



HAWASSA UNIVERSITY
COLLEGE OF NATURAL AND COMPETITIONAL SCIENCE
DEPARTMENT OF CHEMISTRY

REMOVAL OF SELECTED TRACE METALS FROM WASTE WATER
USING SOURSOP (*ANNONA MURICATA L.*) SEED

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HAWASSA, ETHIOPIA
MARCH, 2025

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**A THESIS SUBMITTED TO THE DEPARTMENTS OF CHEMISTRY OF
NATURAL AND COMPUTATIONAL SCIENCE, SCHOOL OF POST
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**IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
MASTER DEGREE OF SCIENCE IN CHEMISTRY**

HAWASSA, ETHIOPIA

MARCH, 2025

DECLARATION

I, Wondimagegn Birhanu the undersigned, declare that this M.Sc. thesis entitled “**removal of selected trace metals from wastewater using soursop (*annona muricata L.*) Seed**” is my original work has not been presented for a degree or diploma to any other university and that all sources or materials for the thesis has been duly acknowledged.

Declared by:

Wondimagegn Birhanu

Signature: _____

Date: _____

This thesis has been submitted for examination with my approval as university advisor.

Advisor:

Ermias Haile (Assistant professor)

Signature: _____

Date: _____

HAWASSA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ADVISOR'S APPROVAL SHEET-I

This is to certify that the thesis entitled “**Removal of selected trace metals from wastewater using soursop (*annona muricata L.*) Seed** submitted in partial fulfillment of requirements for the degree of Master of Science in Chemistry at Hawassa University. A record of original research carried out by Wondimagegn Birhanu (I.D.NO:CHEM/101/ 09, under my supervision, and no part of the thesis has been submitted for any other degree or diploma. The assistance and help received during the course of thesis investigation have been duly acknowledged. Therefore, I recommended that it be accepted as fulfilling the thesis requirements.

Ermias Haile (Assistant professor)

Name of advisor

Signature

Date

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LIST OF ABBREVIATIONS AND SYMBOLS

AC	Activated carbon
FAAS	Flame Atomic Absorption Spectrometry
FTIR	Fourier Transform Infrared spectrometry
SEM	Scanning Electron Microscope
UV-VIS	Ultra violet Spectrometry

ABSTRACT

The effective removal of heavy metals from industrial wastewater is among the most important issues for many industrialized countries. Removal of lead (II), nickel (Ni) and copper (II) from aqueous solutions were studied using adsorbent prepared from soursop (annonamuricata l. Seed. The surface groups present on the adsorbent surface were determined by the Fourier Transform Infrared Spectroscopy (FTIR) analysis. Batch adsorption experiments were performed as a function of pH, contact time, initial concentration, temperature and adsorbent dose. The optimum pH required for maximum adsorption was found to be 6,6 and 5 for lead (II), nickel (Ni) and copper (II) respectively. The maximum contact time for the equilibrium condition is 90 min at the sorbent dose rate of 0.16 g. The maximum efficiencies of lead, Nickel and copper removal by adsorbent were 92%, 93 % and 94 %, respectively. Thermodynamic investigation stated endothermic and spontaneous nature of the system with the participation of a chemical adsorption process. Equilibrium data were represented better by the Freundlich model than the Langmuir model by which describes multilayer adsorptions. The linear regression analysis of kinetic data confirmed that pseudo-second order rate expression.

Keywords: Adsorption, Heavy metal, Pollution, Removal efficiency, Soursop

1. INTRODUCTION

1.1. Background of Study

Water bodies are imperative for human existence, support aquatic life and sustain other uses relies on some trace elements present in the water body. However, water pollution is one of the growing concerns of worldwide. Wastewater discharged into the environment from various industries and households constitute the major causes of water pollution. Metallic ions in wastewater is of a great concern of water pollution because their presence and accumulation cause toxicity which affect many lives, (Ko et al, 2000).

Direct discharge of wastewater containing metallic ions with concentrations above the permissible limits will have severe toxicological effects on humans' health the_deteriorate water quality and aquatic ecosystem (NWQRL, 2020). Toxic metallic ions can enter the food chain, accumulate in the aquatic ecological system, and cause harmful effects on humans, plants, animals, and the environment (Afroze&Sen 2018). The use of various industrial products over the past few decades has seriously contributed to a rise in the flow of metallic compounds into household wastewater and has raised significant ecological and human health threats (Syafiq*et al*, 2021). An increase in population the aquatic ecosystem Thus, analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health.

Because of their toxicity and non-biodegradability properties, trace metals in wastewater have many opposing effects. The release of trace metals in wastewater has many adverse impacts on environmental and human health problems (European Commission, 2002). The health difficult of trace metals are bioaccumulation or magnification, which may raise concentration to poisonous level (Corcoran, E 2010).

Nevertheless extreme environmental pollution and human health problems caused by toxic trace metals can result in endless contaminated stages of exposure and consequently clinical poisoning (Morel,and Price,2003).Wastewater discharged from domestic use and industrial effluent may contain many toxic heavy or trace metals. Metals existing in high or even low concentrations must be effectively removed from the waste water.

Numerous techniques have already been implemented to remove trace metals concentration in aqueous solutions, including ion exchange, chemical precipitation, electrochemical deposition,

ultra-filtration (Zafar et al., 2020; Chuanbin et al., 2022). Conventional wastewater treatment methods have high cost of labor, chemicals consumption and sludge handling problem (Chan *et al.*, 2009). Nevertheless, the high cost of these technologies makes them unfeasible for widespread use, especially in developing nations. Adsorption in particular is much preferred due to high and fast removal efficiency, relatively low cost, and design simplicity (Karimi et al. 2019). The biosorption technique is another alternative method to solve such problems because of its portability, low cost, and potent efficacy (Haidong&Ke, 2020).

Conventional biosorbentssuch as activated carbons (ACs) might not be favorable because they are costly to produce and regenerate (Amanda et al., 2021). Thus, the use of natural adsorbents derived from renewable biomaterials with a lower risk to the environment has gained more attention (Li et al. 2007, Wang et al. 2020). Therefore, this study conducted with the aim of determine the removal of selected trace metals (nickel, lead and copper) from aqueous solutions using Soursop (*Annona Muricata*) seed

1.2. Statements of the Problem

Wastewater from different sources is a widely known source of metal pollution in aquatic bodies as well as surface contamination. Trace metals in wastewater are the major causes of water and environmental pollution. Trace metals are toxic, persistent, carcinogenic and mutagenic in nature. In the last few decades, industrialization in many regions has increased the discharge of trace metals in wastewater into the environment and aquatic ecosystems. Because of their toxicity and non-biodegradability properties trace metals in wastewater have many opposing effects. The release of trace metals in wastewater has many adverse impacts on the environmental and human health problems (European Commission, 2002). Thus, removing trace metals from wastewater using safe, eco-friendly, easily available and low-cost adsorbents have become important. Therefore, this study was conducted to remove selected trace metals from wastewater using Soursop (*Annona Muricata*) seed.

1.3. Objectives of the study

1.3.1. General objective of the study

- ❖ The general objective of this study was to determine the removal of selected trace Soursop (Annona Muricata) seed and evaluate their efficiency to remove heavy ions Pb (II), Ni (II) and Cu (II) from contaminated water.

1.3.2. Specific objectives of the study

The specific objectives of this study were

- pH and temperature.
- To remove selected trace metal ions from contaminated water.
- To describe adsorption capacity of using Soursop (Annona Muricata) seed to remove nickel, lead and copper ions.
- To study the adsorption isotherm by Langmuir and Freundlich isotherm.
- To undergo thermodynamic and kinetic Analysis.

1.4. Significance of the study

This study is significant for the following reason Suggests the effectiveness using Soursop (Annona Muricata) seed as adsorbents to remove trace metals from waste water Provides practical information on how effective using Soursop (Annona Muricata) seed to remove toxic metal ions from waste water. Serve as reference for anyone who is interested to study further on the issues.

1.5. Scope of the study

The scope of this study were to collected the locally available adsorbents of Soursop (Annona Muricata) seed, optimize the operating parameter, validate the polluted purification, test the removal of Pb, Ni, and Cu by FAAS, and results were calculated and fitted using the two adsorption isotherm model.

2. LITERATURE REVIEW

2.1. Waste water

Waste water is any water that human uses have contaminated. Waste water is used water from any combination of domestic, industrial, commercial or agricultural activities surface runoff or storm water and any sewer inflow or sewer infiltration (Babel , and Kurniawan , 2003). Waste water can contain Trace metals, physical, chemical and biological pollutants. Water is mainly polluted with organic and inorganic sediments, radioactive elements and Trace metals (El-Said et al ,2012). Trace metals can frequently be found in manufacturing wastewater and their release to the environment carries a serious threat due to their harmfulness to aquatic and global life which contains humans.

2.2. Trace Metals

Trace metals are natural elements characterized by their rather high atomic mass and their high density. Trace metal is entirely applied to a group of metals and metal-like elements with density greater than 5 g/cm³ and atomic number above 20 is toxic or poisonous at low concentrations (Karvelas, M., Katsoyiannis, A., & Samara, C. (2003). Trace metals are elements having atomic weights between 63.5 and 200.6 g. (Duffus, J. H. 2002). Trace metals such as lead, copper, Zinc, chromium and cadmium are associated with environmental pollution and human health problems. According to the Lasat MM (2000), Trace metals of urgent environmental concern are lead, chromium, mercury, cadmium, copper, zinc, and iron (Duffus, J. H. 2002). Trace metal poses a great health risks to all living organisms upon long-term exposures (Volesky B, 2003). On the other hand toxic metals for example Pb, Cd, As and Hg are not required by the body and they produce deleterious effects upon exposure even at very low concentrations (Pivetz BE (2001).

2.3. Effects of Trace Metals on Humans and Environment

Some trace metals have bio-importance as trace elements but the biotic effects of many of them inhuman biochemistry are of great concern. Hence there is a need for proper understanding of the mechanism involved such as concentration and oxidation states, which make them harmful. The release of heavy metals from industry on a large-scale had an adverse impact on the environmental health (Zein, R and Suhaili, F 2010). It is also important to know their source, leaching process, chemical conversions and their mode of deposition in polluting the environment, which essentially supports life. These metals are released to the environment by

both natural and anthropogenic means, especially mining and industrial activities, and automobile exhausts. They leach into underground waters, moving along water pathways and eventually depositing in the aquifer, or are washed away by run-off into surface waters there by resulting in water and subsequently soil pollution. Poisoning and toxicity in ecosystem occur frequently through exchange and co-ordination mechanisms. When ingested, they form stable bio-toxic compounds, thereby mutilating their structures and hindering bio- reactions of their functions (Samarghandi, M, 2007)

2.4. Adsorption

Conventional wastewater treatment methods have high cost of labour, chemicals consumption and sludge handling problem (Chan *et al*, 2009). The biosorption technique is another alternative method to solve such problems because of its portability, low cost, and potent efficacy (Haidong&Ke, 2020). Adsorption method is an important process in the physicochemical treatment of municipal wastewater' a treatment which can be economically low cost meet today's higher effluent typical and water reuse necessities.

Different materials have been used as adsorbents but many of them are not without drawbacks. Conventional biosorbents such as activated carbons (ACs) might not be favourable because they are costly to produce and regenerate (Amanda et al., 2021). Synthetic materials such as polymers have been developed as adsorbents for heavy metals removal. However, prolonged and extensive use of synthetic adsorbents will lead to secondary pollutants in the form of by-products (Wang et al. 2020).

The use of natural adsorbents derived from renewable biomaterials with a lower risk to the environment has gained more attention (Li et al. 2007, Wang et al. 2020). *Annonamuricata* L. fruit or soursop has many functional groups such as -OH (hydroxyl), -NH₂ (amino), -COOH (carboxylic acid), C-O-C (ether), and aromatic rings (Sawant&Dongre 2014, Anaya Esparza &Montalvo-González 2020), which play a dynamic role in the metal binding mechanisms. These functional groups originate from chemical components such as lignin, cellulose, hemicellulose, fatty acids, lipids, sugars, and proteins (Menzes et al. 2019). Untreated and chemically treated *A. muricata* L. seeds have been used as an adsorbent to remove heavy metal ions (Obboh&Aluyor 2008, Kurniawan et al. 2014) from their aqueous solutions. Obboh&Aluyor (2008) studied the

adsorption of four heavy metal ions using untreated *A. muricata*L. seeds powder under batch mode.

2.5. Factors affecting adsorption capacity

2.5.1. Effect of Contact Time on Metal Ions adsorption

Metal Ions adsorption was performed based on the effect of contact time against an initial concentration and an optimum pH of each metal. The assay was carried out by various contact time 15-90 minutes with a 15 minute interval. Adsorption by using Electric Arc Furnace Slag shows the maximum value after 300 minutes (X Chen, WH Hou, GL Song, and QH Wang, 2011), Adsorption by using Xanthium Pensylvanicum shows the maximum value after 90 minutes (JaberSalehzadeh, 2013)

2.5.2. Effect of pH on Metal Ions adsorption

Metal adsorption on the surface of biomass materials has been described in the molecular mechanisms which may include the exchange of cations in the interlayer, and the specific adsorption due to the surface complexation. Hydrogen ions affect metal complexation because it has a great affinity for adsorption. It was well-established that the adsorption of heavy metal ions by bio sorbent depends on the pH (Olu-owolab BI, Oputu and OU Adebowale) 2012).

In a very acidic pH, ion acts as a positive charged species (Umar Farooq, Janusz A. Kozinski, Misbahul 2010). Neutralizations of negative charges reduce the hindrance to diffusions and leads to more active adsorption sites. With increase in pH from 5 to 9, the degree of protonation of the adsorbent functional group decreased gradually and hence removal was decreased. A close relationship between the surface basis of the adsorbents and the anions is evident. This is similar to the findings of others, where the interaction between oxygen-free Lewis basic sites and the free electrons of the anions, as well as the electrostatic interactions between the anions and the protonated sites of the adsorbent are the main adsorption mechanism (Leon et al., 1992; Radovic et al., 1997; Faria et al., 2004).

2.5.3. Effect of Temperature on Metal Ions adsorption

Adsorption involves specific relations between the properties of activated carbon and the solute temperature. Therefore, the quantitative effects of temperature are not the same with all carbon and solutes. The extent of adsorptions should increase with decreasing temperature because the

adsorptions reactions are exothermic. However, increased temperature also increases the rate of diffusions of the solute through the liquid to the adsorptions sites, which eventually leads to increased adsorptions. An important difference in the adsorptions of solutes versus gases is found in the role of temperature. An increase in temperature increases the tendency of a gas to escape from the interface and thus diminishes adsorptions.

2.6. Kinetics of Adsorptions

In an adsorptions system, equilibrium is established between the adsorbent and the adsorbate in the bulk phase. The definitions of adsorptions kinetics is the rate of approach to equilibrium. Adsorptions equilibrium does not appear instantaneously because the rate of adsorptions is usually limited by the following mass transport mechanisms and depends both on the properties of the adsorbent and the adsorbate. The adsorption data of will be analyzed using the non-linear and linear kinetics models to further investigate the rate of metal ions adsorption. The non-linear pseudo-first-order (PFO) and pseudo-second-order (PSO) models (Ho & McKay 1998).

2.7. Adsorption Equilibrium Study

The successful representation of the dynamic adsorptive separation of solute from solution by an adsorbent depends upon a good description of the equilibrium between the two phases. Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed. The equilibrium adsorption isotherms were depicted by plotting solid phase concentration (q_e) against liquid phase concentration (C_e) of solute. The adsorption capacity at the equilibrium state was plotted against the equilibrium concentration of metal ions.

The equilibrium adsorption capacity increased with the increase in the initial metal ions concentration possibly due to the increased rate of mass transfer of adsorbate on the adsorbent (Anbalagan et al. 2016)

2.8. Langmuir Isotherm

The original derivation of adsorption isotherm by Langmuir was from Kinetics, with the following assumptions: i) adsorption occurs at definite localized sites, ii) each site can accommodate only one entry, and iii) the energy of the adsorbed entity is the same at all sites on the surface, and is independent of the presence or absence of other adsorbed entities at

neighboring sites. As can be seen from these assumptions, the Langmuir isotherm is valid only for mono molecular adsorption. The Langmuir isotherm is applicable to homogeneous sorption where the sorption of each adsorbate molecule on to the surface has equal sorption activation energy and is represented as follows (Langmuir 1918). The Langmuir isotherm is defined by the following equation:

$$q_e = \frac{Q_o}{1 + bC_e} bC_e$$

Where q_e is the amount of metal adsorbed (mg/g, mmol/g, meq/g), Q_o is the maximum metal uptake by the adsorbent, b is the Langmuir constant and C_e is the final (equilibrium) concentration of the metal. The b parameter reflects the affinity (the lower the b value, the higher the affinity) of the adsorbent for the metal. The Langmuir model is useful in metal adsorption studies because it gives the Q_o and b information.

Generally, higher Q_o and lower b values are required in adsorbents. Also, the equation shows that at low adsorbate concentrations, it efficiently reduces to a linear isotherm. Alternatively, at high adsorbate concentrations, it forecasts a constant monolayer adsorption capacity.

2.9. Freundlich Isotherm

The Freundlich isotherm is usually used to quantify the equilibrium relationship between the amount of adsorbate adsorbed on the carbon and the adsorbate concentration remaining in the solution (Freundlich 1906). Mathematically,

$$qe = K_F C_e^{1/n}$$

where, q_e is the solid phase concentration in equilibrium, C_e is the liquid phase sorbent concentration at equilibrium, K_F is the Freundlich constant and $1/n$ is the heterogeneity factor.

3. MATERIALS AND METHODS

3.1. Chemical and instruments

3.1.1 Chemicals

All the required solutions are prepared with analytical reagents and distilled water. Stock standard solutions (Buck scientific pornographic calibration standards, USA) containing 100 ppm of the metals Cu, Ni, and Pb from which 1000 ppm of intermediate standards obtained were used for 99 % Pb (NO₃)₂ (ALPHA), 98 % Ni(NO₃)₂ (NICE), 95 % Cu(NO₃)₂ (FINKEM), and 37 % HCL, analytical reagents of 97 % NaOH (Central Drug house) of Ltd, INDIA), were used. Distilled water was used rise the apparatus prior to analysis, dilution and preparation of all solutions throughout the experiment.

. 3.1.2. Instruments

Digital analytical balance (ADAM, Model AFP110L, and England) with 120 g loading capacity and \pm 0.0001 precision. Flame atomic absorption spectroscopy (Buck scientific, Model 210VGPAAS, USA) equipped with a deuterium background corrector and air-acetylene flame atomizer was used for the determination of the selected metals (Ni, Cu, and Pb) in water samples.

Fourier Transform Infrared spectrometry (Perkin Elmer Spectrum 65 FTIR spectrometer) and Scanning Electron Microscope (SEM), (Jeol-JSM-IT300LA). Volumetric flask (50 and 1000 ml) was also used during the dilution of sample and preparation of metal standard. An analytical mill (IKA[®], Model A11 basic, IRA), grinding small millmachine were used for grinding and homogenizing the seed sample powder adsorbents and Portable pH meter (Model HI9024, HANNA Instrument) were used.

3.2. Preparation of Soursop seeds *Annona Muricata* L.

Annona Muricata seeds were brought from Hawassa town of Sidama Regional State. The collected seeds were washed with distilled water, and dried at room temperature for 3 days. Dried *Annona Muricata* seeds were peeled to get the seed core and the seeds were grounded the and the seeds were ground in the grinding mill. The ground sour sop seeds were sieved and are of particle size 0.25 to 0.5 mm. This is to allow for shorter diffusion path, thus allowing the

adsorbate (sour sop seeds) to penetrate deeper into the effluent more quickly, resulting in a higher rate of adsorption (Adeyinka et al., 2007).

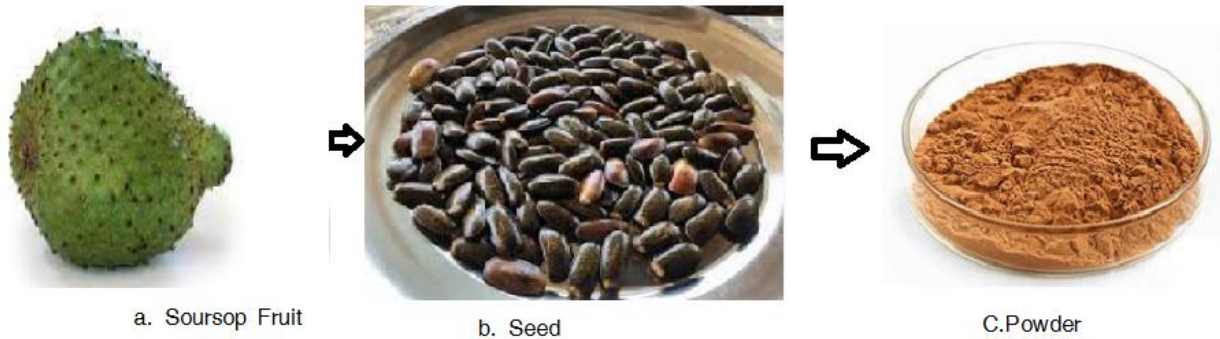


Figure 1: (a) Soursop fruit sample (b) Soursop seed (c) powdered dried sample of soursop

3.2.1 Experimental Design for Preparation of Activated Carbon



Figure 2: (i) powdered dried sample of *Soursop*



Figure 3: (ii) Activated carbon of *Soursop*

- The *Soursopseed* , known locally as 'Gishita,' gathered from the hawassa town for the preparation of activated carbon.
- The material was cleansed by washing with distilled water to eliminate impurities, then dried in an oven at 100 degrees Celsius for 24 hours.
- The dried bark was crushed and grinded. the study and stored in a glassbottle.
- Then, the powder was soaked with different chemicals such as (H₂SO₄, H₃PO₄, and KOH) solution overnight followed by decantation through 0.5 μm sieve and repeated. Then, the filtrate was dried over night at 100 C in a tabular oven.
- Then the activated *soursop* powder was subjected to carbonization at different temperature ranging from 400°C to 700 °C in a tubular furnace for 2 hour.

- After completing the carbonization process it was cooled in desiccators; crushing and sieving to desired mesh size 0.25 to 0.5 μm to eliminate the effect of sieve size in the study and stored in a glass bottle.

3.3. Preparation of metal solutions

All chemicals used were of analytical grade. Stock standard solutions, having concentrations of 1000 ppm. of Ni (II), Cu (II) and Pb (II) were prepared by dissolving 3.18 g of Nickel nitrate ($\text{Ni}(\text{NO}_3)_2$); 1.5980 g of lead nitrate ($\text{Pb}(\text{NO}_3)_2$); 3.801 g of hydrated copper (II) nitrate, ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), and 2.896 g of hydrated Zinc (II) nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) respectively. Then, the solutions were diluted to a final volume of 1000 ml. these solutions were used to prepare working solutions of various concentrations by appropriate dilution.

3.4. Soursop Adsorption experiment

The experiments were carried out in batch mode for the measurement of adsorption capabilities. The bottles with 500 ml capacity were filled with 25 ml of the synthetic wastewater 1 gram of sour-sop seeds (grind). The bottles were shaken for a predetermined period at room temperature in a reciprocating shaker for 2 h at 300 rpm. The separation of the adsorbents and solutions was carried out by filtration with Whatman filter paper No. 42 and the filtrate stored in sample cans in a refrigerator prior to analysis. The rate of adsorption and determination of maximum adsorption capacity of sour-sop seeds were determined using kinetics and isotherm models, respectively.

3.4 Characterization study

3.4.1 FT- IR (Fourier Transform Infrared spectrometry)

The FTIR study was conducted on Soursop adsorbent sample to determine the various organic and inorganic groups on the surface before adsorption. Then FTIR was also conducted after adsorptions so that the organic and inorganic group which participates in the adsorption process was determined by watching the change in frequency that occurred due to the adsorption of heavy metals on adsorbent.

3.4.2 Scanning Electron Microscope (SEM)

Scanning electron microscope is a type of microscope which that is used for the visualization of the porous structure of a material. The Soursop sample was analyzed in a SEM to visualize the porous structure. The magnification was adjusted to get a clear picture.

3.5. Batch adsorption study using Soursop prepared at optimum point

3.5.1 Effect of adsorbent Dose

The adsorption of heavy metal by adsorbents of Soursop was investigated using the following adsorbent doses: 0.04, 0.08, 0.12, 0.16, 0.20, and 0.24 g was added to different conical flask containing 25 ml of 30 ppm heavy metal solution, the flask was closed and placed in a laboratory shaker, used by keeping other variable constant (at optimal contact time and temperature). After the adsorption time was completed, the adsorbents were centrifuged and removed from the solution, and the concentration of residual heavy metal in each solution was determined using AAS.

3.5.2 Effect of contact time

The effect of contact time on the removal of heavy metal was studied for a period of 105 min. 0.16 g of the adsorbents Soursop was added to a different conical flask containing 25 mL of 30 ppm heavy metal solution, the flask was closed and placed in a laboratory shaker, for each of the different contact times chosen (0, 20, 40, 60, 80, 100, 120, and 140 minute). The content of each flask was filtered and the concentration of residual heavy metal in each solution was determined using FAAS.

3.5.3 Effect of pH

The effect of pH on the heavy metal adsorptions onto Soursop was studied at pH range of 3.0 to 10.0. For this 25 mL of heavy metal solutions with a initial concentration of 30 ppm, was taken in 50 mL Erlenmeyer flasks, and pH was adjusted to pH of 3.0- 9.0 using the required quantity of 1N HCL or 1N NaOH before mixing the adsorbent. Then 0.16 g of Soursop was added to the solutions and shaken in a laboratory shaker at room temperature and at optimum time.

3.5.4 Effect of Temperature

Adsorption involves specific relations between the properties of Soursop and the solute temperature. Therefore, the range of temperature is 25, 30, 35, 40, 45, 50, 55, and 60 C°. The extent of adsorptions should increase with decreasing temperature because the adsorptions reactions are exothermic. However; increased temperature also increased the rate of diffusions of the solute through the liquid to the adsorptions sites, which eventually leads to increased adsorptions. An important difference in the adsorptions of solutes versus gases is found in the

role of temperature. An increase in temperature increases the tendency of a gas to escape from the interface and thus diminishes adsorptions.

3.5.5 Isotherm study/equilibrium study

Equilibrium isotherms were studied by taking 25 ml of 30 ppm mixture of Pb (II), Ni (II), and Cu (II) solutions of (10, 20, 30, 40, 50, and 60ppm) in 50 ml Erlenmeyer flasks. Then 0.16 g of Soursop was added respectively to the solutions and shaken in laboratory shaker. Flame Atomic Absorption spectrophotometer was employed to determine the remaining concentrations of metal ions in each sample after adsorption at the desired time intervals. To establish the adsorptions capacity of adsorbents experimental data was fitted against Langmuir and Freundlich isotherm equations.

3.5.6 Thermodynamics Study

Thermodynamics study were conducted by taking 25 ml a mixture of Pb (II), Ni (II), and Cu (II) solutions with initial concentrations of 30 ppm in 50 ml Erlenmeyer flasks. Solutions was shaken at different temperature (293, 308 and 318 K) and the filtrate was analyzed for the remaining Pb (II), Ni (II), and Cu (II) concentrations. Flame Atomic Absorption spectrophotometer was employed to determine the remaining concentrations of metal ions in each sample after adsorption at the desired time intervals.

4. RESULT AND DISCUSSION

4.1 Characterizations of Adsorbent

4.1.1 FT-IR and SEM analysis

The active functional groups responsible for the adsorption of the metal ions on the surface of the prepared adsorbents were identified by FTIR spectroscopy. Figure. 1 shows the FT-IR spectra of activated carbon of sour-sop seeds samples. The absorption bands in the spectrum showed several functional groups, including carboxyl, aromatic, alkene, hydroxyl, and carboxyl. The spectra of activated carbons exhibited broad peaks attributing to O-H stretching group at 3457 cm^{-1} and intensive peaks of conjugated ketone at 1635 cm^{-1} . The peak that was observed at 2935 cm^{-1} and attributed to the symmetric or asymmetric C-H stretching vibration of aliphatic acids; The peak at 1165 cm^{-1} was related to aromatic C-N stretching. In summary, there were a large number of functional groups in activated carbon, such as C-N, COO-, O-H bonds, which were conducive to the adsorption of heavy metals. After adsorption, the peak intensity shifts this indicated the adsorption process.

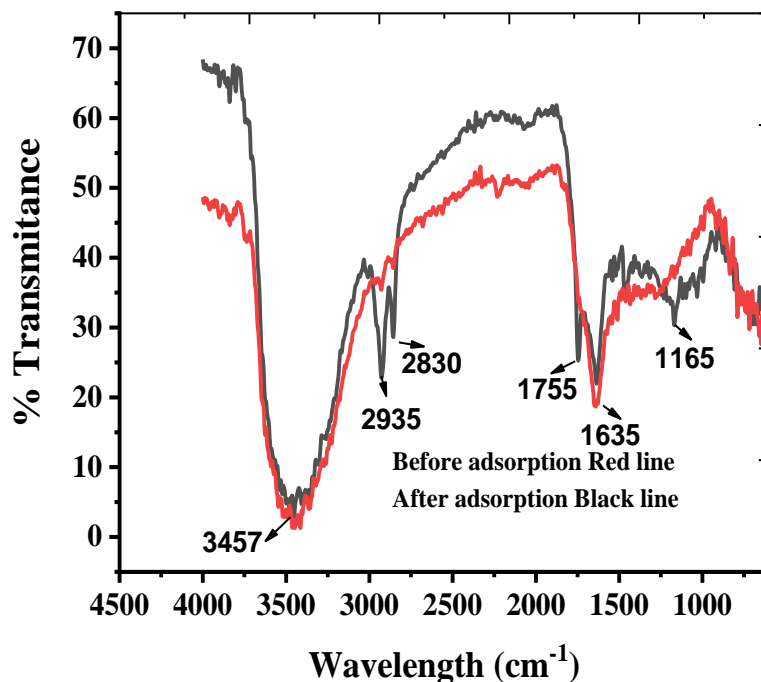


Figure 1: FTIR spectra of adsorbent before adsorption red line and after adsorption black line

4.1.2 SEM analysis

The scanning electron microscopic images were taken with the help of a JEOLJSM-5910 (Japan) at Adama science and Technology University, and the images are shown in Figure 2. It is clear the adsorbent show fairly smooth surfaces for the adsorption of the metal ions.

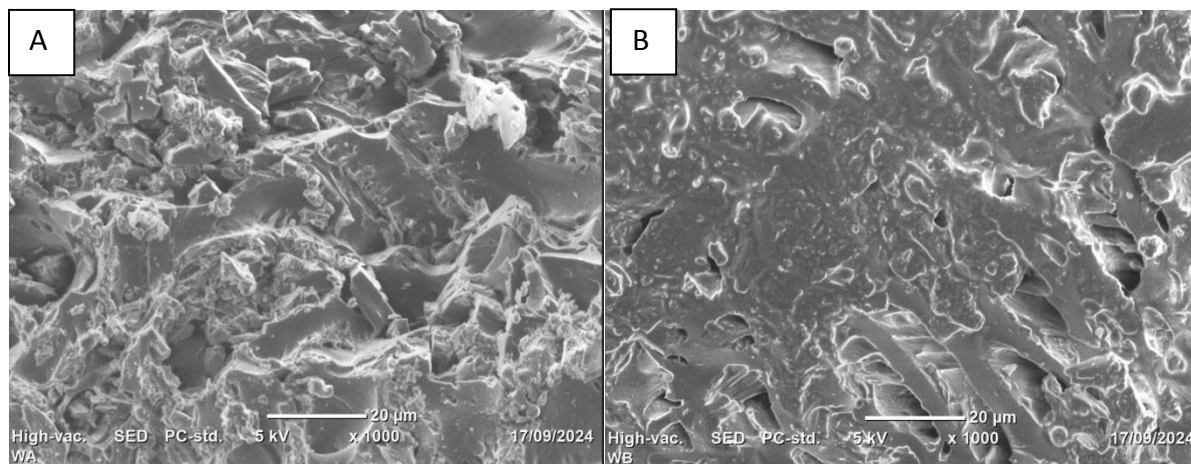


Figure 2: SEM image of adsorbent (A) before adsorption and (B) after adsorption

4.2. Optimization of experimental parameters

4.2.1 Effect of Adsorbent dose

It is important to fix the amount of the adsorbent to design the optimum treatment systems and for a quick response of the analysis. To achieve this aim, a series of batch experiments were conducted with the adsorbent dose of 0.04, 0.08, 0.12, 0.16, 0.20, and 0.24 g per 25 ml of test solution. When the addition of the adsorbent dose increased, the percentage removal of metal ions also increased. A maximum removal of 92% of lead, 93% of nickel, and 94.6% of copper, respectively, was obtained at 0.16 gram of the Soursop. It can be seen from Figure 3 that an adsorbent dose of 0.16 gram is sufficient for optimal removal of metals in aqueous solutions. A further increase in the quantity of biocarbon dose was not have any significant effect on the removal of lead, nickel and copper ions from the solution.

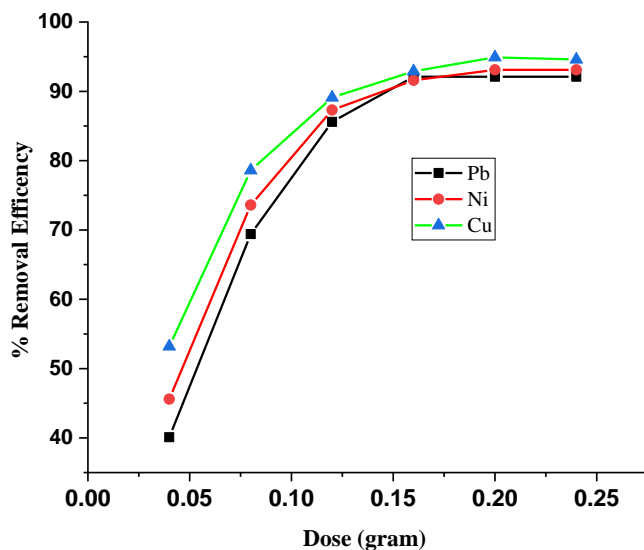


Figure 3 effect of dose of adsorbent

4.2.2 Effect of metal ions concentration

The metal uptake mechanism is particularly dependent on the heavy metal concentration. Initial concentrations of 10 to 50 mg/l of metal ions were selected for the comparative study for the removal of Pb (II) , Ni (II) and Cu(II). Figure 4 shows the effect of metal concentration on the removal of lead, nickel and Copper ions. At the metal ion concentration of 10 mg/l and the optimum dose of 0.16 g of the Soursop the maximum removal of Pb (II), Ni (II) and Cu (II) was achieved within 90 min. The heavy metals are adsorbed by specific sites provided by the acidic functional groups on the biocarbon, while with increasing metal concentrations the specific sites are saturated and the exchange sites due to the excessive surface area of the carbon are filled. It is clear that with increasing initial concentrations, the metal removal decreases.

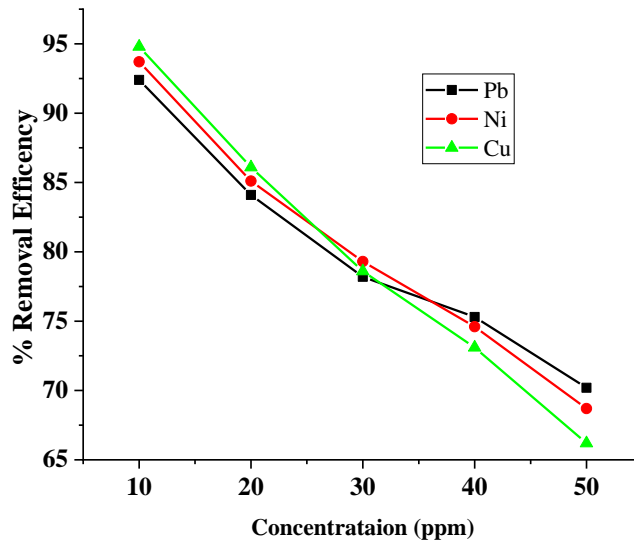


Figure 4: Effect of initial concentration

4.2.3 Effect of contact time

After optimization of the adsorbent dose at 0.16 gram per 25 ml test solution the effect of contact time for the efficient removal of metal ions was studied. The metals showed a steady rate increase of sorption during the sorbate-sorbent contact process and the rate of removal became most insignificant due to a quick exhaustion of the adsorption sites. The rate of metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals. In these studies, 92.6 % removal of lead 93.7 % removal of nickel and 94.8 removal of copper were achieved at 100 min. Further, no significant changes were observed in the removal of both metal ions from the solution after 24 h of equilibration figure 5.

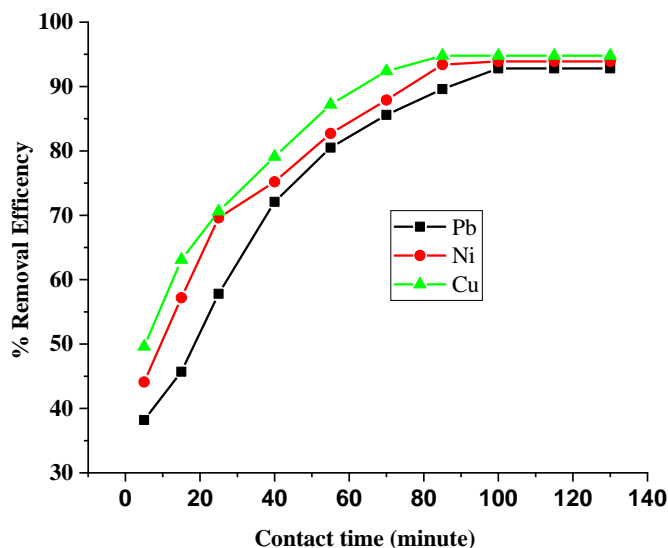


Figure 5 Effect of contact time

4.2.4 Effect of pH

The pH is one of the most important parameters of bio sorption of heavy metals. The biosorption of lead, nickel and copper by activated bio carbon at different pH values is presented in Figure. 6. In the present investigation, the rate of removal of Pb (II), Ni (II) and Cu (II) ions in synthetic wastewater is mainly controlled by pH of the solution. The optimal pH for Pb (II), Ni (II) and Cu (II) removal was 6, 6 and 5, respectively. At pH higher than 6 both metals were precipitated due to the formation of hydroxides and removal due to sorption was very low. At low pH the Concentration of protons was high and metal binding sites became positively charged repelling the Pb (II), Ni (II) and Cu (II) cations. With an increase in pH, the negative charge density on the biocarbon increases due to deprotonation of the metal binding sites, thus increasing metal biosorption.

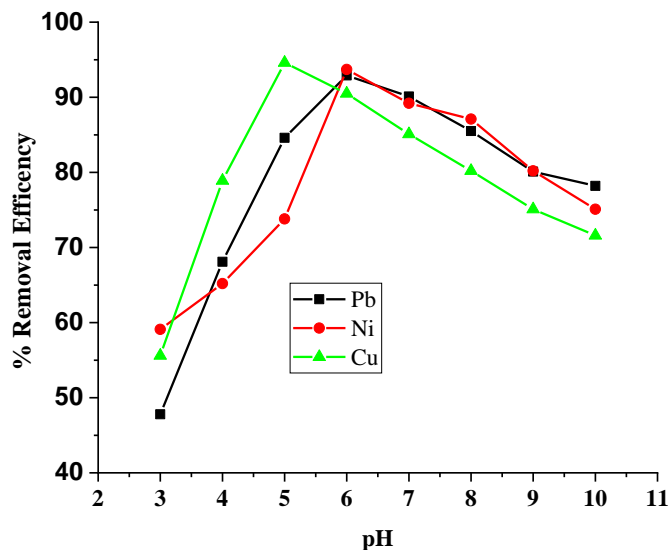


Figure 6 Effect of pH

4.2.4 Effect of temperature

The temperature has strong effects on the intermolecular forces between the adsorbate and adsorbent particles. At low temperature, the kinetic energy of the particles is low and the intermolecular attractive forces are strong, therefore, the adsorbate molecules are easily and strongly attracted to the surface of the adsorbent resulting in the more pronounced adsorption. As the temperature increases, the kinetic energy of both the adsorbate and adsorbent particles increases and the intermolecular interaction between them decreases. As a result, the adsorbate molecules are gradually desorbed from the surface of the adsorbent to decrease the rate of adsorption. As can be seen from Figure 7, the rate of adsorption Pb, Ni and Cu decreases as the temperature increases. Clearly, the rate of adsorption of Pb, Ni and Cu is high at 45°C and decreases as the temperature increases.

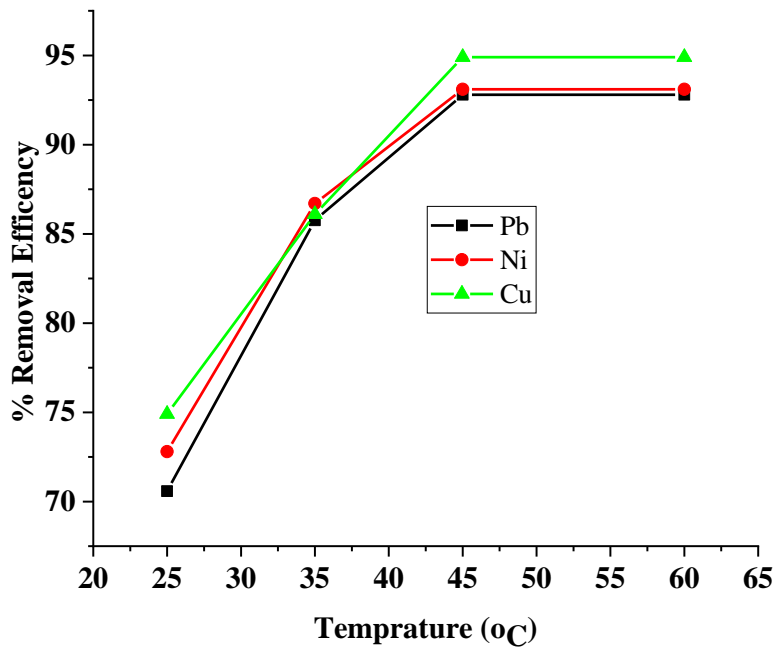


Figure 7 Effect of temperature

4.3 Adsorption Isotherm

Many adsorption models are available in the literature to fit the experimental adsorption data. In this study, the data were fitted using Langmuir and Freundlich models. Each of these models makes use of a parameter q_e (i.e. adsorption capacity per unit mass of the adsorbent at equilibrium) in mg/g.

4.3.1 Langmuir adsorption isotherm

$$q_e = V \frac{(C_0 - C_e)}{w}$$

C_0 =Initial concentration of metal ion (mg/L):

C_e =Equilibrium concentration of in (mg/L)

V =Volume of solution in L

x =Amount of adsorbent used in g the linear form of Langmuir expression:

$$\frac{c_e}{q_e} = \frac{c_e}{q_0} + \frac{1}{b Q_0}$$

Where C_e is the equilibrium concentration of metal solution (mg/L), q_e is the equilibrium capacity of metal on the adsorbent (mg/g), Q_0 is the monolayer adsorption capacity of the adsorbent (mg /g), and b is the Langmuir adsorption constant (L/mg) and is related to the free

energy of adsorption. Langmuir model was fitted to the experimental data as shown in the Table 1 below. The adsorbent was taken as 0.16 g for different concentration of metal solution. The solution inside the conical flask was kept in shaker for 90 min.

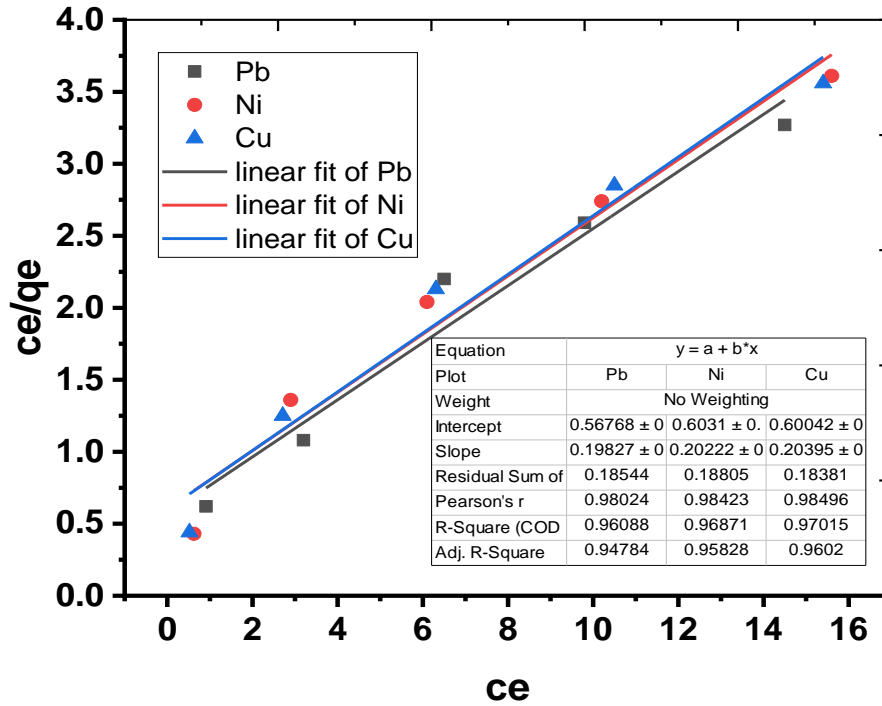


Figure 8: equilibrium study using Langmuir isotherm for activated carbon

4.3.2 Freundlich adsorption isotherm

Table 1, show that the adsorption of metals on adsorbent fits well with the Langmuir model. The fact that the Langmuir model is a good fit to the experimental adsorption data suggests physical adsorption as well as a heterogeneous distribution of active sites on the AC surface. The other Freundlich constant, n , is a measure of the deviation of the adsorption from linearity. If the value of n is equal to unity, the adsorption is linear. If the value of n is below unity, it implies that the adsorption process is unfavorable, and if the value of n is above unity, adsorption is favorable. In the present study, the values of the dimensionless factor, R_L , were between 0 and 1. This also suggested a favorable adsorption between activated carbon and Pb, Ni and Cu.

Table 1: Langmuir and Freundlich Adsorption isotherm constant for the adsorbent for the removal of Pb, Ni and Cu

	Lang	Freund						
	Q_e (mg/g)	bL (L/mg)	R_L	R^2	K_F L/mg	$1/n$	R^2	
Pb	5.05	0.110	0.47	0.94	2.40	2.53	0.97	
Ni	4.92	0.120	0.45	0.95	2.95	2.91	0.97	
Cu	4.95	0.130	0.43	0.96	2.45	2.63	0.99	

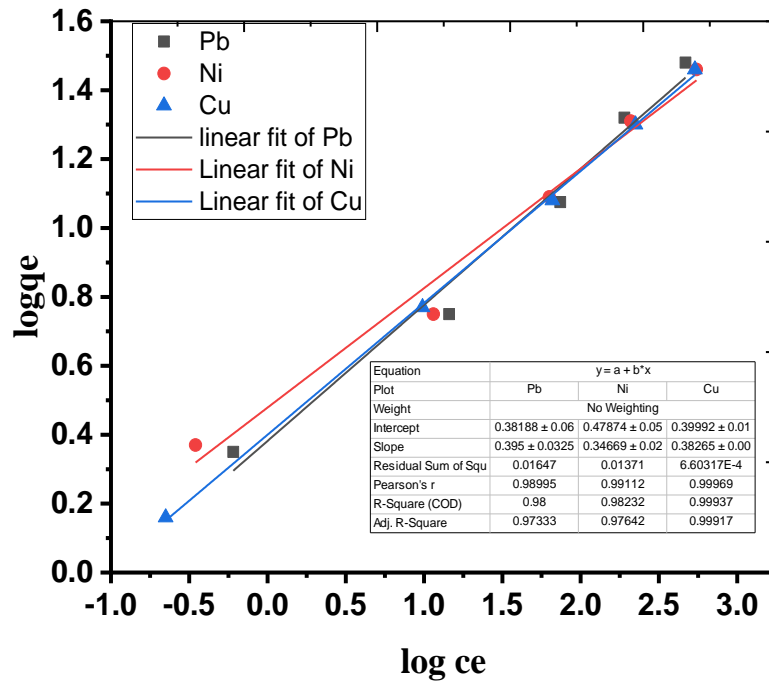


Figure 9: equilibrium study using Freundlich isotherm for the adsorbent

4.4. Adsorption Kinetic Studies

In order to evaluate the kinetic parameters, Pseudo first order and Pseudo second order models were implemented to analyze the experimental data. The pseudo first order equation can be expressed as:

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t$$

Where, q_e and q_t represent the amount of adsorbed (mg/g) at equilibrium and at any time t , k_1 is the first order rate constant (min^{-1}). From the plots of $\log(q_e - q_t)$ versus t in Figure 10, k_1 can be calculated from the slope and theoretical q_e can be obtained from intercepts. Pseudo second order equation can be given by

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

Where, K_2 is the rate constant of second order adsorption. The linear plots of $\frac{t}{q_t}$ versus t determine $1/q_e$ as slope and $\frac{1}{K_2 q_e^2}$ intercepts. The linear plots of pseudo first and pseudo second order model are shown in Figure 10 and 11. But the calculated q_e (mg/g) values obtained from Pseudo first order kinetics did not agree well with the experimental (mg/g) values were shown in

Table 2. Thus, it can be concluded that it is not appropriate to use the Pseudo first order kinetic model to predict the adsorption kinetics for Pb, Ni and Cu the adsorbent for the entire adsorption period. On the contrary, the correlation coefficient, R^2 for the pseudo second order kinetic model were almost equal to unity (0.99) for all the concentrations signifying the applicability of the model. Moreover, the calculated q_e (mg/g) values obtained from Pseudo second order kinetics were in good agreement with the experimental (mg/g) values (Table 2). Thus, it appeared that the system under study is more suitably described by pseudo second order kinetics which was based on the assumption that the rate limiting step may be chemisorption concerning valences forces through sharing and exchange of electrons.

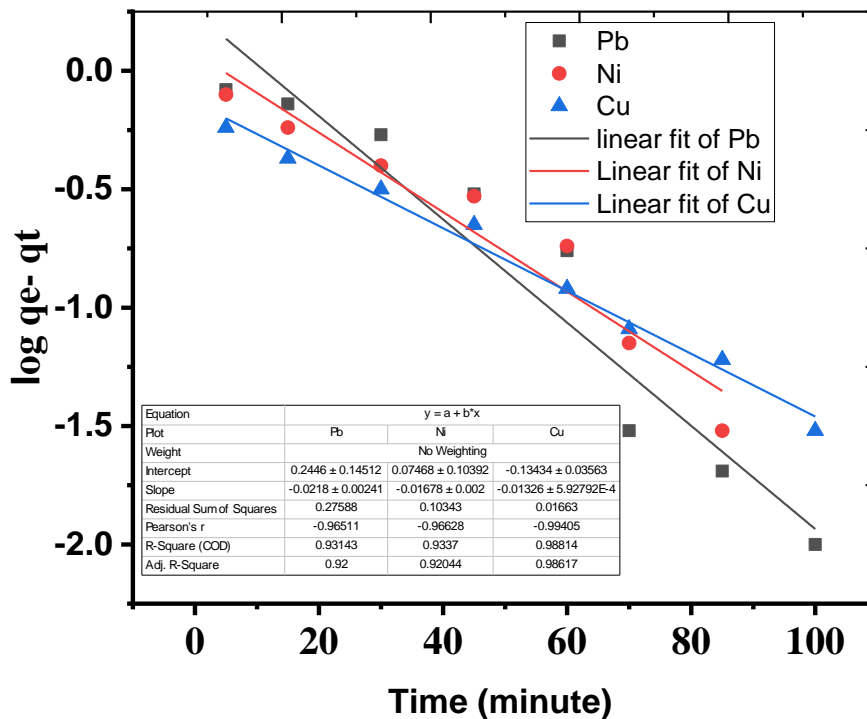


Figure 10: Pseudo first order kinetics model for Pb, Ni and Cu

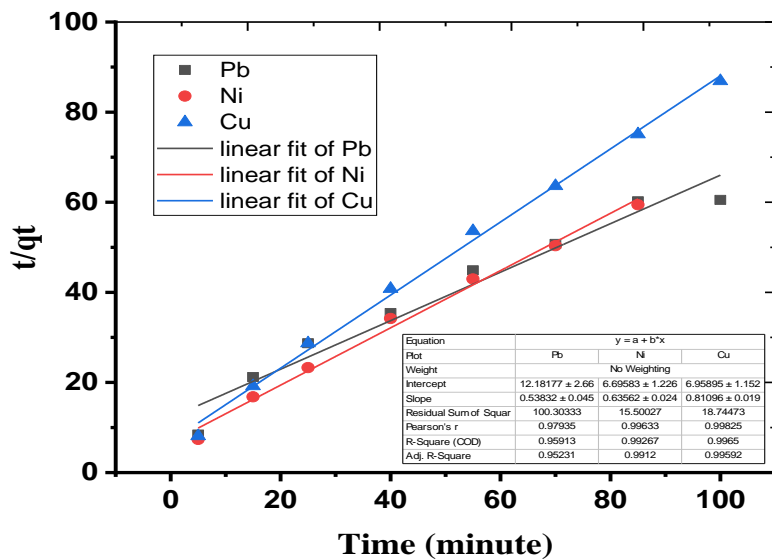


Figure 11: Pseudo second order kinetics model for Pb, Ni and Cu

Table 2: Kinetics parameters for the adsorption of Pb, Ni and Cu at 25 °C

Metal ion	Pseudo first order			Pseudo second order			
	qe(mg/g)	K ₁	R ²		qe(mg/g)	K ₂	R ²
Pb	1.75	0.0218	0.92	Pb	1.88	0.023	0.95
Ni	1.18	0.0167	0.92	Ni	1.58	0.062	0.99
Cu	1, 36	0.0132	0.97	Cu	1.23	0.091	0.99

4.5 Thermodynamic study

The thermodynamic parameters that help us to understand the nature of the adsorption of Pb, Ni and Cu on adsorbents are the standard change in Gibbs free energy (ΔG°), the standard change in entropy (ΔS°), and the standard change in enthalpy (ΔH°). These can be determined using the following equations:

$$\Delta G = -RT \ln K_c$$

Where R is the gas constant (8.314 J/mol. K),

T is the absolute temperature in Kelvin; And K_c (L/g) is the standard

Thermodynamic equilibrium constant defined by q_e/C_e . Similarly, the enthalpy change (H°) from 298 to 318 K was computed from the following equation:

$$\ln K_c = \frac{q_e}{ce}$$

ΔH° ($\text{kJ}\cdot\text{mol}^{-1}$) and ΔS° ($\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) were calculated from the slope and intercept of the linear plot of $\ln k_c$ versus $1/T$. However, the calculated values of thermodynamic parameters are listed in Table 3. The positive value of enthalpy change confirms the endothermic nature of the adsorption process. The enthalpy value for adsorption process may be used to distinguish between chemical and physical adsorption. For chemical adsorption, values of enthalpy change is highest while for physical adsorption is medium. The lowest values of ΔH give clear evidence that the interaction between Pb, Ni and Cu and adsorbent was weak. On this basis we concluded that Pb, Ni and Cu adsorption by activated carbon is a physical adsorption process. The positive value of entropy, ΔS° represents an increase in the degree of freedom of the adsorbed species. The positive value of ΔS° also reflects that some changes occur in the internal structure of adsorbent during 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 -71.84 to -3492.5 KJ/mol for physical adsorption and -247.75 to -274.60 KJ/mol for chemical adsorptions. In this study, the ΔG° values ranged from -0.792 to -3833.58 KJ/mol, indicating that adsorption is mainly physical.

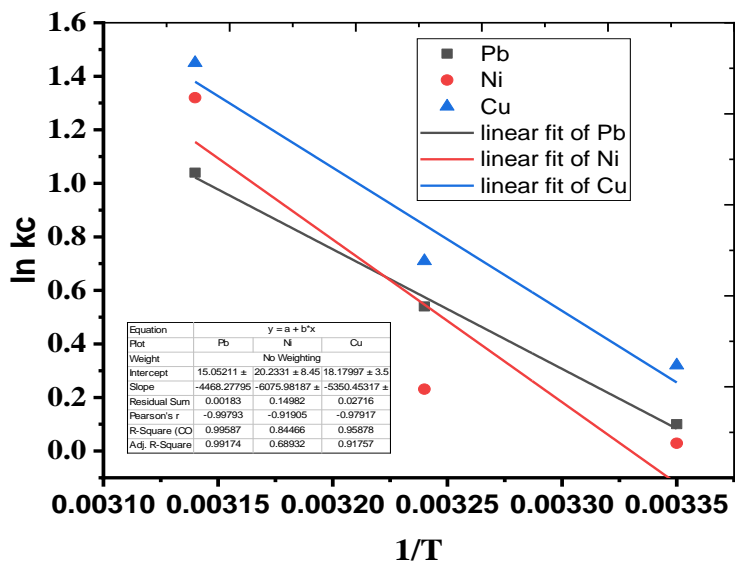


Figure 12: Van't Hoff plot for the determination of thermodynamic parameters

Table 3: Thermodynamic parameters for the adsorption of Pb²⁺, Ni²⁺ and Cu²⁺ at different temperatures.

Metal	T(K)	lnKc	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol.k)
Pb	298	0.10	- 247.75	37146.9	125.12
	308	0.54	- 1382.78		
	318	1.04	- 2749.60		
Ni	298	0.029	- 71.84	50507.5	168.19
	308	0.231	- 591.5		
	318	1.321	-3492.52		
Cu	298	0.32	- 792.82	44479.9	151.06
	308	0.71	- 1818.10		
	318	1.45	- 3833.58		

Table 4: Comparison heavy metal up take capacity using different bioadsorbents at the same pH=6

Heavy Metal	Adsorbents	Removal Efficiency	Reference
Pb(II)	<i>Oriza sativa husk</i>	98 %	(A.Saeed,et al,2005)
	<i>Passiflora Edulis</i>	95.07 %	
	This study	91.58%	
Cu(II)	Banana peel	91.5 %	(G. K and P.S koblewsk, et al, 2010)
	Passflora edulis	93.11 %	
	This study	94.1%	
Ni(II)	Coconut husk	85 %	(C. RajI, et al, 1997)
	This study	93.4%	

4.7. Treatment of contaminated water

Contaminated water sample was used to assess the removal efficiency of Cu(II), Pb(II) and Ni(II) using adsorbent. The adsorption efficiencies of the adsorbents were tested at optimum operating parameters(dose=0.16g, time=90min). The concentrations of selected heavy metal ions in wastewater samples were determined using FAAS. Quality control measures were taken to assess contamination and reliability of data. As indicated in the Table, it has been found that almost 82.78 ± 0.02 , 87.92 ± 0.022 and 85.59 ± 0.074 mg/l metal ion were removed.

Table 5: Results of contaminated water sample Analysis for Pb(II) , Cu(II), and Ni(II).

Heavy metal	*Concentration in contaminated water sample(mg/L)	Adsorbent	*Concentration at equilibrium(mg/L)	%Removal
Cu(II)	5 ±0.016	Soursop Seed	0.9 ±0.05	82.78 ±0.02
Pb(II)	1.49 ±0.2699	Soursop Seed	0.18±0.065	87.92 ± 0.022
Ni(II)	4.06 ± 0.209	Soursop Seed	0.37 ±0.034	90.75 ± 0.074

5. CONCLUSIONS AND RECOMMENDATION

5.1 Conclusion

This study describes the adsorption of Metal ions from aqueous solution by using adsorbent prepared from soursop (*Annona Muricata*) seed. The adsorption was found to be strongly influenced by pH, contact time, initial concentration and temperature. The optimum conditions were maximum removal efficiency occur was at dose of 0.16 gram, initial concentration of 10 ppm, contact time of 90 minutes, pH of 6 and temperature of 45° for removal of Pb (II), Ni (II), and Cu (II) from aqueous solutions. Furthermore, this adsorbent had several reactive surface groups including hydroxyl, and ketone. Both Freundlich and Langmuir models were used to fit the data and estimate model parameters but the overall data is better fitted by Langmuir isotherm at the studied temperature range reflecting surface homogeneity of the adsorbent. The pseudo-second order kinetic model was found to be a better fit for the adsorption of Metal ions by adsorbent. Thermodynamic studies predict that the adsorption is feasible, spontaneous and endothermic in nature at temperatures of 293, 308 and 318 K.

5.2 Recommendation

Based on the result of the study the following ideas were recommended

- Widespread study should be carried out to produce better surface characteristics through different routes
- Utilization the adsorbent to treat various other pollutants present in water contaminated with heavy metals should be undertaken.
- The future studies should be intensive on applicability of the adsorbent to the real situation on where large volume of waste effluent is being discharged.
- Furthermore, desorption experiments should be carried out in order to recover the adsorbent.

Reference

- Adeyinka A, Liang H, Tina G (2007). Removal of Metal Ion form Waste Water with Natural Waste.School Eng. Technol. 1-8(33): 4.
- Afroze and Sen (2018). A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorpants
- Amanda, L., Geoffrey D., F.& Nigel J.D., G. (2021). Insights into chemical regeneration of activated carbon for water treatment. Journal of Environmental Chemical Engineering, 9, 105555 <https://doi.org/10.1016/j.jece.2021.105555>
- Babel S, Kurniawan TA (2003) Various treatment technologies to remove arsenic and mercury from contaminated groundwater: an overview. In: Proceedings of the First International Symposium on Southeast Asian Water Environment, Bangkok, Thailand, 24-25 October: 433-440.\
- Chang, F.R., and WU Y.C., (2001).Novel cytotoxic annonaceousacetogenins from Annonamuricata. Journal Natural Product, 64 (7): 925-931.
- Corcoran, E 2010.Sick Water: The Central Role of Wastewater Management in Sustainable
- Duffus, J. H. (2002). Heavy Metals"-A Meaningless Term? (IUPAC Technical Report) Pure Appl. Chem., 74(5), 793-807.Kuva:PasiValkama
- Duffus, J. H. (2002). Heavy Metals"-A Meaningless Term? (IUPAC Technical Report)Pure Appl. Chem, 74(5), 793-807.
- El-Said AG, Badawy NA, Garamon SE (2012) Adsorption of Cadmium (II) and Mercury (II) onto Natural Adsorbent Rice Husk Ash (RHA) from Aqueous Solutions: Study in Single and Binary System, International Journal of Chemistry 2012: 58-68. 36.
- European Commission.(2002). DG ENV. E3, Project ENV.E3/ETU/2000/0058, Heavy Metals in Waste. Final Repo
- Gong R, Ding Y, Liu H, Chen Q, Liu Z (2005). Lead biosorption and desorption by intact and pretreated Spirulina maxima biomass. Chemosphere. 58(1): 125-130.

- Haidong, H.&Ke, X. (2020). Chapter 8 - Physicochemical technologies for HRP's and risk control. In H. Ren& X. Zhang (Eds.), High-Risk Pollutants in Wastewater (pp. 169-207): Elsevier.
- Ho, Y.S.,and McKay, G., (2000).The kinetics of sorption of divalent metal ions onto Sphagnum peat moss. *Water Resources*, 34:735-742.
- JaberSalehzadeh. Leonardo *Journal of Sciences* 2013;97-104.
- Karimi, S., Yaraki, M.T. and Karri, R.R. 2019.A comprehensive reviewof the adsorption mechanisms and factors influencing the adsorptionprocess from the perspective of bioethanol dehydration. *Renew. Sust.Energ. Rev.*, 107: 535-553.
- Karvelas, M., Katsoyiannis, A., & Samara, C. (2003).Occurrence and fate of heavy metals in the wastewater treatment process. *Chemosphere*, 53, 1201-1210.
- Ko DCK, Porter JF, Mckay G (2000). Optimized Correlation for the Fixed Bed Adsorption of Metal Ions on Bone Char, *Chem. Eng. Sci.* 55: 5819-5829.
- Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica,and platinum. *J. Am. Chem. Soc.*, 40: 1361-1403
- Lasat MM (2000). Phytoextraction of metals from contaminated soil: a review of plant/soil/metal interaction and assessment of pertinent agronomic issues. *J. Hazard. Subst. Res.*, 2(5): 1-25.
- Lee, S.-Y.& Choi, H.-J. (2018). Persimmon leaf bio-waste for adsorptive removal of heavy metals from aqueous solution. *Journal of Environmental Management*, 209, 382-392
<https://doi.org/10.1016/j.jenvman.2017.12.080>
- Leon Y, Leon CA, Solar JM, Calemma V, Radovic LR (1992).Evidencefor the protonation of basal plane sites on carbon.*Carbon*. 30: 797-811.
- Li, Q., Zai, J., Zhang, W., Wang, M. and Zhou, J. 2007. Kinetic studiesof adsorption of Pb(II), Cr(III), and Cu(II) from aqueous solutionby sawdust and modified peanut husk. *J. Hazard Mater.*, 141:163–167.

- Menzes, E.G.T., Oliveira, E.R., Carvalho, G.R., Guimaraes, I.C., and Queiroz, F. 2019. Assessment of chemical, nutritional and bioactive properties of *Annona crassiflora* and *Annona muricata* wastes. *Food Sci. Technol.*, 39(2): 662-672.
- Morel, F. M. M. and N. M. Price. 2003. The Biogeochemical Cycles of Trace Metals in the Oceans. *Science*. 300(5621):944-947. DOI: 10.1126/science.1083545.
- NWQRL (2020). Atlas of Rivers and Open Waterbodies Monitoring Activities, National Water Quality Reference Laboratories (NWQRL), Department of Water Quality Control and Sanitation, *Federal Ministry of Water Resources*, Abuja.
- Oboh and Aluyor (2008). Phenol-formaldehyde cationic matrices substitutes by bagasse – Charcoal. *Res. Ind.* 29:293-297.
- Olu-owolabi BI, Oputu and OU Adebawale. *Sci Res Essays* 2012;7(15):1614-1629.
- Pivetz BE (2001). Phytoremediation of contaminated soil and groundwater at hazardous waste sites. EPA Ground Water Issue, EPA/540/S-01/500.
- R Zein, R Suhaili, F Earnestly, Indrawaty and E Munaf. *Hazardous materials* 2010;181:52-56.
- Samarghandi, M.; Nouri, J.; Mesdaghinia, A.R.; Mahvi, A.H.; Nasser, S.; Vaezi, F. Efficiency Removal of Phenol, Lead and Cadmium by Means of UV/TiO₂/H₂O₂ Processes. *Int. J. Environ. Sci. Technol.* 2007, 4, 19–26. [CrossRed]
- Sawant, T.P. and Dongre, R.S. 2014. Bio-chemical compositional analysis of *Annona muricata*: A miracle fruit's review. *Int. J. Univers. Pharm. Bio Sci.*, 3(2): 82-104.
- Syafiq A.; O. Norzila; A.H.A Wahid; S.K Faisal; A.B. Norshila; T. Muhammad and S.S. Eddy. (2021). A Review on Adsorption of Heavy Metals from Wood-Industrial Wastewater by Oil Palm Waste. *Journal of Ecological Engineering* 2021, 22(3), <https://doi.org/10.12911/22998993/132854> ISSN 2299-8993, License CC-BY 4.0, pp 249–265.
- Wang D. S. Tang H. X. 2001 Modified inorganic polymer flocculants-PFSi: its precipitation, characterization and coagulation behavior *Water Research* 35 3473-3581

Wang, X., Cui, Y., Peng, Q., Fan, C., Zhang, Z. and Zhang, X. 2020. Removal of Cd(II) and Cu(II) from aqueous solution by Na⁺-Modified Pisha Sandstone. *J. Chem.*, 28: 579.

X Chen, WH Hou, GL Song, and QH Wang. *ChemBiochemEng* 2011;25(1):105-114.

Zafar, S., Khan, M.I., Lashari, M.H., Khraisheh, M., Almomani, F., Mirza, M.L., and Khalid, N. 2020. Removal of copper ions from aqueous solution using NaOH-treated rice husk. *Emerg. Mater.*, 3: 857-870.