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Research Article

Adsorption Studies of Pb^{2+}, Cu^{2+} and Cr^{3+} from Aqueous Solution Using *Azadirachta Indica* (Neem) Seed Husk and *Adansonia Digitata* (Baobab) Seeds

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Abstract

The adsorption of Pb^{2+}, Cu^{2+} and Cr^{3+} from aqueous solution using Neem seed husk (NSH) and baobab seed (BS) were studied through the use of batch adsorption system. The adsorbents were prepared by drying at 120°C for 24hours and were characterized using FT-IR, XRD, and SEM analysis. The FTIR spectroscopy revealed the presence of O-H, N-H, C-H, C=C, C=O, and C-O stretching; XRD revealed the particle sizes as 44.51nm for NSH and 42.61nm while the morphology of the NSH and BS were revealed by SEM to be porous for NSH and BS. Various parameters such as, initial metal ion concentration, adsorbent dosage, contact time, Temperature and pH of metal ion solution were investigated in a batch-adsorption System. The adsorption uptake was found to increase with increase in adsorbent dose, contact time and temperature but decreases with the initial concentration. The uptake of the metal ions increases and reaches optimum at pH of 4-6. The maximum adsorption capacity was found to be Pb-NSH (15.267mg/g) and Cu-NSH (19.46mg/g). Adsorption of Cu^{2+}onto NSH fitted Langmuir isotherm model with ($R^2 > 0.93$) while Adsorption of Pb-NSH Fitted Freundlich isotherm Model with ($R^2 > 0.99$). Kinetic data fitted pseudo-second-order model ($R^2 > 0.98$) which was more suitable in explaining the adsorption rate. Thermodynamic data showed that Gibb's free energy (ΔG°) values for all metal ions were negative indicating feasibility and favorability of adsorption. Positive enthalpy change (ΔH°) and Entropy change (ΔS°) values indicate endothermic processes and increase in randomness.

Keywords

Adsorption Studies, Aqueous Solution, Azadirachta Indica (Neem) Seed Husk, Adansonia Digitata (Baobab) Seeds

1. Introduction

Heavy metals are generally referred to those metals which possess a specific density of more than 5 g/cm^3 and adversely affect the environment and living organisms [1]. These are group of pollutants, which are non-bio-degradable in living organisms. [1]. They constitute a very heterogeneous group of elements widely varied in their chemical properties and biological functions The most common heavy metal contaminants are copper, iron, zinc, lead, cadmium, arsenic, manganese, cobalt, chromium, mercury and nickel [2].

Although it is acknowledged that, heavy metals have many adverse health effects and last for a long period of time, heavy metal exposure continues and is increasing in

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many parts of the world. Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for environmental reasons Heavy metals enter the surroundings by natural means and through human activities. Various sources of heavy metals include soil erosion, weathering, leaching and volcanic eruption. Anthropogenic source of heavy metals which result from human activities such as mining, agricultural activities, fossil fuel combustion, refineries, textile and paper industries e.t.c. [1].

This accumulation of the heavy metals is harmful to the environment because these metals generally accumulated in their most stable oxidation states, i.e., As^{3+}, Pb^{2+}, Hg^{2+}, Cd^{2+}, $Cu^{2+}$and Cr^{3+} which further react with body bio-molecules to generate extremely stable bio-toxic compounds which are very difficult to dissociate [3].

The release of heavy metals into the natural environment has resulted in various environmental challenges due to their non-biodegradable and persistent characteristics [4]. The toxicity of heavy metals in humans may result in damage to various physiological systems, such as the central nervous, cardiovascular, and gastrointestinal systems, as well as the lungs, kidneys, liver, endocrine glands, and bones, which may increase the prevalence of degenerative illnesses and cancers [2].

Various methods have been developed for the removal of heavy metals from water, including chemical precipitation, electro dialysis, ultrafiltration, ion exchange, reverse osmosis, phytoremediation, membrane separation, aerobic and anaerobic degradation, chemical oxidation, coagulation, and flocculation. Some of these methods have been shown to be effective, however they have some limitations such as excess amount of chemical usage, accumulation of concentrated sludge that has serious disposal problems, formation of toxic compounds during the process, high cost, and incomplete removal of certain ions and takes long time for heavy metal removal. The adsorption technique, which is based on the transfer of pollutants from the solution to the solid phase, is known as one of the efficient and general wastewater treatment method [5].

The major advantages of adsorption over these conventional treatment methods are low cost, high efficiency, minimization of chemicals, no additional nutrient requirement, and reuse of adsorbent for further metal uptake and possibility of metal recovery [2].

Lowcost adsorbent such as rice husk, maize cob, banana peels, orange peels, wheat shell, water hyacinth, hazelnuts shells, orange peel pith, sunflower, coconut husk, groundnut husk, coconut shell, palm fibres, are used for removal of heavy metals from industrial waste water.

This research, explore the potential of Neem seed husk for possible use as adsorbent for removal of Pb^{2+}, and Cu^{2+} ions from waste water.

Aim

The aim of this work is to determine the potentials of *Azadirachta indica* (Neem) seed husk, and *Adansonia Digitata* (Baobab) husk for the removal of Pb^{2+}, Cu^{2+} and Cr^{3+} ions from aqueous solution for possible use as an adsorbent for heavy metals removal from the environment.

Objectives

The objectives of the study are:

i. To characterize the adsorbents using FTIR, SEM and XRD.
ii. To study the effect of initial concentration, adsorbent dose, time, temperature and pH on adsorption of Pb^{2+}, Cu^{2+} and Cr^{3+}ions.
iii. To study and understand the adsorption equilibrium isotherms for Pb^{2+}, Cu^{2+}, and Cr^{3+} ions removal by Neem seed husk, Baobab seeds and Mahogany leaves.
iv. To study and understand the kinetics of the adsorption process and the thermodynamic parameters for removal of $Cu^{2+,}$ Pb^{2+} and Cr^{3+} ions.

2. Materials and Methods

2.1. Reagents

All reagents used were of analytical grade. These include: $Pb(NO_3)_2$, $CuSO_4$, $Cr(NO_3)_3$, NaOH, and HNO_3

2.2. Preparation of Stock Solutions

1000g/L Stock solutions of $Pb(NO_3)_2$, $CuSO_4$ and $Cr(NO_3)_3$ were prepared according to standard procedures by dissolving 1.5980g, 2.5117g and 4.5775g each in 1L of deionize water. Serial dilution method from the stock solution to obtain different concentration by using the formula below, equation (1).

$$C_1V_1=C_2V_2 \quad (1)$$

Where

C_1 is the concentration of stock solution, V_1 is the volume of the stock solution, C_2 is the concentration of the dilute solution and V_2 is the volume of the dilute solution.

2.3. Sample Collection and Preparation

Neem Seed Husks samples and Baobab seeds were collected within Gombe State University Area. The samples were prepared by using slightly modified method of [6, 7]. The samples were washed with ordinary water thoroughly and with distill water in order to remove impurities and debris present. The sample was dried in oven at about 120°C for 24 hrs. These dried samples were then crushed to a fine powder and sieved with 150mm mesh size sieve. The prepared adsorbents were kept in an airtight bottle awaiting subsequent experiments.

2.4. Sample Characterization

Neem Seed Husk and Baobab Seeds samples were characterized using X-ray diffraction analysis (XRD), Scan Electron Microscopy (SEM) and FT-IR spectroscopy.

2.5. The Batch Adsorption Experiment

Batch adsorption experiment was carried out in order to study the effect of change in initial metal concentration of metal ions, adsorbent dose, contact time, temperature and pH on the adsorption of the Pb^{2+}, Cu^{2+} and Cr^{3+}. The effect of each parameter was studied by keeping others parameters constant. The solutions were then filtered and the filtrates were subjected to AAS analysis.

i. Effect of Initial Metal Concentration

The effect of initial metal concentration on adsorption of Pb^{2+}, Cu^{2+} and Cr^{3+} ions was determine at different concentration of 50, 100, 150, 200, and 250mg/L at room temperature (~25°C). 0.5 g of adsorbents was added 50ml the metal ion solution in each conical flask. The solutions were shaken for 30min at 150rpm. The solutions were filtered using Whatman filter paper and the filtrates were analyzed with AAS.

ii. Effect of Adsorbent Dose

Effect of adsorbent dose on Pb^{2+}, Cu^{2+} and Cr^{3+} ions were determined at different amounts of dosage ranging from 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2g. For each experiment, an accurate quantity of the adsorbents were added to 50 mL of metal ions solution at 100mg/L, at 25°C in 250 ml conical flasks. The solutions were shaken at 150 rpm for 30minutes. The solutions were filtered with Whatman filter paper and the filtrates were analyzed using AAS.

iii. Effect of Contact Time

The effect of contact time on the adsorption process of Pb^{2+}, Cu^{2+} and Cr^{3+} was studied at the following time intervals 10, 20, 30, 40 and 60mins at optimum concentration of 100mg/L for the metal ions, adsorbent dose of 0.5g at temperature of 25°C. 50 ml of the metal ions were transferred into 250ml conical flasks. The solutions were shaken at 150 rpm at different time intervals. The solutions were filtered using Whatman filter paper and filtrate was analyzed with AAS.

iv. Effect of Temperature

The effect of temperature on the adsorption process of Pb^{2+}, Cu^{2+} and Cr^{3+} ions were examined at the following temperatures 25, 30, 35, 40 and 60°C. Then 50ml of 100mg/L metal ions solutions were transferred into 250ml conical flasks, 0.5g of the adsorbents were added in to the flasks. The solutions were shaken at 150 rpm for different temperatures. The filtrates were then filtered and analyzed using AAS.

v. Effect of pH

The effect of pH on the process of adsorption Pb^{2+}, Cu^{2+} and Cr^{3+} ions by the adsorbents was determined at different pH value of 2, 3, 4, 5, and 7 and optimum concentrations of metal ions of at room temperature (~25°C). The pH was adjusted using 0.1M HNO_3 and 0.1M NaOH. 50ml of 100mg/L solutions of metal ions were transferred into 250ml conical flasks, 0.5 g of absorbents samples were added and the solutions were shaken for 30 min at 150rpm. The solutions were filtered whatman No1 filter paper and the filtrate was analyzed with AAS.

2.6. Data Evaluation

The data obtained by AAS was carried out to analyze the amount Pb^{2+}, Cu^{2+} and Cr^{3+} ions adsorbed. The equations 2 and 3 were used to calculate the amount of metal ions adsorbed per unit mass of the adsorbent and percentage removal of metal ions.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

Where

$q\,e$ is the amount of ions adsorbed (mg/g) at equilibrium, C_0 is the adsorbate initial concentration (mg/l) and Ce is adsorbate final concentration (mg/l) at equilibrium, V is the solution volume (l) and M is the adsorbent dosage (g).

2.7. Adsorption Equilibrium Studies

The experimental data was modeled using Freundlich and Langmuir isotherms (equations 4 and 5) separately to determine maximum adsorption capacity and adsorption mechanism. The model with the highest R^2 value best fitted the adsorption data.

I Langmuir Isotherm

The Langmuir isotherm model equation is expressed as:

$$\frac{1}{qe} = \left(\frac{1}{qmax}\right) + \left(\frac{1}{qmaxKL}\right)\frac{1}{Ce} \quad (4)$$

Where

qe is the equilibrium dye concentration on the adsorbent (mg g^{-1});

Ce is the equilibrium dye concentration in solution (mg L^{-1});

q_{max} is the monolayer capacity of the adsorbent (mg g^{-1});

K_L is the Langmuir constant.

The value of K_L and q_{max} are determined from the slope and intercept of the plot of 1/qe against 1/Ce.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by equation 5,

$$R_L = \frac{1}{1 + KLc_0} \quad (5)$$

Where

C_0 (mg/L) is the highest initial concentration of adsorbate.

The value of R_L indicates the shape of the isotherm to be either unfavorable (R_L>1), linear (R_L = 1), favorable (0< R_L< 1), or irreversible (R_L =0) (Olgun and Atar, 2012).

II Freundlich Isotherm

The Freundlich isotherm model equation is expressed as in equation 6:

$$\text{Lnqe} = \text{LnK}_F + \frac{1}{n}\text{LnCe} \quad (6)$$

Where

K_F (mg/g) and n are the Freundlich constants related to adsorption capacity and intensity, respectively. A linear plot of Lnq_e against Ln C_e gives K_F and n values.

2.8. Adsorption Kinetics Studies

In order to obtain a suitable rate equation and investigate the controlling mechanism of adsorption process, two main types of adsorption kinetic models, pseudo-first order and pseudo-second order models were considered.

I The Pseudo First-Order Kinetic Model

The first-order rate expression is given in equation 7:

$$\text{Ln}(qe - qt) = \text{Lnqe} - k_1 t \quad (7)$$

where

qt (mg/g) is the amount of the metal ion absorbed at time t. The value of k_1 is the pseudo-first-order rate constant and can be obtained from the slope of the plot of ln(qe−qt) versus t.

II The Pseudo Second-Order Kinetic Model

The pseudo second-order rate expression is given in equation 8:

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where

qe is the maximum adsorption capacity (mg g^{-1}), qt is the amount of metal ion adsorbed at time t (mg g^{-1}) and k_2 is the pseudo-second order kinetic rate constant (g mg^{-1} min^{-1}).

2.9. Thermodynamic Parameters of Adsorption

Thermodynamic parameters for the adsorption process, such as Gibbs-free energy (ΔG°), change in enthalpy and (ΔH°) change in entropy (ΔS°) were obtained from the experiments carried out at different temperatures in equations 9 - 10.

The free energy change ΔG, enthalpy changes ΔH and entropy changes ΔS are determined using fallowing equations 9 - 10.

$$\Delta G = -\text{RTlnKd} \quad (9)$$

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

Where

Kd is the distribution coefficient of the adsorbate, (Kd = Ce/ qe), R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (K). The plot of ln Kd as a function of 1/T yields a straight line from which ΔH and ΔS are obtained.

3. Result and Discussion

3.1. FTIR Analysis

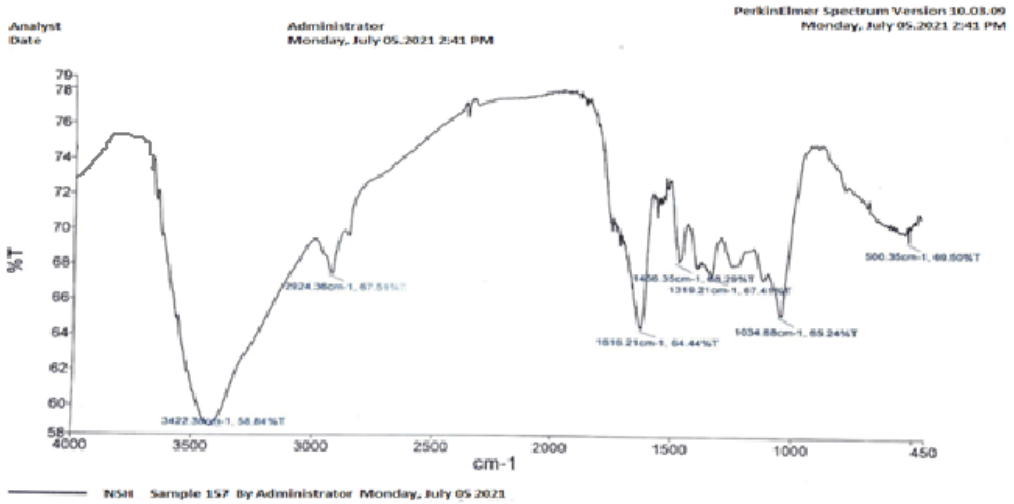

Figure 1. *FTIR Spectra of NSH.*

FTIR analysis was carried out to identify functional groups present on the surface of NSH. The FT-IR spectrum shows a peak around 3422 cm^{-1} indicate the presence of O-H and N-H groups. Peak around 2924 cm^{-1} indicate presence of C-H stretch of alkane. The peak around 1616 cm^{-1} and 1456cm^{-1} in the spectra depict mainly C=C stretch bands of alkene. Peak around 1034 cm^{-1} is attributed to C-O bending band. The results obtained are in agreement with the works reported by [8].

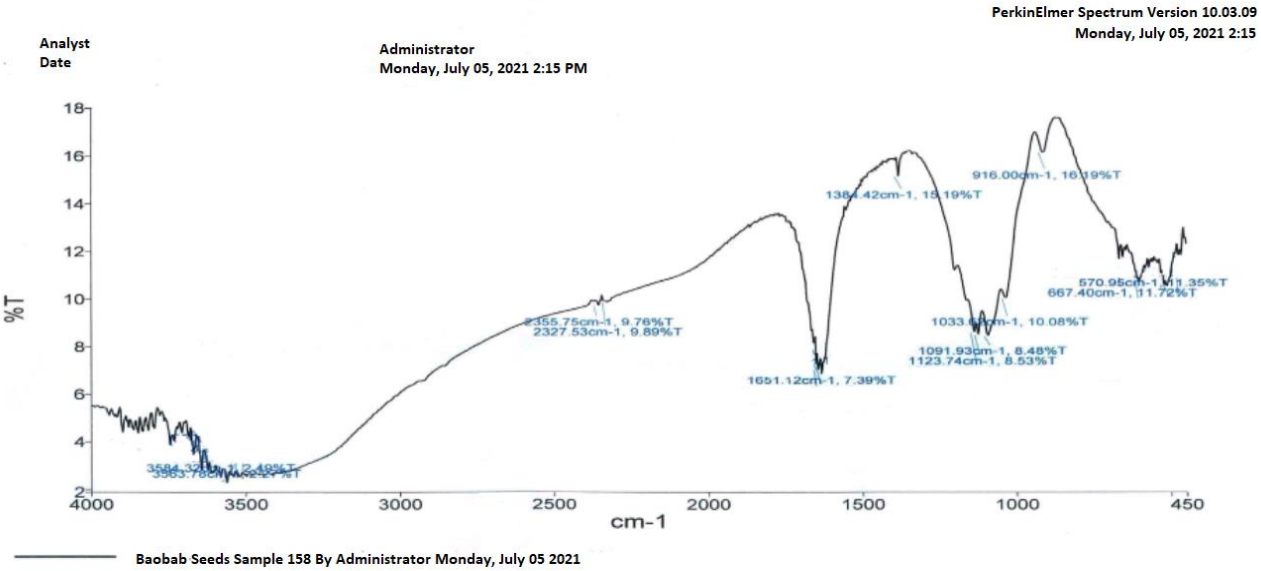

Figure 2. *Shows the FTIR result for BS.*

The FT-IR results for Baobab seed is shown in Figure 2. Peaks at 3563cm^{-1} represent O-H stretch due to alcohol and phenols and also free hydroxyl group. The peak at 1653 cm^{-1} indicate C=O and C=C while that of 1124cm^{-1} represents C-O. Similar results were reported by [8].

3.2. Sem Analysis

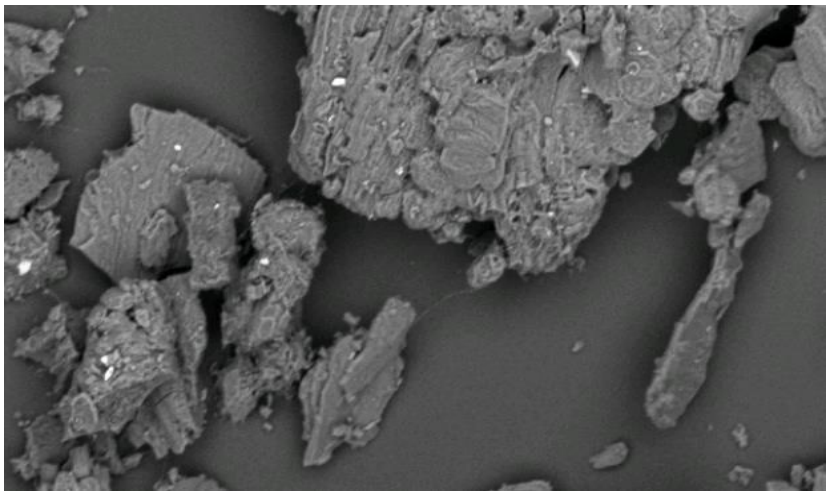

Figure 3. *Shows the SEM result for NSH.*

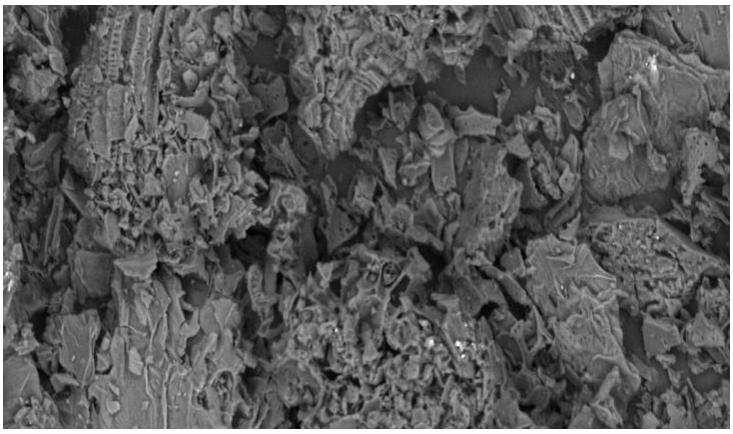

Figure 4. *Shows the SEM result for BS.*

Figures 3 and 4 show the SEM image of NSH and BS. The images showed an irregular and well developed porous structure indicating relatively high surface area. The porous nature of NSH makes it an efficient adsorbent.

3.3. XRD Result

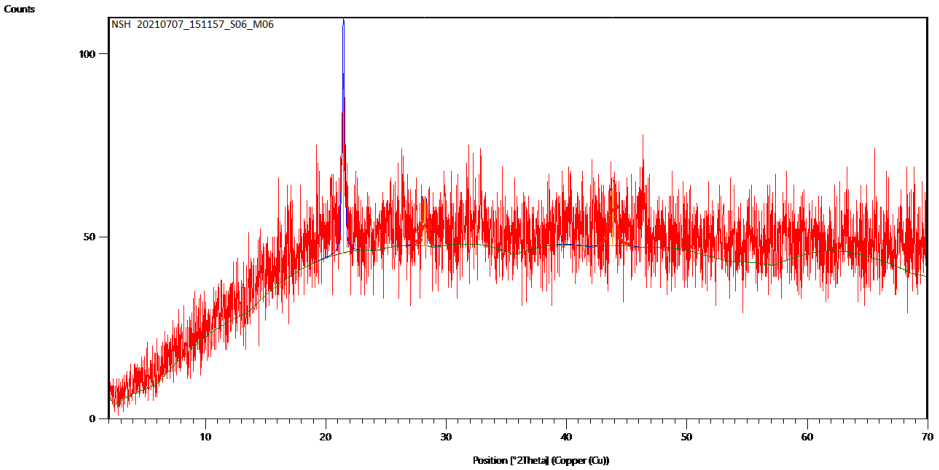

Figure 5. *Shows XRD Spectra of NSH.*

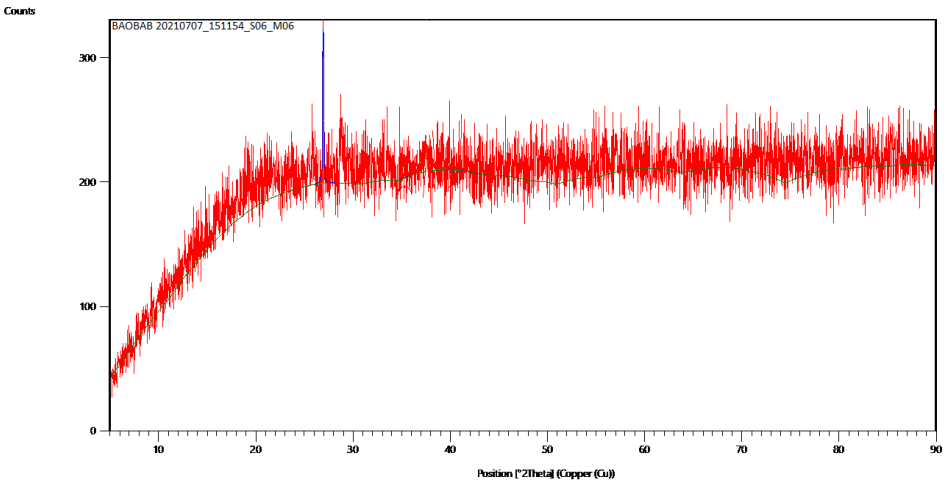

Figure 6. *Shows XRD image of BS.*

XRD analysis was carried out using Cu-Kα radiation, λ = 1.54059 A ° at 25°C. Figures 5 and 6 show the patterns for NSH, and BS with peaks at 2θ = 21.96 and 22.48° respectively. The average crystal size was calculated to be 44.51 and 42.61nm for NSH and BS.

3.4. The Effect of Initial Concentration

The effect of initial metal ion concentration on percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} ions was investigated at different initial concentrations (50, 100, 150, 200 and 250 mg/l) metal ions and keeping the other parameters constant. The results are shown in Figures 7 and 8. The percentage removal of the metal ions decreases with the increase in the concentrations of the metal ions. This is because, at lower concentration, the number of metal ions is low when compared to the available adsorbent active sites; therefore, adsorption is more frequent. When the metal ion concentration is increased, more ions are crowded on the surface of the adsorbents and the active sites are quickly occupied by them. This result in the saturation of the adsorption sites which decreases the rate of adsorption at higher concentration [9].

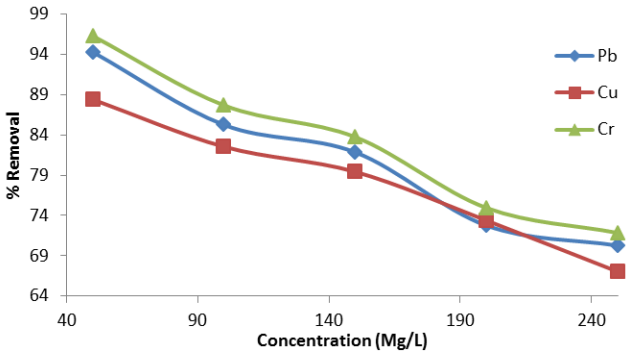

Figure 7. *Effect of Initial Concentration the percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} by NSH.*

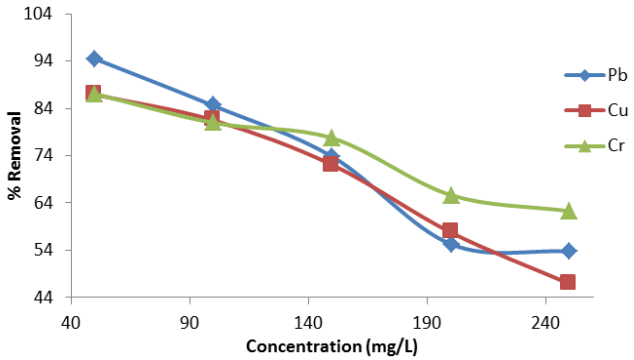

Figure 8. *Effect of Initial Concentration on the percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} by BS.*

3.5. The Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption of Pb^{2+}, Cu^{2+} and $Cr^{3+}$was investigated from range 0.2-1.2g while other parameters were kept constant. The plots of percentage removal against adsorbent dosage are presented in figures 9 and 10. It is clear from the results that an increase in the adsorbent dosage led to a corresponding increase of the percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} adsorbed. This is because as the amount of adsorbent is increased the number of available adsorptions sites increased which directly increases the rate of adsorption [10].

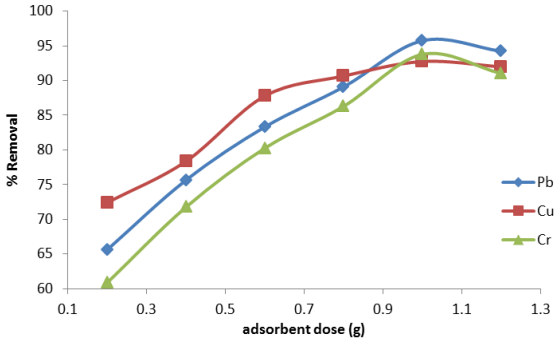

Figure 9. *Effect of adsorbent dose on the percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} by NSH.*

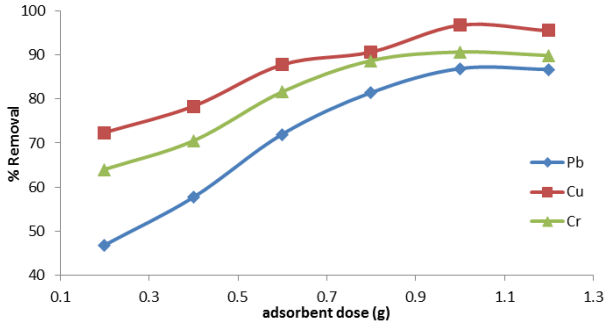

Figure 10. *Effect of adsorbent dose on the percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} by BS.*

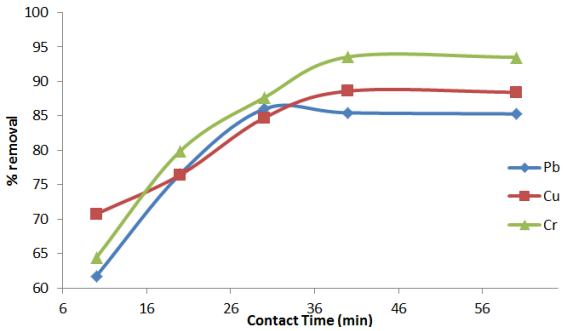

Figure 11. *Effect of contact time on the percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} by NSH.*

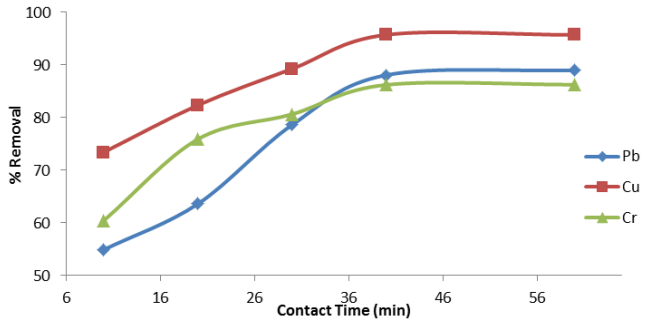

Figure 12. *Effect of contact time on the percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} by BS.*

3.6. Effect of Contact Time

The effect of contact time on the adsorption of Pb^{2+}, Cu^{2+} and Cr^{3+} by the adsorbents was studied using time interval from 10-60 minutes, while other parameters were kept contact. The results were shown in figures 11 and 12. It is clear that the percentage removal of the metal ions increased with increasing the contact time to a point where it reached equilibrium at 40 minutes, beyond which, there was almost no further increase in the adsorption. At initial stages, there are available adsorbent surface sites that rapidly adsorb metal ions. At equilibration time, active sites are exhausted limiting the number of metal ions that can be adsorbed [11-13]. Completion of adsorption occurs when equilibration time is achieved at a specific time of adsorption [14].

3.7. The Effect of Temperature

The effect of temperature on adsorption Pb^{2+}, Cu^{2+} and Cr^{3+} ions onto the adsorbents was carried out at five different temperatures ranging from 25°C to 60°C while other parameters were kept contact. The results in Figures 13 and 14 show that the percentage removal of metal ions increases with rise in temperature indicating the endothermic nature of the process and was further explained by evaluation of thermodynamic parameters. A similar trend was also observed by [15].

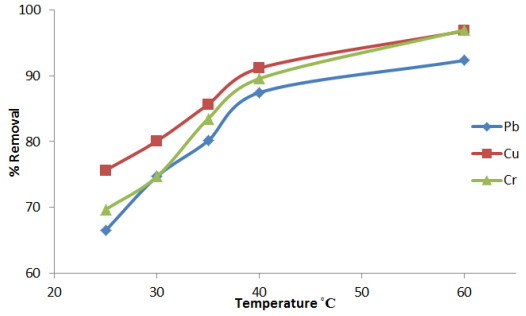

Figure 13. *Effect of Temperature on the percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} by NSH.*

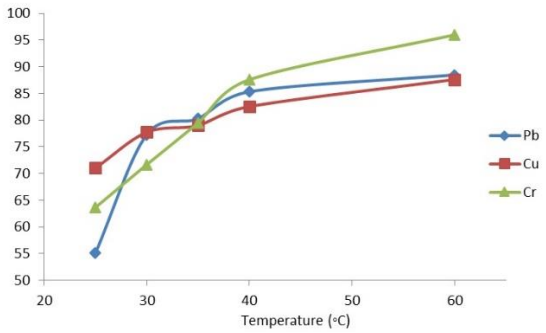

Figure 14. *Effect of Temperature on the percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} by BS*

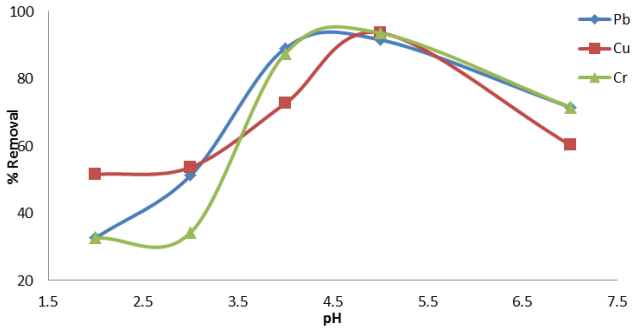

Figure 15. *Effect of pH on the percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} by NSH.*

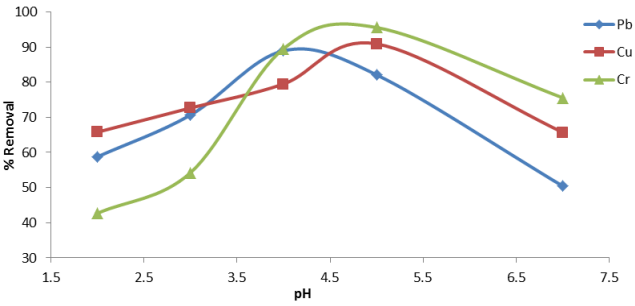

Figure 16. *Effect of pH on the percentage removal of Pb^{2+}, Cu^{2+} and Cr^{3+} by BS.*

3.8. Effect of pH

The pH solution is one of the most important factors affecting the adsorption of metal ions. The acidity of the medium affects the competition of the hydrogen ions and the metal ions for the active sites on the adsorbent surface [16]. The effect of pH on the adsorption of the Pb^{2+}, Cu^{2+} and Cr^{3+} ions onto the adsorbents was studied by changing pH values within the range 2–7 for the metal ion solution. The results are presented in Figure 7. The results showed that the adsorption of metal ions increased from within the pH range 2–5. An appreciable decrease in adsorption was observed after pH 5, which continued till pH 7. A similar result was observed by [16]. At lower pH the adsorption of metal ions was low due

to competitions between protons and metal ions for the available sites [11]. As the pH increased from 2-5, there were fewer protonated active sites leaving more negatively charged active sites. The decrease in adsorption at pH> 5 could be attributed to the formation of insoluble hydroxyl complexes.

3.9. Adsorption Isotherms

The equilibrium of the adsorption of Pb^{2+}, Cu^{2+} and Cr^{3+} on to NSH and BS is established when the concentration of metal ions in bulk solution is in dynamic balance with that on the liquid-adsorbent interface. The relationships between the concentrations of adsorbed metal and metal in solution at a given temperature are known as adsorption isotherms. Langmuir and Freunlich isotherm model were used to describe the equilibrium data. The Langmuir isotherm constant K_L and q_{max} were calculated from the slope and intercept of the plot between 1/qe and 1/Ce. While the Freundlich constants K_F and 1/n where obtained from the slope and intercept of a plot of $logq_e$ against log C_e. The values of Langmuir parameters (q_{max}, K_L and R_L) and Freundlich parameters (K_F and 1/n) together with the correlation coefficients (R^2) for both models are presented in Tables 1 and 2.

Table 1. *Isotherm models for adsorption of Pb^{2+}, Cu^{2+} and Cr^{2+} ions onto NSH.*

Isotherm Model	Adsorbates		
	Pb^{2+}	Cu^{2+}	Cr^{3+}
Langmuir			
q_{max}	15.267	19.46	14.75
K_L	0.152	0.0498	0.253
R_L	0.294	0.167	0.038
R^2	0.9512	0.9921	0.9400
Freundlich			
K_F	3.0549	1.867	3.769
1/n	0.7192	0.381	0.547
R^2	0.9912	0.9261	0.9922

The results in the table 1: showed that the Langmuir isotherm model best fitted the adsorption of Cu^{2+} onto NSH due to higher correlation coefficient R^2 value 0.9921 as compared with the Freundlich Isotherm model (0.9261). This indicate a monolayer adsorption which mostly due to the formation of a fixed number of local sites on the surface of the adsorbent [17]. The Freundlich adsorption model fitted well for the adsorption of Pb^{2+} and Cr^{3+} ions with R^2 value 0.9912 and 0.9922 respectively. The Freundlich model assumes that the adsorption occurs on a heterogeneous surface with non-identical sites with different distributions of heat of adsorption over the surface, and the adsorption sites are distributed exponentially with respect to the heat of adsorption [18]. The maximum adsorption capacity (qmax) of adsorption for Pb^{2+}, Cu^{2+} and Cr^{3+} onto NSH was observed to be 15.267mg/g, 19.46mg/g and 14.75 mg/g respectively. It was observed that the value of R_L in the range 0–1 confirms favourable adsorption processes.

Table 2. *Isotherm models for adsorption of Pb^{2+}, Cu^{2+} and Cr^{3+} ions onto BS.*

Isotherm Model	Metal ions		
	Pb^{2+}	Cu^{2+}	Cr^{3+}
Langmuir			
q_{max}	30.864	16.155	12.048
K_L	0.048	0.134	0.2304

Isotherm Model	Metal ions		
	Pb^{2+}	Cu^{2+}	Cr^{3+}
R_L	0.116	0.067	0.0416
R^2	0.9789	0.977	0.9770
Freundlich			
K_F	3.0549	3.138	3.8415
1/n	0.7192	0.398	0.2618
R^2	0.9512	0.9235	0.9512

Table 2: shows different values for Langmuir and Freundlich adsorption isotherms. The Langmuir isotherm fitted the experimental data very well for the adsorption Pb^{2+}, Cu^{2+} and Cr^{3+} on to BS with R^2 value 0.9789, 0.9770 and 0.9770 respectively which is greater than the R^2 for Freundlich Isotherm. This confirmed the monolayer coverage of Pb^{2+}, Cu^{2+} and Cr^{3+} onto BS and also the homogeneous distribution of active sites on the adsorbent, since the Langmuir equation assumes that the surface is homogeneous. This is consistent with the result obtained by [19].

The R_L and 1/n values less than 1 also confirm favorable adsorption of the metal ions onto BS. The maximum adsorption capacity for adsorption for Pb^{2+}, Cu^{2+} and Cr^{3+} onto BS was observed to be 30.864mg/g and 16.155mg/g and 12.048 mg/g respectively.

4. Kinetic Studies

In investigating the adsorption kinetic process of the metal ions in solutions, the experimental data obtained were tested with pseudo-first-order and pseudo-second-order kinetic models to identify the controlling mechanism. The linear graph of pseudo-first order was plotted from ln (qe-qt) against t (mins), and the graph of pseudo-second order was plotted from t/qt against t (min). The q_{cal}, K_1, K_2, and R^2 were obtained from the plots and are presented with the q_{exp} in tables 3 and 4.

Table 3. *Kinetics of Pb^{2+}, Cu^{2+} and Cr^{3+} ions adsorption on NSH.*

Kinetic Model	Parameters	Adsorbates		
		Pb^{2+}	Cu^{2+}	Cr^{3+}
Pseudo-First order				
	q_{exp} (mg/g)	8.524	8.917	8.7660
	K_1 (min^{-1})	0.0438	0.0246	1.7615
	q_{cal} (mg/g)	4.772	36.509	0.8270
	R^2	0.9021	0.9856	0.9908
Pseudo-Second order				
	K_2 (min^{-1})	0.0164	1.0299	1.5893
	q_{cal} (mg/g)	8.945	8.7873	8.4817
	R^2	0.9895	0.9939	0.9942

Table 4. Kinetics parameters of Pb^{2+}, Cu^{2+} and Cr^{3+} ions adsorption on BS.

Kinetic Model	Parameters	Adsorbates		
		Pb^{2+}	Cu^{2+}	Cr^{3+}
Pseudo-First order				
	q_{exp} (mg/g)	8.455	8.930	7.366
	K_1 (min^{-1})	0.0345	0.0303	0.7841
	q_{cal} (mg/g)	2.8519	19.638	0.9036
	R^2	0.9372	0.9923	0.9947
Pseudo-Second order				
	K_2 (min^{-1})	0.0277	1.6466	2.4172
	q_{cal} (mg/g)	8.606	9.0009	7.5529
	R^2	0.9984	0.9970	0.9994

From tables 2 and 3, the experimental data processed using the pseudo-first-order kinetic model gave a low correlation coefficient, R^2 values for the adsorption of Pb^{2+}, Cu^{2+} and Cr^{3+} ions by NSH, BS and ML. Therefore, the adsorption of Pb^{2+}, Cu^{2+} and Cr^{3+} onto NSH and BS cannot be adequately described by the pseudo-first-order model. The wide variance between the experimental adsorption capacity (qexp) and calculated adsorption capacity (qcal) values also support this assertion. The pseudo-second order model fit well for the adsorption of the Pb^{2+}, Cu^{2+} and Cr^{3+} onto NSH and BS due to higher R^2 values as well as the relative agreement between qcal and qexp. The pseudo-second-order model assumes that the rate is proportional to the square of the number of remaining free surface sites [11]. This result trend is in consistent with [10, 15, 19, 20].

5. Thermodynamic Studies

Table 5. Thermodynamic parameters for adsorption of Pb^{2+}, Cu^{2+} and Cr^{3+} ions onto NSH.

Model	Metal ion		
	Pb^{2+}	Cu^{2+}	Cr^{3+}
ΔG° ($KJ.mol^{-1}$)			
25°C	-0.4665	-0.9655	-0.0153
30°C	-0.8994	-2.0486	-0.32143
35°C	-1.2289	-2.9288	-0.59872
40°C	-2.1354	-3.9544	-0.97635
60°C	-2.7753	-4.7526	-1.02944
ΔH° ($KJ.mol^{-1}$)			
	+18.8528	+29.8389	+8.7131
ΔS° ($KJ.mol^{-1}.K^{-1}$)			
	+0.05487	+0.08717	+0.02962

Table 6. Thermodynamic parameters for adsorption of Pb^{2+}, Cu^{2+} and Cr^{3+} ions onto BS.

Model	Metal ion		
	Pb^{2+}	Cu^{2+}	Cr^{3+}
ΔG° (KJ.mol-1)			
25℃	-0.05396	-0.233	-0.19854
30℃	-0.5959	-0.51166	-0.66506
35℃	-0.84665	-1.05825	-1.12888
40℃	-1.19037	-1.43191	-1.27545
60℃	-1.61301	-1.91713	-1.72442
ΔH° (KJ.mol^{-1})			
	+11.8832	+13.90683	+11.6133
ΔS° (KJ.mol^{-1}.K^{-1})			
	+0.040584	+0.04757	+0.04016

The values of the thermodynamic parameters for the adsorption of Pb^{2+} and Cu^{2+} onto NSH and BS are given in Tables 5 and 6. These results showed negative values of ΔG° which indicate spontaneous processes. The values of ΔG° become more negative with increasing temperature, which shows that adsorptions are more favourable at high temperatures. The positive values of enthalpy indicate endothermic process. The positive values of the entropy (ΔS) indicate an increase in the degree of randomness. Similar findings were obtained by [15].

6. Conclusion

This study presents a simple, cost-effective, and efficient adsorption process for removing heavy metals from wastewater and the environment. The parameters of initial concentration, temperature, contact time, dosage and pH affected the removal of the three metal ions. The maximum adsorption capacity was found to be for Pb^{2+}, Cu^{2+} and Cr^{3+} onto NSH was observed to be 15.267mg/g, 19.46mg/g and 14.75 mg/g respectively. Also the maximum adsorption capacity Pb^{2+}, Cu^{2+} and Cr^{3+} onto BS was observed to be 30.864mg/g and 16.155mg/g and 12.048 mg/g respectively. The equilibrium data were well-fitted with the Langmuir isotherm model for adsorption of Cu^{2+} while the Freundlich isotherm model best fitted the adsorption of Pb^{2+}. The kinetics study of the adsorption of three metal ions fitted pseudo-second-order model compared to the pseudo-first-order. Thermodynamic parameters, change in the free energy (ΔG°), the enthalpy (ΔH°), and the entropy (ΔS°), show that the overall adsorption processes were spontaneous, endothermic in nature, and proceeds with increase in randomness as the value of entropy is positive. Based on this study NSH and BS could be used as a natural adsorbent to remove Pb^{2+}, Cu^{2+} and Cr^{3+} from wastewater and environment due to their high removal efficiencies.

Author Contributions

Nasiru Pindiga Yahaya: Conceptualization, Data curation, Formal Analysis, Investigation, Supervision, Validation, Writing – original draft, Writing – review & editing

Yahaya Aliyu Saad: Methodology, Project administration, Resources, Visualization

Conflicts of Interest

The authors declare no Conflicts of Interest.

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