carbon prepared through chemical activation in adsorbing metal ions from aqueous solution. The adsorption abilities of both adsorbents were carefully studied and compared. Four different activated carbons were prepared from *Zea mays* stem using NaOH, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, and KOH. The maximum removal percentages that were obtained for all the three metal ions at pH 5-6 were 97.44% for Pb(II), 98.37% for Cu(II), 89.37% for Cr(III) and there was no adsorption for mercury ions. Pb(II) and Cr(III) also showed a well-defined adsorption even at low pH, with 98.13 % and 69.92 % adsorption respectively. From the results obtained, it is evident that activated carbon prepared from *Zea mays* stem using sulphuric acid via chemical activation method is a good adsorbent for removal of Pb(II), Cu(II), and Cr(III) from aqueous solution.

Results obtained from adsorption experiments indicated that activated carbon from *Zea mays* stem is not good enough for the removal of Hg(II) and it was clear that the adsorption of Pb(II), Cu(II), Cr(III) ions is pH, contact time, and concentration dependent. The optimal conditions for all metal ions removal were pH = 5-6, 2 hours of contact time, 2 g of adsorbent, 110 rpm, and initial concentration of 200 ppm. Although Pb(II) and Cr(III) reached equilibrium adsorptions at 30 minutes and 60 minutes of contact time, when compared with the untreated *Zea mays* material, the activated carbon have high surface area and pore volumes with better adsorption capacity. The metal ions adsorption trend was in this order: Pb(II)>Cu(II)>Cr(III)>>Hg(II) and the adsorptive abilities of the activated carbons

prepared from sulphuric acid and potassium hydroxide were significantly higher. This is confirmed by the results obtained from the iodine number and adsorption percentages calculated from the experiments.

The pH of the solution still remains the most contributing factor on the adsorption of metal ions. It is believed that at low pH levels, the rivalry between hydrogen proton ( $H^+$ ) in the solution and the dissolved metal ions for proton acceptor or ligands such as carbonyl, hydroxyl, aromatics, and carboxyl on the surface of the activated carbon turn out to be the most significant factor and it hinders the removal on metal ions. Two mechanisms were proposed for the adsorption of metal ions in this study viz. (i) The *metal ion-adsorbent complex model* due to the chemical interactions between the surface ligands mentioned above and metal cations dissolved. (ii) The *metal ion – ion-exchange adsorbent complex model* which is due to the presence of ion-exchangeable elements (Ca, Mg, K, Na, C, and S) on the surface of some activated carbon. The presence of these elements was confirmed from the EDS spectrum. Electrostatic forces and Van der Waals forces are also believed to be the driving forces for the latter mechanisms in this research as the ionic compound were intermingling with oppositely charged adsorbent surface (dipole interaction). The Langmuir model fitted well in most of the cases with  $R^2 > 0.99$ . Consequently, the adsorption of Pb(II) and Cu(II) followed Langmuir isotherm model and that of Cr(III) was best defined by Freundlich isotherm model.

## 4.2 Conclusion

The adsorptive abilities of *Zea mays* stem and its activated carbon were investigated in this study. It was observed that different activated carbons adsorbed metal ions at various optimal conditions. Pb(II), Cr(III), and Cu(II) were easily adsorbed by the activated carbon and showed good adsorption capacity. The adsorption of Pb(II), Cr(III), and Cu(II) by raw *Zea mays* stem was significantly less than that of activated carbon. It is therefore concluded that adsorption of metal ions by chemically prepared activated carbon is far better than that of its precursor. Possible adsorption sites were investigated and found to be in two categories: Ligands such as  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{S}^{2-}$  that were found in the activated carbons surface area and ion-exchangeable elements K, Na, Ca which are believed to be exchangeable sites for metal ions. Langmuir and Freundlich models both defined the adsorption of the three metal ions, where Langmuir model fitted well for adsorption of both the Pb(II) and Cu(II) ions, than Freundlich for Cr(III) ion.

## 4.3 Recommendations for further studies

Although much work has already been done on the processes and mechanisms involved in the removal of metal ions using biomaterials and modified agricultural by-products, but there is still a need for the understanding of the following aspects of the adsorption processes using these materials.

- ❖ The effect of the chemical activation method and activating agent on the adsorptive performance of the prepared activated carbon, particularly from *Zea mays* stem.
- ❖ Thorough investigation on the linearity of the pseudo-first-order and pseudo-second-order models on the adsorption process of each metal ion.

- ❖ Extensive investigation of the kinetic isotherms for the adsorption of each metal ion by activated carbon.
- ❖ Since diffusion is one of the most important principle involved in the adsorption process, there is a need to understand which of the three phases of diffusion drive the mechanism of adsorption.