KINETIC, ISOTHERM AND THERMODYNAMIC STUDIES OF THE BIOSORPTION OF LEAD (II) FROM SOLUTION BY SHEA-NUT SHELL

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ABSTRACT

Biosorption of Pb(II) from dilute aqueous solution using seed shell of shea tree (*Vitallaria paradoxa*) was investigated. Batch experiments were carried out to assess biosorption kinetic and equilibrium behaviour of Pb(II) by varying parameters such as pH, contact time and initial metal ion concentration at 30ºC. The optimum pH obtained was in the range pH 5 - 6. The kinetic study shows that uptake of Pb(II) increased with time and that maximum biosorption was obtained within 90 min of the process. The result obtained showed that the pseudo second order model correlated with the experimental data better than the pseudo-first order model. Freundlich and Langmuir isotherm models were used to analyse the experimental data of the biosorption process with the adsorption isotherm obeying the later model better than the former. These results indicate that seed shell of shea tree has potential for the removal of Pb(II) from industrial wastewater.

Key words: Biosorption, Pb(II), isotherm, seed shell, shea tree, kinetic studies

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1.0 INTRODUCTION

Pollution of water by heavy metals through the discharge of industrial wastewater is particularly one of the major environmental problems threatening the ecosystem. Rapid industrialization has contributed to the release of toxic heavy metals into water bodies (Sun et al, 2006). Removal of trace amounts of these heavy metal ions from wastewater and drinking water is of great importance due to their high toxicity to human, animal and aquatic lives (Addul-Ghani et al, 2007).

Many traditional methods have been applied for the removal of these metals from wastewaters. These include chemical precipitation, ion-exchange, membrane separation, reverse osmosis, evaporation, and electrolysis (Goel J et al., 2005; Kavitha et al., 2007). These conventional techniques can reduce metal ions, but they do not appear to be highly effective due to the limitations in the pH range as well as the high material and operational costs. The use of activated carbon is however more popular and different grades are available but is quite expensive and the regeneration of the carbon is not always possible. Activated carbon has been used as an adsorbent for the removal of lead by many researchers (Goal et al,2005; Issabeyeva et al. 2006; Issabayeva et al, 2007) but the process has not been used extensively due to its high cost. Thus the use of low cost agricultural materials as an alternative to commercial activated carbon has greatly increased overtime (Randall et al, 1975).

Activated carbon prepared from shea nut has been utilized for the sorption of methylene blue dye and for textile wastewater treatment. There are however no documented report on the utilization of the seed shell of shea tree. In the present work, we have studied the potential of lead (II) biosorption unto pre-treated shea-nut shells.

2.0 MATERIALS AND METHODS

2.1 Preparation of the biosorbent

The nut shells of shea tree (*Vitellaria paradoxa*) used for this research work were collected from Gwagwalada, Abuja Nigeria. The method of sample treatment by (Fan et al, 2003) was adopted. These sample was washed with ordinary water and then with de-ionized water to remove dirt. They were later oven-dried at 80°C for 12 h. The dried samples were pulverized in a mortar and pestle and thereafter sieved using a 400-mesh copper sieve. The prepared biosorbent was then preserved in air-tight polyethylene bags.

2.2 Biosorption studies

Series of the batch biosorption experiments was carried out by contacting the biomass with the metal ions under different conditions for a period of time in a glass tube. Studies were conducted at 27ºC to determine the effects of initial solution pH, contact time and initial ion concentration on the biosorption of Pb(II) ions. Each experiment was conducted in a thermostated water bath (Haake Wia model) and the residual metal ions analysed using Atomic Absorption Spectrophotometer (SOLAAR 32 AA). The amount of metal ion biosorbed from solution was determined by difference and the mean value was calculated for each set of experiments.

2.3 Effect of pH

The effect of pH on the biosorption of metal ions was carried out within the range that would not be influenced by the metal precipitated (Pavasant et al., 2006). As a result, the suitable pH ranges for Pb which is between 2-9.5 was used. The procedure used is similar to those earlier reported (Vasuderan et al., 2003; Xu et. al., 2006; Babarinde et al., 2006). Experiments were conducted at 25ºC to study the effect of initial solution pH on the biosorption of Pb(II) by contacting 1.00 g of the shea nut shell with 50 mL of 100 mg L-1 Pb(II) solution in a glass tube. The pH of each of the solutions was adjusted to the desired value with 0.1 M sodium hydroxide and /or 0.1 M nitric acid. The studies were conducted at pH values of 2-9. The glass tubes containing the mixture were left in a water bath for 24 hours. The biomass was removed from the solution by decantation and the residual Pb(II) concentration in the solution was analyzed. All studies were conducted in triplicates and the mean value was determined for each.

2.4 Effect of contact time

The biosorption of the Pb(II) by nut shells of shea tree was studied at various time intervals (5-90 min). A constant concentration of 100 mg L^{-1} was used. 1 g nut shells of shea tree were weighed into glass tubes and 50 mL of solution at the optimum pH was added into each tube. The nut shells of shea tree in each tube was removed from the solution by decantation after a given time interval and the residual ions in the solution was determined. The amount of metal ions biosorbed was calculated for each sample. The mean of the three results for a particular time was then calculated and plotted against time.

2.5 Effect of concentration

Batch biosorption study was carried out using a concentration range of 5 - 100 mg L^{-1}. 1 g of the nut shells was weighed into each of the glass tubes employed and 50 mL of the metal ion solution at the optimum pH of 5.5 was added. Three glass tubes were used for a particular concentration. The biosorption mixture was then left in a water bath to maintain the temperature at 27ºC for a period of optimum contact time required to reach equilibrium. The nut shells were removed from the mixture by decantation and the residual ions in the solution were determined. The biosorption capacity (qe) of the sludge is expressed as milligrams of biosorbed ions per gram of dry mass of the biomass (mg g^{-1}) and the removal efficiency of metallic ion (%E) were calculated by equations (1) and (2), respectively.

$$q_e = \left(\frac{C_i - C_e}{m}\right)V \quad ....(1)$$

$$\%E = 100\,\frac{C_i - C_e}{C_i} \quad ....(2)$$

where Ci is the initial metal ion concentration (mg L^{-1}); Ce, the equilibrium metal ion concentration (mg L^{-1}); m, the mass of the biosorbent (g); V, the volume of the solution (L). The results obtained were analysed using both Freundlich (Freundlich, 1906) and Langmuir (Langmuir, 1918) isotherms. The Freundlich isotherm in linearised form is;

$$\log \phi = \frac{1}{n}\log c_e + \log K \quad ....(3)$$

where n and K are Freundlich constants. The linearised form of the Langmuir isotherm is

$$\frac{1}{\phi} = \frac{1}{b_m}\frac{1}{C_E} + \frac{1}{\phi_m} \quad ....(4)$$

Where bm is a coefficient related to the affinity between the sorbent and sorbate, and ϕ_m m is the maximum sorbate uptake under the given condition.

2.6 Fourier Transform Infrared (FTIR) analysis of shea nut shell

The Fourier transform infrared (FTIR) spectrometer was used to identify the functional groups present in the activated shea nut shell. The biomass samples were examined using SHIMAZU FTIR spectrometer within the range of 500-4500^{-1}. All analyses were performed using KBr as background material. In order to form pellets, 0.002g shea nut shell was mixed with 0.3g KBr and pressed at 6-8 bar pressure.

3.0 RESULTS AND DISCUSSION

3.1 Effect of pH on adsorption efficiency

Figure 1 shows that the percentage of Pb(II) ions removal was relatively low at pH 2.0 when compared to higher pH values. This can attributed to the fact that the high concentration of H$^+$ ions compete with Pb(II) for active site at low pH (≤ 2.0) with an apparent preponderance of H$^+$ ions, resulting in the suppression of Pb(II) adsorption on the surface of adsorbent (Demirel *et al*, 2002). Therefore, increasing the initial concentration of proton in aqueous solutions resulted in the decrease of Pb(II) removal.

The result from figure 1 also shows that adsorption of Pb(II) ions decrease when the pH was > 7.0. High pH conditions reduce the mobility of Pb(II) due to the decrease in the exchangeable form, resulting in a decrease in the contact probability between adsorbent and adsorbate (Chem *et al*, 2007). At high pH value (pH 9.0), no interference of lead hydroxide precipitation was observed in this study. From figure 1 the maximum efficiency of Pb(II) ions removal was found to be 53% at pH 5.5 for a total time of 90 minutes. Thus, pH 5.5 was used for further batch experiments.

3.2 Effect of contact time on adoption efficiency

Figure 2 shows that the percentage of lead is higher at the initial stage. This is probably due to the larger surface area of the shea nut shells being available at the initial stage for the adsorption of Pb(II) ions. Figure 2 also shows that as the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the absorbent particles. Optimum lead removal was obtained after about 90 minutes of shaking time (Demirel *et al,* 2002).

3.3 Effect of initial concentration on adsorption efficiency

Adsorption characteristics indicated that percentage of Pb(II) ion removal was fairly dependent on the initial concentration of Pb(II) ions. (Horsfall et al; 2005) reported that adsorption sites take up available metal more quickly at low concentrations. However, at high concentrations metals need to diffuse to the adsorbent surface by intra-particle diffusion and greatly hydrolyzed ions will diffuse at a slower rate.

The result of batch experiments from figure 3 shows that the percentage of Pb(II) ions removal increased when the initial concentration of Pb(II) ion per 100ml of solution was increased from 5 to 30ppm for each agitation period. Figure 3 also shows a sharp decrease in the percentage of Pb(II) ions removal for the solution containing 100ppm of lead ions. This was basically due to the saturation of adsorbent above an initial Pb(II) ions concentration of 30ppm (Horsfall et al; 2005).

3.4 Effect of adsorbent dosage on adsorption efficiency

Experimental results observed from figure 4 generally shows that as the adsorbent mass increased from 0.5 to 1.0g, the percentage lead ions removed also increased up to a total contact time of 90 minutes. This can be attributed the fact that the number of adsorption sites or surface area increases with the weight of adsorbent, resulting in a higher percent of metal removal at a high dose (Conrad *et al*, 2007). However, figure 4 also reveals that further increase in the adsorbent mass from 1.0 to 4.0g did not yield any significant difference in the efficiency of Pb(II) ions removal after a total contact time of 90 minutes. This is because the equilibrium adsorption capacity is attained at higher adsorbent dosage.

3.5 FTIR Characterization of shea nut shell

The FTIR spectra of shea nut shell show a broad peak at 3475.8cm^{-1} which indicates the presence of –OH and –NH groups. The peak at 2154.56cm^{-1} indicates the stretching of the OH group bound to methyl radicals. The peak located at 1624.12cm^{-1} is a characteristic of carbonyl stretching from aldehydes and ketones. The peak observed at 1057.03cm^{-1} are due to C-H bonds. The presence of carbonyl and carboxylic groups confirms their importance as adsorption sites (Volesky, 1986).

3.6 Langmuir Isotherm

The Langmuir model is based on the assumption that maximum adsorption occurs when a monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecule in the surface plane (Patel *el al*, 2008).

Plotting $\frac{1}{q_e}$ against $\frac{1}{c_e}$ yield a straight graph with slope $\frac{1}{K_e q_m}$ and intercept $\frac{1}{q_m}$ as shown in figure 5, from which K_e and q_m are calculated. To confirm the favourability of the adsorption process to Langmuir isotherm, the essential features of the isotherm was expressed in terms of a dimensionless constant separation factor or equation parameter, R_L, which was calculated as:

$$R_L = \frac{1}{1 + k_L c_o} \quad \text{................................(5)}$$

Where C_o = initial concentration of adsorbate. The value of R_L indicates whether the isotherm is irreversible ($R_L = 0$) favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$).

The graph as shown in figure 5 is linear with a reasonably high regression co-efficient (R^2) value (0.9034) suggesting that the adsorption process obeys the Langmuir model. Also, R_L value of 0.141, shows that the Langmuir isotherm is favourable for describing the adsorption process. (Mattson *et al*, 1971).

3.7 Freundlich Isotherm

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a solid surface and assumes that different sites with several adsorption energies are involved (Faust *et al*, 1987). The constants, k_f and n were determined by plotting log C_e on the abscissa and log q_e on the ordinate as shown in figure 6. A best fit of the experimental data provides values for n and k_f based on the slope and the y-interception respectively.

Where $\frac{1}{n}$ is a heterogeneity factor, which is a measure of intensity of sorption or affinity of adsorbate for the adsorbent and is less than 1 if the adsorption process is favourable.

The plot in figure 6 give a correlation co-efficient (R^2) of 0.9002 which is close to 1 and also 1/n value obtained is 0.895 (i.e. < 1) suggesting that this model is also suitable for the description process.

3.8 Pseudo-First order model

The pseudo first order equation is generally expressed (Nassa, 1997) as:

$$\frac{dq_t}{d_t} = K_1 (q_e - q_t) \text{ ....(6)}$$

A plot of log (q_t - q_e) versus t as seen from figure 7 gives a straight line. K_1 and q_e are determined from the slope and intercept of the plot, respectively. A comparison of the results with the correlation coefficients in figure 7 shows that the correlation coefficient for the pseudo-first order kinetic model obtained from the study is low (0.8252). The theoretical q_e value found from the pseudo-first order kinetic model did not give reasonable values (1.55). This suggests that this adsorption system is not a first order reaction.

3.9 Pseudo-Second order model

The pseudo second order adsorption kinetic rate equation as expressed by (Ho *et al,* 2000) is

$$\frac{dq_t}{d_t} = K_2 (q_e - q_t)^2 \text{ ....(7)}$$

A plot of $\frac{t}{qt}$ versus t as shown in figure 8 gives a straight line, which shows that this model obeyed the sorption process. From the slope and intercept of the plots, q_e and K_2 are determined respectively. The correlation coefficient for the second order kinetic model obtained is 0.9969 and the calculated q_e values (3.03) also agree with the experimental data. This indicates that the adsorption system studied belongs to the pseudo-second order kinetic model.

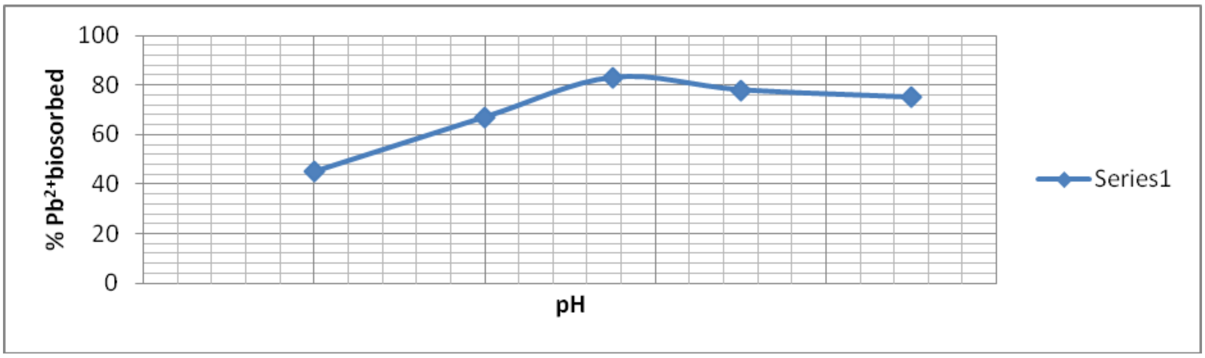

Figure 1. Effect of pH on biosorption of Pb^{2+} by shea nut shel at 100 mg L^{-1} and 27°C.

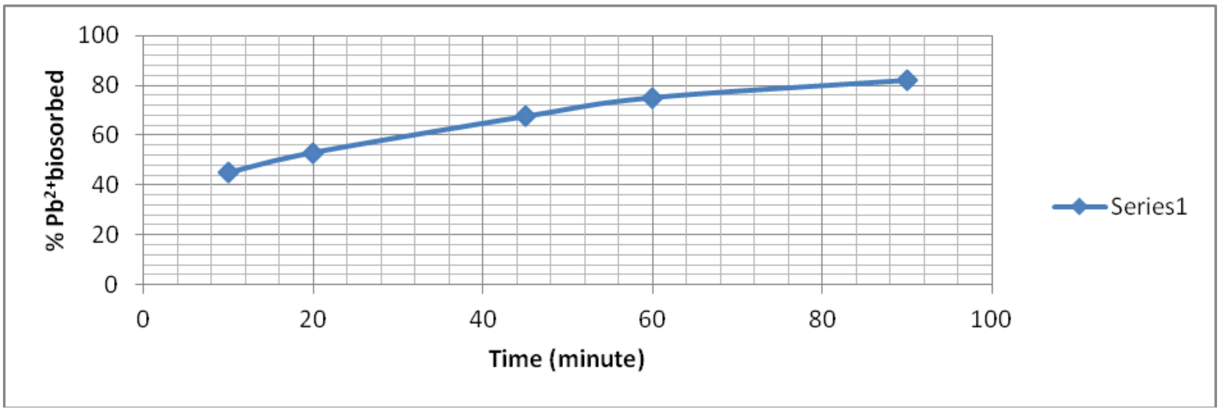

Figure 2. Time course of Pb^{2+} biosorption shea nut shell at 100 mg L-1, 30°C and pH 5.5.

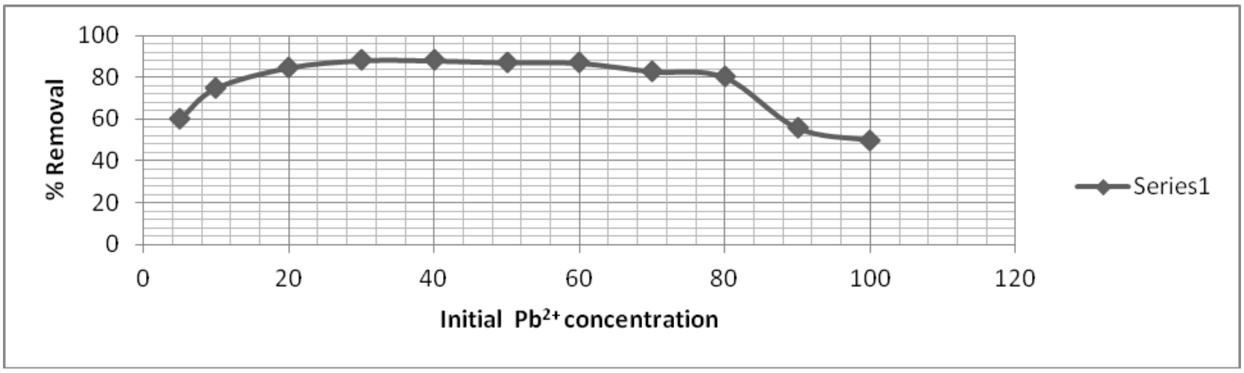

Figure 3. Effect of initial concentration on the biosorption capacity of Pb^{2+} by shea nut shell.

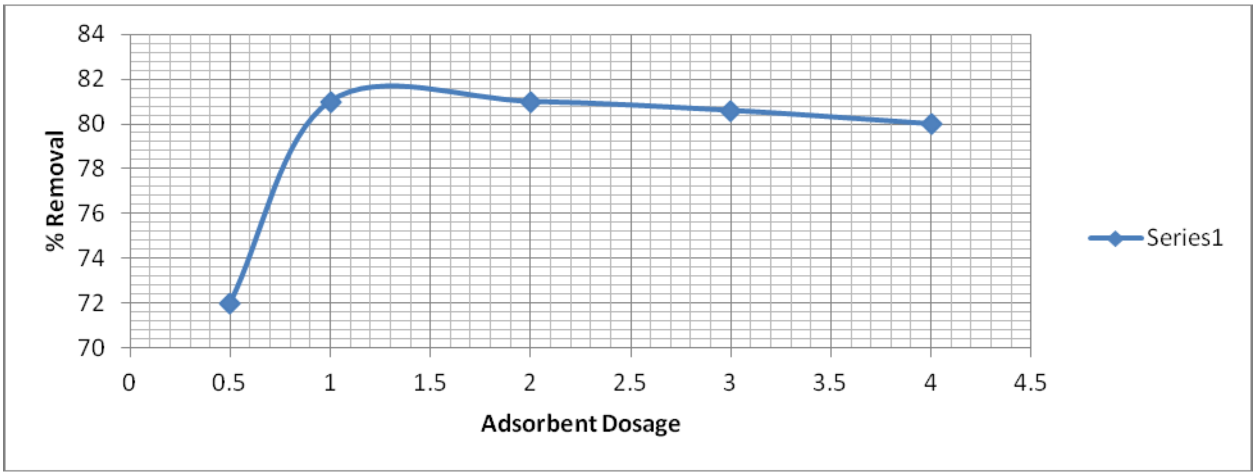

Figure 4. Effect of adsorbent dosage on the biosorption capacity of Pb^{2+} by shea nut shell.

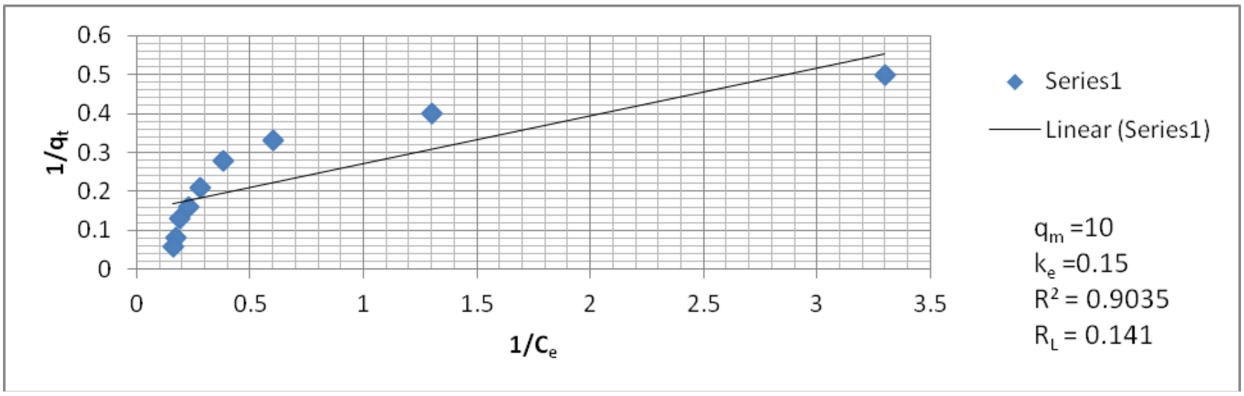

Figure 5. The linearized Langmuir biosorption isotherm of Pb^{2+} by shea nut shell at 27°C and pH 5.5.

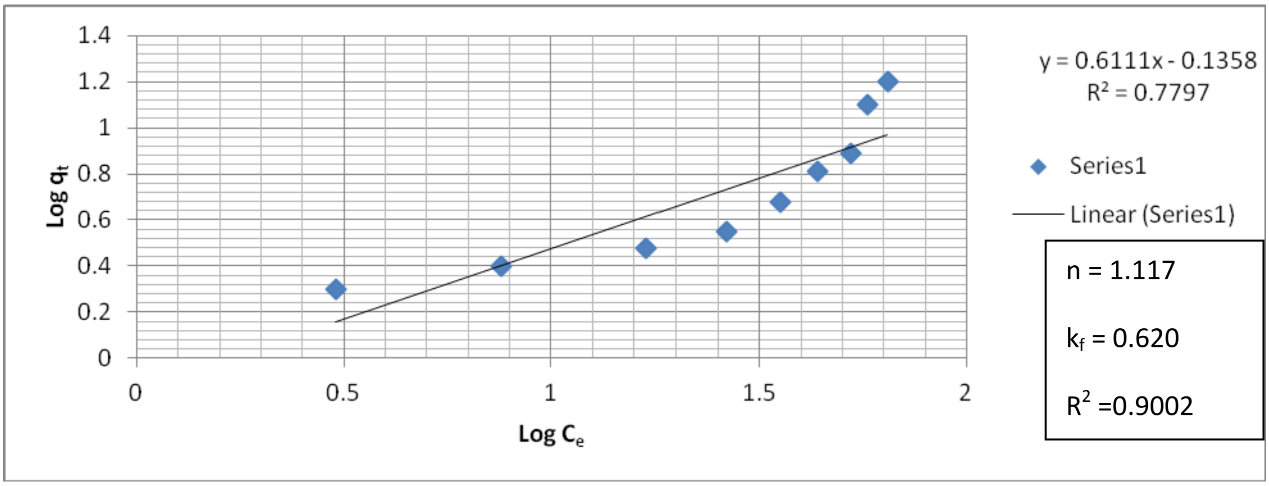

Figure 6. The linearized Freundlich biosorption isotherm of Pb^{2+} by shea nut shell at 27°C and pH 5.5.

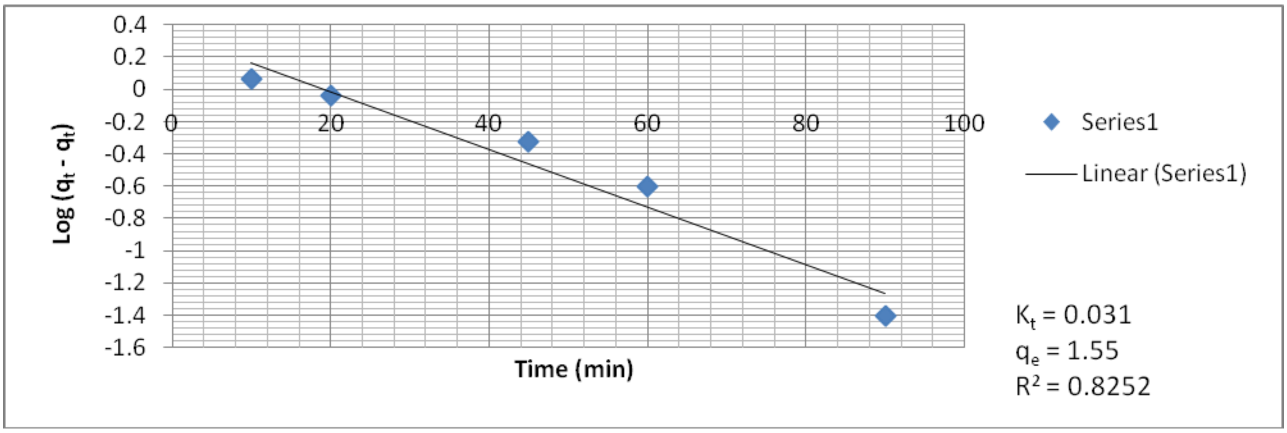

Figure 7. Pseudo-first order plot for the biosorption isotherm of Pb^{2+} by shea nut shell at 27°C and pH 5.5.

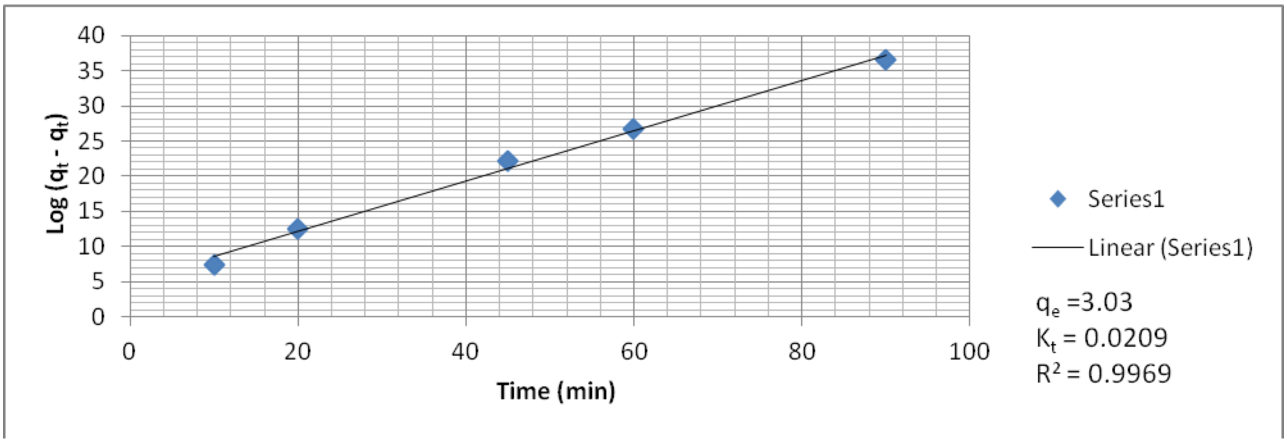

Figure 8. Pseudo-second order plot for the biosorption isotherm of Pb^{2+} by shea nut shell at 27°C and pH 5.5.

4.0 CONCLUSION

The batch biosorption studies have shown that the biosorption is pH dependent and the optimum pH for the removal of Pb^{2+} by shea nut shell is in range 5 - 6. Maximum biosorption was obtained within the first 90 minute of the process. Kinetic study also showed that the biosorption is well represented by pseudo-second order equation. The amount of lead ions biosorbed increased with increase in initial metal ion concentration. Isothermal analysis showed that the adsorption process fits into the Langmuir isotherm. Shea nut shell, an agricultural waste could therefore, be used as potential biosorbent for the removal of Pb (II) from aqueous solutions.

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