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Biosorption Kinetics and Isotherm Investigation of Co (II), Zn (II) and Pb (II) Ions on Gourd Cell Seed Husk Adsorbent

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ABSTRACT

Heavy metals contamination from industrial wastewaters into the environment is a serious environmental problem. Activated carbon adsorption is the most effective means of removing heavy metals from industrial effluents before discharge into the environment but is expensive. Several low cost adsorbents have been utilized as alternatives for heavy metal removal. However a thorough literature search revealed a dart of information on the use of Gourd Cell Seed Husk (GCSH) as adsorbent for heavy metals. This study therefore investigates the performance of GCSH for the biosorption of Co (II), Zn (II) and Pb (II) ions from aqueous solution. The adsorbent was characterized by the Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM). Batch biosorption was used to determine the effect of pH, metal ion concentration, adsorbent dose and contact time on metals sequestration. Isotherm was analyzed by the Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich models. Kinetic mechanism of biosorption was analyzed using the Pseudo-first order, Pseudo-second order, Intra-particle diffusion and Film diffusion rate equations. FTIR and SEM showed the presence of surface functional groups and a porous surface of GCSH. The trend of metal biosorption was Co (II)>Pb (II)>Zn (II) ions. The results of this study revealed a good performance of GCSH for the removal of the three metal ions from solution. This indicated the usefulness of GCSH as an alternative low cost adsorbent.

Keywords: Biosorption, Cobalt, Lead, Zinc, Equilibrium isotherm, Kinetics

INTRODUCTION

The Pollution of the environment with heavy metals has become a serious environmental problem. The is due to the fact that heavy metals are highly toxic at certain concentrations in water, non-biodegradable, and bio-accumulate resulting in health problems in humans, animals and aquatic organisms [1]. Heavy metals usually get to the environment from industrial effluents from textile, pharmaceutical, metallurgical, paints, batteries, ceramic glazes, dye and pigment industries [2]. As a result of the high cost involved in the removal of heavy metals from industrial effluents, most industries in developing nation discharge the effluents directly without treatment into receiving water bodies. This poses serious concern to environmentalist. As a result several methods have been utilized in the treatment of effluents contaminated with heavy metals such as solvent extraction, ion exchange, membrane filtration, reverse osmosis, precipitation, evaporation, chemical oxidation or reduction, electrochemical treatment, filtration, sedimentation and activated carbon adsorption [3]. However most of these techniques are inefficient at certain metal concentrations, complex, require skilled personnel and expensive. Among these separation methods, adsorption using activated carbon has been reported to be the most effective for metal removal from industrial effluents [4]. However, the use of activated carbon is expensive which limits its wide spread application and use [5]. This led to the search of cheaper alternative adsorbents to activated carbon. As a result, several low cost adsorbents such as agricultural waste or biomass, clays, soils, sawdust and microorganisms have been utilized extensively by many researchers for heavy metal removal [1-6].

In Nigeria, there is an abundance of Gourd cell in which the waste materials or seed husk can be utilized as a low cost adsorbent for heavy metals. However, a thorough literature search revealed limited information on the use of Gourd Cell Seed Husk (GCSH) for the removal of heavy metals from solution. This study therefore aims to establish the biosorption performance of GSCH for the attenuation of Pb (II), Zn (II) and Co (II) ions from aqueous solution. The material was used without chemical modification or treatment in order to keep the process cost low. Equilibrium and kinetic sorption mechanism analysis were carried out.

MATERIALS AND METHODS

Adsorbate preparation

All the chemicals used in the study were of analytical grade and were used without further purification. Stock solution of concentration 1000 mg/L cobalt (II), lead (II) and zinc (II) ions were prepared by dissolving appropriate weights of $Co(NO_3)_2$, $Pb(NO_3)_2$ and $Zn(NO_3)_2$, respectively in de-ionized water. Lower concentrations of the metal ions which include 200, 400, 600, and 800 mg/L were then prepared from the stock solution by serial dilution.

Preparation and characterization of gourd cell seed husk adsorbent

The Gourd cell was obtained from Orie market, Emene, Enugu, Nigeria. The Gourd cell was then sliced and the seeds were removed manually. The seeds were sundried for 21 days and then dried in the oven at 80ºC for 2 h in order to aid the drying process and get rid of moisture. The seed husks were then removed manually and further sundried for 14 days. The dried Gourd cell seed husk was then ground and the powder was passed through 100 µm mesh sieve to obtain to Gourd Cell Seed Husk (GCSH) adsorbent. This adsorbent was stored in appropriate plastic containers until use.

The surface functional groups on the GCSH were analyzed by the Fourier Transform Infrared (FTIR) spectrophotometer (Shimadzu FT-IR 8400s)**.** The morphology of the adsorbent was obtained by the use of the Scanning Electron Microscope (SEM) (Hitachi S4800 model).

Biosorption study

The batch biosorption technique was applied to determine the effect of pH, initial metal ion concentration, adsorbent dose and contact time on the adsorption of Co (II), Pb (II) and Zn (II) ions on GCSH as described;

Determination of the effect of pH

In order to determine the effect of pH on adsorption of metal ions, the metal solution of concentration 400 mg/L was used and adjusted to different pH values of 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 by the drop wise addition of 0.1 M NaOH or 0.1 M HNO_3 when required and checked by the help of a pH meter ((Mettler Toledo, Model MP 220) to determine the pH. Several 100 mL plastic bottles were purified by washing with detergent then rinsed with distilled water and dried in the oven at 40ºC. 0.1 g of GCSH was placed in each plastic bottle. 20 mL of each solution was then added to the separate plastic bottles and labeled appropriately. The plastics were corked, agitated for 5 s and then left for a contact time of 120 min at a room temperature of 300 K. At the end of a given contact time of adsorption the solution was filtered into another empty plastic bottle using Whatman no.1 filter paper placed in a funnel. The filtrate was then taken to the Atomic absorption spectrophotometer (AAS) (Buck scientific model 210VGP) to determine the residual metal ion concentrations in solution**.** Each experiment was performed in triplicate and mean result was taken.

Determination of the effect of initial metal concentration

Several solutions of Co (II), Pb (II) and Zn (II) ions of concentrations 200, 400, 600, 800 and 1000 mg/L were prepared. The pH of all the solutions were adjusted to 6.0 by the drop wise addition of 0.1 M HNO_3 or 0.1 M NaOH when required using a pH meter (Mettler Toledo, Model MP 220). 0.1 g of GCSH was then weighed each in several 100 mL plastic bottles after which 20 mL of each solution was added. The plastic bottles were corked then agitated for 5 s and left to stand for 120 min at a room temperature of 300 K. The solutions were then filtered using a funnel containing a fitter paper into empty plastic bottles and taken to the AAS to determine the concentration of metal ions remaining in solution after adsorption. The experiment was performed three times and the mean result was calculated.

Determination of the effect of adsorbent dose

The effect of adsorbent dose was determined by weighing different doses of GCSH of weights 0.1, 0.2, 0.3, 0.4 and 0.5 g into several 100 mL plastic bottles. 400 mg/L concentrations of each solution at pH 6.0 were used. 20 mL of each solution was added to the separate plastic bottles, one solution for each bottle, then corked, agitated for 5 s and left to stand at 120 min at a room temperature of 300 K. The solution was then filtered and the filtrate taken to the AAS to determine the residual metal ion concentrations remaining in solution. The experiment was performed in triplicate and the mean computed in order to ensure quality assurance.

Determination of the effect of contact time

The effect of contact time on adsorption was determined using 400 mg/L concentration of the solution of metal ions at pH 6.0. 0.1 g of GCSH was placed in several 100 mL plastic bottles. 20 mL of the metal solutions of Co (II), Pb (II) and Zn (II) ions was added to the bottles, agitated for 5 sec after been corked and left to stand at different contact times of 5, 10, 15, 20, 30, 40, 50, 60, 90, 120 min. At the end of the given contact time for each experiment, the solution was filtered and the residual concentration of metal ions in the filtrate was determined by the AAS. Each experiment was performed three times and the mean result was computed to ensure reproducibility of the results.

Descriptive statistics

The biosorption percentage removal of Co (II), Pb (II) and Zn (II) ions on GCSH and its adsorption capacity for metal ions were calculated from the equations [3].

$$\text{Biosorption Removal (\%)} = \frac{100\,[Co - Ce]}{Co} \qquad (1)$$

$$qe\ (mg/g) = \frac{v[Co - Ce]}{m} \qquad (2)$$

Where qe (mg/g) is the biosorption capacity of GCSH, Co (mg/L) is the initial metal ion concentration, Ce (mg/L) is the residual metal ion concentration at equilibrium, v (L) corresponds to the volume of solution used for biosorption and m (g) is the biomass weight used [6].

RESULTS AND DISCUSSION

Characterization of gourd cell seed husk

The characterization of GCSH was performed using the Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM) to determine the surface functional groups and morphology, respectively. FTIR allows the determination of the surface groups in the range 400-4000 cm^{-1} responsible for biosorption of metal ions [3]. The FTIR spectrum of GCSH is shown in Figure 1. The presence of –OH stretching group on the surface of the adsorbent was observed by the broad and intense peak at 3419.9 cm^{-1}, which indicated the presence of active –OH groups for binding of metal ions [4]. Peaks at 2943.5 cm^{-1}, 2359 cm^{-1} and 2029.2 cm^{-1} are related to the C-H vibration of CH_3 and CH_2 groups of side chains and aromatic methoxyl groups [7]. The strong peak at 1639.6 cm^{-1} showed the presence of carbonate group while the characteristic band at 1126.5 cm^{-1} correspond to the C-O stretching vibration [4]. The band at 667.4 cm^{-1} could be attributed to the C-Cl stretching vibration and could also be attributed to the C-H out of plane bands of alkanes [6,7].

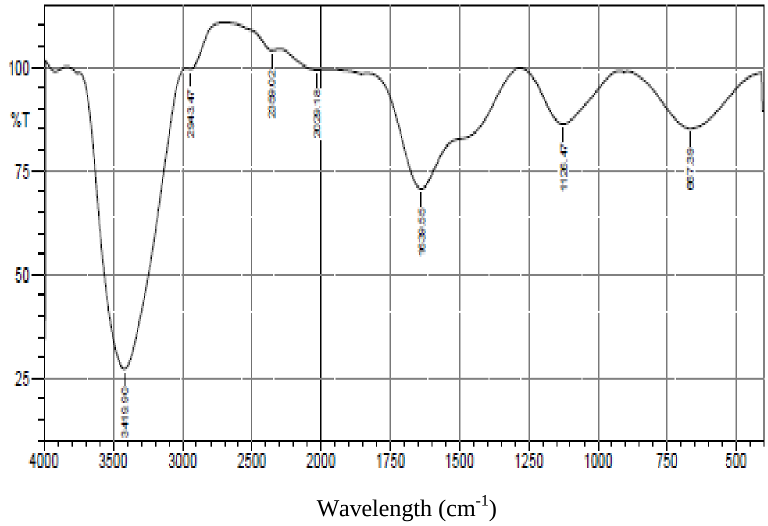

Figure 1: Fourier transform infrared spectra of GCSH

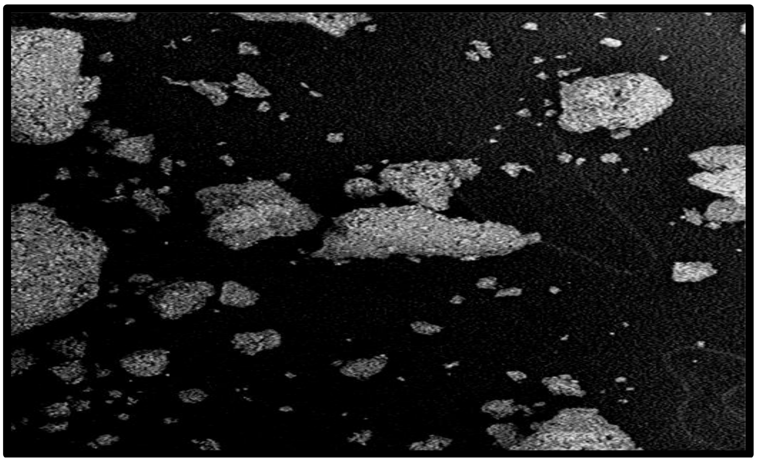

Figure 2: Scanning electron microscopy of GCSH

The SEM morphology helps to reveal the level of porosity of an adsorbent material, as a porous material would be more effective for adsorption than a non-porous one [4,6]. The SEM morphology of GCSH is shown in Figure 2. The surface morphology revealed a porous nature, considerable number of heterogeneous pores, an irregular surface and particle aggregation of various shapes and sizes for metal ions to be trapped and adsorbed. The diffusion of metal ions to the surface of the adsorbent is also enhanced by a porous surface which in turn favors biosorption of metal ions [3].

Influence of pH

The initial pH of solution is significant in biosoption because it affects the surface charge on the adsorbent and the ionization of metal ions [8]. Heavy metal form complexes with groups such as OH, and the extent of this formation varies with pH thereby affecting biosorption [2,8]. The influence of pH on the biosorption of metal ions on GCSH is shown in Figure 3.

An observed increase in biosorption of metals with increase in pH of solution was obtained. With increase in pH of solution from 2.0 to 8.0, an increase in the percentage biosorption for Co (II), Pb (II) and Zn (II) from 7.25 to 72.5%, 5.25 to 67.25% and 6.25 to 62% on GCSH was achieved respectively. It was noticed that Pb (II) recorded highest biosorption at pH values of 3.0 to 5.0 than Co (II) and Zn (II), also attaining an optimum pH of adsorption at 5.0.

For Co (II) and Zn (II) ions optimum biosorption was achieved at pH 6.0. The trend of metal ions biosorption was Co>Pb>Zn ions. pH 6.0 was chosen and utilized for subsequent biosorption experiments since optimum removal was achieved. Higher pH values were avoided in order to avoid the precipitation of metal ions in the form of insoluble metal hydroxides which could occur [9]. The biosorption increase with increase in pH is due to the decrease in competition of metal ions with protons for the active sites of BFSH. Also the repulsive forces between the protons and metal ions were greater at lower pH values due to similar charge hindering the biosorption process [10]. Similar results have been reported in literature [2-4,8,9].

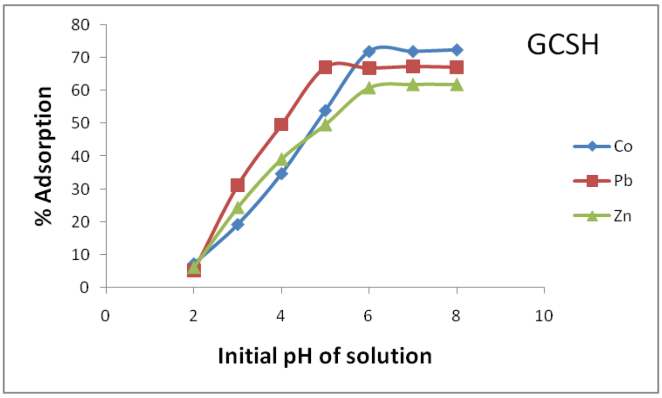

Figure 3: Effect of initial pH of solution on the percentage adsorption of heavy metals on GCSH

Influence of metal concentration

The initial concentration of metal ions in solution determines the amount of metal ions adsorbed [10]. In this regard its influence on the adsorption capacity of GCSH for Co (II), Pb (II) and Zn (II) ions was determined as shown in Figure 4. An increase in the biosorption capacity with increase in initial metal ion concentration was recorded. In fact the adsorption capacity of GCSH for Co, Pb and Zn ions increased with increase in metal concentration (200–1000 mg/L) from 35.8 to 90 mg/g, 34.4 to 86 mg/g and 32.6 to 81.8 mg/g respectively. The increase in adsorption capacity with increase in metal concentration is due to increasing concentration gradient which generates a driving force to overcome resistance of metal ions to mass transfer [11]. In general, higher concentration suggests higher metal ions fixed at the surface of BFSH and maximum utilization of its active sites [3].

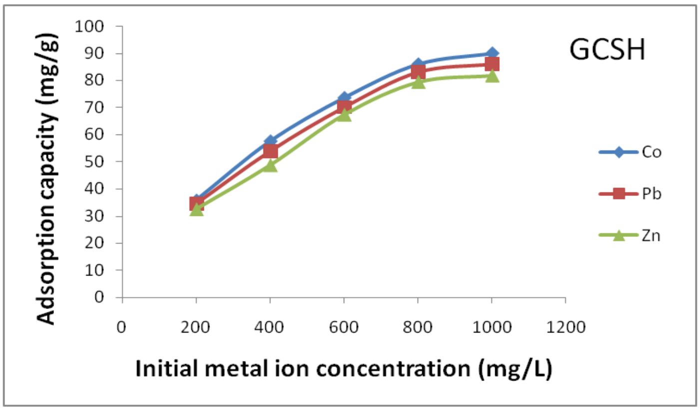

Figure 4: Influence of metal ion concentration on the adsorption capacity of heavy metals

The influence of metal concentration on the percentage adsorption of Co (II), Pb (II) and Zn (II) ions on GCSH is shown in Figure 5. It was clearly seen that an opposite trend to that of adsorption capacity in which a decrease in percentage biosorption of the three metal ions with increase in metal concentration was obtained. As metal concentration was increased from 200 to 1000 mg/L the percentage biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH decreased from 89.5 to 45%, 86 to 43% and 81.5 to 40.9% respectively. The decrease in adsorption with increase in metal ion concentration is due to the saturation of the active sites on the adsorbent surface [9,10,12]. The trend of metal biosorption on GCSH was the adsorbents was Co>Pb>Zn ions. It has been reported that the electronegativity of metal ions, ionic radius of the metals, pKOH of the metal hydroxides in solution and the strength of acidity of metals affects the biosorption of a metal ions [3,9]. The trend of adsorption recorded could be explained based on the electronegativity of the metal ions; Co (II) (1.88)>Pb (II) (1.87)>Zn (II) (1.65) as metals with higher electronegativity tend to have more favorable biosorption [9,12]. The higher biosorption of Co (II) than Pb (II) is due to the smaller ionic radius of Co (II) (0.74 Å) than Pb (II) (1.20 Å) which allowed for an easy diffusion [3]. Similar results have been reported by many researchers [4,7-9,12].

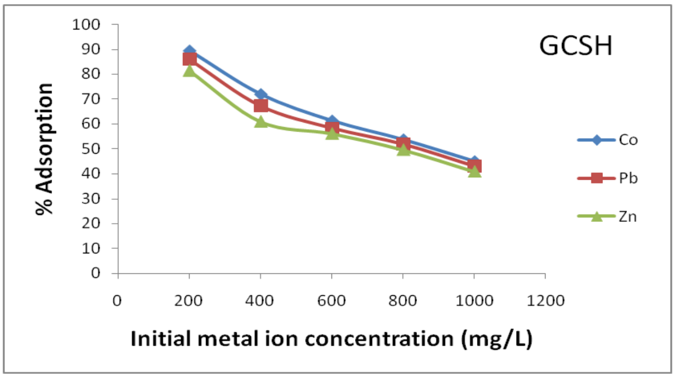

Figure 5: Effect of initial metal ion concentration on percentage biosorption

Biosorption equilibrium isotherms

Equilibrium isotherms are models describing the phenomenon governing the mobility of a substance from the aqueous phase or aquatic environment to a solid phase at a constant temperature and pH [13]. In more specific terms, they give description of how metal ions interact with adsorbents and are important in optimizing the use of adsorbents. Equilibrium biosorption isotherms are basic requirement for designing any adsorption system [14]. An accurate mathematical description of equilibrium adsorption capacity is indispensible for reliable prediction of adsorption parameters and quantitative comparison of adsorption behaviors for different adsorption systems or for varied conditions within any given system [9]. These parameters of equilibrium isotherms often provide fundamental information on both sorption mechanism and surface properties and affinity of the adsorbents, which helps to determine the applicability of the sorption process as a unit operation [6,10]. Therefore, it is important to establish the most suitable correlation of equilibrium curves in order to optimize the conditions for designing adsorption systems [14]. In this regard, several researchers have utilized many equations for analyzing experimental adsorption equilibrium data [4,5,8,11,12]. In this work, the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models analysis were applied for the biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH. The equilibrium isotherm parameters obtained from the four models are shown in Table 1. The most suitable isotherm is determined by the linear regression coefficient (R^2). The closer the R^2 value of the model plots to one the best the fit of the model [6,12].

Table 1: **Biosorption equilibrium isotherm constant parameters**

Isotherm/Adsorbent	**Co (II)**	**Pb (II)**	**Zn (II)**
Langmuir			
q_L (mg/g)	100	100	100
K_L (L/mg)	0.016	0.012	0.009
R^2	0.992	0.989	0.98
Freundlich			
K_F	14.69	11.78	8.87
N	3.42	3.13	2.82
R^2	0.994	0.989	0.972
Tempkin			
B (mg/g)	17.14	17.93	18.94
A (L/g)	0.338	0.211	0.129
R^2	0.98	0.968	0.946
Dubinin-Radushkevich			
qm (mg/g)	76.55	73.11	69.41
B (mol^2/J^2)	6×10^{-5}	0	0
R^2	0.811	0.793	0.761

The Langmuir isotherm assumes a monolayer adsorption occurring only at a fixed number of definite localized sites that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites [3,6,10]. This isotherm refers to a homogenous adsorption in which each molecule possess constant enthalpies and sorption activation energy and is restricted to a monolayer adsorption, with no transmigration of the adsorbate in the plane of the surface [4,9]. The linear form of the Langmuir isotherm model is given as [6]:

$$C_e/q_e=1/q_LK_L+C_e/q_L \qquad (3)$$

Where q_e (mg/g) represents adsorption capacity of the adsorbent, K_L (L/mg) is the Langmuir adsorption constant related to the energy of adsorption, q_L (mg/g) is the maximum monolayer adsorption capacity of GCSH [6]. The Langmuir isotherm is applicable to the adsorption process if the plot of C_e/q_e versus C_e is linear and passes through the origin. The constants q_L and K_L were obtained from the slope and intercept of the plot respectively [3]. The Langmuir isotherm plots for the adsorption of Co (II), Pb (II) and Zn (II) ion on GCSH are shown in Figure 6 and the isotherm parameters obtained are presented in Table 1. It was deduced that linear regression coefficient (R^2) were high and gave suitable fits to the biosorption (R^2 values <0.9). The good fits indicated that the biosorption may be attributed to a monolayer one on heterogeneous surface of GCSH.

This however could only be verified by comparing the R^2 values of this model with that of the Freundlich model in order to know which best represented the biosorption. However, the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant or separation factor (R_L) defined by the relationship [10].

$$R_L=1/[1+K_LC_o] \qquad (4)$$

The value of the separation factor provides useful information about the nature of biosorption. The biosorption is said to be irreversible (R_L=0), favorable (0<R_L<1), linear (R_L=1) and unfavorable (R_L>1) [4,12]. The values of R_L obtained for the adsorption of Co (II), Pb (II) and Zn (II) ions on GCSH was within the range of favorable biosorption, indicating the suitability of GCSH for heavy metals biosorption.

The Freundlich isotherm describes non-ideal and reversible adsorption which is not restricted to the formation of monolayer [14]. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. In this perspective, the amount adsorbed is the summation of adsorption on all sites, in which the strong binding sites are occupied first, until adsorption energy are exponentially decreased upon the completion of adsorption process [4,10,12]. The linear form of the Freundlich isotherm model is given as [15].

$$\log q_e=\log K_f+[1/n]\log C_e \qquad (5)$$

Where K_f (mg/g) represents the Freundlich constant and n is related to the adsorption intensity of the adsorbent [16]. This isotherm is applied by a linear plot of $\log q_e$ versus $\log C_e$ and the constants n and K_f are determined from the slope and intercept respectively [6].

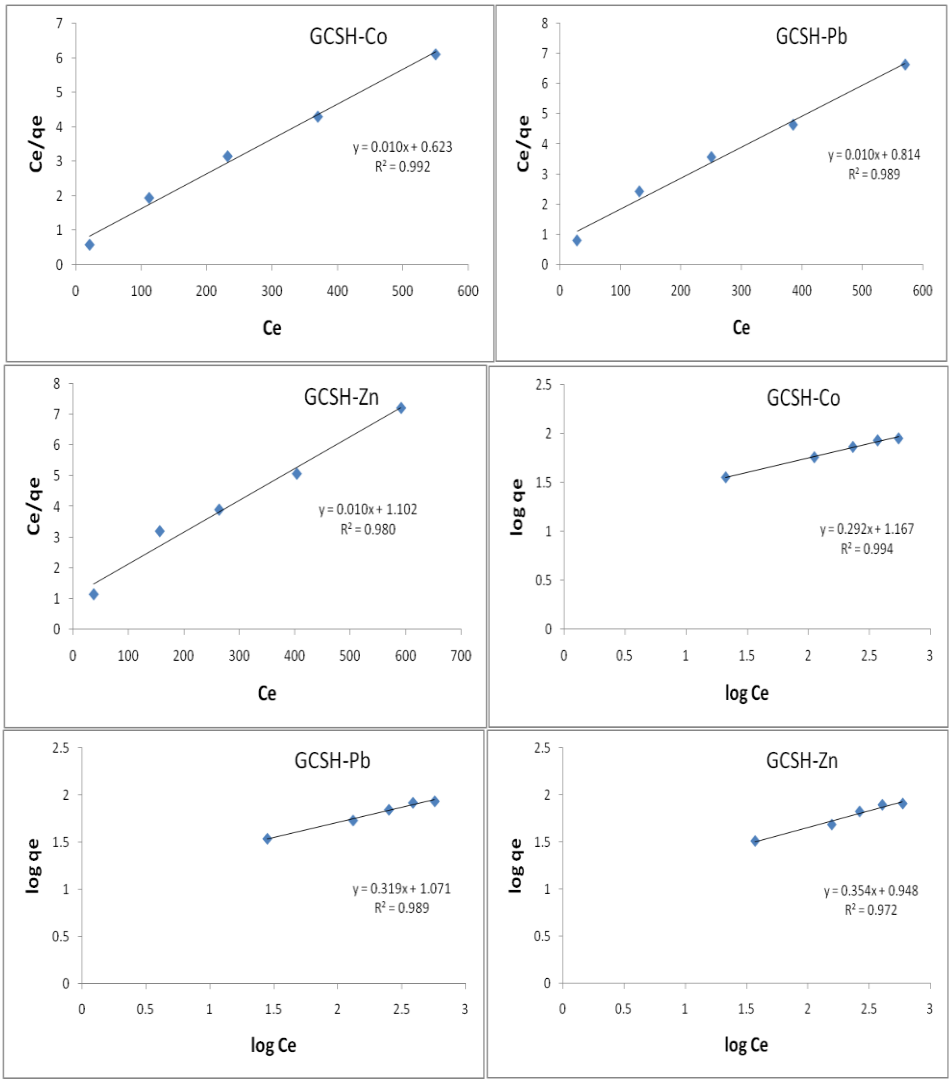

Figure 6: Langmuir and Freundlich isotherm model plots for the biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH

The Freundlich isotherm model plot for the adsorption of Co (II), Pb (II) and Zn (II) ion on GCSH are shown in Figure 6 and the constant parameters are presented in Table 1. The Freundlich isotherm was also found to provide a good fit to the biosorption process for the three metal ions on GCSH as R^2 values were all greater than 0.9. The Freundlich model was found to provide better fit than the Langmuir model. An exception was obtained for the adsorption of Zn (II) ion in which the Langmuir R^2 value of 0.980 was greater than that of the Freundlich of 0.972. This indicated that the biosorption of Zn (II) ions was a monolayer sorption unto a homogenous surface of GCSH in which there was no interaction between the adsorbed Zn ions [16].

Also, in the biosorption of Pb (II) ion on GCSH both the Langmuir and Freundlich isotherm showed similar R^2 values of 0.989, however this biosorption was likely on a heterogeneous surface of the adsorbent as the FTIR analysis showed the presence more than one type of active functional group on the surface of GCSH. In general, the better fits presented by the Freundlich model plots than the Langmuir plots indicated that the biosorption of the metal ions on the adsorbents except Zn (II) on GCSH was a multilayer one on a heterogenous surface of the adsorbents and not a monolayer homogenous adsorption as suggested earlier when good fits were obtained with the Langmuir model plots [4,12]. If the values of *n* lies between 1 and 10, it indicates a favorable biosorption process [10,17]. The values of *n* obtained for the biosorption process was within the range for a favorable process which corroborated the result of the Langmuir R_L obtained. This again indicated the suitability of GCSH as an adsorbent for heavy metals.

The Tempkin isotherm was also used to analyze the experimental data. The Temkin isotherm model unlike the Langmuir and Freundlich isotherm, takes into account the interactions between adsorbents and metal ions to be adsorbed [3,9,14]. This model assumes that the heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage [17]. The linear form of the Temkin isotherm equation is represented as [12,14].

$$q_e=BlnA+BlnC_e \qquad (6)$$

Where B=RT/b_T, and T (K) is the absolute temperature, R is the ideal gas constant (8.314 J/molK) and b_T (J/mol) is the Temkin constant. The constant B is related to the heat of adsorption and A (L/mg) is the equilibrium binding constant [4,9,10]. The constants A and B were determined from the intercept and slope of the linear plots of q_e versus lnC_e [3]. The Tempkin isotherm model plots for the biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH are shown in Figure 7 and the constant parameters are presented in Table 1. The R^2 obtained for the three metal ions on GCSH were also high and presented good fits (R^2>0.9) but lower than those of the Langmuir and Freundlich isotherm.

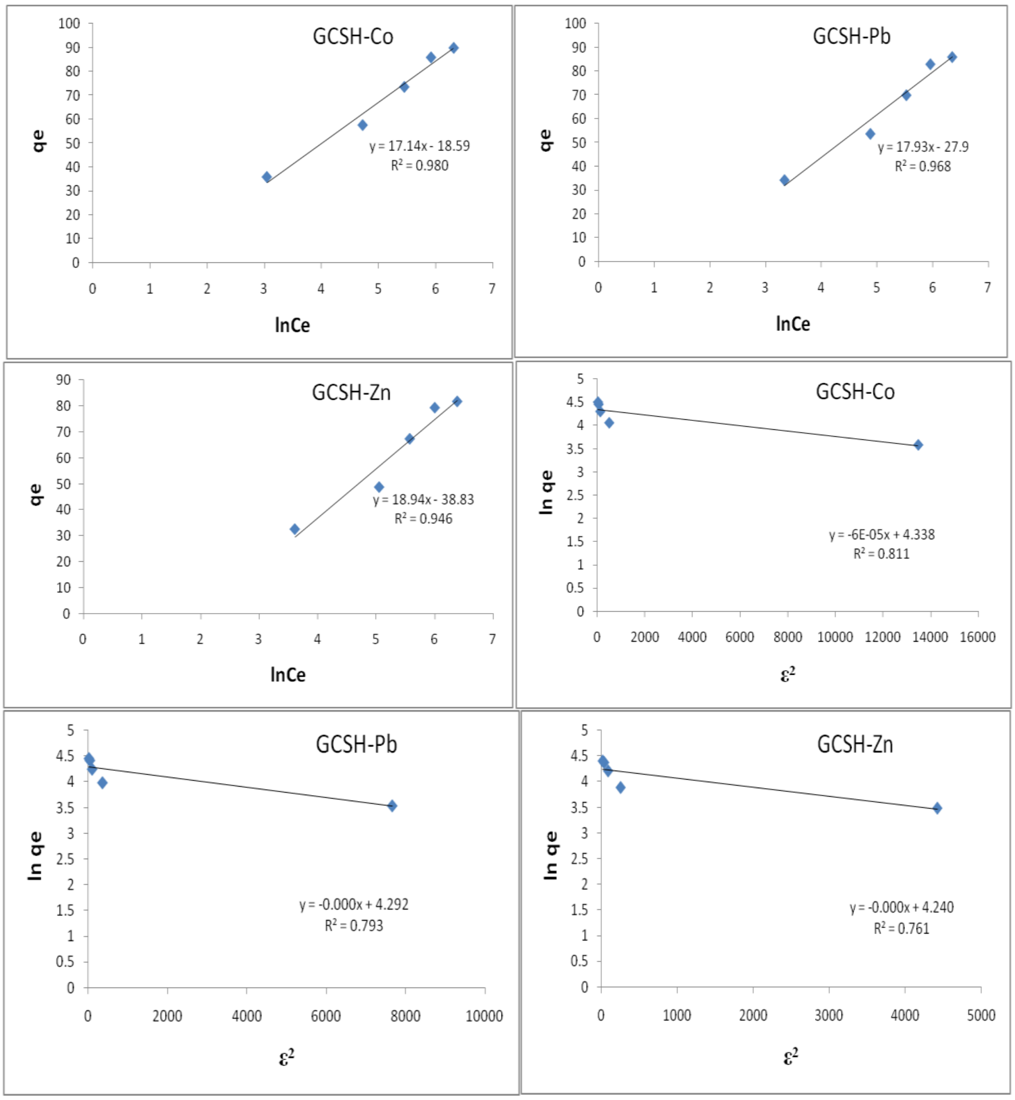

Figure 7: Tempkin and Dubinin-Radushkevich isotherm model plots for the biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH

The Dubinin-Radushkevich (D-R) isotherm is an empirical model generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [6]. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well [16].

This model does not assume a homogenous surface or a constant adsorption potential as the Langmuir model [10]. One of the unique features of the D-R isotherm lies on the fact that it is temperature dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed versus the square of potential energy, all suitable data will lie on the same curve, called the characteristic curve [3,9]. The linear form of the D-R isotherm is given as [4].

$$ln q_e = ln q_m - \beta\varepsilon^2 \quad (7)$$

Where q_e (mg/g) is the adsorption capacity, q_m (mg/g) is the theoretical saturation capacity, β (mol^2/J^2) is a constant related to the mean free energy of adsorption per mole of the adsorbate and ε is the Polanyi potential expressed as [12,14,17].

$$\varepsilon = RTln(1+1/C_e) \quad (8)$$

The D-R isotherm model plots obtained for the biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH are shown in Figure 7 and the isotherm parameters are presented in Table 1. The R^2 indicated that this model did not provide a good fit to the biosorption process as the values were less than 0.9. This model therefore presented the least fit for the biosorption and is therefore not suitable in the description of the biosorption process.

Influence of gourd cell seed husk dosage

The influence of the dosage of GCSH on its adsorption capacity for Co (II), Pb (II) and Zn (II) ions is shown in Figure 8. An observed decrease in the biosorption capacity of GCSH for the three metal ions with increase in dosage was recorded. With increase in adsorbent dose from 0.1 to 0.5 g a decrease in the adsorption capacity of GCSH from 57.6 to 13.6 mg/g, 53.8 to 13.4 mg/g and 48.8 to 13.08 mg/g for Co (II), Pb (II) and Zn (II) ions were obtained respectively. This decrease is as a result of the higher biosorbent dose providing more active adsorption sites which resulted in the adsorption sites remaining unsaturated during the biosorption process [3,6,18]. It could also be due to decrease in the total adsorption surface area and increase in diffusion path length resulting from aggregation of adsorption sites [6,10]. The aggregation becomes increasingly significant as the weight of the adsorbent increase. Similar results have been reported by some scientists [5,9,12,13,18].

On the contrary, an opposite pattern was achieved with the influence of GCSH dosage on the percentage biosorption of the three metal ions as shown in Figure 9. It was observed that an increase in percentage adsorption of metal ions on GCSH was obtained. With increase in adsorbent dose from 0.1 to 0.5 g the percentage adsorption of Co (II) increased from 72 to 85%, For Pb (II) ions increase from 67.25 to 83.75% while for Zn (II) ions from 61 to 81.75% was recorded. The increase is attributed to an increase in the number of available active biosorption sites and surface area of GCSH [4,17]. It is also attributed to increase in negative charge and decrease in the electrostatic potential near the solid surface that favours sorbent-solute interactions [6]. Therefore in order to optimize the use of a given amount of adsorbent i.e., obtain both a high adsorption capacity and high percentage removal, the adsorbent is implemented in several adsorption units in parallel rather than in a single large adsorption unit [3,12,14]. The maximum biosorption capacity of an adsorbent could be determined from column experiment by the use of excess of the adsorbate (metal ions) [6,9,16]. The trend of biosorption of Co>Pb>Zn was also obtained. The adsorbent dose of 0.1 g was chosen and utilized for optimum utilization of the adsorption sites of GCSH.

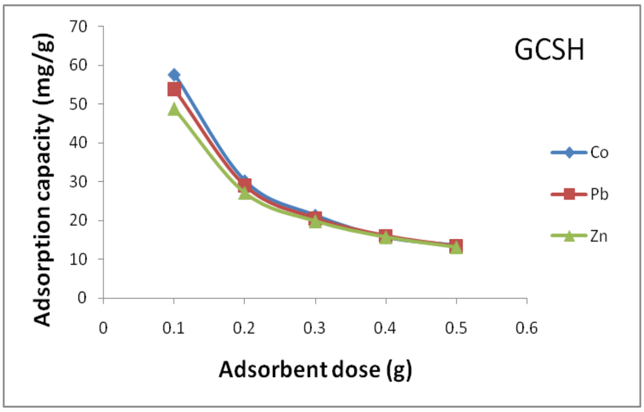

Figure 8: Effect of adsorbent dose on the adsorption capacity of GCSH for heavy metals

Influence of contact time

It is necessary to determine the time dependence of an adsorption system because it provides information on the process mechanism [19]. In this regard it was determined in his study. The influence of contact time on the biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH is shown in Figure 10. It was clearly seen that the rate of removal of metal ions was initially rapid and then diminished gradually until an equilibrium time was attained. This is attributed to the rapid filling of the abundant active sites of GCSH at the start of biosorption by metal ions which became saturated with time attaining equilibrium [10,20]. Similar results have been reported by many researchers [6,7,11,14,16,21]. Equilibrium contact time of 30, 60 and 40 min was recorded for Co, Pb and Zn ions. In fact at equilibrium time of 30 min for Co (II) ions, the percentage removal increased from 17.5 to 72%, For Pb (II) ion from 5 to 60 min the biosorption increased from 4.75 to 67.25%, while for Zn (II) ions from 5 to 40 min an increase from 7 to 61% was recorded.

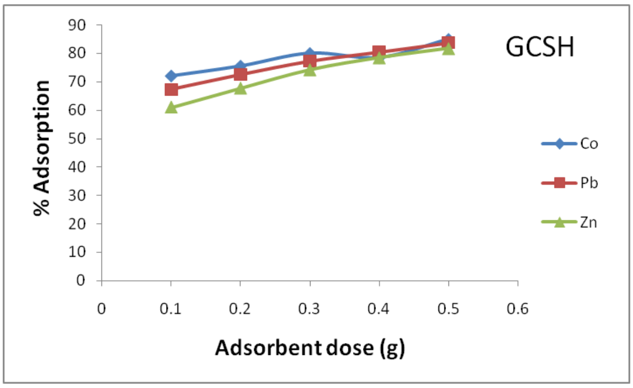

Figure 9: Effect of GCSH dosage on the percentage adsorption of heavy metals

It has been reported that the nature of the adsorbent and its available sorption sites affects the time needed to reach equilibrium [4,6,12]. Despite the facts that the metals were sorbed on the same adsorbent, their equilibrium biosorption times were different. The ionic radius of metal ions has been reported to play the most significant role in determining the equilibrium adsorption time attained by metal ions on an adsorbent [9,10]. Metals with smaller ionic radii tend to diffuse faster and get to the surface of the adsorbent and vice versa [4]. Looking at the ionic radius of the three metal ions; Co (0.74 Å), Zn (0.74 Å) and Pb (1.20 Å) and the equilibrium times recorded Co (30 min), Zn (40 min) and Pb (60 min). It was observed that Co and Zn ions were adsorbed faster than Pb ions due to their relatively smaller sizes. The faster biosorption equilibrium attainment rate of Co than Zn ion was due to the higher electronegativity of Co (1.88) than Zn (1.65) [9,10]. A biosorption contact time of 120 min was selected to obtain equilibrium and optimum removal of metal ions on GCSH adsorbent.

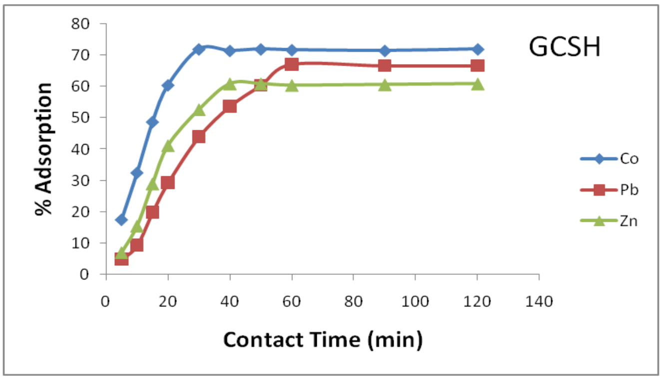

Figure 10: Effect of contact time on the percentage adsorption of heavy metals on GCSH

Kinetic model analysis

An ideal adsorbent for the adsorption of heavy metals should not only have a high adsorption capacity but also a fast rate of removal [6]. Adsorption kinetics describes how fast the adsorption occurs and also gives information on the factors affecting the rate of adsorption. Kinetic modeling has been exploited to evaluate the mechanism of adsorption and its potential rate-controlling steps, which include chemical reaction, diffusion control and mass transfer [20]. In addition, information on the kinetics of metal uptake is required to select the optimum condition for full-scale batch metal removal processes [10]. Predicting the rate of adsorption for a given system is among the most important factors in adsorption system design, as the system kinetics determines adsorbate residence time and the reactor dimensions [4].

Generally, three steps are involved during the adsorption process onto porous adsorbents: (i) Solute transfer from the bulk solution to the external surface of the adsorbent through a liquid boundary layer (film diffusion), (ii) Solute transfer from the sorbent through the pores to the intraparticle active sites (Intraparticle or pore diffusion) and (iii) Interactions of the solute with the available active sites of the adsorbent (sorption process or reaction resistance) [4,9,12,14]. One or more of the above mentioned stages may control the rate at which the solute is adsorbed and the amount of solute that is adsorbed onto the adsorbent. Therefore the adsorption rate is usually controlled by film diffusion or intraparticle diffusion or both [4,10]. In this study, the kinetics of sorption that defines the efficiency of biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH were analyzed by the pseudo first order, pseudo second order, intraparticle diffusion and film diffusion rate equations.

The first order kinetics is due to electrostatic attraction between the metal ions and the external surface of the adsorbent which is likely a physical adsorption mechanism [3]. The pseudo first order kinetic model was developed to correlate the experimental data when kinetic adsorption occurs due to a driving force generated by a concentration gradient of the adsorbate [6]. This model is based on the assumption that the rate of adsorption site occupation is proportional to the number of unoccupied sites and also assumes that one metal ion is sorbed onto one sorption site on the adsorbent surface [4]. The linear form of the Lagergren model is given as [14]:

$$\log(q_e - q_t) = \log q_e - (K_1 t / 2.303) \quad (9)$$

Where q_e and q_t in mg/g are the amounts of metal ions adsorbed at equilibrium and time t, respectively. K_I (min^{-1}) is the pseudo first order rate constant. K_I and q_e were determined from the slope and intercept of the linear plot of $log(q_e - q_t)$ versus t [16].

Table 2: Kinetic parameters for the biosorption process

Kinetic/Adsorbent	**Co (II)**	**Pb (II)**	**Zn (II)**
qe_{exp} (mg/g)	57.6	53.8	48.8
Pseudo-first-order			
qe_{cal} (mg/g)	80.72	75.86	73.28
K_I (min^{-1})	0.104	0.048	0.076
R^2	0.973	0.983	0.98
Pseudo-second-order			
qe_{cal} (mg/g)	66.67	125	66.67
h(mg/g min)	6.803	1.189	2.283
K_2(g/mg min)	0.002	7.6×10^{-5}	5.1×10^{-4}
R^2	0.983	0.561	0.883
Intraparticle diffusion			
K_d (mg/g min$^{1/2}$)	4.465	6.548	5.076
C	20.04	-6.06	5.112
R^2	0.623	0.861	0.725
Film diffusion			
K_{fd}	0.104	0.05	0.077
D	0.338	0.344	0.406
R^2	0.973	0.983	0.98

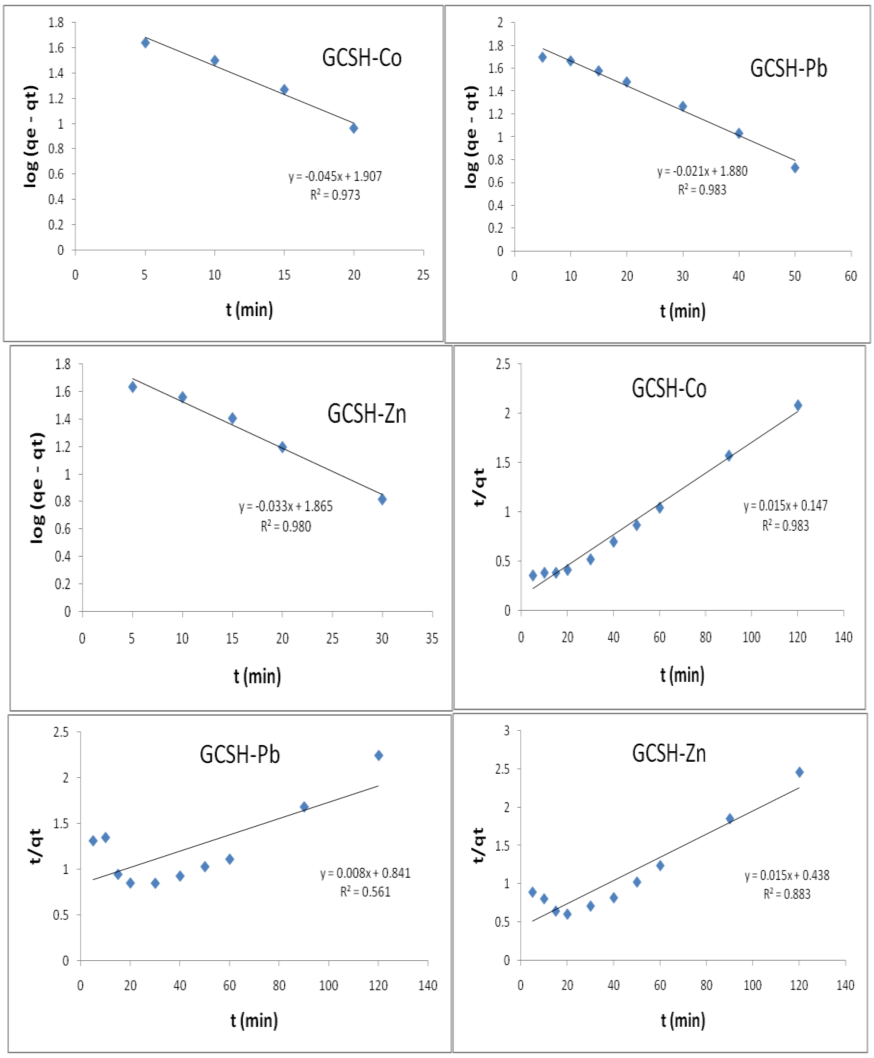

Figure 11: Pseudo first and Pseudo second order model plots for the biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH

The pseudo second order model assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites [20]. It is also based on the assumption that chemisorption is the rate controlling step [6]. The linear form of the pseudo second order model is given as [14]:

$$t/q_t=1/K_2q_e^2+t/q_e \qquad (10)$$

Where q_t and q_e in mg/g are the adsorption capacity at time, t and equilibrium respectively. K_2 (g/mg min) is the equilibrium constant of pseudo-second order adsorption [3]. The initial sorption rate (h) can be calculated from [4].

$$h=K_2q_e^2 \qquad (11)$$

The pseudo second order model was applied by the plots of t/q_t versus t and the constants q_e and K_2 were calculated from the slope and intercept of the plots, respectively [17]. The pseudo second order plots for the biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH is shown in Figure 11 and the constant parameters are presented in Table 2. This model also presented a very good fit (R^2>0.97) for the biosorption of Co (II) than the pseudo first order model, but did not provide good fits for Pb (II) and Zn (II) as the R^2 values were low. The experimental qe values were close to the calculated qe values for Co (II). This showed the pseudo second order model best describes the biosorption of Co (II) indicating chemisorptions [9]. However, the pseudo first order model best describes those of Pb (II) and Zn (II) indicating physisorption [4]. The initial sorption rate (h) showed a faster rate of adsorption of Co (II) followed by Zn (II) and a much slower rate for Pb (II) ions. The faster rate of Co (II) biosorption is due to its small ionic radii (0.74 Å) and higher electronegativity (1.88) while the slower rate obtained for Pb (II) was due to its higher ionic radii (1.20 Å) making for a more difficult diffusion to the surface of the adsorbents. Similar results have been reported previously [4,9,10].

To determine if intraparticle diffusion is the mechanism of biosorption, the intraparticle diffusion model was applied and given in its linear form as [10].

$$q_t=K_dt^{1/2+}C \qquad (12)$$

Where K_d (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant. Intra-particle diffusion is the sole rate limiting step if the regression of q_t versus $t^{1/2}$ is linear and passes through the origin ($C=0$) [14]. The occurrence of the intercept (C) reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption (film diffusion) in the rate controlling step [4,10]. The intraparticle diffusion model plots obtained for the biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH are shown in Figure 12 and the constant parameters are presented in Table 2. The R^2 values were low (R^2<0.9) suggesting a poor fit of the intraparticle diffusion model. The plots did not pass through the origin which means intra-particle diffusion cannot be the sole rate determining step [20]. These suggested that film diffusion might be the major determining mechanism of the biosorption of metal ions on GCSH. Although the intraparticle diffusion model did not give good fit to this biosorption process, it has been found to provide good fits in most adsorption studies, one of such is the sorption of trivalent chromium unto novel cassava peel modified kaolinite clay [21].

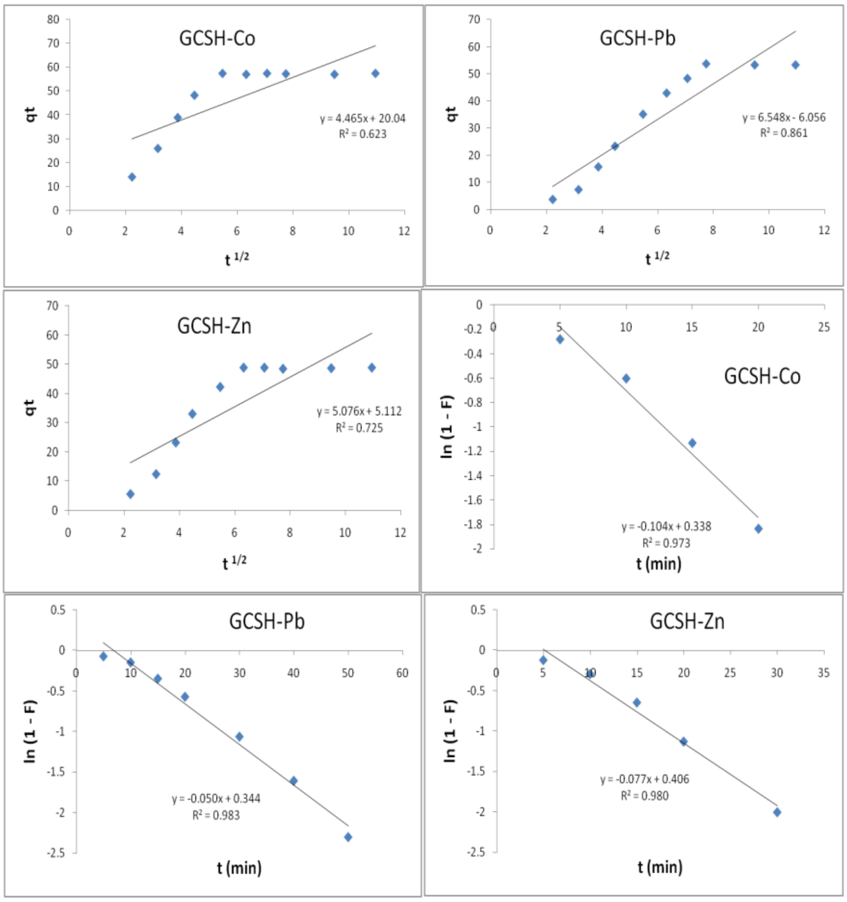

Figure 12: Intraparticle diffusion and Liquid film diffusion plots for the biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH

The liquid film diffusion model plots for the biosorption of Co (II), Pb (II) and Zn (II) ions on GCSH are shown in Figure 12 and the constant parameters are presented in Table 2. The R^2 values obtained were high (>0.9) and better than those of the intraparticle diffusion model. This indicated that film diffusion is a major mechanism of biosorption of the metal ions on GCSH. Previous studies have reported similar results [10,20].

CONCLUSION

The result of this study showed that gourd cell seed husk was suitable as effective adsorbent for the removal of Co (II), Pb (II) and Zn (II) ions from solution. The trend of biosorption of heavy was Co (II)>Pb(II)>Zn (II) ions. The FTIR spectra showed the presence of surface functional groups such as OH, -C=O, C=C and C-Cl responsible for the binding of the positively charged metal ions on the adsorbent surface. SEM morphology revealed a porous surface structure. The influence of solution pH showed low biosorption of metal ions at lower pH values. However, the adsorption increased with increase in pH up to pH 6.0 after which it became fairly stable. The effect of initial metal ion concentration on biosorption showed an increase in the adsorption capacity and decrease in the percentage removal of metal ions. In fact the adsorption capacity of GCSH for Co, Pb and Zn ions increased with increase in metal concentration (200–1000 mg/L) from 35.8 to 90 mg/g, 34.4 to 86 mg/g and 32.6 to 81.8 mg/g respectively. Four adsorption isotherm models, namely; the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherms were applied to the experimental equilibrium data. The Freundlich isotherm was found to give the best fit for the biosorption, except for Zn (II) ions on GCSH which was better described by the Langmuir isotherm model. The best fit presented by the Freundlich model indicated a multilayer adsorption of metal ions on heterogeneous surfaces of the adsorbents. An increase in the percentage removal of metal ions and a decrease in the adsorption capacity were obtained when the effect of adsorbent dose was investigated. The effect of contact time on the biosorption of Co the metals showed a rapid initial rate of removal after which it became constant with the attainment of equilibrium. Equilibrium times of 30, 40 and 60 min were established for the biosorption of Co (II), Zn (II) and Pb (II) ions, respectively. The ionic radius of the metal ions (Co (0.74 Å), Zn (0.74 Å), Pb (1.20 Å) was found to play a major role in the rate at which equilibrium sorption was achieved. Kinetic modeling was performed by the application of the pseudo first order, pseudo second order, intraparticle diffusion and liquid film diffusion rate equations. The pseudo first order model was found to be applicable in the adsorption of Pb (II) and Zn (II) ions which indicated a physical adsorption process. On the other hand, the pseudo second order model was applicable for Co (II) adsorption on the adsorbents suggesting a chemical adsorption mechanism. The diffusion mechanism was found to be controlled by film diffusion rather than intraparticle diffusion. The results of this study therefore suggest the potentials of GCSH as suitable low cost adsorbent for the biosorption of Co (II), Pb (II) and Zn (II) ions from their contaminated solutions or effluents. This adsorbent could be applied to solve the problem of high cost involved in the use of activated carbon.

REFERENCES

[1] R. Lakshmipathy, N.C. Sarada, N. Jayaprakash, *Inter. J. Chem. Tech. Res.*, **2015**, 8, 25-31.
[2] H. El-Hassouni, D. Abdellaoui, S. El-Hani, R. Bengueddour, *J. Mater. Environ. Sci.*, **2014**, 5, 967-973.
[3] K.G. Akpomie, F.A. Dawodu, K.O. Adebowale, *Alexandria Eng. J.*, **2015**, 54, 757-764.
[4] F.A. Dawodu, K.G. Akpomie, *J. Mater. Res. Technol.*, **2014**, 3, 129 -141.
[5] A.G. Hadi, *Inter. J. Chem. Tech Res.*, **2016**, 9, 343-351.
[6] Z. Yao, J. Qi, L. Wang, *J. Appl. Surf. Sci.*, **2010**, 174, 137-145.
[7] J.O. Nwadiogbu, P.A.C. Okoye, V.I.E. Ajiwe, N.J.N. Nnaji, *J. Environ. Chem. Eng.*, **2014**, 2, 1699-1708.
[8] M.R. Lasheen, N.S. Ammar, I.S. Hanan, *J. Solid State Sci.*, **2014**, 14, 202-209.
[9] F. Lawson, Y. P. Ting, I. G. Prince, *J. Biotechnol. Bioeng.*, **1991**, 37, 445-452.
[10] K.G. Akpomie, F. A. Dawodu, *J. Adv. Res.*, **2015**, 6, 1003-1014.
[11] A.R. Kumar, K. Sobha, *Inter. J. Chem. Tech. Res.*, **2015**, 8, 1769-1778.
[12] K.G. Akpomie, F.A. Dawodu, *Trans. Royal. Soc. South. Afr.*, **2015**, 70, 83-88.
[13] C. Raji, T.S. Anirudhan, *Ind. J. Chem. Technol.*, **1997**, 4, 157-167.
[14] S. Larous, A.H. Meniai, M.B. Lehocine, *Desalination.*, **2005**, 185, 483-492.
[15] Y. Nuhoglu, E. Malkoc, *Bioresor. Technol.*, **2009**, 100, 2375-2387.
[16] B. Das, N. K. Mondal, *Univ. J. Environ. Res. Technol.*, **2011**, 1, 515-525.
[17] A.B. Etukudoh, K.G. Akpomie, N.D. Obi, P.E. Chimezie, A.E. Agbo, *Der Pharma Chemica.*, **2016**, 8, 9-15.
[18] A.N. Babu, G.V.K. Mohan, K. Ravindhranath, *Inter. J. Chem. Res.*, **2016**, 9, 506-512.
[19] N.Y. Fairooz, *Inter. J. Chem. Tech. Res.*, **2016**, 9, 495-452.
[20] S.R. Taffarel, J. Rubio J, *Min. Eng.*, **2009**, 22, 336-246.
[21] K.G. Akpomie, O.A. Odewole, C.U. Ibeji, O.D. Okagu, I.I. Agboola, *Der Pharma Chemica.*, **2017**, 9, 48-55.