

JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
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DEPARTMENT OF CHEMISTRY



A RESEARCH PAPER ON

DETERMINATION OF THE LEVEL OF COPPER AND CADMIUM IN
DRINKING WATER SAMPLES FROM JIMMA TOWN AND THEIR
REMOVAL USING ACTIVATED CARBON PREPARED FROM
PUMPKIN SEED SHELLS

October, 2014
Jimma, Ethiopia

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PUMPKIN SEED SHELLS**

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Abbreviations and Acronyms

AAS	Atomic Absorption Spectroscopy
AC	Activated Carbon
ASTM	American Society for Testing and Materials
PSS-AC	Pumpkin Seed Shell Activated Carbon
FT-IR	Fourier Transforms Infrared
MPL	Maximum Permissible Limit
MC	Moisture Content
SEM	Scanning Electron Microscope
EDX	Energy Dispersion X-ray
WHO	World Health Organization of the United Nations
EPA	The Federal Environmental Protection Authority of Ethiopia
ΔG°	Standard Gibbs free energy change
ΔH°	Standard Enthalpy change
ΔS°	Standard Entropy change

Abstract

This study was designed for the determination of the level and the removal methods of heavy metal contaminants in drinking water samples from Jimma town, South Western Ethiopia using chemically activated carbon prepared from pumpkin seed shells (*Telfairia occidentalis*) by H_3PO_4 . The activation was done by heating the mixture in an electrical furnace at 800°C for 3 hrs. Three type of drinking water samples (raw, treated and distribution) had been collected from six different sites having a total of about twenty one samples and they were analyzed using Atomic Absorption Spectrophotometer (AAS). Two heavy metals, copper and cadmium had been studied and their concentration in some of the water samples was found to be (0.3 mg/L for Cu (II) and 0.0072 mg/L for Cd (II)) which is above the maximum permissible levels (MPL) in World Health Organization of the United Nations (WHO) data that was 0.2 mg/L and 0.005 mg/L for copper and cadmium respectively. Adsorption experiments were carried out as a function of pH, contact time, initial Cu (II) and Cd (II) ion concentrations, adsorbent dosage and temperature of the solution for the removal of the ions. The equilibrium data better fitted to the Langmuir isotherm model for studying the adsorption behavior of the ions with correlation coefficient (R^2) of > 0.999 . Kinetic studies of the data showed that the adsorption follows the pseudo-second order kinetic model. Thermodynamic parameters such as Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were also calculated for the uptake of Cu (II) and Cd (II) ions. This parameter showed that adsorption on the surface of activated carbon prepared pumpkin seed shells was non spontaneous and feasible; and endothermic between temperatures of 25°C and 45°C .

Keywords: heavy metals, drinking water, activated carbon, pumpkin seed shells.

1. INTRODUCTION

Water is one of the most essential resources for all living systems, industrial processes, agricultural production and domestic uses on the earth. It is the most frequently and easily analyzed environmental compartment, because unlike air or soil, it already exists in liquid phase. It comes from different sources which include ground water such as aquifers, surface water such as rivers, streams and glaciers; and other sources including rain, hail and snow, biological sources such as plants and sea through desalination. In its pure form, water is colorless, odorless and tasteless; and should also be free from hazardous compounds¹.

Water could be exposed to different contaminants on its sources as or its way of journey with elements created by human activities, effluents from chemical industries, human and animal waste, dissolved gases, etc. The acid rain is another natural major water contaminant. In addition, water contains some amount of mineral constituents such as iron (Fe), magnesium (Mg), lithium (Li), zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni), cobalt (Co), vanadium (V), arsenic (As), molybdenum (Mo), selenium (Se), lead (Pb) and so many other elements².

Heavy metals in nature are not hazardous to the environment and human health if their amounts are not substantial; furthermore some heavy metals are required at lower concentrations as catalysts for enzyme activities in human body. Some of these metals are vital to keep up life such as calcium, magnesium, potassium and sodium, which are necessary for common body functions and others including cobalt, copper, Iron, manganese, molybdenum and zinc are needed at low levels as catalysts for enzyme activities³⁻⁵. However, if their level is elevated to higher than the permissible ranges, their way cause malfunction and result in toxicity to human body.

The use of water increases with growing population, putting increasing strain on the water resources: oceans, lakes, surface and underground water sources. An adequate supply of high quality drinking water is one of the major prerequisites for healthy human life and that of acceptable quality is essential for agricultural, domestic and commercial uses. However, all these activities are also responsible for further pollution of the water sources⁶. Although water availability is not a problem on a global scale, there might be a problem of finding an adequate supply of fresh water that meets the ever increasing needs; and maintaining its quality is becoming a problem in the required quantity⁷.

Water pollution is a worldwide environmental problem and mostly caused by industrial, agricultural (commonly soil erosion, large-scale use of insecticides, pesticides and other agrochemicals), domestic waste from urban and rural areas, radioactive and chemical wastes. The pollutants could be adsorbed using the soil and then to rivers, lakes, etc. has caused a serious problem to human health such as accumulative poisoning, cancer, brain damage, etc. when they exceed the acceptable limits⁸. Water pollution due to chemical pollutants is one of the most important environmental problems that have frequently causes waterborne diseases and have posed a great threat to the safety of water supplies in developing countries. Patel, K.C. and his ∞ workers reported that about 80 percepts of the diseases in the world are created because of poor quality of drinking water⁹.

The natural concentration of metals in raw water which has not been treated or purified varies from state to state, country to country depending on many factors such as geological structures, the soil, the acidity of the water and the particulate matter. Most metal species in natural fresh water occur in organic compounds, organic complexes or colloids¹⁰. From the point of view of health, metal could be divided into two categories:

- i. Metals with undesirable effect such as iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), cobalt (Co), barium (Ba), silver (Ag).
- ii. Metals with a negative toxic effect such as arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se).

Heavy metals enter our body through drinking, eating, inhaling, and skin and eye contact; and once they enter into the body, they damage on the cellular level by causing dangerous free radicals production that can cause cancer and many other diseases. Unlike organic pollutants, the majority of which are susceptible to biological degradation and do not degrade into harmless end products¹¹. Determination of the level of heavy metals in environmental samples like water and food is of great importance nowadays due to the non-degradability, bioaccumulation and high toxicity of heavy metals in the environment and living organisms.

Knowledge of the concentration and removal methods of heavy metal contaminants from drinking water is vital to distinguish the role of nutrient and pollutant elements; and has been a subject of scientific environmental research for a long time¹². The removal of heavy metal in an effective manner from water and wastewater is ecologically very important. There are many reported and established conventional methods for the recovery of heavy metal ions from wastewater, which included precipitation, oxidation and reduction, ion exchange, filtration, electrochemical treatment and evaporative recovery. However, these high-technology processes have significant disadvantages, including incomplete metal removal, requirements for expensive equipment and monitoring systems, high-cost reagents, energy requirements, generation of toxic sludge and other waste products that require disposal¹³.

In recent years, many researchers have been intensified on studying for low-cost agricultural by-products as adsorbents for the removal of heavy metal ions from water sources; that have high metal binding capacities. These include peat, wood, pine bark, banana pith; soybean and cotton seed hulls, peanut shells, hazelnut shell, rice husk, saw dust, wool, orange peel, compost and leaves are used as the starting materials to prepare activated carbon¹⁴. The advantage of using agricultural by-products as raw materials for manufacturing activated carbon is that these raw materials are renewable and potentially less expensive to manufacture.

Pumpkins, from low cost of agricultural by-products, have received great attention from academics and practitioners due to their economic and environmental benefits. Pumpkin are creep vegetative shrubs that spread low across the ground with large lobed leaves and long twisting tendrils. Pumpkin seeds, also known as pepitas, are flat and variable in size, color, shape and weight. Some are encased in a yellow-white shell, although some varieties of pumpkins produce seeds without shells. The seed shell constitutes the largest morphological part of the plant. Seeds and leaves of this fruit have been investigated¹⁵. The adsorption of capacity of activated carbons prepared from pumpkin seed shells towards Cu (II) and Cd (II) ions were investigated in this study.

Both Cu and Cd are among the heavy metals that are used in a number of geological or human activities leaving aqueous solutions with elevated metal ion concentrations. Cu (II) is found in naturally occurring minerals principally as sulfides, oxides, or carbonates. It makes up approximately 0.01 % of the earth's crust and is obtained commercially from such ores as chalcopyrite (CuFeS_2). It is also found in biological complexes such as hemocyanin and is one of the essential bimetals necessary for the growth and development of the human body like the synthesis of hemoglobin, melanin, and the mineralization and development of bones; and proper functioning of important enzymatic systems. Copper enters water supplies through the natural process of dissolution of minerals, through industrial effluents, through its use, as copper sulfate, to control biological growth in some reservoirs and distribution systems, and through corrosion of copper alloy water pipes. Copper-containing enzymes include ceruloplasmin, SOD, cytochrome-c oxidase, tyrosinase, monoamine oxidase, lysyl oxidase and phenylalanine hydroxylase¹⁶. The lack of Cu (II) can lead impaired growth in children and several metabolic problems in adults. Whereas, its excess amount in the human body can cause stomach and intestinal distress such as nausea, anemia, vomiting, diarrhea, and stomach cramps. In pure water, the Cu^{2+} ion is the more common oxidation state and will form complexes with hydroxide and carbonate ions. The formation of insoluble malachite [$\text{Cu}_2(\text{OH})_2\text{CO}_3$] is a major factor in controlling the level of free Cu^{2+} ion in aqueous solution which is the major species in water up to pH 6. According to WHO standards, its maximum allowable concentration in drinking water is 0.2 mg/L¹⁷. In order to protect humans and the environment, removal of Cu (II) ions from environments such as water, sanitation and flood is important when its level exceeds the permissible level.

Cadmium on the other hand can occur naturally in zinc, lead, copper and other ores which act as source to ground and surface waters. It can be released into drinking water from the corrosion of some galvanized plumbing and water main pipe material¹⁸. Cd shows no sign of being essential element in biological processes; on contrary, it is highly toxic and carcinogenic metal to humans even in trace amount like mercury, cadmium and its compounds are black-listed materials, which by international agreement should not be discharged or dumped into the environment because it has accumulative poison that can cause renal dysfunctions, hypertension and diabetes; and a maximum level of 0.005 mg/L¹⁹ is permitted for drinking water.

Due to the harmful and toxic effects of high level of Cu and Cd from industrial and/or household waste discharges directly or indirectly through leakages in sewage systems into water sources that cause excessive pollution in surface and underground water, it is necessary to determine and monitor their content in water¹⁷; since the quality of water sources can be judged only by comparing the concentrations of various constituents present in the water with the acceptable limits of different International Organizations such as USEPA, WHO, EPA¹⁹.

Clean water coverage of Jimma town is low. As a result of low level of water production, access to clean water is low even though the majority of households have tap water lines. Thus, the majority of the city populations are still using water irregularly from unprotected wells for various purposes such as cleaning utensils, washing clothes, bathing and even for drinking²⁰. So far, no sufficient study has been conducted on the analysis of the level of heavy metal contamination of drinking water on Jimma town. Thus, due emphasis is given on analysis of these contaminants and AAS was used to determine the level of these heavy metals in drinking water samples collected from different points in Jimma town (Ethiopia); and their removal techniques, adsorption using activated carbon prepared from pumpkin seed shells was used.

1.1. Statement of the problem

Heavy metals have great concern because of their extreme toxicity when they exceed the permissible limits; and pollution of drinking water with heavy metals has become an increasingly important problem in all over the world. Thus, knowledge of the level and removal techniques for the metals is essential to understand the role of nutrient and pollutant elements in water. Currently, some of the people in Jimma town do not have access to safe drinking water supply and frequently experienced water-borne diseases²¹. Nevertheless, a comprehensive investigation of the level of heavy metals of drinking waters sources particularly the water treatment plant and distribution water from different points on the town, is infrequent.

Even though, activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse kinds of pollutants, this study specifically answers the following basic questions.

- Can a pumpkin seed shell is used as a precursor for preparation of AC?
- How much efficient is the PSS-AC for the removal of heavy metals, Cu (II) and Cd (II)?
- What are the removal methods responsible for adsorption the metal ions using PSS-AC?

1.2. Objectives of the study

1.2.1. General Objective

To study the level of Cu (II) and Cd (II) in drinking water samples collected from different points in Jimma town and to provide their removal methods when found beyond the permissible level.

1.2.2. Specific Objectives

- ✓ To determine the level of Cu (II) and Cd (II) in the water samples collected from Jimma town using AAS.
- ✓ To prepare activated carbon from pumpkin seed shells and determine adsorption efficiency of Cu (II) and Cd (II) from water samples,
- ✓ To determine the effects of pH, contact time, initial concentration and adsorbent dose on the adsorption of activated carbon for the maximum removal of Cu (II) and Cd (II) ions from aqueous solution.

1.3. Significance of the study

The study was focused on the determination of the level of trace metals Cu (II) and Cd (II) and on the methods how to remove these contaminants in drinking water using activated carbon prepared from pumpkin seed shells if their level APL. Pumpkin seed shells are locally available agricultural by-products which are selected because of their high cellulose content, the presence of carboxylic acids and their availability in my study area. The study helps to:

- ✓ know and monitor the level of heavy metals Cu (II) and Cd (II) in the water samples and has an importance for improving drinking water safety,
- ✓ contribute alternative operational method of advanced technologies for removal Cu (II) and Cd (II) by activated carbon prepared from locally available agricultural by-products called pumpkin seed shells,
- ✓ and also it will give more information on adsorption of different pollutants to treat water pollution by using pumpkin seed shells activated carbon for further study.

2. LITERATURE REVIEW

Water pollution is versatile process that leads to changes in water composition, aquatic flora and fauna, and may result in a poor condition water quality for economic and recreational use and being dangerous to human health²²⁻²⁴. Water is mainly polluted with organic, inorganic, sediments, radioactive materials and heavy metals. Among these pollutants, the contribution of heavy metal ions from the transition series such as Cu, Ni, Pb, Hg, Cd, etc. is of major concern because of their toxicity for many life forms, bioaccumulation, persistence and non-biodegradability causing various diseases and disorders. Few of these metals such as Pb, Hg and Cd have been included in the U.S. Environmental Protection Agency's list of priority pollutants²⁵. Interestingly, small quantities of heavy metals are nutritionally essential for a healthy life but they become toxic when they are not metabolized by the body and accumulate in the soft tissues.

2.1. Heavy metals

Heavy metals in water refers to the heavy and dense metallic elements that occur in trace levels, but are very toxic and tend to accumulate, hence are commonly referred to as trace metals. Heavy metals normally occurring in nature are not harmful to our environment because they are only present in very small quantities²⁶. However, if the levels of these metals are higher than the recommended limits, their roles change to a negative dimension. Human beings can be exposed to heavy metal ions through direct and indirect sources like food, drinking water and exposure to industrial activities²⁷. Thus, drinking water can be considered as one of the major sources of heavy metals for humans.

The natural concentration of metals in raw water may vary depending upon the metal concentration in the soil and the underlying geological structures, the acidity of the water, its humus content and particulate matter concentration²⁸. Recently, several methods of analysis were developed for determination of the level of heavy metals in different water samples such as voltammetry²⁹, atomic absorption spectrophotometry and X-ray fluorescence spectrometry^{30, 31}.

2.2. Adsorption

Adsorption is a mass transfer process which involves the accumulation of atoms, ions or molecules at the interface of two phases, such as, liquid-liquid, gas-liquid, gas-solid or liquid-solid adhere using a surface of the adsorbent. It is a surface-based process where a film of adsorbate is created on the surface. It is one of the easiest, safest and most cost-effective separation methods for the removal of heavy metals in which certain components of the fluid phases are transferred to the surface of the solid adsorbents³²⁻³⁴. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term adsorption encompasses both processes, while desorption is the reverse process. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification³⁵.

The success of heavy metal uptake by agricultural products is believed to be dependent on a number of factors, one of which is chemical composition³⁶ which is a feature of successful heavy-metal adsorption products that is due to the presence of ligno-cellulosic biomass. Ligno-cellulosic biomass refers to plant biomass that contains cellulose, hemi-cellulose, and lignin. Another characteristic of successful agricultural products is the presence of acidic groups such as carboxylic and phenolic groups³⁷.

The removal of toxic metals from water sources is a matter of great interest in the field of water pollution, which is a serious cause of water degradation. Thus, there are a number of technologies are available; chemical precipitation, ion exchange, coagulation, and bioremediation, adsorption etc. Of all these techniques, adsorption at solid substrate is preferred because of its high efficiency, easy handling and cost effectiveness as well as availability of different adsorbents³⁸. The high adsorption capacity is mainly due to the high surface area and the existence of functional groups on its active sites. AC production costs can be reduced by either choosing a cheap untreated material and/or by applying a proper production method³⁹.

2.2.1 Types of Adsorption

Adsorption involves two types of forces as physisorption (characteristic of weak Van der Waals forces) or chemisorption (characteristic of covalent bonding).

Physisorption: It is a result of intermolecular forces of attraction between molecule of the adsorbent and adsorbate. Physical adsorption occurs when the intermolecular attractive forces between molecules of a solid and the gas are greater than those between molecules of the gas itself. Furthermore, it occurs lower or close to the critical temperature of the adsorbed substance.

Chemisorption: It is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption. Commercial adsorbents rely on physical adsorption; catalysis relies on chemisorption. Chemisorption occurs only as a monolayer and substances chemisorbed on solid surface are hardly removed because of stronger forces. The driving force for adsorption process is surface affinity, chemical reactivity, pH, surface area for adsorption per unit volume and reduction in surface tension is key parameter for adsorption. The adsorption operation can be batch, semi-batch and continuous⁴⁰.

2.2.2 Application of Adsorption

Adsorption plays a significant role in the environmental pollution control and life supporting systems or planetary bases, where adsorbents may be used to process the habitat air or to recover useful substances from the local environments. Adsorption processes are good candidates for separation and purification by virtue of high reliability, energy efficiency, design flexibility, technological maturity and the ability to regenerate the process by regenerating the exhausted adsorbent. Development and application of adsorption cannot be considered separately from development of technology used to manufacture adsorbents applied both on laboratory and industrial scales. The adsorbent can take a broad range of chemical forms and different geometrical surface structures. A large specific surface area of the adsorbent pores provides a large adsorption capacity. The creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. Materials such as activated carbon and zeolite can be specifically engineered with precise pore size distributions and hence tuned for a particular separation application⁴¹.

2.3 Activated Carbon

Activated carbon (AC) is a common term used for a family of highly carbonaceous material that is processed and prepared by carbonization process to have amorphous, highly porous and large surface area for adsorption of industrial influents as organic compounds, heavy metals, herbicides and dyes, among many others toxic and hazardous compounds⁴². Commercial AC's are expensive materials manufactured by the pyrolysis and activation of high-cost starting materials, such as wood, petroleum and coal⁴³. More recently, researchers have been showing interest in the preparation of low-cost AC's with intensified metal binding capacities from low or no cost waste materials and readily available agricultural by-products as precursors. Some of these precursors used with success for the production of activated carbons include guava seeds⁴⁴, black stone cherries⁴⁵, orange peel⁴⁶, Peanut shell⁴⁷, etc.

2.3.1 Preparation of Activated Carbon

Any carbonaceous materials (animal, plant, or mineral origin) with a high concentration of carbon can be changed into AC by either physical or chemical activation processes. Physical activation consists of two steps in which the precursor is developed into AC by one or a combination of the two processes: a carbonaceous material is carbonized under oxygen-free atmosphere (carbonization) and then activated with an activating gas such as CO₂ and H₂O (activation).

In chemical activation, both carbonization and activation processes occur simultaneously at lower temperature and shorter time than in physical activation. Different activating agents such as H₃PO₄, KOH, ZnCl₂, HNO₃ and CO₂ can be used to improve the adsorption properties of the ACs. Among the activating agents, H₃PO₄ and ZnCl₂ are usually used for the activation of agricultural by-products for water purification⁴⁸. H₃PO₄ activation is widely preferred over ZnCl₂ because ZnCl₂ has bad environmental impact and the AC produced cannot be used in the food and pharmaceutical industries⁴⁹. However, H₃PO₄ is widely used activating agent for the preparation of activated carbons for wastewater treatment probably due to its ease of removability after carbon activation by either washing with hot or cold water besides its other operational and environmental advantages⁵⁰.

2.3.2 Applications of Activated Carbon

There are enormous applications for AC. Its important use is for gasoline vapor emission control containers in automobile. It can also act as a filter material in air cleaning filters for removal of gases and vapors in the industrial environment. Especially impregnated grades are used in cigarette filters to adsorb some of the harmful components of tobacco. Heavy metal ions such as Hg, Pb, Cr and Cd in drinking water are very dangerous even in trace amount, and adsorption method for removing these metal ions can be essential for treatment of water contaminated by heavy poisonous metal ions²⁵.

2.4. Adsorption Experiments

The adsorption process can provide vital information about mechanism of the reaction between the adsorbate and the adsorbent; and is useful in understanding the process. Equilibrium adsorptions are described by isotherms governing the distribution of a given adsorbate between the liquid phase and the adsorbent where, Freundlich and Langmuir models were developed and used to analyze the data for the adsorption of the ions by pumpkin seed shell activated carbons. A kinetics study was carried out to determine the equilibrium time required for the uptake of metals from a liquid solution. The kinetic results obtained from batch experiments were analyzed using Lagergren pseudo-first order and pseudo second order kinetic models⁵¹. Thermodynamic parameters such as Gibbs free energy, ΔG^0 , enthalpy, ΔH^0 and entropy, ΔS^0 of adsorption were evaluated⁵².

The initial metal ion concentration in the test solution and the adsorbent dosage were varied to investigate their effect on the adsorption kinetics. All experiments were carried out in triplicate analysis, and the concentrations given are average values. The amount of Cu (II) and Cd (II) adsorbed at a time t , q_t (mg/g) was calculated using the relation on the following Equation (1).

$$q_t = \frac{(C_0 - C_t)V}{W} \dots \dots \dots (1)$$

where C_t (mg/L) is the liquid phase concentrations of metal ion at any time, C_0 (mg/L) corresponds to the initial concentration of each metal ion. V (L) is the volume of the solution and W (g) is the mass of the adsorbent.

Under the experimental conditions, the adsorption capacities of all the adsorbents for each concentration of Cu (II) and Cd (II) ions at equilibrium were calculated as follows⁵³ by difference and the mean value was calculated as Equation (2):

$$q_e = \frac{(C_0 - C_e)V}{W} \dots \dots \dots (2)$$

where C_0 (mg/L) corresponds to the initial concentration of each metal ion, and C_e (mg/L) to the concentration at equilibrium. V (L) is the volume of the solution, and W (g) is the mass of the adsorbent. The removal efficiency percentage of Cu (II) and Cd (II) ions was calculated⁵³ for each run by using the following Equation (3):

$$Removal (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \dots \dots \dots (3)$$

where C_0 (mg/L) corresponds to the initial concentration of each metal ion and C_e (mg/L) to the concentration at equilibrium.

2.4.1. Adsorption Isotherms

Adsorption isotherm is one of basic requirements for the design of an adsorption system. It provides information on the capacity of the adsorbent or the amount required for removing a unit mass of pollutant under the operating conditions. Usually the amount adsorbed is only a fraction of a monolayer. The degree of the adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases. Among the several models that are often employed to interpret the equilibrium data of isotherm studies, Langmuir and Freundlich equations are early used adsorption models and are still most frequently used⁵⁴; and are utilized at the present study. The Langmuir equation was modeled using the Equation (4) below:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_L} \dots \dots \dots (4)$$

where C_e (mg/L) is the equilibrium concentration of Cu (II) and Cd (II) in solution, q_e (mg/g) is the amount each ions adsorbed at equilibrium from the solution on the adsorbent. Langmuir constants, which are related to the adsorption capacity (q_m) and energy of adsorption (b_L) can be calculated from the slope of the linear plot of C_e/q_e versus C_e ; a slope $1/q_m$ and intercept of $1/q_m b_L$ is obtained.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L which is given in Equation (5) as:

$$R_L = \frac{1}{1 + b_L C_o} \dots \dots \dots (5)$$

Freundlich model was assumed to estimate the adsorption intensity of the metal ions on the carbon adsorbent surface. The Freundlich equation was presented as Equation (6).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots \dots \dots (6)$$

where K_f (mg/g) and n are Freundlich constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of the adsorption.

2.4.2. Adsorption Kinetics

The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the fluid-solid mass transport process. The kinetics of sorption processes were studied by carrying a set of sorption experiments between the metal ions and activated carbon samples at constant temperature by monitoring the amount adsorbed with time. The sorption kinetics normally include two phases: a rapid removal stage followed by a much slower stage before the equilibrium is established. In order to ascertain which model fitted better to the experimental data, the Lagergren pseudo first-order and pseudo-second order kinetic models were applied⁵⁵. The linear form of the pseudo-first order equation was generally expressed as Equation (7) below:

$$\log(q_e - q_t) = \log q_e - \frac{K_f}{2.303} t \dots \dots \dots (7)$$

where q_e and q_t are the values of amount adsorbed per unit mass (mg/g) at equilibrium and at any time t respectively, and K_f is the pseudo first order sorption rate constant (min^{-1}). The K_f value could be obtained by plotting $\log(q_e - q_t)$ versus t . In order to find a more reliable description of the kinetics, second order kinetic equation was applied as the linear (Equation 8)⁵⁶.

The procedure for the pseudo-second order is more likely to predict the behavior over the whole range of adsorption process which was based on the assumption that the rate limiting step may be physisorption due to the presence of weak forces of attraction between adsorbent and adsorbate.

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{t}{q_e} \text{----- (8)}$$

where k_s is rate constant for the second order kinetics (g mg/min).

2.4.3. Thermodynamic Study

The thermodynamic parameters that help us to understand the nature of adsorption of heavy metal ions Cu (II) and Cd (II) are the standard change in Gibbs free energy, ΔG° (kJ/mol), the standard change in entropy, ΔS° (J/mol K) and the standard change in enthalpy, ΔH° (kJ/mol). These can be determined using the following equations⁵⁷. The Gibbs free energy indicates the degree of spontaneity spontaneous nature of sorption of Cu (II) and Cd (II) by the activated carbon, and the higher negative value reflects a more energetically favorable adsorption. The enthalpy value for adsorption process may be used to distinguish between chemical and physical adsorption. For chemical adsorption, values of enthalpy change range from 83 to 830 kJ/ mol, while for physical adsorption they range from 8 to 25 kJ/ mol⁵⁸.

$$\Delta G^\circ = -RT \ln K_c \text{----- (9)}$$

The values of ΔH° (J/mol) and ΔS° (J/mol/K) were calculated from the slope and intercept of the linear plot of $\ln K_c$ versus reciprocal of temperature $1/T$ (Equation 10).

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \text{----- (10)}$$

Where R is the gas constant (8.314 J/ mol. K), T is the absolute temperature in Kelvin (K) and K_c (L/g) is the standard thermodynamic equilibrium constant defined as q_e/C_e .

3. MATERIALS AND METHODS

3.1. Sample collection

Three types of water samples (Untreated, treated and distribution system) were collected from six sites in Jimma town using plastic bottles of 1 L capacity. Untreated and treated water samples were collected from the treatment plant located at Boye; and the distribution system samples were collected from five different sites around the town: Bosa-Adis, Hermata-Mentina, Mendera Kochii, Ginjo-Guduru and Ginjo. Pumpkin seed for the preparation of activated carbon were collected from local merchants in Jimma town using clean plastic bags.

3.2. Chemicals and Reagents

Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Riedel-de Haën, Germany) (98% by wt.) and Cadmium chloride, $\text{CdCl}_2 \cdot 1/2\text{H}_2\text{O}$ (Riedel-de Haën, Germany) (99% by wt.) were used to prepare respective stock standard solutions. H_3PO_4 (Riedel-de Haën, Germany) (85% by wt.) was used as activating agent. Aqueous solution (5% w/v) NaOH (Riedel-de Haën, Germany) and HCl (5% v/v) (Riedel-de Haën, Germany) were used to adjust the pH of solutions to the desire value. All chemicals and reagents used were analytical grade and were used as received without any treatment. Distilled water was used for preparation of stock standard solution.

3.3. Materials and instrument

Apparatus and glass wares used in experimental procedures were: teflon (PTFE) knife, chopping board (PTFE, China), sieve (150 μm), pipette, crucible, test tube, measuring cylinder, beaker, conical flasks (of capacity 25 mL, 50 mL, 100 mL, 250 mL), volumetric flasks (of capacity 5 mL, 10 mL, 25 mL, 50 mL, 100 mL, 500 mL, 1000mL) were used. Mortar and pestle were used for grounding the PSSs, Whatmann No. 42 filter paper and plastic bottles (capacity 1 L). And; the instruments used in the works were: atomic absorption spectrophotometer (AAS) (Model analytikjenanov AA 300), thermostatic water bath shaker (Model GRANT GLS 400, England), digital pH meter (HANNA instruments, pH 211), electronic balance (ADAM AFP-110), Air drying oven (Model GENLAB WIDNES, England), electrical furnace (Model Nabertherm^(R)), Scanning electron microscope (Model JSM 6510LV, JEOL Japan) and Fourier transforms infrared [FT-IR] spectrophotometer (Spectrum 65 FT-IR, Perkin Elmer model).

3.4. Procedure

3.4.1. Drinking water sampling and pre-treatment

The pre-treatment process was conducted before analysis. Three types (untreated, treated and distribution system) of water samples were collected using plastic bottles of 1 L capacity which were prewashed sequentially with detergent, dilute 5% HNO₃ and distilled water and rinsed with the sample water. The sampling was done within two consecutive days. The water samples, after collection, were immediately transported to the laboratory and; 500 mL portion were acidified with 5% (v/v) nitric acid and preserved, at about 4°C in a refrigerator until the analysis was done.

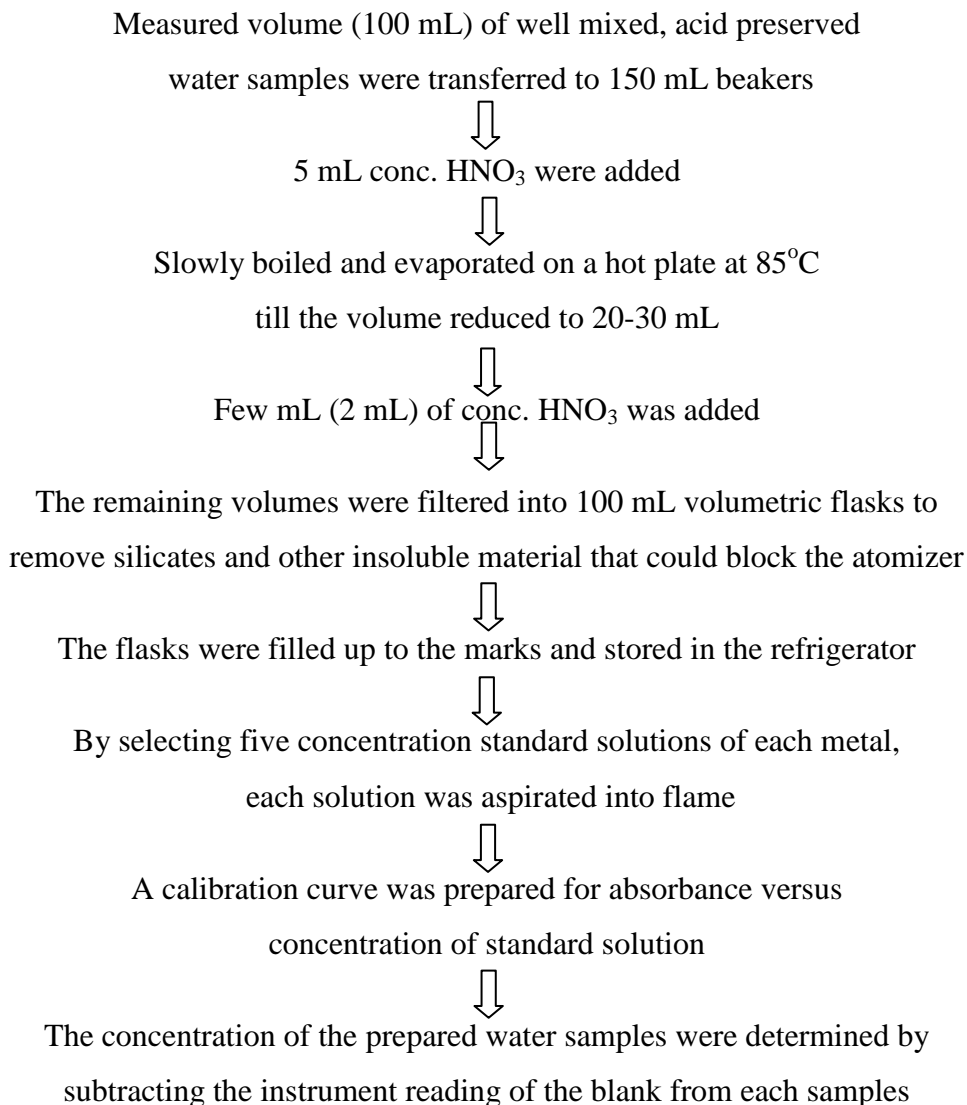
3.4.2. Digestion of the water samples

For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities from reagents and laboratory apparatus are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by:

- i. contributing contaminants through leaching and
- ii. by depleting concentrations through adsorption.

Thus, collection and treatment of the sample prior to analysis requires particular attention. For this purpose, a sample was preserved in the field with nitric acid. The shaken sample aliquot is digested with nitric acid to ensure the removal of organic impurities from the samples and thus to prevent the interference in analysis.

All the three type of water samples including the blanks were digested with concentrated nitric acid as in the Scheme 1 below. After effective digestion, the samples were analyzed for the concentration of the Cu (II) and Cd (II) using AAS.



Scheme 1: Digestion of the blanks, untreated, treated and distribution system water samples with concentrated nitric acid

3.4.3. Preparation of standard solutions

Since standard solutions of the respective concentrations of Cd (II) and Cu (II) ions are necessary to standardize and calibrate the instrument, stock standard solutions of Cd (II) and Cu (II) ions were prepared from hydrated $\text{CdCl}_2 \cdot 1/2\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ salts, respectively. Calibration solutions of the target metal ions were prepared from the stock standard by serial dilution. All chemicals used in this study were of analytical reagent grade and were used without further purification.

3.4.4. Real sample analysis

The digested drinking water samples were analyzed for the level of Cu (II) and Cd (II) using AAS. The air-acetylene flame and the characteristic hollow cathode lamp of the corresponding element were used. The line sources, wavelength for the determination of the ions were 324.7 nm and 288.8 nm for Cu (II) and Cd (II) respectively. The analysis was done in triplicate with the average concentration of metals being displayed in mg/L.

3.4.5. Preparation of activated carbon

The raw pumpkin seed shells were washed with tap water to remove the attached dust and other impurities and then washed with distilled water. It was dried at 105°C for 12 hr, and grinded to increase the surface area. The powdered pumpkin seed shells were soaked with ortho phosphoric acid (85% by v/v) by using the weight ratio of raw material and the acid at 1:1 w/v and the mixture was dried in an air drying oven at 105°C for 24 hr. The dried PSS/ H_3PO_4 mixture then was put on to a crucible and placed in an electrical furnace for carbonization. The heating rate of carbonization was $10^\circ\text{C}/\text{min}$ and continues until the final temperature of 800°C was attained and it was kept at this temperature for 3 hr. The produced activated carbon was then cooled down to room temperature, then washed with 5% aqueous NaOH solution followed by distilled water for several times until the pH of the washing was neutral. It was filtered and dried in an air-drying oven at 105°C for 12 hr. Finally, the activated carbon prepared was crushed and powdered into $150\ \mu\text{m}$ (sieve size) mesh size before adsorption experiments.

3.4.6. Characterization of activated carbon

Proximate analysis for the moisture content, ash content, and fixed carbon were performed at Jimma University. Fourier transform infrared (FT-IR) spectra of dried AC, before and after adsorption of Cd (II) and Cu (II) were recorded in the range 400-4000 cm^{-1} wave number using FT-IR spectrophotometer for determination of the surface functional groups at Addis Ababa University. The surface morphology and porosity of the PSS-AC was analyzed using scanning electron microscope (SEM); and for the determination of the elemental composition of the adsorbent, the energy dispersion X-ray (EDX) analysis were performed at USIF (University Sophisticated Instruments Facility), AMU, Aligarh, India.

3.5. Optimization of the experimental parameters

To find the most favorable conditions of (pH, contact time, adsorbent dose and initial metal ion concentration) for the removal of Cu (II) and Cd (II) metals the adsorption studies were carried out by taking 25 mL of the metal ion solution under different conditions for a period of time in a 250 mL conical flask using thermostatic water bath shaker maintained at 140 rpm and to a temperature of 30°C. The pH of each solution was adjusted to the desired value by dilution with aqueous 5% HCl and/or 5% NaOH solutions. The separation of the residual metal ion from the solution was done by filtration using Whatmann filter paper No. 42 and finally, the residual metal ion was determined using atomic absorption spectrometer (AAS). The optimum concentrations were determined as the concentrations with the highest percent adsorption of each metal ion using Equation (3) in chapter two.

3.5.1. Effect of initial metal ion concentration

The effect of initial metal ion concentration was conducted to find the optimum concentration for the removal of metal ions from solutions. To find the optimum concentrations and time for the removal of the Cu (II) and Cd (II) ions, ten conical flasks containing 0.2 g of PSS-AC within 25 mL of (0.01 mg/L, 0.05 mg/L, 0.2 mg/L, 2 mg/L and 5 mg/L) Cu (II) and (0.002 mg/L, 0.005 mg/L, 0.04 mg/L, 0.2 mg/L and 1 mg/L) of Cd (II) solutions were taken. These conical flasks were kept in thermostatic water bath shaker maintained to 140 rpm at a temperature of 30°C; and each sample was taken out at the time intervals of, 10 min, 30 min, 50 min, 70 min and 90 min.

3.5.2. Effect of pH

pH is one of most important controlling parameters for the removal of heavy metal ions from solutions because it affects the solubility of the metal ions, concentration of the counter ions on the functional group of the adsorbent and the degree of ionization of the adsorbate during the reaction process^{40, 41}. The experiment was done by taking 0.2 mg/L of Cu (II) and 0.005 mg/L of Cd (II) solutions and 0.2 g of the AC with varying pH from 1 to 9. The mixture was left in the thermostatic water bath shaker for 50 min to Cd (II) and 70 min to Cu (II). The optimum pH was determined as the pH with the highest percent adsorption of each metal ion.

3.5.3. Effect of adsorbent dose

The removal efficiency and specific uptake of metals depend on type and quantity of the adsorbent. An experiment on the variation of the adsorbent dosage is an important part of the study to determine the capacity of an adsorbent for a given initial concentration of the metals at the operating conditions. Thus, the effect of adsorbent dosage of PSS-AC was investigated by taking varying the quantity of the adsorbent between 0.05 g and 0.3 g on both Cu (II) and Cd (II) ions at optimum conditions of pH, contact time and initial by keeping the thermostatic water bath shaker at 140 rpm. The optimum dose was determined as the amount with the highest percent adsorption of the ions.

3.5.4. Effect of temperature

In order to investigate the effect of temperature on the adsorption process, the batch adsorptions were done at different temperatures (from 25°C - 45°C) by mixing 0.2 g of activated carbon with 25 mL of 0.2 Cu (II) mg/L and 0.005 mg/L of Cd (II) solution at the optimal pH. The effect of temperature on adsorption depends on thermodynamic parameters such as change in Gibbs free energy, ΔG° , change in enthalpy, ΔH° , and change in entropy, ΔS° of the system.

3.6. Statistical analysis

Triplicate analysis by averaging the values was made for the determination of Cu (II) and Cd (II) ions using the AAS and the curve fittings of the data obtained was performed using Microcal Origin 6.0 software.

4. RESULTS AND DISCUSSION

4.1. Calibration curve and detection limit

The calibration curves were obtained from five calibration standard solutions of different concentration (0.01 mg/L, 0.05 mg/L, 0.2 mg/L, 2 mg/L and 5 mg/L for Cu (II) and 0.002 mg/L, 0.005 mg/L, 0.04 mg/L, 0.2 mg/L and 1 mg/L for Cd (II)) prepared identically by serial dilution from stock standard solutions. Linear calibration curves were obtained with correlation coefficients of the calibration curves > 0.999 and these correlation coefficients showed that there was very good relationship between concentration and absorbance (Table 1 and Figure 1).

Detection limit of an analyte is the smallest quantity (concentration) of the analyte which can be detected but not quantified at a given confidence level. Detection limit of certain method may vary greatly often with matrix and experimental procedures⁵⁹. In this study, method detection limit for Cu (II) and Cd (II) was estimated by digesting six analytical blanks with the optimized procedure for the drinking water samples. Each blank solution was run with AAS for the level of metals in similar manner as the samples and the standard deviations of the blanks' concentration were calculated. The method detection limit for the metal analyte is therefore the concentration in the sample matrix at which analytes signal equals at least three times that of noise ($3\delta_{\text{blank}}$, where δ = standard deviation of the blanks, $n = 6$ for the water samples. The method detection limits were 0.01 mg/L and 0.001 mg/L for Cu (II) and Cd (II) ions respectively which were low enough to detect the presence of the metals⁶⁰. The digested water samples for the analysis of Cu (II) and Cd (II) were aspirated into the flame and the absorbance was measured at their respective wave lengths; and compared to identically prepare standard and blank solutions, using an air-acetylene oxidizing flame.

Table 1: Analytical wavelengths, detection limits, correlation coefficients and calibration equations of the calibration curves for the determination of Cu (II) and Cd (II) using AAS

Metal	Wavelength (nm)	Method detection limit (mg/L)	Correlation Coefficient (R^2)	Calibration equation
Cu (II)	324.7	0.01	0.99999	$Y = 0.0302x + 2.997 \times 10^{-4}$
Cd (II)	228.8	0.001	0.99988	$Y = 0.068x - 6.08 \times 10^{-4}$

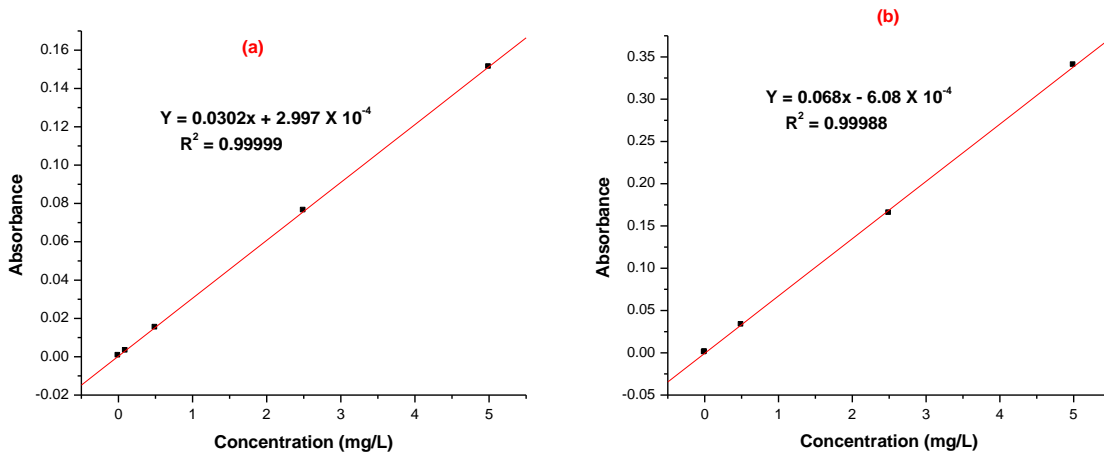


Figure 1: Calibration curves for determination of Cu (II) (a) and Cd (II) (b) using AAS

4.2. Concentration of Cu (II) and Cd (II) in drinking water samples

The result of the concentration of the Cu (II) and Cd (II) in the drinking water samples collected from different sites in Jimma town measured by AAS which is rapid, sensitive, and free from inter-element interferences, is shown in Table 2 below. From the result obtained, the minimum concentration of Cu (II) observed was 0.1 mg/L from Ginjo-Guduru site; and for that of Cd (II) ion it was 0.0012 mg/L (two samples from Bosa-Adis and Ginjo). However, the maximum concentrations obtained were 0.30 mg/L and 0.0072 mg/L (both from Boye) respectively.

For the protection of human health, guidelines for the level of heavy metals in drinking water have been set by different International Organizations such as USEPA, WHO, EPA, and the European Union Commission. Thus, heavy metals have maximum acceptable concentration in drinking water as specified by these organizations^{61, 62}.

According to comparison of the data tabulated in Table 2 and the maximum permissible level (MPL) in the WHO, the concentrations of both Cu (II) and Cd (II) in almost all untreated water samples collected from Boye site were above the permissible limits, 0.2 mg/L for Cu (II) and 0.005 mg/L for Cd (II)^{17, 19}. This was assumed that since water could be exposed to different contaminants on its sources and/or its way of journey mainly with large-scale use of insecticides, pesticides, soil erosion and wastes from urban and rural areas, the pollutants could be adsorbed using the soil from either of those sources and then to rivers.

It also showed higher concentration of Cd (II) from two samples at Ginjo-Guduru and one sample from Hermata-Mentina sites; which might be due to long journey of the water through old water pipe, tobacco smoking's, etc.⁸ The high level of Cd (II) contamination may also be due to soil composition and environmental pollution in the study area. Excessive Cd (II) exposure may weaken the body immune system and can cause lung cancer. This is of concern because some studies suggest it causes prostate enlargement, other studies suggest it may be a reproductive toxin and can cause premature birth, low birth weight, still birth and spontaneous abortion.

Table 2: Concentrations of Cu (II) and Cd (II) in drinking water samples examined from Jimma

Sample site	Sample type	Conc. of Cu ²⁺ (mg/L) ± SD	WHO MPL (0.2 mg/L)	Conc. of Cd ²⁺ (mg/L) ±SD	WHO MPL (0.005 mg/L)
Boye	UW1	0.30 ± 0.0012	APL	0.0064 ± 0.0003	APL
	UW2	0.27 ± 0.0003	APL	0.0072 ± 0.0005	
	UW3	0.19 ± 0.0007	BPL	0.0069 ± 0.0001	
	TW1	0.14 ± 0.0004	BPL	0.0049 ± 0.0001	BPL
	TW2	0.13 ± 0.0001		0.0043 ± 0.0003	
	TW3	0.19 ± 0.0002		0.0046 ± 0.0003	
Mendera Kochi	M-K DW1	0.18 ± 0.0004	BPL	0.0022 ± 0.0009	BPL
	M-K DW2	0.12 ± 0.0002		0.0032 ± 0.0004	
	M-K DW3	0.11 ± 0.0009		0.0041 ± 0.0002	
Bosa-Adis	B-A DW1	0.18 ± 0.0004	BPL	0.0028 ± 0.0007	BPL
	B-A DW2	0.19 ± 0.0006		0.0016 ± 0.0007	
	B-A DW3	0.15 ± 0.001		0.0012 ± 0.0001	
Ginjo-Guduru	G-G DW1	0.19 ± 0.0005	BPL	0.0033 ± 0.0007	BPL
	G-G DW2	0.14 ± 0.0004		0.0056 ± 0.0007	APL
	G-G DW3	0.10 ± 0.009		0.0051 ± 0.0008	APL
Hermata-Mentina	H-M DW1	0.16 ± 0.007	BPL	0.0049 ± 0.0003	BPL
	H-M DW2	0.17 ± 0.006		0.0054 ± 0.0009	APL
	H-M DW3	0.12 ± 0.0012		0.0030 ± 0.0004	BPL
Ginjo	G DW1	0.14 ± 0.004	BPL	0.0022 ± 0.0001	BPL
	G DW2	0.13 ± 0.0018		0.0016 ± 0.0002	
	G DW3	0.15 ± 0.0011		0.0012 ± 0.0005	

Note: -**APL** (Above permissible limit), **BPL** (Bellow permissible limit), **UW** (Untreated water), **TW** (Treated water), **DW** (Distribution water).

4.3 Characterization of the activated carbon

Most carbonaceous materials do have a certain degree of porosity and an internal surface area in the range of 10-15 m²/g. During activation, the internal surface becomes more highly developed and acquired an internal surface area between 700 and 1,200 m²/g that must be accessible to the passage of a fluid or vapor if a potential for adsorption is to exist. Thus, it is necessary that an activated carbon has not only a highly developed internal surface but accessibility to that surface via a network of pores of differing diameters. Activated carbons are widely used adsorbents utilized in recent years for adsorption of pollutants due to their highly porous structure and large surface area that can results in a high capacity for removal of contaminants from gas or liquid streams⁶³.

The proximate analyses of PSS-AC as presented in Table 3 showed lower amount of moisture, ash and volatile matter, indicating that the particle density is relatively small and that the biomaterial should be an excellent raw material for adsorbents to be used in adsorption process. Ash content can also affect activated carbon i.e. it reduces the overall activity of activated carbon. It also reduces the efficiency of reactivation, the lower the ash value therefore the better the activated carbon for use as adsorbent. A higher percentage adsorption for adsorbents having smaller particle size is due to the availability of more surface area⁶⁴.

4.3.1 Moisture content determination

Thermal drying method was used in the determination of moisture content of the samples. 1.0 g of the dried activated carbons were weighed in triplicates and placed in washed, dried and pre-weighed crucible. The crucibles were placed in an oven and dried at 105°C to constant weight for 12 hr⁶⁵. The percent moisture content (% MC) was computed as follows:

$$\text{Moisture (\%)} = \frac{(\textit{lose in wt. on drying})}{(\textit{initial wt.})} \times 100 \dots \dots \dots (11)$$

4.3.2. Volatile matter determination

Thermal drying method was used in the determination of volatile matter of the samples. 1.0 g of the dried activated carbons were weighed in triplicates and placed in washed, dried and weighed crucible. The crucibles were placed in an oven and dried at 105 °C to constant weight for 24 hr. The percent volatile matter content (% VM) was computed as follows:

$$\text{volatile matter (\%)} = \frac{\text{weight of volatile component (g)}}{\text{oven dry weight (g)}} \times 100 \dots \dots \dots (12)$$

4.3.3. Ash content determination

For the determination of ash content, the standard test method for ash content-ASTM D2866-94, was used⁶⁶. A crucible was pre-heated in a muffle furnace to about 800°C, cooled in a desiccator and weighed. Dry 1.0 g activated carbon samples were transferred into the crucibles and reweighed. The crucibles containing the samples were then placed in a cold muffle furnace and the temperature was allowed to rise to 800°C. The furnace was left on for three hours and, after which the crucible with its content was transferred to desiccators and allowed to cool for 30 min. The crucible and content was reweighed and the weight loss was recorded as the ash content of the AC sample (W_{ash}). Then the percent ash content (dry basis) was calculated from the following equation.

$$\text{Ash (\%)} = \frac{\text{ash wt.}}{\text{Oven dry wt.}} \times 100 \dots \dots \dots (13)$$

The lower ash content and volatile matter is attributed to lower inorganic content and higher fixed carbon content. Higher value of fixed carbon shows that the adsorbent has more efficiency and stability. Moisture content of the carbon has no effect on its adsorptive power; it dilutes the carbon which is necessary to use for additional weight of carbon during the treatment process. The samples were determined using standard test methods for ash and volatile matter contents of AC^{67, 68}. The fixed carbon of the PSS-AC sample was calculated from the Equation (14) below.

$$\% \text{ fixed carbon} = 100 - (\% \text{ ash content} + \% \text{ volatile matter content}) \dots \dots \dots (14)$$

Table 3: Proximate analysis of PSS-AC

Parameter	Value
Moisture content (%)	10.06
Volatile matter (%)	4.89
Ash content (%)	21.01
Fixed carbon (%)	74.1
Particle size (μm)	150
pH	6.5 \pm 1

4.3.4. Fourier transforms infrared characterization

Fourier transforms infrared (FT-IR) spectrum analysis is one of essential methods for the identification of the surface functional groups which can significantly enhance the adsorption efficiency of the prepared activated carbon by surface complexation. The spectrum in the near IR region (wave number: 4000-400 cm^{-1}) of PSS-AC exhibits different absorption peaks indicating the presence of different functional groups. A peak around 2935 cm^{-1} was attributed to aliphatic methyl C-H stretching. The peak observed around 1465 cm^{-1} can be attributed to the CH_3 bending and that observed around 1358 cm^{-1} was due to in-plane C-H bending. The very weak absorption band which was observed at around 725 cm^{-1} was attributed to the long chain band of aliphatic alkane. Figure 2 and Table 4 below shows the FT-IR spectra of the activated carbon prepared from PSS-AC before and after adsorption of Cu (II) and Cd (II) ions.

Table 4: The FT-IR Spectral Characteristics of PSS-AC before and after adsorption of Cd (II) and Cu (II)

Metal ion	Absorption bands (cm^{-1})			Functional groups
	Before adsorption	After adsorption	Difference	
Cu (II) Cd (II)	2935	2924	11	O-H stretching
Cu (II) Cd (II)	1465	1461	4	CH_3 bending
Cu (II) Cd (II)	1358	1356	2	in-plane C-H bending
Cu (II) Cd (II)	725	722	3	long chain band of aliphatic alkane

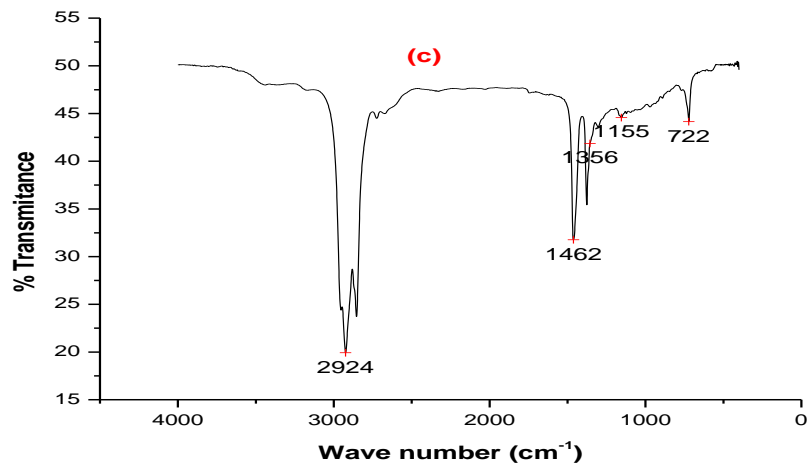
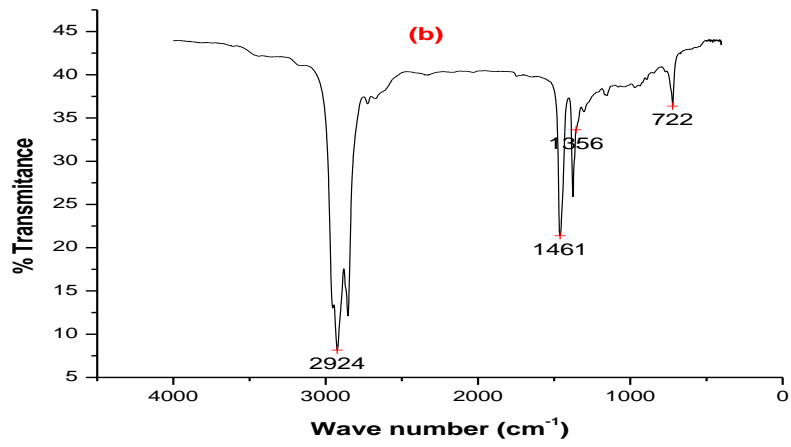
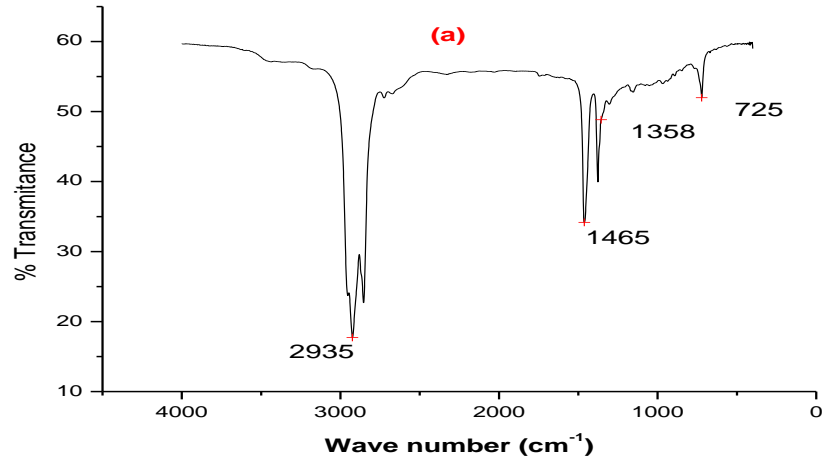


Figure 2: FT-IR spectra of PSS-AC (a) before adsorption, (b) after adsorption of Cu (II) and (c) Cd (II) ions

4.3.5. Scanning Electron Microscope (SEM) and EDX Analysis

The SEM micrographs of PSS-AC, figure 3 (a, b & c), shows the surface having small cavities, pores and more rough surfaces indicating the presence of interconnected porous network. SEM micrographs of Cu (II) loaded PSS-AC shows that the surface is pitted and fragmented due to the Cu (II) uptake. The surface areas of Cd (II) loaded PSS-AC is found to be enhanced by the presence of more porosity, which can hold more solute from solution during adsorption.

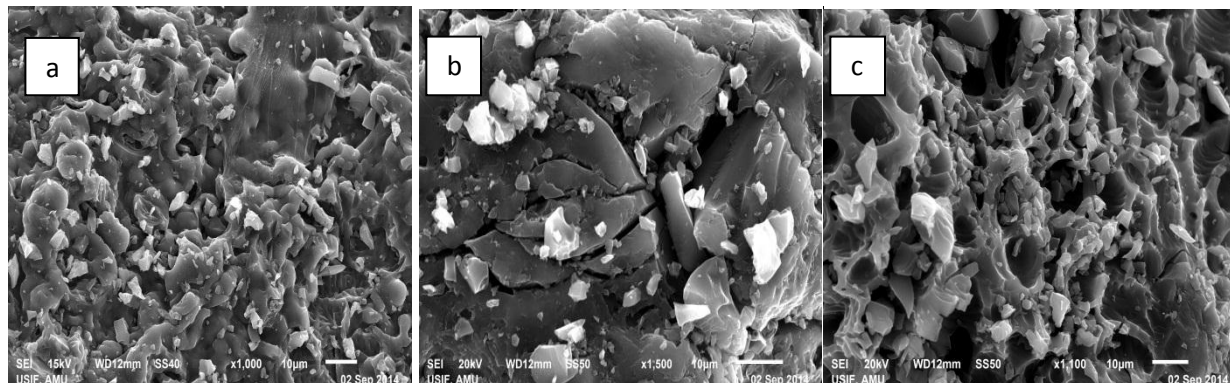
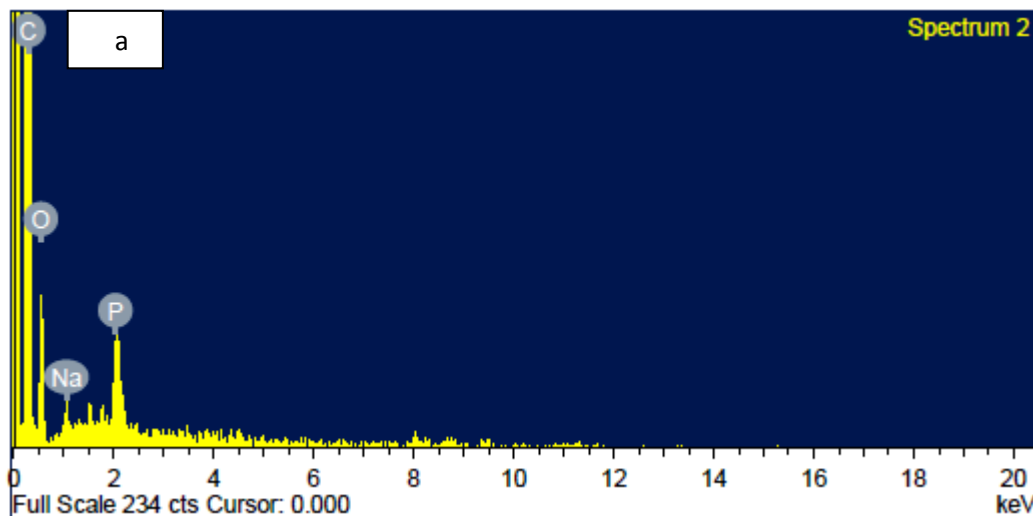


Figure 3: Scanning Electron Microscope (SEM) photographs for PSS-AC: (a) unloaded, (b) loaded with Cu (II) and (c) loaded with Cd (II)

EDX analysis was performed to determine the elemental composition of the activated carbon before and after metal ion adsorption implies the ability of the PSS-AC for Cu (II) and Cd (II) ions binding. Figure 4 presents the EDX spectrum of PSS-AC before and after adsorption of Cu (II) and Cd (II) ions.



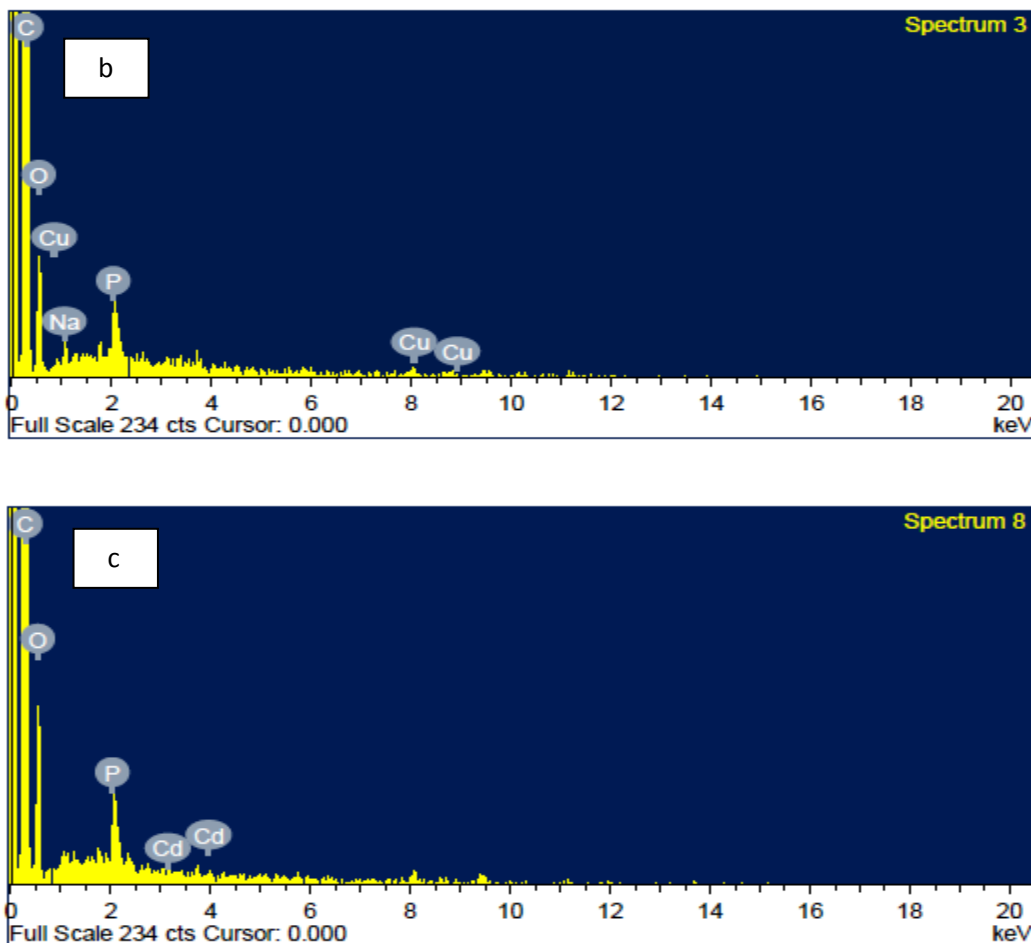


Figure 4: EDX Analysis for PSS-AC before adsorption (a) and after adsorption of Cu (II) (b) and Cd (II) (c) ions

4.4. Adsorption Experiments

4.4.1. Effect of Initial metal ion Concentration

The result of initial metal ion concentrations for the removal of Cu (II) and Cd (II) from aqueous solution is demonstrated in Figures 5 (a and b) below. It clearly indicated the percent adsorption was increased from 90.58% to 98.81% for Cu (II) with increase of initial metal ion concentration from 0.1 mg/L to 5 mg/L; and it increased from 93.52% to 98.99% for Cd (II) with increasing initial metal ion concentration from 0.002 mg/L to 1 mg/L. This should be due to the fact that at lower concentrations, adsorption of the metal-ions occurred slow and further increase in initial metal-ion concentration led to a competition for available bonding sites on the PSS-AC surface by the metal ions and thus increased the adsorption.

After certain time it is found that the percentage removal reaches equilibrium and the removal percentage had fractional deviation from one another. The adsorption equilibrium was reached at 0.2 mg/L for Cu (II) at optimum time of 70 min and for that of Cd (II) it reached at 0.005 mg/L at the optimum time of 50 min. Research works in a similar adsorption procedure have also been reported by other researchers⁷⁰⁻⁷².

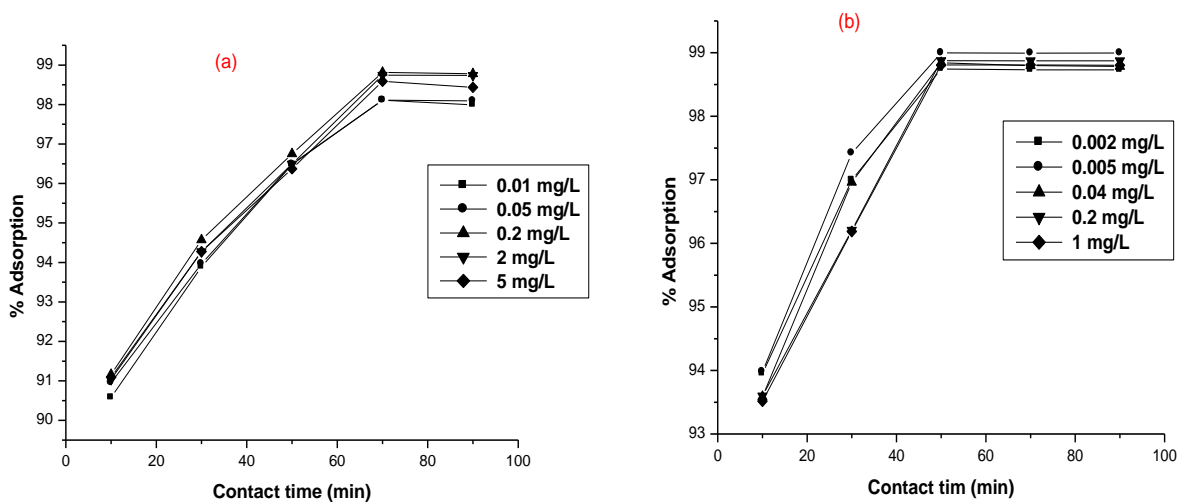


Figure 5: Effect of initial metal ion concentration on the adsorption of Cu (II) (a) and Cd (II) (b) using PSS-AC

4.4.2. Effect of pH

The effect of pH on the adsorption of Cu (II) and Cd (II) from solutions containing PSS-AC was studied by taking optimum concentrations of the metal ion (0.2 mg/L at 70 min for Cu (II) and 0.005 mg/L at 50 min for Cd (II)) to a 0.2 g of the adsorbent and the thermostatic water bath shaker at 140 rpm by varying pH.

The binding of metal ions by surface functional groups was strongly pH dependent and hence at lower pH values, the surface of the adsorbent is positively charged which would be closely associated with hydronium ions (H_3O^+) by electrostatic repulsive forces to the surface functional groups that consequently decrease the percent adsorption of the metal ions. As the solution pH increases, the negative charge on the surface of adsorbent increases and thereby enhances the metal ions adsorption.

When the pH of the adsorbing medium was increased, there was a corresponding increase in the de-protonation of the adsorbent surface leading to a decrease in H_3O^+ ion on the adsorbent surface. This creates more negative charges on the adsorbent surface, which favors adsorption of positively charge species and the positive sites on the adsorbent surface⁷³. With increasing pH, the negative charge on the surface of adsorbent increases there by enhancing the metal adsorption. This replacement occurs after the removal of the outer hydration sphere of metal cations. The results obtained agreed with the findings of some researchers. The solubility of metals is known to be lowered at higher pH (at $pH > 8$) values⁷⁴.

Figure 6 below shows the effect of pH on adsorption percentage of Cu (II) and Cd (II) using PSS-AC and it was found that adsorption of the ions from aqueous solution was pH dependent. The percent adsorption increases from 92.45 % to 98.61 % and from 91.9 % to 98.2% for Cu (II) and Cd (II) respectively with increasing pH. After this pH, it is found that percentage adsorption reaches equilibrium and it had fractional deviation from one another.

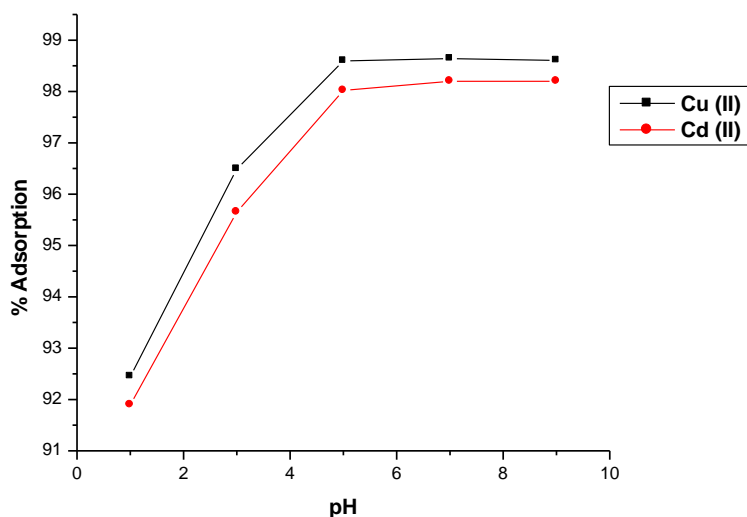


Figure 6: Effect of pH on the adsorption of Cu (II) and Cd (II) using PSS-AC

4.4.3. Effect of Adsorbent Dose

Removal efficiency and specific uptake of metals depends on the type and quantity of adsorbent. The dosage of adsorbent was a key parameter to control both availability and accessibility of adsorption sites. Raise in quantity of AC increases the deduction percentage of both Cu (II) and Cd (II). This was due to extra surface area existing on adsorbent and thus makes the penetration of ions easier to adsorption sites⁷⁵. An experiment on variation of adsorbent dosage is an important part of this study, because it determines the capacity of an adsorbent for a given initial concentration of the adsorbates, at the operating conditions. Thus, the effect of adsorbent dosage of PSS-AC required for the quantitative removal of Cu (II) and Cd (II) from 25 mL of each solution was investigated by varying the quantity of the adsorbent from 0.05 g and 0.3 g at 30°C.

Effect of adsorbent dosage on the removal of Cu (II) and Cd (II) has been presented in Figure 7. It is clear from the figure that percent removal increases with rise in the carbon dosage. After certain dose it was found that equilibrium is reached and had fractional deviation from one another. It was found that percent removal was increasing from 97.3 % to 98.465 % for Cu (II) and from 97.2 % to 98.36 % for Cd (II) and; at 0.2 g of carbon dose; the percent removal has insignificant increase around 98.46 % for Cu (II) and around 98.36 % for the Cd (II). From there onwards, percentage removal of both ions is slightly varying and equilibrium is achieved at 0.2 g at an optimum conditions.

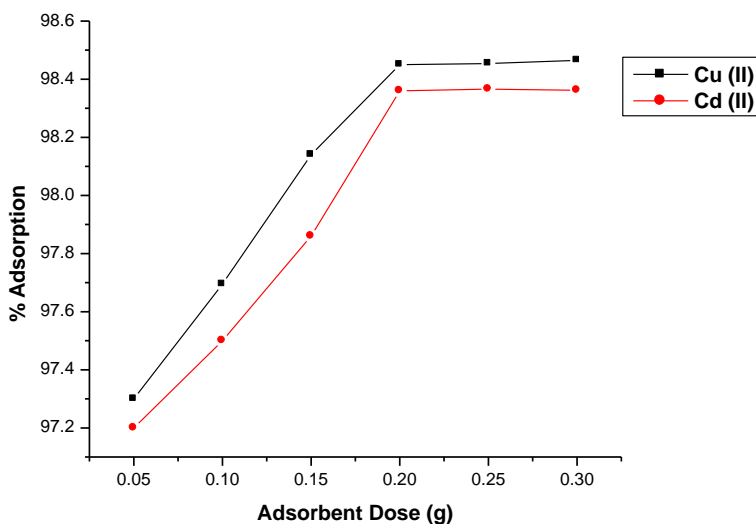


Figure 7: Effect of adsorbent dose on the removal efficiency of Cu (II) and Cd (II) using PSS-AC

4.4.4. Effect of Temperature

It was found that the Cu (II) and Cd (II) adsorption has a steady increases with increasing solution temperature from 25⁰C to 45⁰C, indicating that the adsorption is an endothermic process. Increase in temperature probably weakens the bond formed between the metal ions and the adsorption sites on the adsorbent thereby resulting in an increase in the amount of metal ions adsorbed on the adsorbent. This implies that increase in temperature creates a wider surface area for adsorption at the adsorbent. In addition, at high temperature due to bond rupture of functional groups on adsorbent, be an increase in number of active adsorption sites, which may also lead to enhanced adsorption with the rise in temperature⁷⁶. Similar findings have been reported by different researchers working on removal of heavy metal ions from aqueous solution by activated carbon⁷⁷.

From the results in Figure 8, it was observed that the percentage removal for both Cu (II) and Cd (II) ions was optimum at 30 °C and it had insignificant increase above this temperature from 98.49 % to 98.56 % for Cu (II) and 98.4 % to 98.5 % for Cd (II).

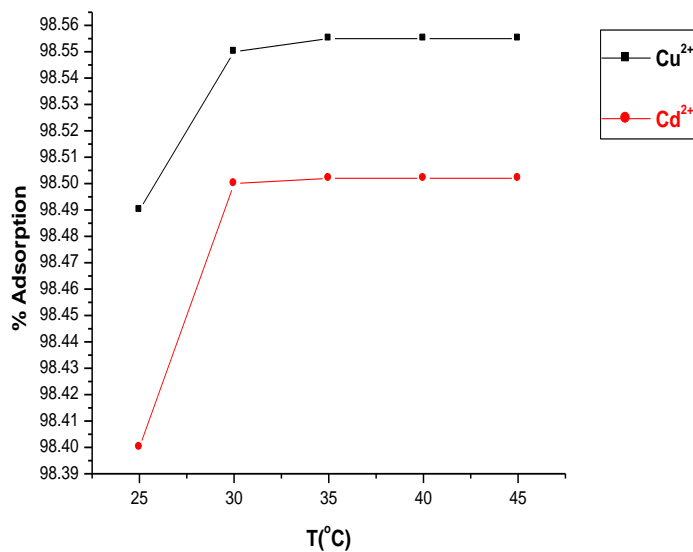


Figure 8: Effect of temperature on removal efficiency of Cu (II) and Cd (II) ions using PSS-AC

4.5. Adsorption Isotherms

The equilibrium study has been conducted based on the early and commonly used monolayer and multilayer isotherm models, Langmuir and Freundlich respectively.

4.5.1. Langmuir Isotherm model

The Langmuir adsorption isotherm model is the best known of all other isotherm models that describe adsorption process and it has been successfully applied to many adsorption processes. Weber and Chakravorti⁷⁸ expressed the Langmuir equation with its essential characteristics and the feasibility of the process in terms of a dimensionless constant separation factor or equilibrium parameter R_L obtained from Equation (5) on chapter two; where R_L values indicates the type of adsorption either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Linear plots of C_e/q_e versus C_e for Langmuir model with a straight line of slope $1/q_m$ and intercept of $1/q_m b_L$ is obtained as shown in Figure 9 where it is clearly seen that an excellent linear relationship exists for both metals indicating that the copper and cadmium adsorption on the PSS-AC follow the Langmuir adsorption isotherm. The values of q_m and b_L were calculated from the slopes and the intercepts are shown for both metals in Table 5.

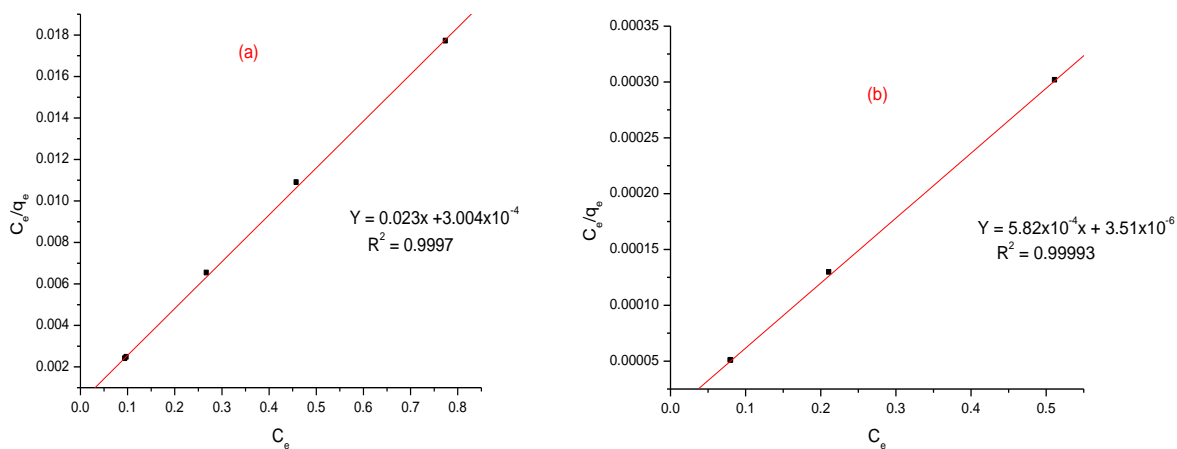


Figure 9: Langmuir plot for adsorption of Cu (II) (a) and Cd (II) (b) using PSS-AC

4.5.2. Freundlich Isotherm model

Freundlich isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption⁷⁹. Freundlich equation does not consider all sites on the adsorbent surface to be equal rather it assumes that, once the surface is covered, additional adsorbed species can still be accommodated⁸⁰. The Freundlich isotherm plot, $\log q_e$ versus $\log C_e$, is shown in Figure 10. If a plot of $\log q_e$ against $\log C_e$ yields a straight line, then the sorption process obeys a Freundlich model. The K_f and $1/n$ can be obtained from the intercept and slope of the straight line. The exponent (n) is an index of the diversity of free energies associated with the sorption of the solute by multiple components of a heterogeneous sorbent. When $n < 1$, the isotherm is concave and adsorbates are bound with weaker and weaker free energies, $n > 1$, the isotherm is convex and more sorbate presence in the sorbent enhance the free energies of further sorption and $n=1$, the isotherm is linear and system has a constant free energy at all adsorbate concentrations⁸¹.

In the present study, the value of n at equilibrium was below unity, suggesting favorable adsorption. Furthermore, the values of the dimensionless factor, R_L , were between 0 and 1. This also suggested a favorable adsorption of Cu (II) and Cd (II) using PSS-AC.

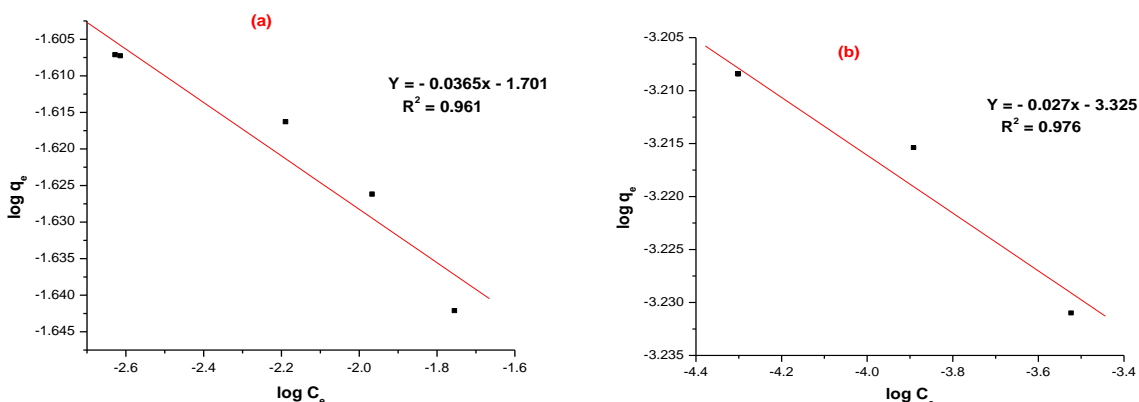


Figure 10: Freundlich plot for Cu (II) (a) and Cd (II) (b) removal using PSS-AC

Table 5: Results of isotherm models for the removal of Cu (II) and Cd (II) ions using PSS-AC at 30°C

Heavy metal ion	Langmuir isotherm			Freundlich isotherm			R_L
	q_m (mg/g)	b_L (dm ³ /g)	R^2	K_f (mg/g)	$1/n$ (L/mg)	R^2	
Cu (II)	43.48	76.56	0.9997	- 0.0365	0.588	0.961	0.061
Cd (II)	172	1656	0.9999	- 0.027	0.300	0.976	0.11

4.6 Adsorption Kinetic Studies

The adsorption kinetics describing the contact time in the removal of Cu (II) and Cd (II) is one of the characteristics defining efficiency of the adsorption. The adsorption kinetics of adsorbent depends on the properties of the adsorbate, the experimental conditions, temperature, concentrations and pH values. Each combination of adsorbent and adsorbate has a unique metal ion-adsorbent interaction. To explain adsorption kinetics of Cu (II) and Cd (II) ions by PSS-AC at 30⁰C both pseudo-first order and pseudo-second order kinetic models⁵⁵ were submitted. The predictability between experimental data and the values expected from the model were expressed by the correlation coefficient (R^2 , whose values close or equal to 1).

4.6.1 Pseudo-first order

The values of q_e and K_1 for the pseudo-first order kinetic model were determined from the intercepts and the slopes of the plots of $\log (q_e - q_t)$ versus time, respectively from Figure 11.

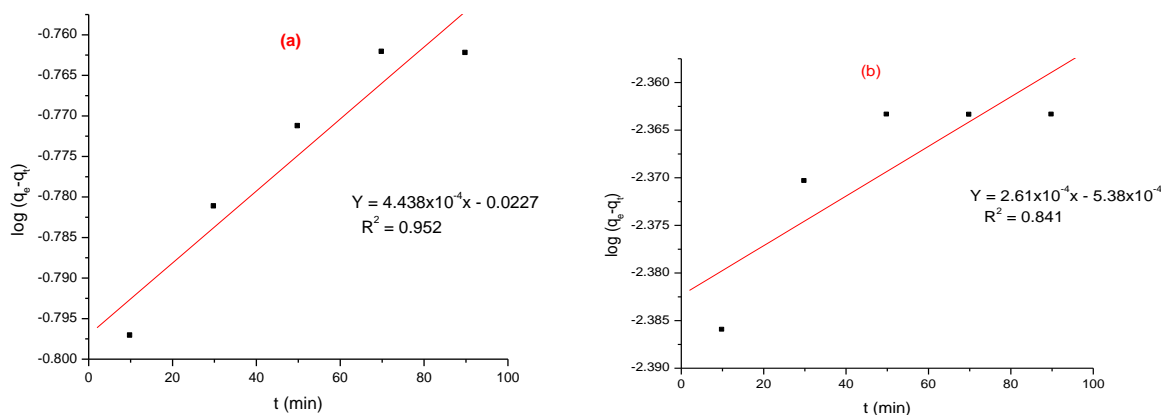


Figure 11: Pseudo-first order sorption kinetics of Cu (II) (a) and Cd (II) (b) using PSS-AC

4.6.2 Pseudo-second order

The pseudo-second-order plot of t/q_t versus t is a straight line as shown in Figure 12. The K_2 and q_e values determined from the slopes and intercepts of the plot respectively are presented in Table 6. The results indicate that the kinetic behavior of Cu (II) and Cd (II) adsorption on activated carbon from pumpkin seed shells can be satisfactorily explained with the pseudo-second order adsorption equation.

Hence, the pseudo-second order model is useful for the kinetic studies in the present investigation which has been successfully applied to several adsorption systems⁵⁶.

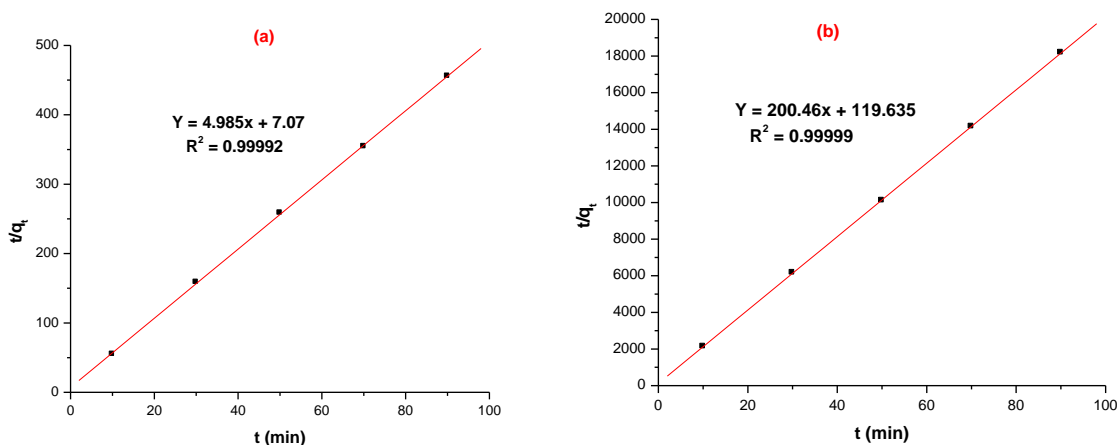


Figure 12: Pseudo-second order sorption kinetics of Cu (II) (a) and Cd (II) (b) using PSS-AC

Table 6: Kinetics parameters for the adsorption of Cu (II) and Cd (II) using PSS-AC at 303 K

Pseudo-first order					Pseudo second order		
Heavy metal ion	q_e exp. (mg/L)	q_e cal (mg/L)	$K_1(\times 10^{-4} \text{ min}^{-1})$	R^2	q_e cal (mg/L)	K_2 (g/mg min)	R^2
Cu (II)	2.5	0.0227	4.438	0.952	2.45	4.985	0.9999
Cd (II)	6.19	0.054	2.61	0.841	5.58	200.46	0.99999

exp. (Experimental result), *cal.* (Calculated values)

4.7 Thermodynamic Study

The thermodynamic parameters were calculated to understand thermodynamic feasibility and to confirm the nature of the adsorption process. The magnitude of Gibbs free energy change, ΔG° obtained is negative demonstrating that the adsorption is rapid and spontaneous. The negative value of ΔG° ensures the feasibility of the process. Generally, ΔG° values range from 0 to -20 KJ/mol for physical adsorption and -80 to -400 KJ/mol for chemical adsorptions⁸². Thus, in this study the $\Delta G^\circ_{\text{ads}}$ values are negative number indicating that the adsorption is mainly physical. $\Delta S^\circ_{\text{ads}}$ and $\Delta H^\circ_{\text{ads}}$ were obtained from the slope and intercept of a linear plot of $\ln K_c$ against $1/T$ respectively (Figure 13).

The low values of ΔH^0 give clear evidence that the interaction between the metal ions and the PSS-AC was weak. On this basis, the adsorption concluded by Cu (II) and Cd (II) with PSS-AC is a physical adsorption process⁸³. The positive value of entropy, ΔS^0 represents an increase in the degree of freedom of the adsorbed species and some changes that occur in the internal structure of PSS-AC during the adsorption process. Similar types of observation were reported previously for removal of lead from waste water by using activated palm ash⁸⁴.

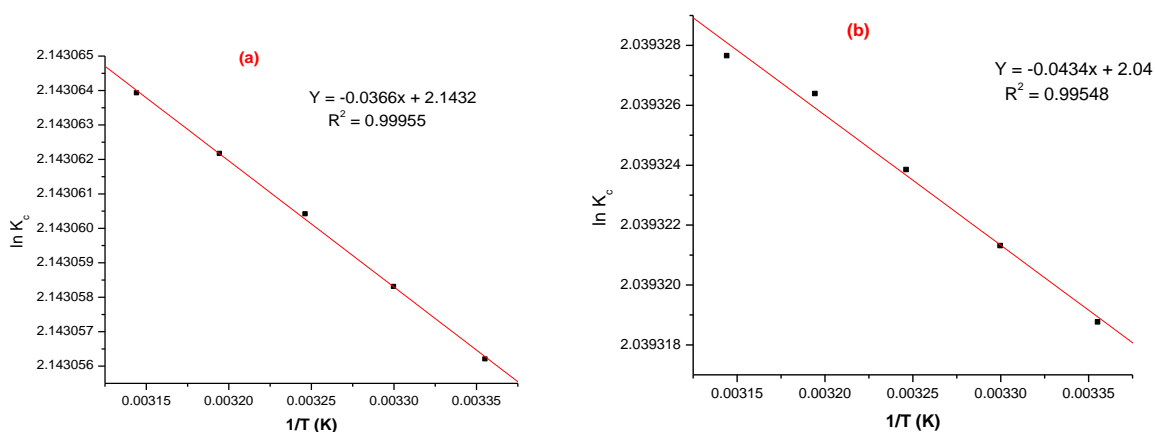


Figure 13: Linear plots of $\ln K_c$ versus $1/T$ for the adsorption of Cu (II) (a) and Cd (II) (b) using PSS-AC

Table 7: Thermodynamic parameters for the a adsorption of Cu (II) and Cd (II) using PSS-AC at different temperatures

Heavy metal	T (K)	$\ln K_c$	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (kJ/mol.K)
Cu (II)	298	8.525453	- 5.31	2.14	-0.0366
	308	8.525489	- 5.49		
	313	8.525504	- 5.58		
	318	8.525519	- 5.67		
Cd (II)	298	7.685372	- 5.05	2.04	-0.0434
	308	7.685411	- 5.22		
	313	7.68543	- 5.31		
	318	7.68544	- 5.39		

5. CONCLUSION AND FUTURE PROSPECTIVE

It is needed to detect Cu (II) and Cd (II) concentration in drinking water by simple, accurate and sensitive method by using AAS and also to provide a suitable, environment friendly and cost effective removal process to save millions of people all over the world from poisoning of these metals. The study indicated that PSS-AC could be used as an effective adsorbent material for the treatment of copper and cadmium from drinking water. It is concluded from this study that the adsorption is a valuable tool for controlling the level of aqueous Cu (II) and Cd (II) pollution.

Characterization of H₃PO₄ activated pumpkin seed shells using FT-IR showed slight differences in the peaks due to the presence of functional groups before and after adsorption of Cu (II) and Cd (II) ions. The majority of the functional groups were aromatic carbon containing in both the cases. The scanning electron microscope (SEM) and EDX analysis clearly indicates significant changes to the surface morphology; and the elemental composition of the adsorbent before and after adsorption of the metals.

The adsorption of Cu (II) and Cd (II) using PSS-AC is found to be contact time, initial metal ion concentration, pH and adsorbent dose dependent. The adsorption kinetics provides better correlation of the sorption data by a pseudo-second order kinetic model than the pseudo-first order model for both metals; this suggests that the pseudo-second order model satisfactorily describe the adsorption process. The Langmuir adsorption isotherm model was better used to represent the experimental data. Adsorption was increased with increasing initial metal ions concentrations and adsorbent. The thermodynamic parameters ΔG^0 , ΔH^0 and ΔS^0 showed a chemically favored, spontaneous and endothermic adsorption.

It is important to remark that pumpkins are very cheap and highly available material. According to the results obtained for the removal of Cu (II) and Cd (II), the pumpkin seed shells can be used for the removal of other metals also like lead, zinc, chromium, etc. Experiments can be performed for these metals also to see how much effective this pumpkin seed shells are for the removal of other metals.

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