NIGERIAN SOCIETY OF CHEMICAL ENGINEERS
(A Division of the NSE)

# PROCEEDINGS

## 46th ANNUAL GENERAL MEETING, INTERNATIONAL CONFERENCE & EXHIBITION

Theme: DEVELOPMENT AND OPTIMISATION OF NIGERIA'S SOLID MINERAL SECTOR FOR NATIONAL ECONOMIC GROWTH:
The Role of Chemical Engineering

Date: Thursday, 17 – Saturday, 19, November 2016

Venue: Yar'adua Center, No. 1, Memorial Drive,
Abuja, Nigeria.

In Partnership with

MINISTRY OF MINES AND
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## OTHER PAPERS

# KINETICS AND THERMODYNAMIC STUDY OF BATCH ADSORPTION REMOVAL OF HEAVY METALS IN A SYNTHESIZED EFFLUENT USING RAW AND ALGINATE-FUNCTIONALISED SHEA HUSKS

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## Abstract

*In this study, adsorption of synthesised solution lead ($Pb^{2+}$), copper ($Cu^{2+}$), cadmium ($Cd^{2+}$) and nickel ($Ni^{2+}$) onto raw shea butter husk (RSBH) and modified shea butter husk (MSBH) was investigated. Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy coupled with energy dispersive analyzer (SEM-EDAX), and Brunauer-Emmett- Teller (BET) surface area analyzer were used for characterization of the adsorbents. FT-IR revealed that the –COOH-, -$NH_2$- and –OH- are the major functional groups responsible for the sorption. The SEM-EDAX morphology indicated the presences of pores, cavities and the appearance of the metal ions after sorption. Batch adsorption study on effect of contact time and kinetics study on the sorption variations of the metal ions were analysed. Pseudo-second order equation gave $q_{e(calc)}$ of amount adsorbed of 23.75 mg/g as against $q_{e(exp)}$ of 23.96 mg/g on sorption of RSBH on Pb (II). Pb (II) recorded the highest percentage removal (90%) for all sorbents indicated. The highest amount adsorbed for most of the metal ions was achieved within a contact time of 5 minutes. Thermodynamic parameters were evaluated and negative value of free Gibbs energy ($\Delta G^{o}$) -80.37 and -1.146 KJ/mol-1 was obtained for RSBH-Cu and RSBH-Ni respectively, and (-23.56; -32.43 and -0.034 ) for all modified samples with exception of Ni (II) . This depicts the reactions as feasible and spontaneous.*

## 1.0 INTRODUCTION

The recent advocacy on the agro-alimentary and solid mineral industry to be one of economic motor for sustainable development has brought about growth in the small and medium enterprises from these sectors. Mining industries form a large percentage of the small medium enterprise because of the feasibility of starting it in a growing economy like Nigeria. The blacksmith and miners are majorly the artisans' involved in the processing of these natural substances. The ores of these minerals are heavily bonded with other compounds and the extraction processes are carried out in immediate environment or communities where their deposits are found. The resultants are the contamination of the soil, plants and water body. These contaminants range from pathogens, heavy metals and suspended solids amongst which of devastating effects are the heavy metals.

Heavy metals are highly toxic to the environment and constitute serious health effect to the ecosystem and man (Ahmad and Haydar, 2016). Johnson *et al.*, 2008 categorized eleven (11) out of twenty (20) known heavy metals as hazardous. They are cadmium (Cd), selenium (Se), mercury (Hg), uranium (U), chromium (Cr), zinc (Zn), arsenic (As), lead (Pb), cobalt (Co), copper (Cu), and nickel (Ni). Smedley as cited in Podder and Majunder, (2016) gave some of their increase in the environment to be as results of both natural and anthropogenic sources: examples of natural sources to include: volcanic emissions, forest fires, and weathering reactions (Tchounwou *et al.*, 2014). Ahalya *et al.* (2005) gave examples of anthropogenic sources as smelting of irons, mining, electroplating, leatherworking, sludge disposal and so on.

The presence of these metals in our environment has negative impact on human health: plants that are grown on this contaminated soil can accumulate the excesses of these metals and if consumed by man and animals can be transferred to them. Furthermore, they are toxic, non-biodegradable and persistent in nature (Larous *et al* (2005) Recently, Nigeria recorded acute lead poisoning in as a result of mining activities in Zamfara State 2010 (Yahya *et al.*, 2013) and in Niger State in 2015 http://medicalxpress.com/news/2015 05 poisoning children central-nigeriagovt.html).This was as result of mining activities in gold extraction. Plants, animals and man are affected through the bio-accumulation in the food chain. The effect of heavy metals poisoning is more pronounced on children and may include various health disorder such as blindness, paralysis, low IQ, seizures and even death (Grossman, 2012). Discharging such wastewater into the ecosystem is also a source of aesthetic pollution, eutrophication and perturbations to aquatic life (Gupta *et al*., 2011). From these devastating effects, it is imperative to reduce these metal concentrations to standards values of disposals or complete removal from waste effluents before discharging into the water bodies.

In other to effectively reduce the concentrations of these heavy metals, different technologies such as chemical precipitation (Nishimura & Umetsu 2001 as cited by Podder and Majumder, 2016), ion exchange (Figueiredo *et al*., 2016), filtration (Brandhuber and Amy 1998), reverse osmosis (Bhausaheb *et al*., 2011), electro dialysis techniques (Blanes *et al*., 2016) have been employed. However, these processes are expensive, need high energy requirements and sometimes generation of secondary sludge which also poses disposal challenges (Abdollahi *et al*., 2016). The possibility of developing low cost wastewater treatment materials from low cost agricultural waste materials has prompted a lot of researchers into biosorption techniques in recent times. (Benerjee *et al*., 2012. Amirnia *et al*., 2016, Matin-lara *et al*., 2016). The use of agricultural by-products such as oil palm waste (Daud and Ali, 2004), cassava waste biomass (Horsfall and Abia, 2004) and defatted papaya seed (Gilbert *et al*., 2010) to mention a few. in wastewater treatment have also been reported. This study seek to use an agricultural wastes matter (shea butter seed husk) for the removal of heavy metals such as cadmium, nickel, copper, and lead from synthetic wastewater using the batch modes of sorption. This differs from previous studies because of the modification using calcium alginate for enhanced sorptive sites and also simultaneous removals of other competing heavy metal ions.

The kinetics and thermodynamic adsorption rate was evaluated as well.

## 2.0 MATERIALS AND METHODS

The stock solutions containing Cd, Cu, Pb and Ni were prepared by dissolving known mass of cadmium, copper, lead and zinc nitrate salt, $3CdSO_4 \cdot 8H_2O$, $CuCl_2.2H_2O$, $Pb(NO_3)_2$ and $NiCl_2.6H_2O$ in distilled water. All the reagents used for analysis were of analytical reagent grade. The metal concentration was analyzed by fast sequential atomic absorption spectrometer with auto sampler Varian SPS3, SpectrAA240 FS, (Varian, England).

Fresh shea butter fruits were collected between the month of July and August, from Gidan Kwanu farmland in Niger state, Nigeria. The fruits weighing approximately 1 kg were washed thoroughly with water followed by distilled water to remove impurities like dusts and inorganic matters from the surface. After washing, de-pulping was carried out to remove the fleshy mesocarp. This was followed by drying in an oven for 48 hrs at a temperature of 50 °C to reduce moisture content to as low as 6-7%. The drying process facilitates de-husking, which helps to remove the hard shell covering the endoderm that contains the oil. The dried husks were crushed with a jaw crusher and sieved using an electrical sieve shaker to obtain a powder less than 250 μm particle sizes. The particles were then stored in polyethene bags for further use. This sample was called the raw shea butter husks (RSBH).

To prepare modified shea butter husk (MSBH), 1 g of sodium alginate was dissolved into 100 ml of distilled water kept on hotplate magnetic stirrer at a temperature of 65 °C (Fiol *et al*., 2006). The dissolved jelly-like solution was continuously stirred at approximately 100 rpm until it was cooled down to room temperature (27 ±2 °C). A 2 % (w/v) composition of shea butter husk was chosen as it was found to be the most efficient for the encapsulation procedure (Fiol *et al*., 2003; Escudero, *et al*., 2006), was added into the jelly-like solution under an intense agitation at 150 rpm in order to produce homogeneous mixture of alginate and the husk particles. The mixture was carefully added drop wise through the nozzle of diameter 0.2 mm syringe into a solution of 0.1 M calcium chloride. The alginate chains in the mixture wrapped up the sorbents to form beads (Khorrambadi *et al*., 2011). The entrapped RSBH with the calcium alginate (CA) beads was cured in the $CaCl_2$ solution for 24 hours. The emerging hard spherical beads of 2 % (w/v) of RSBH now called modified shea butter husk (MSBH) were filtered and thoroughly rinsed with distilled water until the pH of the rinsed water is at neutral thus ensuring complete removal of excess $Ca^{2+}$ ions and stored in a refrigerator at around 4 °C for further use.

## 3.0 CHARACTERISATION OF THE ADSORBENTS

Raw shea butter husks and cake were characterized for various properties. The functional groups of the raw sorbents were determined using the Fourier transform-infrared spectrophotometer (8400S Schimadzu, Japan). The surface morphology of the sorbent at the raw state and after adsorption was studied with high resolution scanning electron microscope. The BET test for RSBH and for the loaded metal ions (Cu II and Cd (II)) was done using the BET analyzer (NovaWin Quantachrome, 2013) for surface area and pore volume analysis.

### 3.1 Batch Adsorption Procedure

The measurement of metal ions uptake onto shea butter husks (RSBH) and modified shea butter husk (MSBH) were determined by batch adsorption technique using a multi-purpose flask shaker at a speed of 200 rpm and temperature of 303 ±1K (Akhtar *et al*., 2010) to obtain rate and equilibrium data (Lugo-Lugo *et al*., 2009).

### 3.2 Effect of contact time

The rate at which adsorption takes place is very important in equilibrium study as it determines the saturation point. The experimental runs were performed on each adsorbate at higher concentration of 250 mg/L. This was chosen in order to account for highly polluted effluents. 50 ml of the adsorbate solution was introduced into a flat bottom flask with capacity 250 ml containing 40 beads of the MSBH and 0.5 g for RSBH. These were agitated at approximate 200 rpm and filtered at fifteen minutes time intervals (0-240 mins). The concentration in the liquid phase was analyzed using the atomic absorption spectrophotometer and sorption uptake and percentage removal calculated as:

$$q_e = (C_i - C_e)\frac{V}{N} \qquad (3.1)$$

$$\%R = \frac{C_i - C_e}{C_i} \times 100 \qquad (3.2)$$

where, $q_e$ is the sorption capacity, (mg/g), V is the volume of the solution in liter (L) and N is the amount of beads or weight of adsorbent in (g) when the raw sample is used. % R is the percentage of the metal removed.

### 3.3 Effect of temperature

The effect of temperature on the sorption of metal ions unto the biosorbent was studied by measuring out 50 ml of the adsorbate solution into flask containing 40 beads of the MSBH or 0.5 g of RSBH. These were agitated for 120 minutes at a speed of approximately 200 rpm, 27 °C (300 K) and then filtered. The procedure was repeated at 40 °C (313 K), 50 °C (323 K) and 60 °C (333 K). The thermodynamic parameters, heat of adsorption, ΔH, entropy, ΔS and free Gibbs energy, ΔG for the adsorption process were obtained from the relation:

$$InK_C = -\frac{\Delta H''}{RT} + \frac{\Delta S''}{R} \qquad (3.3)$$

and

$$\Delta G'' = -RTInKc \qquad (3.4)$$

A plot of $InK_c$ ($q_e/C_e$) versus 1/T (K) should yield an equation whose slope is ΔH and intercept is ΔS (Naiya *et al*., 2009).

where, $K_c$ is the equilibrium constant; R is the universal gas constant (8.314 J/mol K); and T (K) is the absolute temperature, $q_e$ is sorption capacity (mg/g), while $C_e$ is the equilibrium concentration (mg/L) in the solution.

## 4.0 RESULTS AND DISCUSSION

The RSBH had BET surface area of 5.493 $m^2/g$. The BET surface area for the adsorbed metals (Cu (II) and Cd (II) however, decreased to 2.073 and 5.333 $m^2/g$. This was as a result of reduction in the pore area and volume after adsorption with the metal ions which indicated the coverage of the sorptive sites.

The IR spectra of Figure 4.1 indicate that the RSBH possess surface structures of absorption above 3000 $cm^{-1}$ which suggests that they are unsaturated (contains C=C). Absorption is also at the lower end of the range (i.e below 1700 $cm^{-1}$) this suggest that the compound is probably amide or carboxylate. There are additional moderate band in the range 1200 $cm^{-1}$-1000 $cm^{-1}$ and 800 $cm^{-1}$ - 600 $cm^{-1}$ that implies simple hydroxyl compound. The shifting of the band of the O-H (Phenol) at 1376.26 $cm^{-1}$ for RSBH to above 1400 $cm^{-1}$ of the loaded sample is attributed to O-H (phenol) bonding. There is complete disappearance of the aliphatic nitro-compounds from the loaded sample which also indicated adsorption of the metal at 1510.31 $cm^{-1}$ for RSBH. A shift in the sharp peak at 1635.69 $cm^{-1}$ for RSBH and to tiny broad peaks at 1637.62 $cm^{-1}$ for Pb- loaded (Figure 4.1 B) sorbent as an example can be attributed to the stretching of C=O corresponding to carbonyls, olefinic C=C stretching frequencies of hemicelluloses, lignin and amino groups (Bansal *et al.*, 2009). Emergence of new tiny broad bands on the modified sorbents at frequency from 3400 $cm^{-1}$ to above 4600 $cm^{-1}$ may be attributed to binding of –OH group with the polymeric alginate structure.

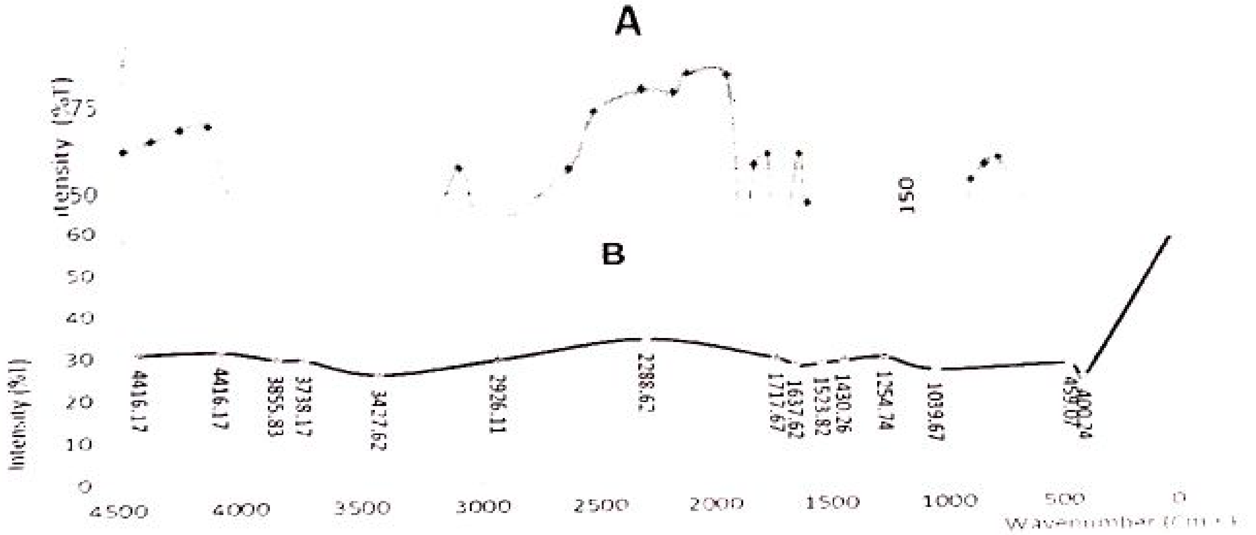

Figure 4.1: FT-IR Spectra of raw shea butter husk (A) and Pb-loaded sorbent (B)

The SEM micrographs at 1000x magnification for the MSBH (see Figure 4.2 A) clearly depict the entrapped sorbents as shown by its white surfaces. Noticeable are the entrapment of the husk within the alginate and the numerous pores for adsorption to take place.

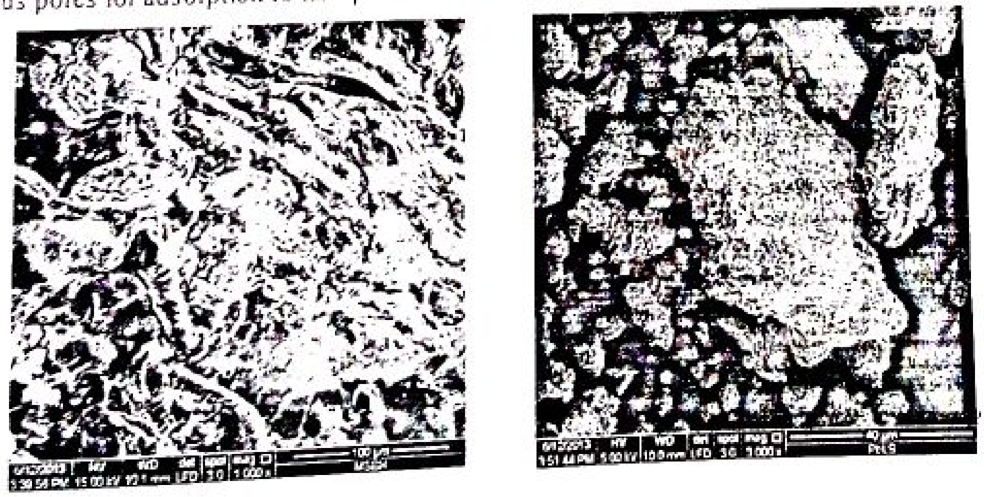

**Figure 4.2: SEM micrographs of MSBH and PbLS at mag A (1000x); B (3000x)**

The EDAX-spectrum for the metal ions after adsorption processes for the lead loaded sorbent (PbLS) is shown in Figur [illegible] while the EDAX (Figure 4.3) depicts the presence of Pb (II) after adsorption. The dense structure of the adsorbed lead can be vividly seen on the micrographs.

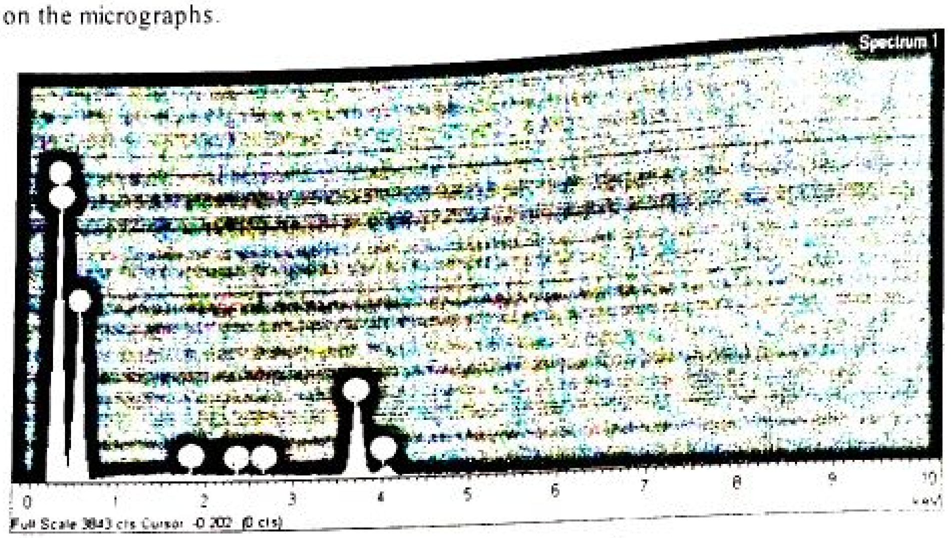

Figure 4.3: Spectrum of lead loaded sorbent (PbLS)

## 4.2 The effect of contact time

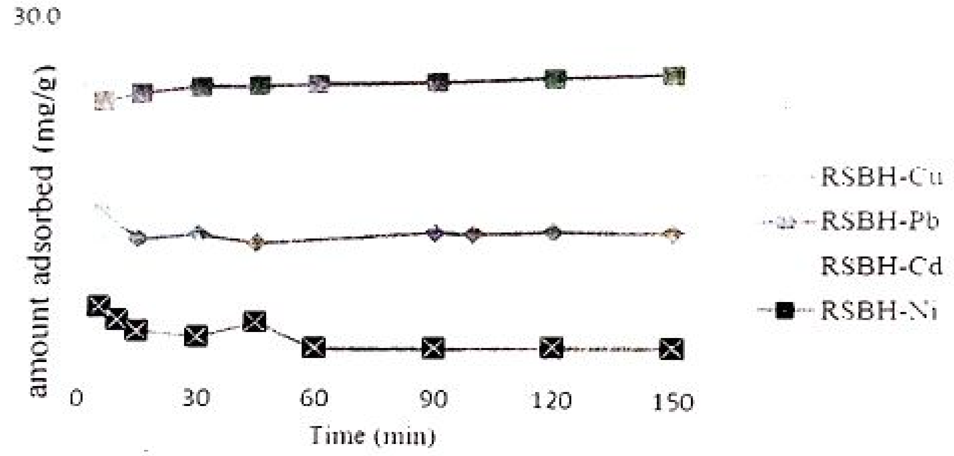

Figure 4.4: Amount adsorbed of Pb (II), Cu (II), Cd (II) and Ni (II) by RSBH at varying Time (mass of sorbent=0.5 g, $V_{sol}$=50 ml, agitation speed 200 rpm, concentration 250 mg/L)

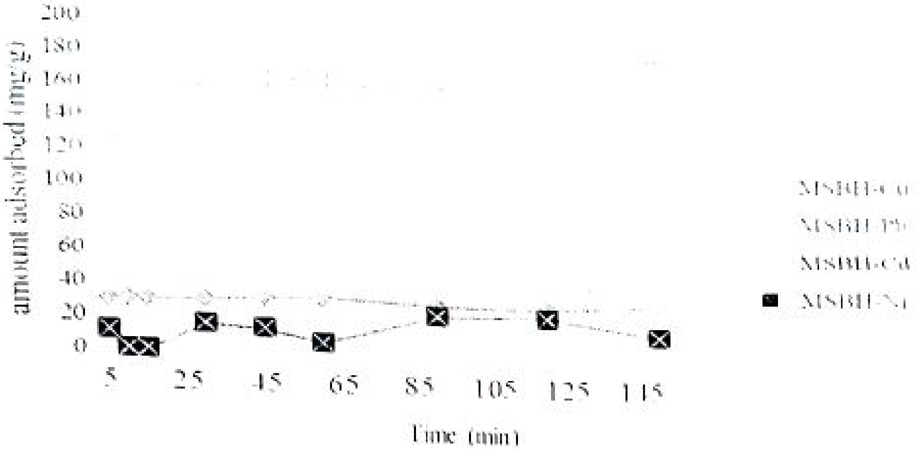

**Figure 4.5: Adsorption capacity of heavy metals by MSBH at different time intervals (no of MSBH=40 beads, $V_{sol}$=50ml, concentration, 250 mg/L)**

Th utes of agitation and these increased for Pb (II) to 22.59 mg/g at same time interval with the initial metal ion concentration kept constant at 250 mg/L. Correspondingly, Cd (II) amount adsorbed by RSBH was 11.40 mg/g with Ni (II) having 4.84 mg/g. (see Figure 4.4). It can be seen that the rate of metal ion removal is found to be very rapid within the first 5 minutes of agitation, thereafter, amount adsorbed becomes almost constant as time increases. No significant change in metal ion removal was observed after 30 minutes. The amount adsorbed for these metals were higher and faster at the beginning firstly because of the strong affinity the adsorbates have for the sorbent. Farinella *et al* (2008) observed 5 minutes using grape bagasse for Cd (II) and Pb (II) adsorption which corresponded well with this adsorbent used. Secondly, the almost constant value achieved after 30 minutes of contact time with the RSBH is as a result of coverage of the sorptive sites and the impossibility of the remaining vacant sites to be occupied due to the repulsive force between the adsorbates on the sorbent surface and the one in the bulk solution (Srivastava *et al.*, 2006). On attachment of the metal ion onto the sorptive sites there is a gradual exhaustion of the capacity of the adsorbent.

The rapid metal ion removal at smaller time range has significant economic importance in the scale-up process as this will facilitate the use of smaller quantity of sorbent to ensure maximum efficiency (Villaescusa *et al.*, 2004)

The adsorption capacity of MSBH for the metal ions is remarkable. Notably on the plots is the arising of the plateau indicating exhaustion of the vacant sites. The amount adsorbed for all the metals ions was higher than the RSBH with MSBH-Pb having values from 126.41 mg/g at 5 minutes of contact to 175.49 mg/g after two (2) hours of vigorous shaking. These increments were recorded for the other metals too. There is relative stability in the adsorption capacities as time progresses and this may be attributed to the enhanced structure of the sorbent. Studies have shown that modification helped to reduce interference from the organic constituents due to their immobilization with calcium alginate. The alginate itself is porous as illustrated in the SEM analysis and thus improves efficiency of the adsorption process (Khorrambadi *et al.*, 2011). Comparing the adsorption capacities amongst the metals, there are pronounced differences in the order Pb (II) > Cu (II) > Cd (II) >Ni (II). Several authors have reported this behaviour (Haug 1965 as cited in Papageorgiou *et al.*, 2006). These maybe attributed to their electronegativity of which Pb (II) is the highest. Their position is not clearly defined using this as Ni (II) which had the lowest adsorption capacity is more electronegative than Cu (II) and Cd (II). The stereo-chemical effects could also be a factor in the coordination of the oxygen atom surrounding the metal ions. The active sites on the sorbent contain oxygen atoms as indicated on the FT-IR results. These have been referred to as hard base from the Pearson's Hard Soft Acid theory (HSAB) and preferentially, this will react with hard acids (the metals in solution). Ni (II) in solution is not as acidic as compared to Pb (II) which is more acidic (Martinez *et al.*, 2006). The important role that can be ascertain through the contribution of the alginate to the sorbent is the rigidity, stability and the conversion of the sorbent to bio-degradable substances because of its biological origin. All this are offered to the sorbent during adsorption (Khoo and Ting, 2001; Mata *et al.*, 2009).

### 4.3 Kinetic studies

Kinetics studies of adsorption of various metals ions on the sorbents was correlated with the Pseudo-first-order, Pseudo-second-order and Weber-Morris equations. The experimental data were used to determine the rate controlling mechanism of the adsorption processes. Their conformity with model-predicted values was expressed by correlation coefficients ($R^2$) and the root mean square error (RMSE) determined.

### 4.4 Pseudo-first-order model

Kinetics study of the sorbents with the sorbates at varying time intervals and concentrations of 250 mg/L was varied. The $R^2$ values were in the range of 0.1526-0.6333 was low for the two sorbents while the RMSE were high in the range of 0.2522-1.6919 (see Table 4.1). The model which is based on diffusion process as the rate limiting sorption step was unable to describe the sorption process in the studied time range. The rate constant, $k_1$ is extremely low for most of the sorbents-sorbates process. Kosasih *et al.* (2011) stated that higher $k_1$ values results in shorter times for the system to reach equilibrium. As a result of this, calculated amount adsorbed, ($qe_{calc}$) does not equal the experimental amount adsorbed ($qe_{exp}$). Studies such as Hansen *et al.* (2010) reported lower correlation coefficient in adsorption of Cu (II) onto agricultural waste; Ibrahim *et al.* (2010) also observed low correlation coefficient of Pb (II) sorption onto modified soda lignin.

**Table 4.1: Pseudo-first-order parameters of RSBH and MSBH**

| Sorbent | $q_{e(calc)}$ (mg/g) | $q_{e(exp)}$ (mg/g) | K ($min^{-1}$) | $R^2$ | RMSE |
|---|---|---|---|---|---|
| RSBH-Cu | 2.2637 | 10.9796 | -0.0027 | 0.2594 | 0.3435 |
| RSBH-Pb | 1.7783 | 23.9576 | 0.0014 | 0.1526 | 0.2522 |
| RSBH-Cd | 3.8289 | 10.0798 | 0.0023 | 0.0771 | 0.4665 |
| RSBH-Ni | 2.0177 | 1.3317 | -0.0069 | 0.4926 | 0.3415 |
| MSBH-Cu | 7.6199 | 95.5733 | -0.0142 | 0.2519 | 1.6919 |
| MSBH-Pb | 55.0337 | 182.6202 | 0.0127 | 0.6333 | 0.6643 |
| MSBH-Cd | 34.3022 | 106.8524 | 0.0153 | 0.7685 | 0.4922 |
| MSBH-Ni | 6.0142 | 16.1035 | -0.0022 | 0.0358 | 0.8303 |

### 4.5 Pseudo-second-order model

The pseudo-second-order assumption as proposed by Ho *et al.*, (2000) assumes that biosorption is in two distinct phase: in the first phase reaction is usually very fast while in the second phase it takes longer exposure time (Peretz and Cinteza as cited in Khorrambadi, *et al.*, 2011). Majority of the sorbent-sorbate interaction follows this assumption with over 80 % having correlation above 0.9. The calculated $q_e$ almost equals the experimental $q_e$. It was also observed that the initial sorption rate, *h* was higher for the modified sorbents than for the raw sorbents. This may be attributed to the calcium alginate used for entrapping the sorbents. Comparing the initial rate of sorption of each metal to the modified sorbents showed that Pb (II) was the highest (see Figure 4.6 & 4.7) followed by Cd (II) with the lowest to MSBH-Cu (II). Authors that have reported coefficient of correlation greater than 0.9 to mention a few are Wang *et al.*, (2011) ; Çolak *et al.*, (2011) ; Mahmood *et al.*, (2011) on sorption of heavy metals on different adsorbents .

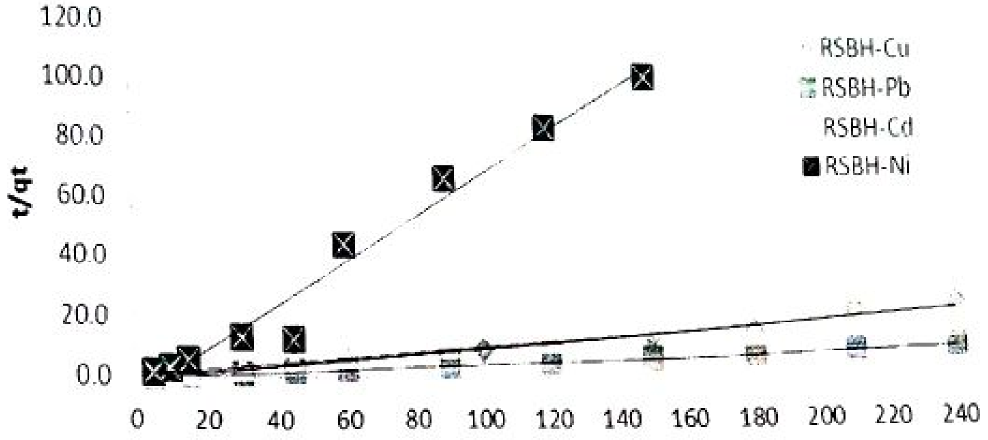

**Figure 4.6: Pseudo-second-order plots of Pb (II), Cu (II), Cd (II), and Ni (II) adsorption by RSBH at 250 mg/l.**

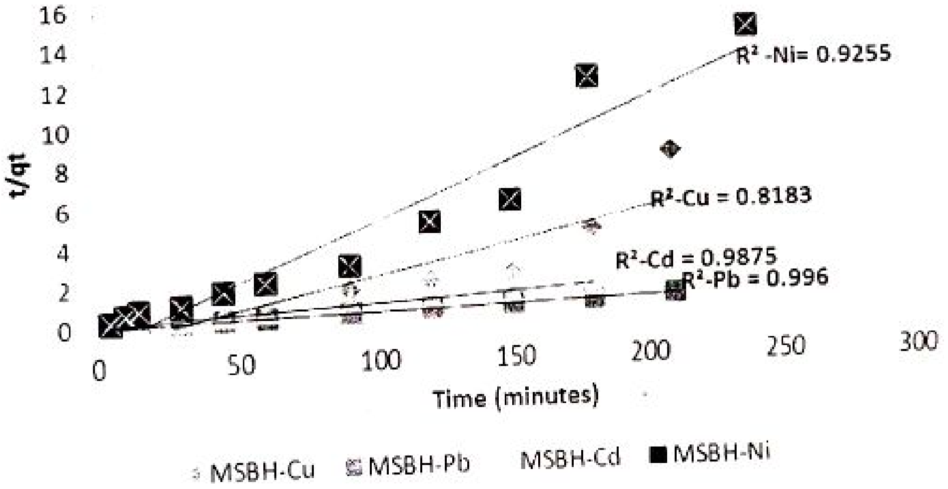

**Figure 4.7: Pseudo-second-order plots of Pb (II), Cu (II), Cd (II), and Ni (II) adsorption by MSBH at 250 mg/L.**

**Table 4.2: Pseudo-second-order parameters of RSBH and MSBH**

| Sorbent | $qe_{(calc)}$ (mg/g) | $qe_{(exp)}$ (mg/g) | k (g/mg.min) | h (mg/g.min) | $R^2$ | RMSE |
|---|---|---|---|---|---|---|
| RSBH-Cu | 9.8260 | 10.9796 | -0.0159 | -1.5305 | 0.9803 | 1.1046 |
| RSBH-Pb | 23.7474 | 23.9576 | -0.0740 | -41.7143 | 0.9994 | 0.0831 |
| RSBH-Cd | 10.3409 | 10.0798 | 0.0161 | 1.7215 | 0.9417 | 1.4142 |

| Sorbent | $q_{e(calc.)}$ (mg/g) | $q_{e(exp.)}$ (mg/g) | k (g/mg.min) | h (mg/g.min) | $R^2$ | RMSE |
|---|---|---|---|---|---|---|
| RSBH-Ni | 1.3132 | 1.3317 | -0.0864 | -0.1489 | 0.9734 | 6.1134 |
| MSBH-Pb | 185.7311 | 182.6202 | 0.0010 | 35.8492 | 0.9960 | 0.0236 |
| MSBH-Cd | 106.7330 | 106.8524 | 0.0013 | 14.3090 | 0.9875 | 0.0620 |
| MSBH-Ni | 16.2183 | 16.1035 | -0.0041 | -1.0766 | 0.9255 | 1.2998 |

## 4.6 Weber-morris intraparticle diffusion model

Kinetic data for Pb (II), Cu (II) Cd (II) and Ni (II) were carried out on all the sorbents to test for this model. The sorption of these metals on MSBH can be seen on Figure 4.8. If the plots qt versus t^0.5 passes through the origin, then the intra-particle diffusion is the rate-limiting step during sorption processes, if it does not pass through the origin, it may be combination of several steps like the film diffusion with the pore diffusion or any of the steps enumerated (Weber, and Morris, 1963). The experimental data exhibited a multiple of linear plots meaning that more than one steps influence the sorption process. This implies that the process occur in various stages as they all had a distinct y-intercept (Chen *et al.*, 2013). The first portion is the diffusion of the metal ions to the film boundary of the sorbents (Ugurlu *et al.*, 2005 as cited by Zulfikar *et al.*, 2013). This indicates the thickness of the boundary layer when extrapolated to the y-axis as the intercepts (see the black arrows on the Fig 4.8). Higher intercepts implies higher boundary layer thickness (Laskhmi *et al.*, 2009). This can be be indicated for example with Pb (II) having the highest intercept of 22.59 while Ni (II) has the lowest of 4.84. The raw sorbents all had lower film diffusion with Ni (II) almost starting at the origin. Contrarily, the film diffusion stage was much higher for the modified sorbents (see Fig 4.9); the second linear portion is the gradual equilibrium stage dominated by intra-particle diffusion as a result of the near saturation of the metal ions on the exterior then the metal ions molecular enters into the pore within the particle and is therefore adsorbed in the interior surface. As the molecular metal ions diffuses into the pores of the sorbents, the diffusion resistance increases and consequently this decreases the *diffusion rate* (Runping *et al.*, 2008) ; the third portion is the final equilibrium stage where the intra-particle begins to slow down.

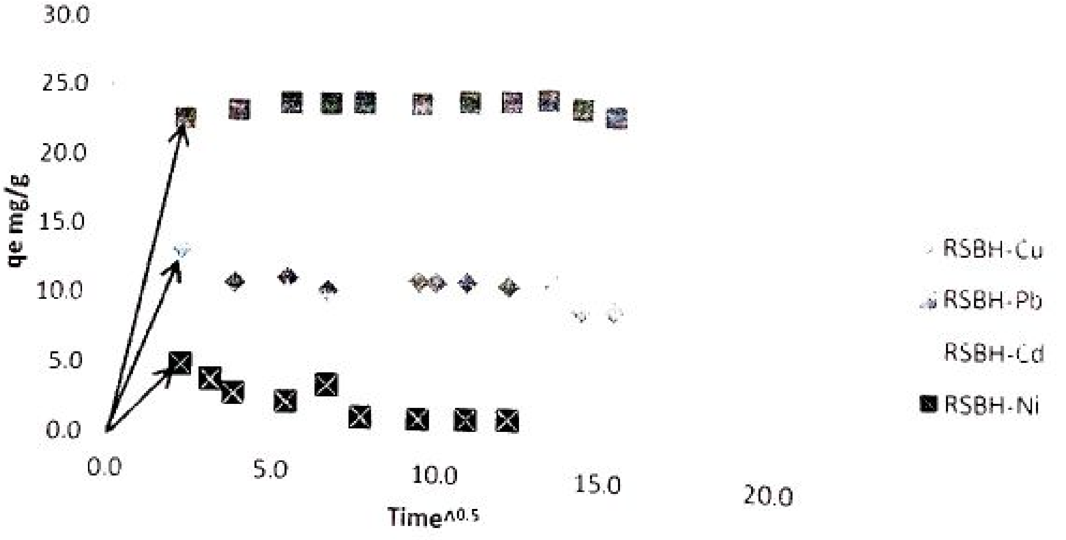

**Figure 4.8: Intra-particle diffusion model plot for the adsorption of Cu(II), Pb(II), Cd(II) and Ni(II) on RSBH at concentration of 250 mg/L and 300 K.**

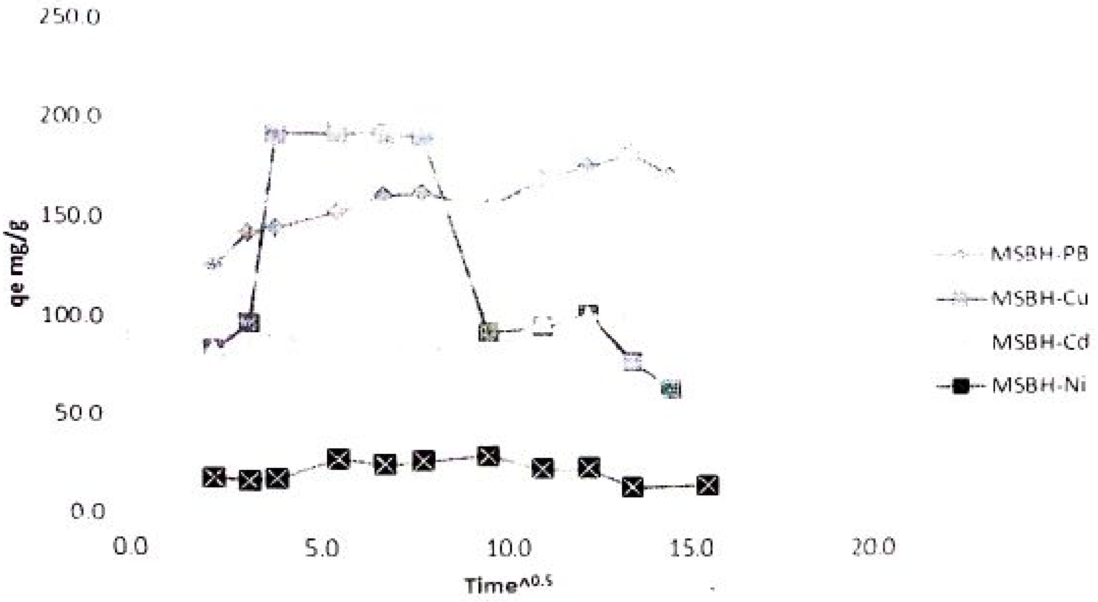

**Figure 4.9: Intra-particle diffusion model plot for the adsorption of Cu (II) RSBH and MSBH at concentration of 250 mg/L and 300 K.**

### 4.7 Thermodynamics Study

Table 4.1 gives thermodynamic parameters of the sorbents onto the metal species at various temperatures. There is a reduction in '*ln K*' which is the adsorption affinity as temperature increases to 323 K before normalizing at higher temperature. This suggests that the reaction may not be favoured by rise in temperature. Although, there was slightly increment in the Gibbs free energy as temperature rises, it indicates the spontaneity of the process (Khan *et al.*, 2011). Bulgariu and Bulgariu, (2012) in his study of heavy metals removal onto algae waste biomass also observed decrease in capacity as temperature rise.

**Table 4.1: Thermodynamic parameters of Pb (II), Cu (II), Cd (II) and Ni (II) sorption**

| Samples | T(K) | ΔG (KJ/mol$^{-1}$) | ΔH (KJ/mol$^{-1}$) | ΔS (J mol$^{-1}$K$^{-1}$) |
|---|---|---|---|---|
| | 313-333 | | | |
| RSBH-Pb | 313-333 | 22.16 | -0.659 | -0.00729 |
| RSBH-Cu | 313-333 | -80.37 | 1.635 | 0.26200 |
| RSBH-Cd | 313-333 | 3.306 | -0.115 | -0.0106 |
| RSBH-Ni | 313-333 | -1.146 | 0.00312 | 0.00367 |
| MSBH-Pb | 313-333 | -23.56 | 0.0684 | 0.0755 |
| MSBH-Cu | 313-333 | -32.43 | 0.0794 | 0.104 |
| MSBH-Cd | 313-333 | -0.034 | 0.00052 | 0.00011 |
| MSBH-Ni | 313-333 | 1.4951 | -0.00729 | -0.0048 |

The negative free Gibbs energy $\Delta G^o$ confirm the spontaneous adsorption of Cu (II) and Ni (II) on RSBH; Cu (II), Pb (II), and Cd (II) on MSBH. The higher negative values of Cu (II) adsorption on RSBH reflect a more energetically favourable adsorption process, (Kosasih *et al.*, 2011). Some of the reactions are exothermic as indicated on the negative $\Delta H^o$ while some are endothermic. This is as a result of combination of two processes: desorption of water molecule in the solvent and the adsorption of the adsorbate species (Srivastava *et al.*, 2007). It has to be remarked that for both types of reaction very low energy is exchanged with less than 1 kJ mol$^{-1}$ released during sorption for the exothermic and less than 1 kJ mol$^{-1}$ adsorbed for the endothermic reaction. Oñate (2009) also reported low energy exchange during sorption of Ni (II). Positive value of $\Delta S^o$ indicates that there is an increase in disorder at the solid-liquid interphase (Bhaumik *et al.*, 2011). It also reflects some structural changes in the adsorbate and adsorbent which thus corresponds to high degree of freedom of the adsorbed species (Lataye *et al.*, 2009). Negative values $\Delta S^o$ correspond to decrease in the randomness which corresponds to the non-spontaneous nature of the reaction. This implies that increase in agitation speed and the addition of stirrer will enhance the spontaneity of reaction. Notably also, is the lower energy associated with the modified sorbent as compared with the raw sorbent. The non-spontaneous reaction was higher for raw sorbent in the order: Ni (II) > Cu (II) > Pb (II) > Cd (II).

## 5.0 CONCLUSION

The results obtained from the batch adsorption process give rise to the following conclusion:

1) The raw sorbents (RSBH) and modified sorbents (MSBH) effectively remove heavy metal ions from a synthesised solution. The FT-IR indicated the presence of functional groups such as; hydroxyl, carboxylic, carbonyls, and phenols groups. The SEM-EDAX revealed the presence of the adsorbed metal species in the sorbents at varying magnifications. The BET test showed that RSBH is highly porous with a surface area of 5.493 m$^2$/g .

2) The Batch adsorption time dependent performance was remarkably fast. At 5 minutes of contact time, the adsorption capacities of RSBH and MSBH for Pb (II) which was the metal with highest affinity were 22.59 mg/g and 126.41 mg/g respectively.

4) *Pseudo-2$^{nd}$* –order successfully described the Kinetic sorption process with calculated amount adsorbed almost equal to experimental amount adsorbed.

5) The thermodynamic parameters of the metal species onto the sorbents indicated that most of the reactions are spontaneous and feasible for Cu (II) and Ni (II) adsorption on RSBH; Cu (II), Pb (II), and Cd (II) adsorption on MSBH. The non-spontaneous reactions were for the raw sorbents adsorption of RSBH-Pb (II) and Cd (II) and only MSBH-NI (II).

The successful utilisation of these raw and modified shea butter husks for the removal of Pb (II), Cu (II), Cd (II) and Ni (II) in the batch adsorption technique has a positive impact on the environmental issues in the solid mineral development.

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