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TABLE OF CONTENTS

SORPTION OF LEAD FROM AQUEOUS SOLUTION ON RAW AND MODIFIED SHEA BUTTER (*VITELARIA PARADOXA)* SEED HUSK

Muibat Diekola Yahya[1] Mohammed-Dabo[2], I.A. Ahmed[2], A.S. Olawale[2], A.S.
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ABSTRACT

The adsorption of Pb from aqueous solution using raw and modified shea butter seed husks was studied. Encapsulation technique was employed to modify the husks.Instrumental analysis such as FT-IR, XRD, BETand SEM were used to characterize the sorbent.The functional groups responsible for metallic biosorption were the –OH, -COOH and –NH$_2$.Batch adsorption process was used to study the effect of various parameters ranging from the effect of initial metal ion concentration; pH; equilibrium time; andtemperature. Optimum pH was 6 and equilibrium time was 30mins.Adsorption isotherm was applied to experimental data by Langmuir, Freundlich, Temkin, and Dubunin- Radushkevich (D-R) isotherms. The Langmuir best fits the data with the highest correlation coefficient 0.99 for RSBH. The maximum sorption capacity was 22.222mg/g for RSBH and2222.22mg/g for MSBH. The mean free energy Ein the range of 0.45 to 4.5 KJ/molobtained by D-R isotherm indicated that the process of adsorption is physiosorption. The calculated amount adsorbed of the Pb(II) was approximately equal to the experimental amount adsorbed by the Kinetic model of Pseudo-second-order. The thermodynamic properties indicated that the Gibbs free energy is spontaneous and feasible for both sorbents. The results obtained showed that the shea butter seed husks and the modified one can serve as potential adsorbent for the removal of Pb(II) ions.
KEYWORDS: Adsorption, Encapsulation, husks, isotherms studies, lead.

INTRODUCTION

Heavy metal pollution is becoming alarming throughout the world especially in Nigeria due to the rapid increase in population and growth of small and medium scale enterprise. [1]reported that of the total metals on the earth crust, at least 20 metals are classified as toxic and 50% of these are emitted in large quantities that pose risks to human health. Electroplating and Mining industry forms a large percentage of the small medium enterprise because of the ease and feasibility of starting it in a growing economy like ours. The effluents from this enterprise are indiscriminately being discharged into the water bodies thereby increasing the threshold limits of these metal ions. Among this effluent is Lead(Pb).[2] gave the maximum allowable limits for lead as 0.01mgL[-1]while a chronic lead toxicity can lead to paralysis of the peripheral motor nerves, anaemia, kidney damage, sterility both in males and females, abnormal fetal development, abnormal neurological function, brain damage in children[3].

Various techniques have been employed for the removal of heavy metals from aqueous solution. These are the electro-chemical precipitation, coagulation, flotation, adsorption, ion-exchange and reverse-osmosis or electrodialysis, etc [4]. However, in many instances these processes do not work effectively and the high costs limit their usage [5]. Wastes from agricultural processes have been proven to have the potential to be used as low cost adsorbents to mention a few such as rice husk [6], maize bran [7], saw dust of various plants [8], cassava wastes[9]. One potential adsorbent material is the Shea butter husks. The Shea tree is widely spread across the

semi-arid zone of sub- Saharan Africa with large amount in Nigeria. Some heavy metals had been tested using the shea butter husks and have shown positive results in their adsorptive capacity such as Fe (II) ions, and Zn (II) ions [10].Developed Countries now have pilot plants that have been constructed for the applicability of using an adsorbent as a basis for metal sequestering processes. In order to stabilize and enhance the mechanical properties and the chemical resistance for potential technological use, immobilization of the adsorbent is sometimes required [11]. Immobilization helps to create a material with the right size, rigidity and porousity necessary for the sorption process. However, there is limited. or no information on immobilization of the shea butter seed husk. Calcium alginate has been chosen as a polymer that will serve as an entrapper for the husk in order to enhance its sorptive sites. Grape stalk powder immobilized in calcium alginate has shown high efficiency in Cr(VI) removal [12]. This study therefore seek to study the uptake of Pb(II) using both raw and modified shea butter husks for future scale-up and serves as a database for further research.

MATERIALS AND METHODS
Preparation of Shea butter husks
The shea butter fruits were collected from the farmland of Sabon-Daga community area in Minna, Niger state, Nigeria.
The collected biomaterials was sorted out and the good ones were thoroughly washed with tap water to remove soil and dusts, they were further washed with distilled water and dried in an oven at 80°C until a constant weight is achieved [13].

Dry shea butter seed was dehusked, and the husks crushed with a Moulinex blender and sieved using an electrical sieve shaker (Octagon 2000 Endecott) to obtain a powder <250μm particle size (Endecotts England BS 410/1986).This shall be called the Raw Shea Butter Husks (RSBH) and then stored in a polyethene bag for further use.

Preparation of Modified Shea butter Husks (MSBH)

To prepare MSBH, 1g ofsodium alginate was dissolved into 100ml of distilled water at a temperature of 65°C [14]. The gel wasallowed to cool down to room temperature (25°C). After complete dissolution, 2g of RSBH (<250 μm) was added and an intense agitation was maintained on a magnetic stirrer in order to produce homogeneous mixture of alginate and the powder. After wards the solution was added drop wise via a syringe to a solution of 0.1M calcium chloride under soft agitation. As a result of this, the alginate chains wrapped up the sorbents to form beads [15]. The entrapped RSBH in the calcium alginate (CA)beads were cured in the CaCl$_2$ solution for 24hr. The emerging hard spherical beads containing 2% (w/v) of RSBH now called MSBH were filtered and rinsed several times with distilled water to remove excess Ca^{2+} ions. These were covered with abundant distilled water and stored in arefrigerator at around 4°C forfurther use.

Preparation of metal solutions

Deionized water was used to prepare all solutions.All reagent used were of analytical grade.Stock solution (1000mg/L) of lead was prepared by approximately dissolving 1.5980g of lead nitrate [Pb(NO$_3$)2] in 100ml of deionized water and dilute to1 liter in a volumetric flask with deionized water.

Characterisation of adsorbent

Raw shea butter husks were characterized using several techniques. The functional groups of the raw sorbents and Pb- loaded sorbent were characterized using the Fourier Transform-Infrared Spectrophotometer (FT-IR-8400S, Shimadzu Japan). The spectral range varied from 4000cm^{-1} to 400cm^{-1}.The surface morphology of the sorbent was studied with High ResolutionScanning Electron Microscope (EVO MA 10 Carl Zeiss). The X-ray diffraction (XRD DY 874 Analytical Empyrean Netherland) analysis was carried out to determine the mineral composition, and crystallinity of RSBH. The Braunaur, Emmet and Teller test (BET) was used to determine the pore area of the raw husks.

Equilibrium Sorption Procedure for Batch Adsorption

The measurement of metal ions uptake onto RSBH and MSBH was determined by batch adsorption technique using a Multipurpose flask shaker (TT 12F Techmel&Techmel, U.S.A) at a speed of 200rpm and 303 ±1K [16]. For this purpose, 40 beads of either MSBH or 0.5g of RSBH were added to 50ml of metal solution at varying concentration in 250ml Erlenmeyer flasks. Experiments were carriedout for a contact time of 240 minute to ensure that the system reaches equilibrium until at saturation where there is no significant change between the final concentrations obtained. After agitation, gel beads were separated from the metal solution by cellulose filter paper and metal concentration in the liquid phase was analysed. In the case of the RSBH the agitated solution were centrifuged at 5000rpm for 5 mins in order to obtain a clear solution before filteration. Quantification of residual concentration of sorbates in metal supernatant solutions was carried out using Flame Atomic Absorption /Emission Spectrophotometer Varian Spectra AA 220FS. The metal concentration in the solid, qe (mg.bead^{-1}) or (mg.g^{-1}) as the case maybe was calculated from the difference between the initial, C_i and equilibrium,C_e metal concentration in solution (mg.L^{-1}). The uptake of the sorbent was calculated according to the next equation:

$$qe = (Ci - Ce)\frac{V}{N} \qquad (1)$$

Where V(L) is the solution volume in liter and N is the amount of beads.N could also be weight of adsorbent in g when the raw sample is used.To compute the sorption percentage,

$$\%R = \frac{Ci - Ce}{Ci} \times 100 \qquad (2)$$

Initial pH effect on Pb sorption

The effect of pH on adsorption capacity of RSBH and MSBH was studied by dispersing 0.5 g of RSBH or 40 beads of MSBH in 50 mL of 250 mg/L of Pbsolution. These were contained in a series of conical flasks in the range from pH1 to pH10. The pH of the adsorbate solution was adjusted with either 1 M NaOH or 0.1 M HCl without increasing the initial volume of the solution significantly. These were agitated for 2 h at 200 rpm at room temperature (298 K)[17]. Table 1 e Values of surface acidity and PZC of defatted C. papaya.

Effect of Temperature

The effect of temperature on the adsorption of Pb^{2+}RSBH and MSBH was studied by repeating the procedure for initial concentration at 313K, 323K, 333K 353K and 363Kat optimum pH value of 6 and adsorbent dosage level of 0.5g or 40 beads. The equilibrium contact time for adsorption was 2 hr.

Effect of Adsorbent Dosage

Adsorbent dosage was varied from 40 beads-240 beads for MSBH and 0.5g-3g for RSBH in 50ml of Pb(II) solution at a concentration of 250mg/L.

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Adsorbent dosage was varied from 40 beads-240 beads for MSBH and 0.5g-3g for RSBH in 50ml of Pb(II) solution at a concentration of 250mg/L.

This was agitated for 120minutes at a speed 200rpm. Solutions were filtered and residual metal concentrations was analysed as stated previously.

RESULTS AND DISCUSSION
Characterisation of the adsorbent material

The IR spectra (Fig. 1) indicate that the RSBH and loaded Pb-RSBH possess different surface structure. There are some emerging bands 3000/cm for the Pb-RSBH which suggests that it is unsaturated (contains C=C). Major band on the Pb-loaded samples are broad which suggest a hydroxyl group. Absorption also occur at lower end of the range (i.e below1700/cm) this suggest that the compound is probably an amide or carboxylate[18].Additional moderate band in the range 1200-1000 implies simple hydroxyl compound. The sharp peak observed at 1738.89 for RSBH and its shift to 1717.67 for Pb-RSBH is assigned to C-O bond.Emerging of new bands on the modified sorbents at 3427.62, 3738.83, 3855.83, 4087.30 and 4416.17 may be attributed to binding of –OH group with the polymeric structure. While small peaks at 606.63 for RSBH and 459.07 for modified sorbents may be assigned to S-O stretching in the sulphonate group.

(a)   (b)
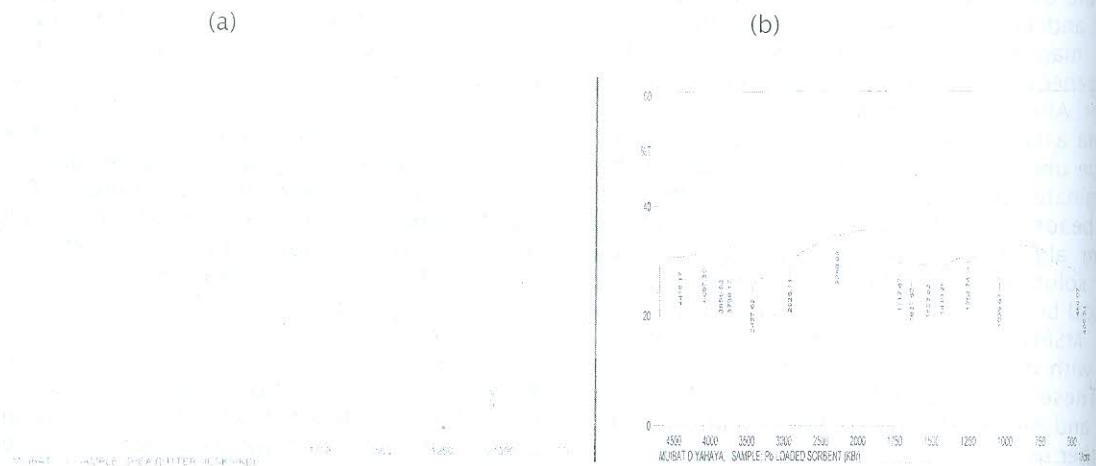
Figure1: FT-IR pattern for (a) raw shea butter husk and (b) Pb-loaded modified shea butter husk

Figure 2 below shows the XRD patterns of the RSBH. The non-appearance of major peaks indicated that the sorbent is amorphous in nature. A very weak peak was observed at 22° 2Θdiffraction angle and was attributed to cristobalite [19].
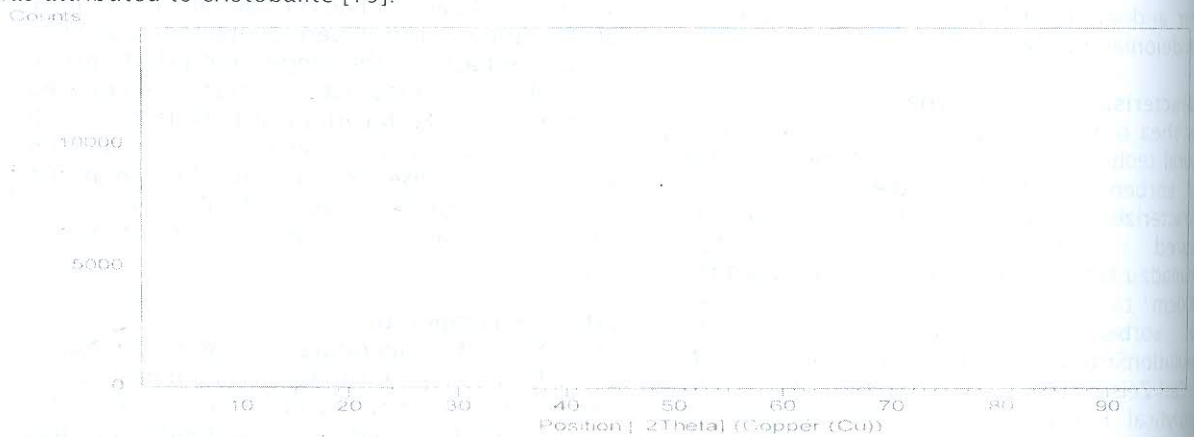
Figure 2: XRD patterns of RSBH

Figure 3 shows the SEM images of the RSBH at different magnification. The micrographs indicated that

the surface was irregular and has hollow cavities.

(a)

(b)

Figure 3: SEM of Shea butter husk (RSBH) at mag (a) 1.00 KK & (b)

The Brunauer-Emmet -Teller (BET) protocol on micromeritics performed on the raw shea butter seed husks was measured at 77Kand gave the average surface area as 1099.6328 m²/g and the pore volumes as 0.4513 cm³/g. This high values indicate the adsorptive sites and porousity of the husks

Effect of pH

The pH governs the speciation of the metals in aqueous solution and also affects the dissociation of active functional sites on the sorbent [20]. Notably is this as shown in Figure 4.The percentage removal of Pb using RSBH increases progressively from 48.1 to 98.3% over pH range from 2.0 to 6.0. The same trend has been reportedin adsorption of lead using rice husks ash [21].This increase in thebiosorption is as a result of decrease in the protons that is

H^+/H_3O^+ generated from the dissociation of waterwhich consequently lowers the electrostatic repulsion between the Pb(II) and surface sites[22].In comparison withmodified shea butter husks(MSBH)the pH values shows that aninsignificant contribution is observed in the percent removal at very low pH value (pH 2) which was 13.7% for MSBH and 48.1% for RSBH. However, this improved steadily from 71.4 % removal at pH of 6 to 96.1% at pH of 10. It has been observed that for Pb(II) adsorption, pH greater than 6 gives hydrolysis products of lead and this can undergo polymerization[23]. Dominant species is $Pb(OH)_2$ at pH>6.0 and Pb^{2+} and $Pb(OH)^+$ at pH<6.0 pH greater than 6 may not be desired and as such pH values less than 6 have to maintained for effective adsorption.
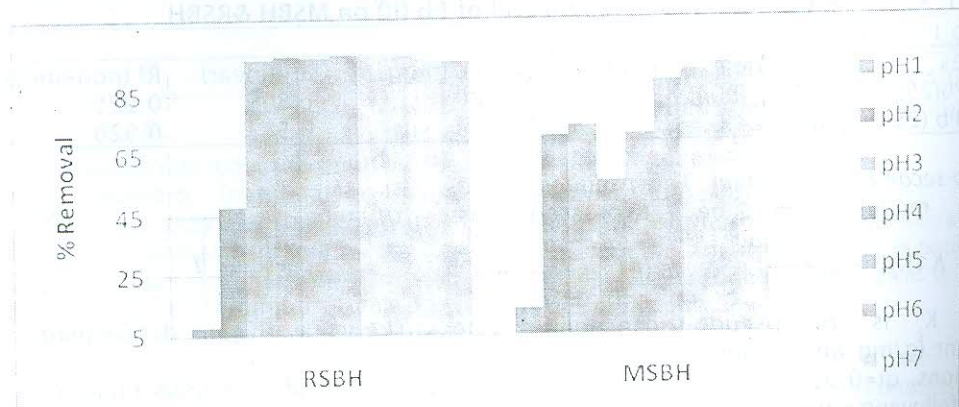
Figure 4: Percentage removal of Pb(II) on RSBH and MSBH at different initial pH

Effect of initial metal ion concentration

The effect of initial Pb^{2+} concentrationon RSBH and MSBH showed the amount adsorbed of Pb(II) in every gram of the husks was high and so also was the percentage removal of the metal ions.At lower initial conc. almost all the sites are filled during adsorption as there is greater interaction between the metal ion and sorptive sites but as the concentration increases more Pb(II) are left un-adsorbed due to saturation of the adsorptive sites . This high rate of adsorption is as a result of increase in concentration values which

provides the driving force that helps to overcome mass transfer resistance between the metal ion and adsorbent [23]. Contrast to the RSBH, the MSBH for Pb(II) uptake gave a better percent removal and amount adsorbed of the metal ion from the stock solution. The stability observed in the adsorption process may be attributed to the calcium alginate. This played an important role in theenhanced porosity of the sorptive sites and helps toprevent leaching of the organic component to the solution.

This is evident in this study as percent removal increased to over 90% as concentration builds as high as 250mg/L. Authors that have used calcium alginate successfully to mention a few are [12];[15];[11].

Effect of Time

The effect of contact time on the removal of Pb^{2+} by RSBH and MSBH at 250mg/L revealed a rapid adsorption in the first 30mins and thereafter adsorption rate decreased gradually. The equilibrium concentration [24], at 4hr contact time was assumed for the sorbent to reach saturation. This followed similar trends in previous studies [17]; [25].The rate of percent metal removal is higher at the beginning firstly because of the affinity the sorbates has for the sorbent. Also, it is due to a large surface area of the husks hasavailable for the adsorption of the metals.This rapid metal ion removal at smaller time range has significant economic importance in the scale-up and design process as this will facilitate the utilisation of lesser quantity of sorbent at maximum efficiency [22].

Effect of Adsorbent Dosage

The amount adsorbed of the metal ions for RSBH and MSBH decreases with increase in adsorbent dose. For instance the amount adsorbed of Pb at 0.5g is 24.34mg/g for RSBH, this then reduces drastically to 3.43mg/g at 3.5 g of the adsorbent mass. This reduction is as a result of using large amount of adsorbent dose which leaves the active sites partially filled and some sites even vacant. Similar observation was reported by[26].The reverse is the case with percent removal of the metal ions from the solution. It rather, increases with increase in biosorbent mass due to larger surface area on the sorbent and thus creates easy penetration of the metal ions to the adsorption sites [23].

Adsorption Kinetic study

In order to investigate the adsorption of Pb^{2+} on the RSBH and MSBH the pseudo-first –order of Lagergren,and pseudo-second-order, kinetic modelsof Hoand Mckay,were used to predict the rate constants. These rate controls the residence time and the mechanism involved in the adsorbate uptake in the solid - solution interphaseX [23]. The conformity between the calculated amount adsorbed and experimental data is determined by correlation coefficient (R^2). 3.5.1 *Pseudo-first-order model*: The pseudo first-order equation is generally expressed as follows

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \qquad (3)$$

Where qe is the amount of adsorption capacity at equilibrium (mg/g), qt is amount adsorbed at time t, K_1 is the pseudo-first-order rate constant (min^{-1}).The values of qe and K_1 for the pseudo-first-order kinetic model were determined from the intercepts and the slopes of the plots of log (qe-qt) versus time, respectively. The values are given inTable 1.

Table 1: Kinetic parameters for the removal of Pb (II) on MSBH &RSBH

Pseudo-1st-order model					
Samples	qe exp. (mgg⁻¹)	qe calc.(mgg⁻¹)	R² (linear)	R² (non-linear)	K₁(min⁻¹)
RSBH-Pb(250mg/l)	79.0495	1.1220	0.809	0.925	-0.3708
MSBH-Pb (250mg/l)	24.0978	1.1454	0.583	0.920	-0.0207

Pseudo-second-order model: The pseudo-second-order model can be expressed as:

$$\frac{dqt}{dt} = K_2(qe - qt)^2 \qquad (4)$$

Where K_2 is the pseudo-second–order rate constant (g/mg min). Integrating with boundary conditions, qt=0 at t=0 and qt=qt at t=t, results in the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 qe^2} + \frac{1}{qe}t \qquad (5)$$

Theinitial sorption rate h (g/mgmin), at $t \rightarrow 0$ can be defined as:

$$h = K_2 qe^2 \qquad (6)$$

Re- arranging and substituting gives

$$qt = \frac{t}{\frac{1}{h} + \left(\frac{1}{qe}\right)t} \qquad (7)$$

The value of *qe* is determined from the slope of the plot of $\frac{t}{qt}$ versus *t* (Fig. not shown), and *h* is obtained from the intercept. The values of qe, K_2, h and R^2 are shown in table 2.The experimental values (qe,exp.) correlated well with the calculated (qe,calc.) values for pseudo-second-order model than the pseudo-first-order, the correlation coefficient is closer to unity and the graphs linear for second-order than that of the first order model.

Nevertheless, the non-linear correlation coefficient for pseudo-first-order was over 90% (figure not shown).Therefore the adsorption can be said to follow pseudo-second-order-model.

Table 2: Kinetic Parameters for the removal of Pb(II) on MSBH and RSBH

Pseudo-2nd -Order-model

Sample	qe(exp.) (mgg^{-1})	qe(Calc.) (mgg^{-1})	R^2	K^2 $(gmg^{-1} min^{-1})$	h $(mgg^{-1} min^{-1})$
MSBH (Pb-250)	85.41141	90.90909	0.995	0.00138	11.405
RSBH (Pb-250)	24.44560	24.39024	0.999	0.09882	58.786

Adsorption Equilibrium Study
In order to ascertain the applicability of an adsorbent, it is important to subject the experimental data to theoretical isotherms. Various isotherm equations have been used to describe the equilibrium characteristics of the adsorption process like Langmuir, Freundlich, Dubunin-Radushkevich and Temkin isotherms.

Langmuir Isotherm
This model is based on the assumption that active surface sites exist on the solid material, to which the metals are adsorbed. The ions are fixed on a monolayer on the surface. This means that there is no penetration of ions into the interior of the adsorbent. The model can be expressed in the following manner:

$$q_{eq} = \frac{q_m C_{eq}}{K_d + C_{eq}} \qquad (8)$$

or

$$\frac{C_{eq}}{q_{eq}} = \frac{K_d}{q_m} + \frac{C_{eq}}{q_m} \qquad (9)$$

where q_{eq} is the equilibrium concentration of the metal on the biomass (mgmetal g^{-1} dry biosorbent), qm is the maximum concentration of the metal on the biomass (mgmetal g^{-1} dry biosorbent), K_d is an adsorption energy related constant (mgL^{-1}) known as Langmuir equilibrium constant and C_{eq} is the equilibrium concentration of metal in the solution (mg L^{-1}).A plot of C_{eq}/q_{eq} versus C_{eq} should be a straight line with a slope $(1/q_m)$ and an intercept as $(1/q_m K_d)$.A dimensionless constant, separation factor, R_L describes the type of Langmuir isotherm as;$R_L = 0$(irreversible);$R_L = 0 < R_L < 1$(favourable); $R_L > 1$(unfavourable);$R_L = 1$(Linear)

$$R_L = \frac{1}{1 + bCi} \qquad (3)$$

Where 'b' is the Langmuir constant(Lmg^{-1}) and Ci is the initial concentration of sorbate(mgL^{-1}). The linear plots of the adsorption of Pb^{2+} is shown in Fig.5. From the plots it is observed that almost all the samples follow the Langmuir isotherm . The correlation coefficient,R^2 are greater than 0.900.The maximum adsorption capacities corresponding to amount adsorbed in mg/wet bead for Pb(II) using RSBH and MSBH are shown on Table 3. The maximum uptake value of 22.222mg/g and 55.555mg/wetbead respectively for RSBH and MSBH far exceeds other adsorbents (see Table 3). The MSBH for Pb(II) adsorption showed tremendous improvement compared to the RSBH and this may compensate for the cost of additional processing. On calculation of the amount adsorbed to mg/gof the sorbent, the maximum adsorption capacity of2222.22mg/g was obtained. The strong affinity can be confirmedfrom $R_L$which was favourable for bothsamples [27].

Freundlich isotherm
Freundlich isotherm is an empirical equation describing the adsorption onto a heterogeneous surface. The Freundlich isotherm is commonly presented as :

$$q_e = K_F C_e^{1/n} \qquad (10)$$

where, K_F and *n* are the Freundlich constants related to the adsorption capacity and the adsorption intensity of the adsorbent, respectively. The values of *n* between 1 and 10 (i.e., 1/n less than 1) represent a favorable adsorption.

Muibat *et al.*
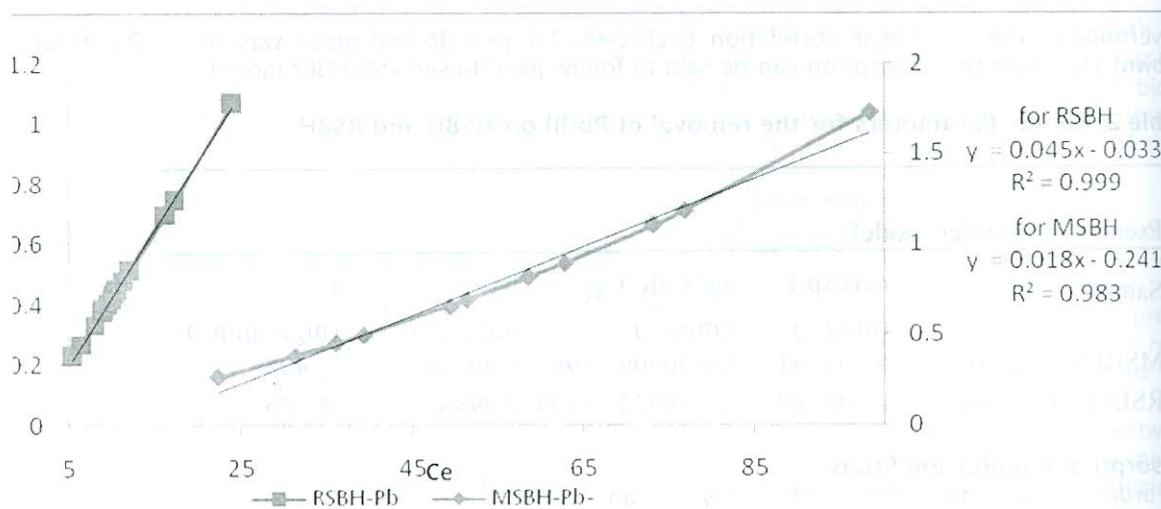
Figure 5:Langmuir Isotherm for Pb removal using MSBH and RSBH at 250mg/L, T=300K and Time-120mins.

The *n* values obtained for the adsorption process represented a beneficial adsorption. From the Freundlich isotherm (Figure 6), the higher the K_f (adsorption capacity mg/g) and n (adsorption intensity) values, the higher the adsorption capacity and notably to say that as high as 54.38 mg/g adsorbate was taken per gram of sorbent. The n values obtained on the overall represented beneficial adsorption [23].
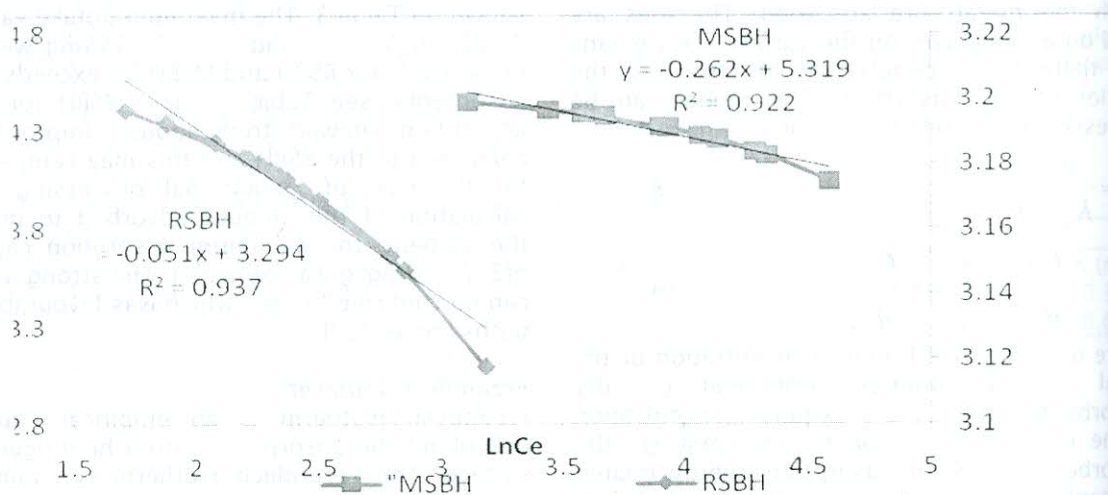
Figure 6: Freundlich Isotherm for Pbadsorbed using MSBH and RSBH at 250mg/L, T=300K and T-120mins.

Temkin Isotherm
Temkin isotherm assumes that the heat ofadsorption of all the molecules in the layer decreases linearly withcoverage due to adsorbate-adsorbate repulsions and that the adsorption has uniform distribution of maximum binding energy. The equation is expressed thus:

$$qe = \frac{Rt}{bt}\log(A_f C_e) \qquad (12)$$

Where $B_T = \left(\dfrac{R_T}{b_T}\right)$ (13)

T is the absolute temperature in *Kelvin* and *R* is the universal gas constant, 8.314 Jmol^{-1} K-1. The constant b_T is related to the heat of adsorption; A_T is the equilibrium binding constant (L g^{-1}) corresponding to the maximum binding energy.

Plot of qe versus log C_e enables the determination of the isotherm constants A_T and b_T as presented in (Table 3) with their values of constants and correlation coefficients. The correlation coefficients obtained were greater than 0.9400 with RSBH having the least. The heat of adsorption is negative indicating that it is exothermic and the binding constant are almost negligible.

Dubunin-Radushkevich(D-R) isotherm
Dubunin-Radushkevich isotherm assumes a fixed volume or sorption space close to the sorbent surface and determines the heterogeneity of sorption energies within the sorption space. It is applied in the linearized form of equation as,

$$ qe = q_D \exp\left(-B_D \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2 \right) $$

(14)

The constant, B_D, is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution and this energy can be computed using the following relationship as given by[28]:

$$ E = \frac{1}{\sqrt{-2B_D}} $$

(15)

Where 'R' is a gas constant in $KJmol^{-1}K^{-1}$, T is the temperature in Kelvin, Ce (mg/L) and q_0 is the sorption capacity in mg/g. The plots of Inq_e

versus $\left(\ln\left(1 + \frac{1}{C_e}\right)\right)^2$ yield the slope to be

equal to $-B_D R^2 T^2$ and the intercept $ln(q_D)$. The linear correlation coefficient was low and the equilibrium data does not fit well. However the correlation coefficient was higher for the non-linear plots. The maximum sorption energy required was 4.075KJ/molfor RSBH and 0.468KJ/molfor MSBH (Table 3) indicating the energy required to pull the sorbate to the sorbent and that the adsorption follows a physiosorption process[13]. The high amount of sorption

capacity q_D shows the generality of the D-R isotherm.

Thermodynamic parameters
The effect of temperature on adsorption experiments was carried out at 30-60°C at pH of 6 and initial metal ion concentration of 250mg/L for 120 mins. The percent removal of $Pb^{(2+)}$ decreases with increase in tempearature for RSBH. The results and Thermodynamic parameters are shown on Table 3. The values obtained were used for the determination of changes in the Gibbs free energy ΔG°, heat of adsorption ΔH°, and entropy of adsorption, ΔS°. MSBH percent removal efficiency reduces as the temperature increases. This reduction is not as significant. At temperature of 40°C, percent removal for lead was 88.6% while at 60°C and 80°C, it was 88.1% and 71.7% respectively. The same trend was observed for RSBH. As the temperature was increased from 30°C to 60°C, the percent removal decreases and so also was the amount adsorbed per unit mass[29]. The thermodynamic parameters, ΔH°, ΔS° and ΔG° for the adsorption process were obtained from the relation

$$ InKc = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} $$ (16)

$$ \Delta G^o = -RTInKc $$ (17)

$$ \Delta G = \Delta H - T\Delta S $$ (18)

Where *Kc*, known as the distribution coefficient of the adsorbate and is equal to (qe/Ce). The plot of *Kc*vs 1/T (T is in K) is linear with the slope and intercepts giving values of ΔH°and ΔS° respectively. Their corresponding values are given in Table 3. The negative value of ΔH°and ΔS° showed that the sorption process for RSBH and MSBH isexothermic and there is a decreasein the randomness at adsorbent - adsorbate interface [29]. The ΔG was also negative showing that the process is spontaneous and highly feasible [16].

Table 3: Equilibrium isotherms for the adsorbtion of Pb(II) on MSBH and RSBH

Langmuir Isotherm			
Samples	Q_{max}	K_L(L/mg)	R_L	R^2
MSBH	55.55(mg/bead)	0.0747	0.051	0.983
RSBH	22.22(mg/g)	1.3637	0.003	0.999

Freundlich Isotherm		
Samples	K_F(L/mg)	1/n	R^2
MSBH	204.179	0.262	0.922
RSBH	26.950	0.051	0.937

Temkin Isotherm		
Samples	B_1	K_T(L/mg)	R^2
MSBH	0.1320	147.4	0.951
RSBH	2.0360	26.76	0.943

Dubunin-Radushkevich Isotherm			
Samples	q_D(mg/g)	B_D	E_D(KJ/mol)	R^2(non-linear)
MSBH	15577.58	-2.2855	0.468	0.9223
RSBH	1408.64	-0.0301	4.075	0.9424

Thermodynamic adsorption-Parameters		
Samples	ΔG(kJmol^{-1})	ΔH(kJmol^{-1})	ΔS(Jmol^{-1}K^{-1})
MSBH	-0.1924	-0.1889	-11.64E-6
RSBH	-668.004	-676.57	-2.83E-2

Table 4: Maximum uptake (q$_{max}$) of Pb(II) for different biosorbent

Sorbent	Langmuir isotherm capacity (mgg^{-1})	Reference
Formaldehyde-treated orange peel	41.99	Lugo-Lugo et al., 2009
Rice husk ash	12.61	Feng et al., 2004
Grape bagasse	88.68	Farinella et al., 2008
Maize bran	142.86	Singh et al., 2006
Saw dust of *pinussylvestris*	15.77	Taty-Costodes et al., 2003
Shea butter husk	22.22	This work
Modified shea butter husk	2222.22	This work

CONCLUSION

Raw shea butter husks and modified shea butter husks has been found to be effective for the removal of Pb($^{2+}$) in an aqueous solution. Entrapment technique using Ca-alginate to produce MSBH gave an improved sorption capacity. The effects of pH was significant for maximum percent removal of Pb(2$^+$), and an optimum value of 6 was obtained before precipitation of lead hydroxyl species. Equilibrium Time was achieved within the first 30 minutes of adsorption. The Equilibrium data fits well with the Langmuir isotherm suggesting a monolayer sorption with maximum capacity on wet basis at 55.555 mg/bead for MSBH and 22.22mg/g for RSBH. This compared adequately well with values obtained in literature. On dry mass basis the sorption capacity for MSBH went as high as 2222.22mg/g of Pb(II).This high value shall compensate for the extra cost for the modification. Other isotherms tested positive especially the Tempkin and Freundlich with correlation coefficient greater than 0.90. The kinetic model of pseudo-second –order experimental adsorption capacity correlated well with the calculated sorption capacity. The mean free energy E in the range of 0.45-4.08 Kj/mol obtained in the Dubunin-Radushkevich isotherm indicated a physio-sorption mechanism. The thermodynamic parameters: free Gibbs energy, enthalpy, and entropy were negative for both sorbents which demonstrate the exothermic, stability and spontaneity of the process. On the overall the raw sorbents and the modified can serve adequately for the removal of Pb(II) in aqueous solution.

REFERENCES

1 Nohambhay S.M., and Palanisamy K. Removal of heavy metal from industrial waste water using chitosan coated oil palm shell charcoal. Elect.J.of Biotech. (2005)8 (1)

2 Nigerian Standard for Drinking Water Quality. Nigerian Industrial Standard. NIS.554 (2007)

3 Ahmedna M., Marshall W.E., Husseiny A.A., Rao R.M.,Goktepe I.The use of nutshell carbons in drinking water filters for removal of trace metals.Water Res.(2004)38 1062-10684

4. Canet L., Llpide Seta M.P. Efficient facilitated transport of lead, cadmium, zinc and silver across a flat sheet-supported liquid membrane mediated by lasalocid A.Sep. Sci. Technol. (2002)37 1851–1860

5   Corbitt R.A. Standard Hand Book of Environmental Engineering, 2nd ed.,McGraw Hill(1999)

6   Han R., Ding D., Xu Y., Zou W., Wang Y., Li Y., Zou L. Use of rice husk for the adsorption of congo red from aqueous solution in column mode.Bioresour. Technol.(2008)99 2938-2946

7   Singh K.K.,Talat M., and Hassan S.H. Removal of lead from aqueous solution by agricultural waste maize bran.Biores. Technol.(2006)97 2124-2130

8   Shukla A., Zhang Y.H., Dubey P., Margrave J.L., Shukla S.S. The role of saw dust in the removal of unwanted material from water.J.of Haz.Mat.(2003)95 137-152

9   Abia A.A., HorsfallJr M., Didi O. The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution.Bioresour. Technol. (2003) 90 345 - 348

10 EromoseleI.C.,Abare L.D. Binding of iron and zinc ions from non-aqueous solution by shea butter (*Butyrospermumparkii*) seed husk.Bioresour.Technol (1998)66 129-132

11 Oñate C.E. Valorisation of Industrial waste for the removal of metals and Arsenic from aqueous effluents. Ph.D Thesis.University de Girona. ISBN:(2009)978 84-692-3178-4 1-18

12 Fiol N.,Poch J.,Villaescusa I. Chromium (VI) uptake by grape stalks wastes encapsulated in calcium alginate beads: equilibrium and kinetics studies, Chem. Spec. Bioavailab.(2004)16 25-33

13 Runping H., Pan H., Zhaohui C.A., Zhenhui Z.,Mingsheng T. Kinetics and isotherms of Neutral Red adsorption on peanut husk.J. of Environ. Sci.(2008)20 1035-104

14 Fiol N., Villaescusa I., MartınezM. N., Miralles J., PochJ., Serarols. Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste, Sep. Purif.Technol.(2006)50 132-140

15 Khorramabadi G.S.,Soltani R.D.C., Rezaee A., Khataee A.R., and Jafari A.J.Utilisation of Immobilised Activated Sludge for the Biosorption of Chromium (VI)Can. J. Chem. Eng.(2011)99991-8

16 Akhtar M., Iqbal S., Kausar A.,Bhanger M.I., Shaheen M.A.An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated rice husk.Colloids and Surf. B: Biointerf.(2010)75 149-155

17 Gilbert U.A., Emmanuel I.U., Adebanjo A.A.,Olalere G.A. Biosorptive removal of $Pb^{2+}$and Cd^{2+}onto novel biosorbent: Defatted Carica papaya seeds. Biomass and bioenergy(2011) 35 2517-2525

18 Coates J. Interpretation of Infrared Spectra, A Practical Approach.*in* Encyclopedia of Analytical Chemistry R.A. Meyers (Ed.)(2000)10815-10837

19 Kumagai S., Ishizawa H., Aoki Y., Toida Y. Molded micro-and mesoporos carbon/silca composite from rice husk and beet sugar. Chem. Engrg. J.(2010)156 270-277

20 KazemipourM., Ansari M., Tajrobehkar S., Majdzadeh M., Kermani H.R. Removal of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone. J. of Haz. Mat. (2008)150 322-327

21 NaiyaT.K.,Chowdhury P., Bhattacharya A.K., DasS.K.Sawdust and Neem barkas low-cost natural biosorbent for adsorptive removal of (II) ions from aqueous solutions. Chem. Engrg. J. (2009)14868-79

22 Villaescusa I.,Fiol N., Martinez M., Miralles N., Poch J., Serarols J. Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, Water Res. (2004)38 992-1002

23 Ibrahim M.N.M., Ngah W.S.W., Norliyana M.S., Daud W.R.W., Rafatullah M., Sulaiman O., Hashim O.,A novel agricultural waste adsorbent for the removal of lead (II) ions from aqueous solutions. J. of Haz. Mat.(2010)182 377-385

24 Kratochvil D.,Volesky B. Advances in the biosorption of heavy metals.Trends Biotechnol; (1998)16 291-300

25 Rocha C.G., Zaia D.A.M., Alfaya R.V., Alfaya A. Use of rice straw as biosorbent for removal of Cu(II), Zn(II) Cd(II) and Hg(II) ions in industrial effluents. J. of Haz. Mat. (2009)166 383-388

26 Hansen H.K., Arancibia F., Gutiérrez C.,Adsorption of copper onto agriculture waste materials. J. ofHaz. Mat.(2010)180 442-448

27 Sekar M., Sakthi V., Rengaraj S. Kinetics and equilibrium adsorption study of lead(II) on activated carbon prepared from coconut shell. J. Coll. Interf. Sci.(2004) 79:307-313

28 Hasany S.M., Chaudhary M.H. Sorption potential of Hare river sand for the removal of antimony from acidic aqueous solution. App. Rad. and Isot.(1996)47 467-471

29 Mane V.S., Mall I.D., Srivastava V.C. Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash. Journ.of Environ. Manag.(2007) 84 390-400