

Copper (II) Adsorption by Calcium-alginate Shea Butter Cake

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Abstract

This study investigated the utilization of modified shea butter cake for the removal of Cu(II) ions from aqueous solution. Instrumental analysis such as Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), X-ray Diffractometer (XRD) was used for the characterisation of the solid sorbent. Batch equilibrium study was carried out to evaluate the adsorption capacity, and process parameters such as initial metal ion concentration, time, pH, and adsorbent dosage. An optimum pH of 5, equilibrium time of 30mins and adsorbent dosage of 40 beads was obtained. The Langmuir and Freundlich isotherms were used to fit the experimental data and values fits the Langmuir more adequately with correlation coefficient unity (1.000) at 10mg/l of initial metal ion concentration. The Kinetic study using the Pseudo-first-order and pseudo-second were used to determine the rate constants and experiments data best fits the pseudo-second –order with calculated amount adsorbed approximately equal to the experimental values. The results indicate that modified shea butter cake could be employed as an adsorbent for the removal of copper (II) ions in an aqueous solution.

Keywords: Shea butter cake, process parameters, kinetics, Copper (II),

Introduction

The activities of man through the growing and development of the small and medium scale enterprise has gradually kept on the increase of copper (II) ions discharge into the environment. Thousands of years ago, the use of copper was limited to making tools and other utensils, but now, it is widely used in electrical wire, coins, ornamental objects, jewellery, pharmaceuticals, fungicides (Odukoya and Ajayi, 1987; Wu *et al.*, 1999) and mining activities (Hansen *et al.*, 2010). These consequently have impact on the threshold limit. Copper toxicity can occur in plants growing in polluted soils, and animals grazing on these plants, through the food chain. In humans about 10-20mg of orally ingested Cu may cause intestinal discomfort, dizziness and headaches, while ingestion of Cu salts in excess of 500-100mg have caused fatal acute poisoning such as vomiting, diarrhoea with bleeding, circulatory collapse, failure of the liver and kidneys and severe haemolysis (Johnson, 1997). The maximum permissible limit of copper in drinking water is 2mg/L (Larous *et al.*, 2005). A wide variety of treatment technologies for the decontamination of this metal-polluted effluent have been investigated and developed. These are chemical precipitation, ion exchange, adsorption, solvent extraction, membrane processes and electrochemical techniques. Adsorption process via the use of agricultural waste material is however been recently utilised because it is readily available, it has low energy consumption, eco-friendly, and cost effective.

The use of the Shea Butter Cake is proposed for the adsorption of copper in this study. Shea butter cake is the residue obtained after the extraction of the butter from the shea butter seed. Nigeria is blessed with the Shea butter tree with an estimated production output of 250,000 metric tonnes per annum (Peter, 2004). Although this has not been optimally utilised, cottage industry are gradually indulging in the shea butter production which obviously will lead to the increase in the cake production. Studies have shown that the presence of the cake into the environment causes nuisance as they are non-bio-degradable and are un-palatable to livestock (He *et al.*, 2007; Nitiema, 2010). Limited work has been reported in the utilisation of shea butter cake for adsorption processes. Yahya *et al.*, (2012) used the cake in the raw and modified form for the removal of Pb (II) ions in an aqueous solution. It is however proposed to use the shea butter cake by modifying it with calcium alginate for the adsorption of copper (II) ions in aqueous solution so as to serve the double benefit of treating a waste polluted water streams and revenue generation to the producing industry. It will also provide a baseline of information and data for further research.

2. Materials and Methods

The shea butter fruits were collected from the farmland of Sabon-Dagaward in Minna, Niger state, Nigeria. The collected biomaterials were thoroughly washed with tap water to remove soil and dusts, and then further washed with distilled water and dried in an oven at 80°C until a constant weight is achieved (Önate, 2009). The dried seed is grinded to smoothness with a blender (Moulinex) and sieved using an electrical sieve shaker (Endecotts England BS 410/1986) to obtain a powder <250µm particle size. Some physical processes such as churning and mixing were done. Warm water was used to press out the oil and overflow the fats. The fat was skimmed and heated to evaporate the excess water molecules. The oil was decanted and filtering was done. The residue obtained after filtration is the Shea Butter Cake. This is air-dried until a constant weight is obtained and stored in a polyethylene bag for further use.

2.1 Preparation of shea butter cake

The Modified shea butter cake (MSBC) was prepared by dissolving 1g of sodium alginate (1% w/v) into 100ml of distilled water at a temperature of 65°C on a constant temperature magnetic stirrer (LabTech 78HW-1) (Fiol *et al.*, 2006). The gel was completely dissolved and allowed to cool down at room temperature (25°C) and thereafter 2g of shea butter cake (<250 µm) was added. An intense agitation was maintained on the magnetic stirrer in order to produce a homogeneous mixture of alginate and the powder. Afterwards the solution was added drop wise via a hypodermic syringe to a solution of 0.1M calcium chloride dihydrate (CaCl₂·2H₂O) under soft agitation. The Calcium atoms from the CaCl₂ will cross link to form salt bridges between the α-L-gulonic acids (G) blocks of the sodium alginate (Onate, 2009). As a result of this, the alginate chains wrapped up the sorbents to form beads (Khorramabadi *et al.*, 2011). The entrapped shea butter cake in the calcium alginate (CA) beads were cured in the CaCl₂ solution for 24hr. Hard spherical beads of similar sizes containing 2% (w/v) of shea butter cake now called modified shea butter cake (MSBC) were filtered and rinsed several times with distilled water to remove excess Ca²⁺ ions. The obtained beads were covered with abundant distilled water and stored in the fridge at around 4°C for further use.

2.2 Preparation of metal solutions

Deionized water obtained from a deionizer was used to prepare all solutions. All glass wares were soaked in 5% nitric acid for 24hr and repeatedly washed with doubly distilled deionized water followed by drying at 353K for 5 hr. so as

to avoid contamination. Stock solution (1000mg/L) of copper was prepared by dissolving 2.6847g of analytical grade copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) in 100ml of deionized water and dilute to 1 litre in a volumetric flask with deionized water.

2.3 Characterisation of adsorbent

The shea butter cake was characterized using the Fourier Transform-Infrared Spectrophotometer (FT-IR-8400S, Shimadzu Japan) in order to determine the functional group. The sample was prepared using KBr discs and the spectral range was varied from 4000cm^{-1} to 400cm^{-1} . The surface morphology of the sorbents was also studied with High Resolution Scanning Electron Microscope (EVO MA 10 Carl Zeiss). The X-ray diffraction (XRD) analysis was carried out to determine the mineral composition, and crystallinity of the cake.

2.4 Batch Equilibrium study

Experiments were carried out in batch mode using series of 250ml conical flasks with cork. 50ml of metal solution in various concentrations ranging from 4mg/l, 6mg/l, 10mg/l, 50mg/l, 100mg/l, and 200mg/l were added to 40 beads of the modified shea butter cake on Stuart Scientific flask shaker at a speed of 200rpm. Agitation was carried out for over 360 minutes to ensure equilibrium although no significant change was recorded after 120 minutes as saturation had been reached. All other parameters studied were therefore fixed at 120 minutes. After agitation, the beads were filtered using Whatman filter paper (110cm) and metal concentration in the liquid phase was analysed using Flame Atomic Absorption Spectrophotometer Varian SpectrAA 220FS.

The metal concentration in the the solid phase q_e (mg.bead^{-1}) was calculated from the difference between the initial, C_i and equilibrium, final, C_e metal concentration in solution (mg.L^{-1}). The uptake of the sorbent was calculated according to the next equation:

$$q_e = (C_i - C_e) \frac{V}{N} \quad (1)$$

Where $V(\text{L})$ is the solution volume and N is the amount of beads

To compute the sorption percentage, $\%R$

$$\%R = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

2.5 Kinetic study on Cu (II) adsorption

Sorption kinetics was studied for initial concentrations of Cu ranging from 4mg/l-to 200mg/l. Metal solutions were prepared by serial dilution and pH of 5 was maintained throughout. For each contact time, content of the flasks was filtered and copper concentration in solution was analysed. The studied time range was fixed at 120 minutes.

2.6 Initial pH effect on Cu (II) adsorption

Effect of initial pH on Cu (II) sorption onto modified Shea butter cake was studied in order to obtain information on the role of H⁺ in Cu(II) uptake. pH values was from 1 to 10 and initial metal concentration was around 250mg/l. 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. Contact time was 120 minutes.

2.7 Effect of Adsorbent Dosage

Adsorbent dosage was varied from 40 beads-240 beads in 50ml of Copper (II) solution at a concentration of 250mg/L. This was agitated for 120 minutes at a speed of 200rpm. Solutions were filtered and residual metal concentrations was analysed as stated previously.

3. Discussions of results

3.1 Characterisation of adsorbent material

The IR spectra (Fig. 1) indicate that the RSBC possess different surface structure. There are some Absorption above 3000/cm which suggests that it is unsaturated (contains C=C). Absorption is at the low end of the range (i.e below 1700/cm) this suggest that the compound is probably amide or carboxylate. Additional moderate band in the range 1200-1000 and 800-600 implies simple hydroxyl compound. The shifting of the band of the O-H (Phenol) at 1374.33/cm to 1440.87 of the loaded sample is attributed to O-H (phenol) bonding. Complete disappearance of the aliphatic nitro-compounds from the loaded sample also indicated adsorption of the metal at 1522.85/cm. A shift in the peak at 1615 to 1633.76 of the loaded sorbent can be attributed to the stretching of C=O corresponding to carbonyls, olefinic C=C stretching frequencies of hemicelluloses, lignin and amino groups. This was more prominent in the loaded sorbent indicating higher sorption due to structural modification (Akhtar *et al.*, 2010). The sharp peak

observed at 1741.78 for shea butter cake is assigned to C-O bond of carboxylic or its ester and its complete disappearance on the Cu-loaded sorbent inferred that the copper metal bonded to the shea butter cake through interaction with active groups OH, COOH (Minamisawa *et al.*, 2004). Emerging of new bands on the modified sorbents at 3154.68; 3458.48; 3777.71 may be attributed to binding of -OH group with the polymeric structure.

Fig. 2 shows the XRD patterns of Shea Butter Cake. The non-appearance of major peaks indicated that the sorbent is amorphous in nature. A very weak peak was observed at $26^\circ 2\theta$ diffraction angle which was attributed to quartz structure of the silica (Kumagai *et al.*, 2010) that may have been introduced during air-drying.

Fig. 3: depicts the SEM image of the Shea butter cake at 1KX and 3KX magnification. The micrographs indicated that the surface was irregular and porous in nature. The micrographs also depict the presence of superficial layers of protective silica and some natural resin.

3.2 Effect of Time and initial metal ion concentration

Fig. 4 shows the effect of Time and initial metal ion concentration; there was a sharp increase in percentage removal of the metal ions from the starting initial concentration value to the next level before saturation is reached. At lower initial concentration almost all the sites are filled during adsorption as there is a greater interaction between the metal ion and sorptive sites but as the concentration increases more Cu(II) are left unadsorbed due to saturation of the adsorptive sites. This high initial rate of adsorption is as a result of increase in concentration which provides the driving force that helps to overcome mass transfer resistance between the metal ion and adsorbent (Ibrahim *et al.*, 2010). The amount of copper (II) ions adsorbed at equilibrium increases from 0.094 mg/g to 4.64 mg/g as the initial metal ion concentration was increased from 4 to 200 ppm.

In relation to time, the rate of metal ion removal is found to be very rapid during the first 30 minutes of adsorption, thereafter, it is almost constant and then gradually decreases at higher concentrations. No significant change in metal ion removal is observed after 120 minutes. Basically for the lower concentration metal ion solution, the maximum percentage removal was achieved within 30 minutes while for the higher concentration metal solution it was after 1 hour of agitation time. The rate of percentage metal removal is higher at the beginning firstly because of the affinity

the sorbates has for the sorbent. Secondly, it may be due to the modification with calcium alginate. This played an important role in the rigidity, enhanced porosity of the sorptive sites, resistance to leaching of the organic component into the solution. This is justified in this study as percentage removal increased to over 90% as concentration builds as high as 250mg/L. Authors that have used calcium alginate successfully for adsorption processes to mention a few are Fiolet *et al.*, (2003); Khorambadiet *et al.*, (2011).

3.3 *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 (Kazemipouret *et al.*, 2008). Notably is this as shown in Fig. 5. The percentage removal of Cu using shea butter cake increases progressively from 1.4% at pH of 2 to 92.3% at pH value of 5. This then gradually drops at pH of 6 and remain almost constant up to pH of 10. At lower pH values (pH 2) biosorption was low as a results of protons (H^+ or H_3O^+) domination to compete with the cations in the aqueous solution to occupy the shea butter cake surface. Increasing the pH from 3 to 5 bring about a progressive increase in the biosorption which is as a result of decrease in the protons and consequently lowering the electrostatic repulsion between the Cu(II) and surface sites. The maximum percentage removal occurred at pH of 5 which agrees quite well with the work of Benaissa and Eloudchi (2011) in their study of Cu(II) from aqueous solution using activated sludge. Beyond pH of 5, insoluble copper hydroxides starts precipitating resulting in lower amount of Cu(II) sorbed at equilibrium (Villaesusa *et al.*, 2004).

3.4 *Effect of Adsorbent Dosage*

Figure 6 shows the adsorption of Cu(II) with modified shea butter cake at varying adsorbent dosage (40beads-200beads), 250mg/L of initial metal concentration and agitation speed of 200rpm at 120mins. Amount adsorbed of the metal ions decreases with increase in adsorbent dose. For example, the amount adsorbed at 40 beads is 0.2525mg/bead this then reduces drastically to 0.070mg/beads at 200beads 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. This was justified by the work of Hansen *et al.*, (2010) who reported that the larger the amount of solid biomass, the lower the equilibrium concentration; Khan *et al.*, (2011) further affirmed this in his study that increasing

the biosorbent dosage may lead to some of the sites unsaturated and consequently decrease in biosorption capacity. The decrease in amount adsorbed may be further explained by the fact that aggregation of adsorbent particle does occur as adsorbent dosage is increased and this results to longer diffusion path length (Zheng et al, 2009). The reverse is the case with percentage 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 (Ibrahim et al., 2010).

3.5 Adsorption Kinetics

In order to investigate the adsorption of Cu(II) on modified shea butter cake (MSBC), adsorption kinetic study using the pseudo-first –order (Lagergren, 1898) and pseudo-second-order, kinetic models (Ho and Mckay, 1999) 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 interphase (Naiyaet al., 2009). 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 of Lagergren is generally expressed as follows:

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

Where q_e is the amount of adsorption capacity at equilibrium (mg/g), q_t is amount adsorbed at time t , K_1 is the pseudo-first-order rate constant (min^{-1}).

The values of q_e and K_1 for the pseudo-first-order kinetic model were determined from the intercepts and the slopes of the plots of $\log(q_e - q_t)$ versus time, respectively. The values are given in Table 1. From the linear regression equation, the correlation coefficient R^2 was 0.5496 at 4mg/L and 0.4333 at 6mg/l. These were quite low and are not shown on the plot except for the non-linear regressions that were above 60% in correlation co-efficient. There is a wide variation between the calculated and experimental values. This shows that the adsorption does not follow the first order which follow similar observation of other authors (Hansen et al., 2010; Kosasih et al., 2010; Gündoğan et al., 2004).

3.5.2 The pseudo-second-order model : This can be expressed as:

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

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:

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

The initial sorption rate, h (mg/mg min), at $t \rightarrow 0$ can be defined as

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

Re arranging and substituting Eq (6) into Eq (5) gives

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

The value of qe is determined from the slope of the plot of $\frac{t}{qt}$ versus t (Fig. 9), and h is obtained from the intercept. The values of qe , K_2 , h and R^2 are shown in Table 2. The graph is linear for second-order than that of the first-order model. 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 R^2 is closer to unity at 4mg/L, 6 mg/l 50mg/l, 100mg/l and exactly 1.00 at 10mg/l . The initial sorption rate h can also be seen to be quite adequate from Table 2 indicating a very fast sorption rate .Therefore the adsorption can be said to follow pseudo-second-order-model adequately which were well justified by the work of Zhang et al 2011; Gündoğan et al., 2004).

3.6 Adsorption Equilibrium Isotherm

Equilibrium data were analysed using the Langmuir and Freundlich isotherm to understand the Cu(II) ions-modified shea butter interaction.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (8)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

Eq.(8) and (9) are Langmuir and Freundlich equations. In these equations, C_e and q_e are the equilibrium concentrations in the solution (mg/l) and on the modified shea butter cake (mg/g) respectively: a_L (l/mg) and K_L (l/g) are the Langmuir constants for the Cu(II) ions-modified equilibrium and monolayer capacity. K_F (l/g) is Freundlich constant and $1/n$ is heterogeneity factor.

From Table 3, parameters obtained after correlation of experimental data to Langmuir and Freundlich showed good correlation coefficient with the best fits for Langmuir model. Li et al., (2004) reported that the Gibbs free energy can be calculated according to the equation $\Delta G = -RT \ln K_L$ and the results shows that at higher Langmuir constant the ΔG was smaller and invariably a higher spontaneity of the adsorption process. At K_L 310.00 L/g, the ΔG was -14.308 and correlation coefficient R^2 was exactly 1.0000. The dimensionless equilibrium parameter or the separation factor R_L (Panda et al., 2007) was also calculated from the Langmuir equation from the expression:

$$R_L = \frac{1}{1 + K_L C_i} \quad (10)$$

Where C_i and is the initial concentration of the Cu(II) ion and K_L is the Langmuir constant. If adsorption is favourable, Then R_L must be within 0 to 1, while $R_L > 1$, $R_L = 1$ and $R_L = 0$, respectively describe unfavourable, linear and irreversible adsorption. Here the R_L value is within 0 to 1 and this indicates that the adsorption of Cu ions is well favoured on the modified shea butter cake.

Freundlich model did not provide as good determination coefficients as the Langmuir model. However, Freundlich model was used to calculate K_F and $1/n$ which are the parameters associated to the adsorption capacity and adsorption intensity respectively. The higher the $1/n$, the higher will be the affinity and heterogeneity of the adsorbent sites. The values of $1/n$ as shown on Table 3 was less than 1 and thus indicate that the adsorption was beneficial (Manet et al., 2007; Naiya et al., 2009).

4. Conclusions

Shea butter cake entrapped in calcium alginate effectively removes copper (II) ions from aqueous solution. Hydrogen ion (H^+) plays an important role on the effect of pH and an optimum pH of 5 was obtained for adsorption of the Cu(II) before precipitation of the hydroxides. The FT-IR analysis indicate the main active groups such as carboxylates, hydroxyl and the phenols as being responsible for the sorption. The Kinetic isotherm of Pseudo-second-order best fits the experimental and correlation coefficient of exactly 1 obtained at 10mg/l of initial metal ion concentration. A very high amount adsorbed (q_{max}) of 161.290mg/g was achieved on subjecting experimental data to the Langmuir equilibrium isotherm which suggest monolayer adsorption, this almost double that obtained for the Freundlich Isotherm. However, on comparison with other agricultural waste (Table 4) for Cu (II) adsorption, the q_{max} was on the high side for both Langmuir and Freundlich isotherms. The entrapment of the Shea butter cake in the calcium alginate gel gave an improvement in the sorption capacity. The thermodynamic property ΔG indicate the spontaneity of the process and reaction is an exothermic one.

References

- Akhtar, M., Iqbal, S., Kausar, A., Bhangar, M.I., Shaheen, M.A. (2010). An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated rice husk. *Colloids and Surfaces B: Biointerfaces* 75 149–155
- Alloway, B. J. and Ayres, D.C. (1997). Chemical Principles of Environmental Pollution. *Blackie Academic and Professional, London*.
- Benaïssa, H. and Elouchdi, M.A. (2011). Biosorption of copper (II) ions from synthetic aqueous solutions by drying bed activated sludge. *Journal of Hazardous Materials* 194 69–78
- Fiol, N. et al., (2006). Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste, *Sep, Purif, Technol.* 50 132–140.
- Fiol, N. et al., (2003). Biosorption of Cr(VI) using low cost sorbents, *Environ. Chem. Lett.* 1 135–139
- Hansen, H.K., Arancibia, F., and Gutiérrez, C. (2010). Adsorption of copper onto agriculture waste materials. *Journal of Hazardous Materials* 180 442–448
- He, Q. et al., (2007). Biodegradability of tannin- containing wastewater from leather industry. *Biodegradation*, 18: 465-472

- Ho, Y.S. and McKay, G. (1999). Pseudo-second-order model for sorption processes. *Process Biochemistry* 34 451-465
- Ibrahim, M.N.M. (2010). A novel agricultural waste adsorbent for the removal of lead (II) ions from aqueous solutions. *Journal of Hazardous Materials*, 182 377–385
- Güngoğan, R., Acemioğlu, B., & Alma, M.H., (2004). Copper (II) adsorption from aqueous solution by herbaceous peat. *Journal of Colloids and Interface Science* 269 303-309
- Johnson, M.A., (1997). Copper. In: Macrae, R. Robinson, R.K. and Sadler, M.J. (Ed.) *Ency. Fd. Sci. Fd. Tech Nutri. Acad. Press, London*. 1237- 1243.
- Kazemipour, M. et al., (2008). Removal of lead, cadmium, zinc, and copper from industrial waste water by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone. *Journal of Hazardous Materials* 150 322-327.
- Khan, M.A. et al (2011). Biosorption and desorption of Nickel on oil cake: Batch and column studies. *Bioresource Technology*.
- Khorrabadi, G.S. (2011). Utilisation of Immobilised Activated Sludge for the Biosorption of Chromium (VI). *Can. J. Chem. Eng.* 9999:1–8.
- Kosasih, A.N. (2011). Sequestering of Cu(II) from aqueous solution using cassava peel (*Manihotesculenta*). *Journal of Hazardous Materials*, 180 366-374.
- Kumagai, S. (2010). "Molded micro- and mesoporous carbon/silica composite from rice husk and beet sugar". *Chemical Eng. Journal* 156 270-277.
- Krishnani, K.K. (2008). Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. *Journal of Hazardous Materials* 153 1222-1234.
- Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar* 24, 1-6.
- Larous, S., Meniai, A.H., and Lehocine, M.B., (2005). Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust. *Desalination* 185 483–490.
- Li, Y.S., Liu, C.C., and Chiou, C.S., (2004). Adsorption of Cr (II) from wastewater by wine processing waste sludge. *Journal of Colloid Interface Science*. 273 95-101
- Lovett P.N., (2004). The shea butter value chain production, transformation and marketing in West Africa *Wath Technical Report* no. 2
- Naiya, T.K., Chowdhury, P., Bhattacharya, A.K., Das, S.K. (2009). Sawdust and Neem bark as low-cost natural biosorbent for adsorptive removal of (II) ions from aqueous solutions. *Chemical Engineering Journal* 148 68–79.
- Nitiema, L.W. et al., (2010). Isolation of a Tannic Acid-Degrading *Streptococcus* sp. From an Anaerobic Shea Cake Digester. *Pak. J. Biol. Sciences*, 13: 46-50.
- Odukoya, O.O., and Ajayi, S.O., (1987). Trace heavy metals in Nigerian fishes II: Copper and Zinc. *Nigerian journal of Nutritional Sciences*. Vol.8. pp 41-49.
- Oñate, C.E., (2009). Valorisation of Industrial waste for the removal of metals and Arsenic from aqueous effluents. *Ph.D Thesis, University de Girona*. ISBN: 978 84-692-3178-4 1-18
- Panda G.C., Dasa, S.K., Bandopadhyay, T.S., Guha, A.K., (2007). Adsorption of nickel on husk of *Lathyrussativus*: Behaviour and binding mechanism. *Colloids and Surfaces B: Biointerfaces* (57) 135–142.
- Villaescusa, I. et al., (2004). Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, *Water Res.* 38 992–1002
- Wu, J. m Laird, D. A., Thompson. M.J., (1999). Sorption and Desorption of Copper on Soil Clay Components. *J. Environ. Qual.* 28: 334-338.
- Yahya, M.D. et al., (2012). Equilibrium and Kinetic study on the removal of Lead from aqueous solution using Raw and Modified Shea Butter Cake. in: 42nd Nigerian Society of Chemical Engineers Conference.
- Zhang, J. et al., (2011). Removal of Cu(II) from aqueous solution using the rice husk carbons prepared by the physical activation process. *Biomass and Bioenergy* 35 464-472.

Table 1: Pseudo-1st-order for the removal of Cu (II) by MSBC at pH5 and 120 (mins)

Ci (mgL ⁻¹)	qe _(exp.) (mgg ⁻¹)	qe _(calc.) (mgg ⁻¹)	K ₁ (min ⁻¹)	R ² (linear)	R ² (non-linear)
4	90.740	108.179	0.0152	0.5496	0.6584
6	137.315	90.386	0.0187	0.4333	0.6495
10	721.83	87.173	0.0119	0.581	0.7352

Table 2: Pseudo-2nd-order for the removal of Cu(II) by MSBC at pH 5 and Time 120(mins)

Ci (mgL ⁻¹)	qe _(exp.) (mgg ⁻¹)	qe _(Calc.) (mgg ⁻¹)	R ²	K ₂ (gmg ⁻¹ min ⁻¹)	h (mgg ⁻¹ min ⁻¹)
4	89.8148	81.8148	0.9996	0.00100	8.1098
6	137.037	136.827	0.9999	0.00015	2.7146
10	229.629	230.032	1.0000	0.00002	1.1226
50	841.967	842.900	0.9895	0.00000	0.1012
100	955.093	876.575	0.9753	0.00000	0.1933

Table 3: Langmuir and Freundlich parameters for Cu(II) sorption onto modified shea butter cake.

Langmuir model Freundlich model									
C _i (mg/L)	q _{max} (mg/g)	K _L (L/g)	R _L	ΔG ⁰ (kJ/mol)	R ²		K (mg/g)	1/n	R ²
4	564.972	4.425	0.0534	-3.709	0.9986		56.36	-0.0679	0.9228
6	86.207	57.999	0.0029	-10.128	0.9987		159.00	-0.0477	0.8794
10	161.290	310.000	0.0003	-14.308	1.0000		88.191	-0.0153	0.9668

Table 4: Comparison of amount adsorbed (q_{max}) of Cu(II) ions on other agricultural wastes

Sorbent	Adsorbent Capacity (mg/g)		Reference
	Langmuir	Freundlich	
Rice Husk ash	2.30±0.2	28.8±0.02	Akhtar et al., 2010
Rice husk biomatrix	10.9	6.21	Krishnani et al., 2008
Herbaceous peat	4.84	8.86	Güdoğan et al., 2004
Rice husk carbons at 40°C	25.25	6.329	Zhang et al., 2011
Modified shea butter cake	161.290	88.191	This work
Grape Stalk	42.92	1.48	Onate, 2009

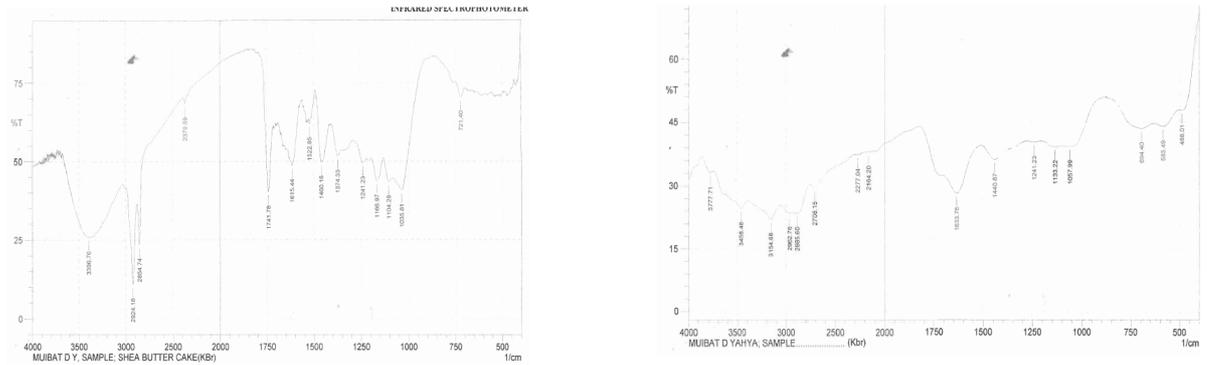


Fig.1: FT-IR spectra: (a) Shea Butter Cake; (b) Cu-loaded modified Shea Butter cake

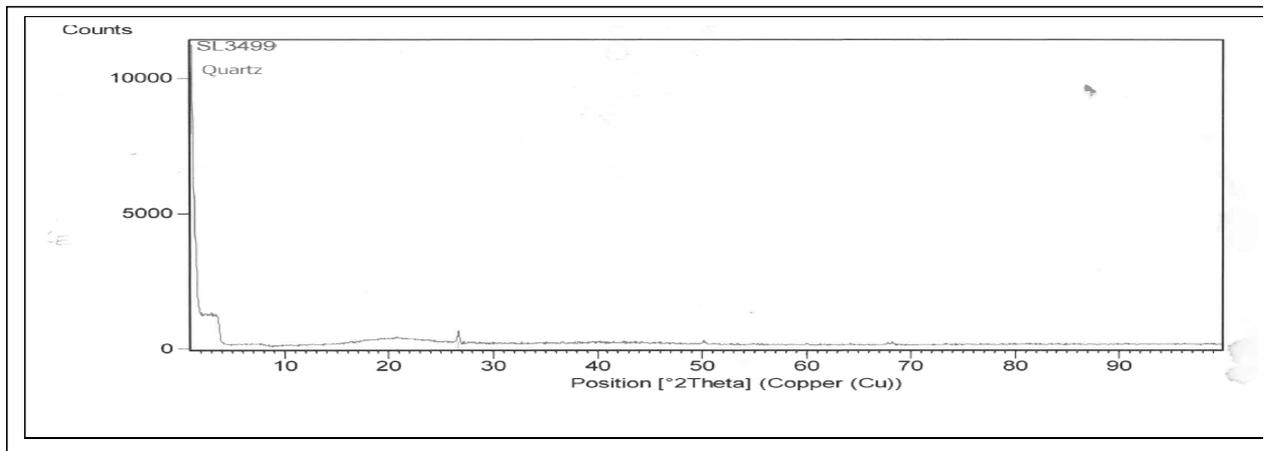


Fig.2: XRD Pattern of Shea butter cake (RSBC)

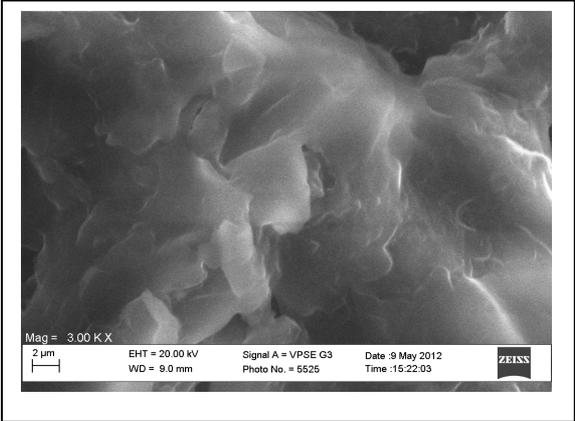
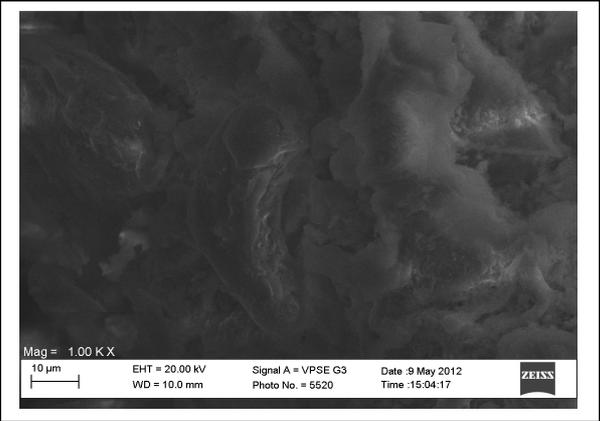


Fig. 3: SEM of Shea butter cake (RSBC) at (A) mag 1.00KX & (B) 3.00 KX

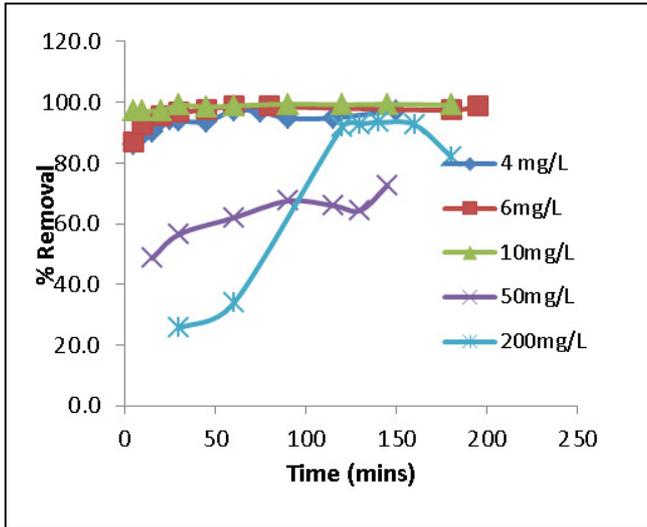


Fig. 4: The percent removal of Cu(II) as a function of time at various concentrations

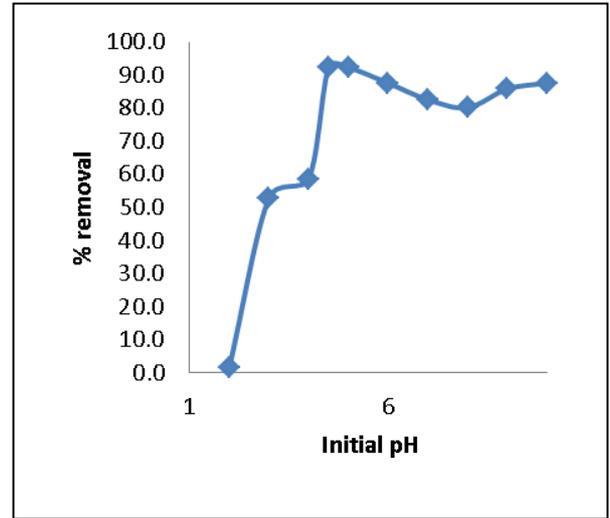


Fig.5: Percent removal of Cu(II) at different initial pH

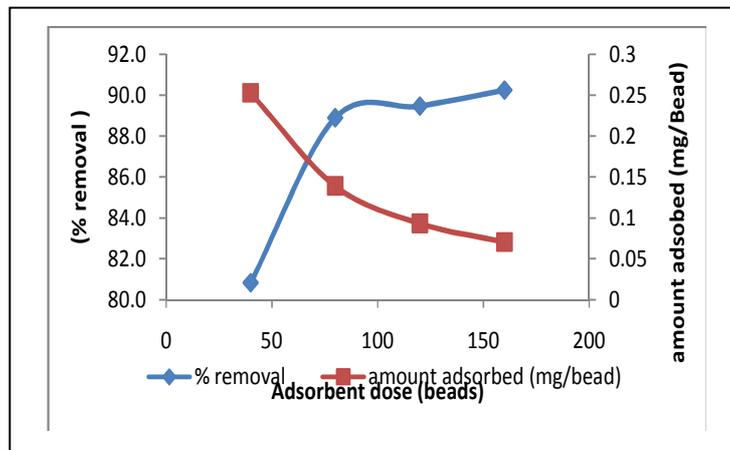


Fig.6: Percentage removal and amount adsorbed of Cu (II) on modified shea butter beads at varying adsorbent dosage

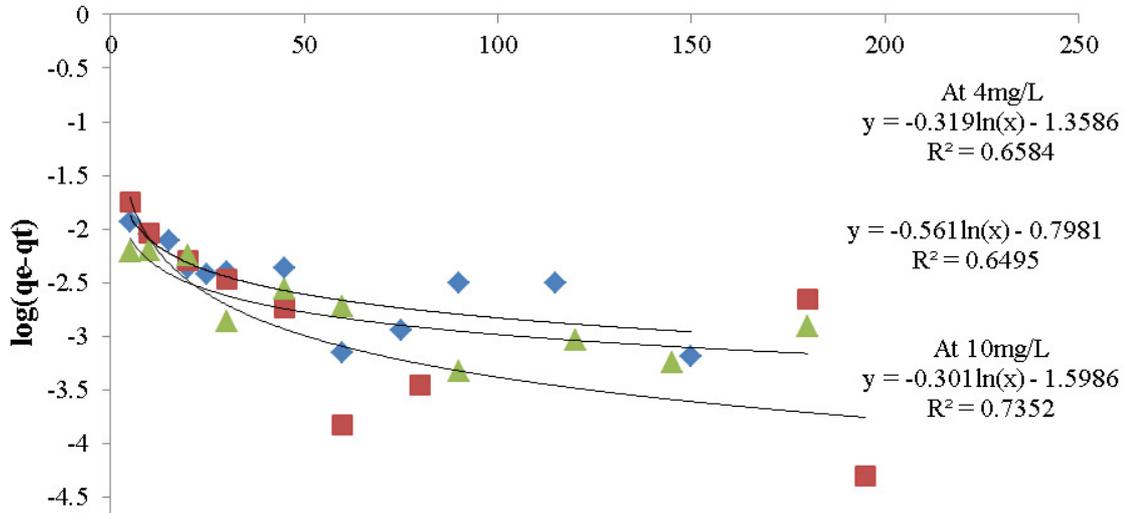


Fig.7: Pseudo-first-order kinetics of Cu(II) adsorption onto modified shea butter cake at 4mg/L and 6mg/L

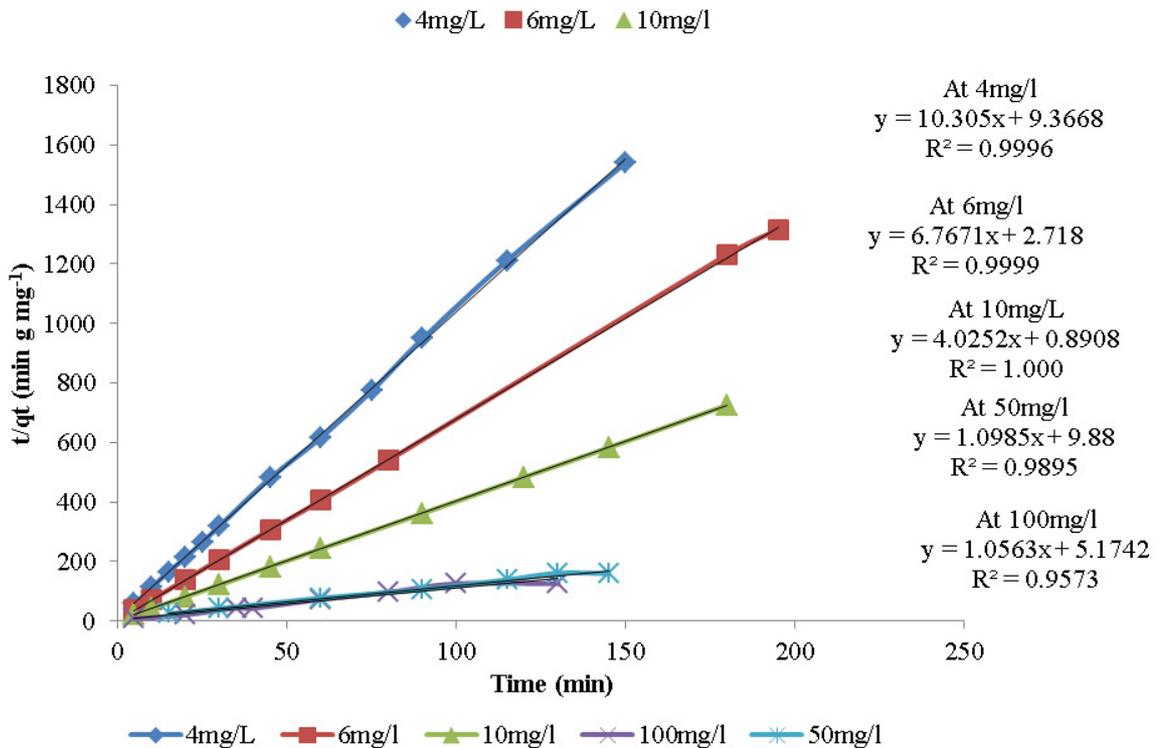


Fig. 8 Pseudo-second-order Kinetics of Cu (II) adsorption onto modified shea butter cake at various initial concentration

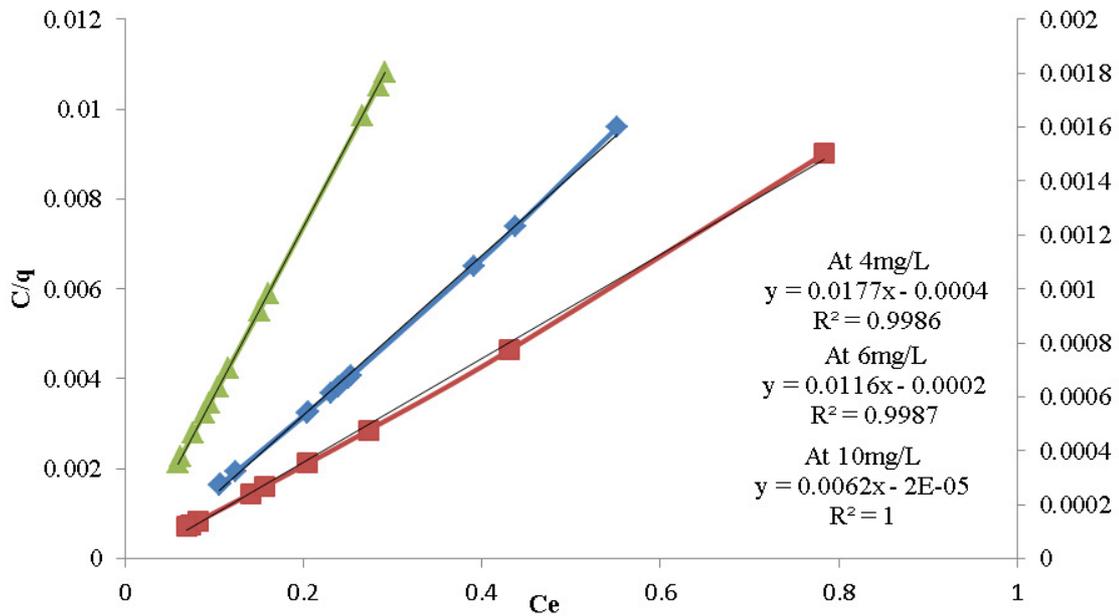


Fig. 9: Langmuir adsorption isotherm at various initial Cu (II) concentrations 4; 6; 10mg/l on modified Shea Butter Cake

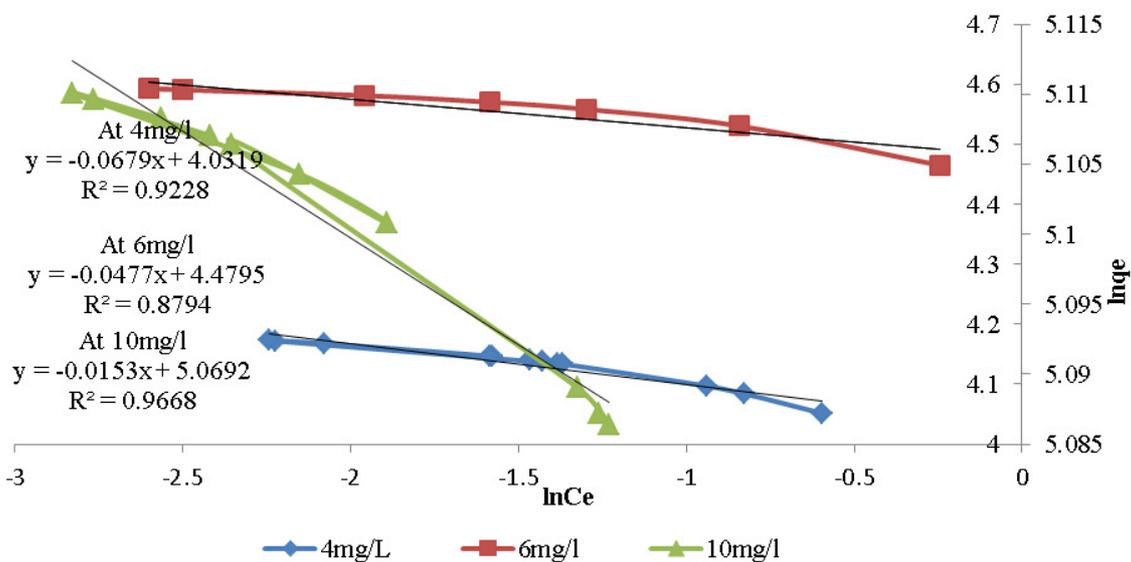


Fig. 10: Freundlich adsorption isotherm at various initial Cu (II) concentrations 4; 6; 10mg/l on modified Shea Butter Cake

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