Accentuated Adsorption of Cu^{2+} and Pb^{2+} from Aqueous Solution Using Activated Macadamia Nutshell

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ABSTRACT

The efficiency of activated macadamia nutshell as an adsorbent for removing lead (Pb^{2+}) and copper (Cu^{2+}) from the water was investigated. The treated macadamia nutshell was characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM). Batch mode adsorption experiments were conducted by varying pH, concentration, adsorbent dose and contact time. The kinetics study of sorption indicates that the pseudo-second-order model provides better correlation of the sorption data (R^2=0.99) than the pseudo first-order model (R^2 = 0.94), confirming the chemisorption of metal ions in solutions on macadamia nutshell. The Freundlich isotherm has a good fit with the experimental data (R^2 close to 1) compared to Langmuir isotherm (R^2=0.96). This study shows that macadamia nutshell is an available, low cost, effective and environmentally friendly biosorbent for the removal of Cu^{2+} and Pb^{2+} ions from aqueous solution. Thermodynamic studies confirmed that the biosorption process was endothermic and the positive value of ΔG° is quite common when an ion-exchange mechanism applies in the biosorption. The positive value of ΔS° suggested an increase in randomness during the biosorption.

Keywords: Heavy metals, macadamia nutshell, adsorption.

INTRODUCTION

Water is a vital resource since it is necessary for all living organism on Earth to live. Roughly 70% of the Earth's surface is made up of water, which exists in many different forms, including rivers, lakes, glaciers, and oceans [1]. Despite the fact that access to clean, potable water is crucial for the health of humans and other living forms, it is anticipated that the majority of the world's population in 2025 has experienced water scarcity [2]. Many sectors, including mining, plating, dyeing, vehicle production, and metal processing, discharge heavy metals into the atmosphere. Numerous environmental issues have been brought on by the presence of heavy metals in the environment. Aquatic plants' photosynthesis will be hampered, their growth will be slowed, and they may even struggle to survive if the concentration of heavy metal ions in the water are beyond the acceptable limit. Heavy metals are carcinogenic, extremely enriched, and difficult to break down. Heavy metal ions can bind strongly with bio-macromolecules, including proteins and enzymes, after being consumed by the body, rendering them inactive. These heavy metal ions that build up in the cells of plants, fish, and mammals pose a major hazard to human health [3].

Controlling the concentration of heavy metals in wastewater is necessary to achieve water quality criteria in the majority of countries. Precipitation, filtration, oxidation-reduction, ion exchange, and membrane separation are examples of traditional physico-chemical treatment techniques for eliminating heavy metals. Adsorption is one of these techniques that has been shown to be an efficient way to remove harmful ions from contaminated water due to its simplicity, excellent performance, and low operating cost. However, these techniques usually become inefficient or costly when metals are dissolved in large volumes at relatively low concentrations [4]. Therefore, there is a need for the development of a low cost process to remove heavy metals economically.

Adsorbents have been made from a variety of materials and resources. For instance, harmful metal pollution has been remedied using biomass waste, industrial waste, carbon-based nanomaterials, oxides, natural and synthetic polymers, and surfactants [5–7]. Because of its microporous structure, large surface area, numerous reactive sites, and high adsorption capacity, biochar is a typical carbon-based class of nanomaterials generated from biomass which is widely employed as an efficient and reasonably priced metal ion adsorbent [9]. After Australia and Hawaii, South Africa is the world's third-largest producer of macadamia.

The current study describes the use of macadamia nutshells to create a more affordable and efficient adsorbent for the removal of copper (Cu) and lead (Pb) ions from aqueous solutions. Additionally, this study will ascertain how acid treatment affects macadamia nutshell adsorption characteristics and how it affects the nutshell's capacity to extract Pb^{2+} and Cu^{2+} from solution. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to prepare and characterize the adsorbent. The effects of solution pH, dosage, initial concentration, and contact time were examined. By fitting the adsorption data to kinetic and isotherm models, the removal capacity of macadamia nutshell was investigated.

MATERIAL AND METHODS

All reagents were of analytical and HPLC grade (Merck, South Africa). Anhydrous sodium sulphate, 99.5% pure, was deactivated by drying in the muffle furnace at 400 °C for 3 h before use. All solvents were subjected to distillation three times before use and were in a range of 99.0 to 99.5% pure. Kieselgel Merck Typ 77754, 70 to 230 mesh 100 μm was purchased from Sigma-Aldrich, South Africa. Macadamia nutshells were supplied by Eastern Produce Estates—SA (Pty) Ltd (Louis Trichardt, South Africa).

Macadamia homogenization

Macadamia nutshells were washed thoroughly with deionized water to remove dirt and then dried in the vacuum oven at 105 °C overnight. The shells were crushed and ground to a fine powder and then sieved through a pore size of between 90 and 150 μm. This sample was labelled as untreated Macadamia nutshell (AC). The AC sample was treated with 0.1 M HCl (Stirred for 3 h) to remove all the nutrients from the shells and labelled treated Macadamia nutshell (TAC). TAC was washed with deionized water through a funnel until the water coming out of the funnel was neutral. The samples were then dried in a vacuum oven at 105 °C overnight.

Batch contact adsorption experiments

Parameters controlling the adsorption of Cu^{2+} and Pb^{2+} ions by macadamia were evaluated in batch experiments. The influence of solution pH (pH 2–9), initial concentration (0.2–1.2 g/L), adsorbent dosage (0.05–0.30 g) and stirring time (0–60 minutes) was investigated. Solid material was separated from the solution after adsorption by first centrifugation and then filtered through a Whatman #4 filter paper. Then the concentration of Cu^{2+} and Pd^{2+} was determined using an atomic absorption spectrophotometer.

Data Management

The experiments were carried out in replicates (n=3), and blanks were performed. The adsorption capacity (q_e, mg/g) and the percentage removal (%R) of adsorbate by adsorbent were calculated from equations (1) – (3), respectively:

$$q_e = \frac{(C_0 - C_e)}{M} V \quad \text{............} \quad 1$$

$$q_t = \frac{(C_0 - C_t)}{M} V \quad \text{............} \quad 2$$

$$R = \frac{(C_0 - C_e)}{C_0} \, x \, 100 \quad \text{............} \quad 3$$

Where C_o is the initial concentration (g/L), C_e is the equilibrium concentration (g/L), C_t is the Cu^{2+} & Pb^{2+} concentration at any time (g/L), m is the adsorbent amount (g), q_e is the amount of adsorbed metal ion (mg/g adsorbent) on the sorbent and V is the volume of solution (L).

Adsorption kinetic modelling

The successful adsorption process depends on the kinetic parameters. By understanding the adsorption kinetics, the process may be designed and carried out more effectively. Several kinetic models are used to investigate the processes controlling biosorption of adsorbate as well as the rate of mass transfer. Pseudo-first order (PFO) and pseudo second order (PSO) were employed to fit the experimental data. The equations for the models in their non-linearized form are given below.

The PFO rate equation (also, known as Lagergren equation) and the PSO kinetic model [10] are represented in Eqs. 4 and 5.

$$log(q_e - q_t) = log q_e - \frac{k_1 t}{2.303} \quad \text{.......} \quad 4$$

$$\frac{t}{q_t} = \frac{1}{k_1 q_{e^2}} + \frac{t}{q_e} \quad \text{.......} \quad 5$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). k_2 is the pseudo-second-order rate constant (g/mg/min), q_e is obtainable by a linear regression analysis of the $t / q_t = f(t)$ function.

Adsorption thermodynamics

To understand the adsorption process, the three main adsorption thermodynamic parameters, standard free energy (ΔG^0), standard enthalpy (ΔH^0), and standard entropy (ΔS^0), were calculated. The thermodynamic equilibrium constant is approximately equal to the Langmuir adsorption constant [11]. The thermodynamic parameters were calculated through the following equations:

$$\Delta G = -RT\, InK_L \quad \text{.......} \quad 6$$

Where K_L is the equilibrium constant obtained from the Langmuir model, T is the absolute temperature (K) and the universal gas constant $R=8.314\times10^{-3}$ kJ/K/mol. The relationship between K and thermodynamic parameters of ΔH and ΔS can be described by the Van't Hoff correlation in the following equation [12,13]:

$$InK = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{.......} \quad 7$$

RESULTS AND DISCUSSION

Characterization of the macadamia

The main functional groups present in the macadamia nutshell were characterized by infrared material analysis. The FTIR, was used to confirm the potential applicability of adsorption of pollutants on macadamia with sufficient and satisfactory removal efficiency.

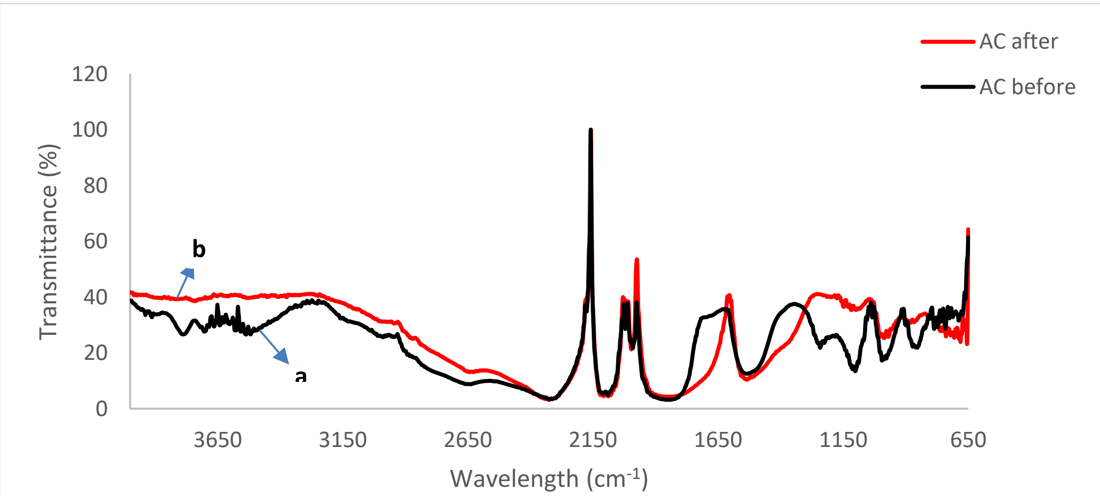

Fig. 1 FTIR spectrum of macadamia nutshell (AC-activated carbon)

It has been found that the AC raw powder shows a stratified structure with wrinkle surface and wide crack between layers. With the exception of variations brought on by the treatments, the TAC spectra prior to adsorption displayed comparable features. Prior to adsorption, the TAC spectra showed a broad absorption band at 3000–3500 cm^{-1}, with a maximum at roughly 3255 cm^{-1}, which is attributed to the O–H stretching vibrations of hydrogen-bonded hydroxyl groups [14]. Aliphatic C–H stretching vibration is found as a very weak peak at 2845 cm^{-1} while the asymmetric vibration of CH_2 group appears at 2926 cm^{-1} (Figure 1).

A broad asymmetric band further characterized the spectra of TAC before adsorption at 1621 cm^{-1} ascribed to the presence of carboxylate group [15, 16]. The broadband decreased in intensity after metals loading signifying its involvement in Cu^{2+} and Pb^{2+} ions removal. The shoulder at 1038 cm^{-1} can be ascribed to C–OH stretching of phenolic groups [17]. The differences observed in FTIR spectra of TAC before and after adsorption of metals confirm the participation of functional groups in the removal of Cu^{2+} and Pb^{2+} ions by macadamia nutshell.

Surface morphology of macadamia

Scanning electron microscopy (SEM) was used to analyse the morphology and structure of treated macadamia prior to adsorption; the micrographs are displayed in Figure 2. The material had a flaky long fold-like structure, which is characteristic of plant-based materials, according to the SEM image shown in Figure 2. Since they maintained their flakiness, the material's structural backbone was not significantly changed, indicating that the treatment was not too severe to destroy the material. Interconnected networks demonstrate the material's porosity. A closer examination of the surface reveals elongated pores, confirming that macadamia maintained the structure of plant materials based on lignocellulose and demonstrating that more non-carbon elements were eliminated throughout the activation process [18].

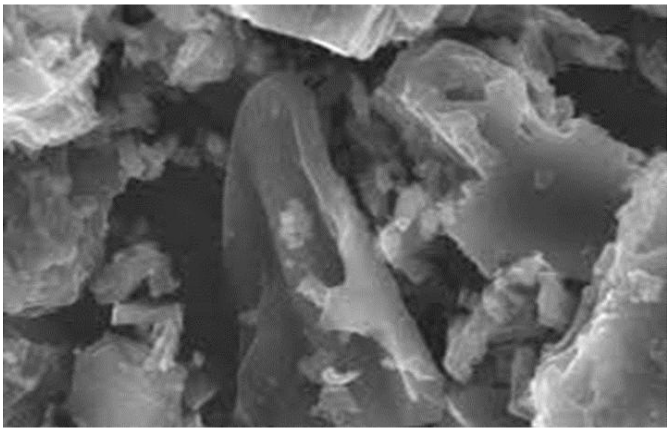

Fig. 2 SEM image of the treated macadamia nutshell Effect of contact time

Since contact time is directly related to the quantity of metal ions extracted from aqueous solution, it is a crucial factor in calculating the equilibrium time needed for the sorption of metal ions on a sorbent. The optimal time to adsorb Cu^{2+} was 30 min with an efficiency of 82.4%, which became saturated at 40 min of processing time, after the efficiency increased at 50 min and slightly decreased at 60 min. The absorbing capability for Pb^{2+} had the highest efficiency of 95.4% after 35 min of adsorption time, as shown in Figure 3.

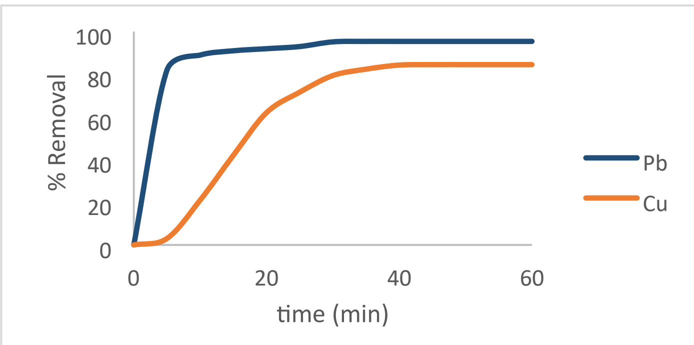

Fig. 3 Effect of adsorption time on Cu^{2+}& Pb^{2+} removal efficiencies Effect of solution pH

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The pH of the solution has been identified as the most important variable affecting metal adsorption onto the adsorbent. This is partly because hydrogen ions themselves are strongly competing with the adsorbate. The removal of $Cu^{2+}$and Pb^{2+} as a function of hydrogen ion concentration was examined at pH 2–9. The removal efficiency was found to be highly dependent on the hydrogen ion concentration of the solution. The effect of pH on adsorption efficiency is shown in Figure 4. The Cu^{2+} ions are usually soluble in an acidic pH and the maximum removal of cadmium was obtained in a pH of 5. The optimal pH for Pb^{2+} removal by the macadamia was 4,5.

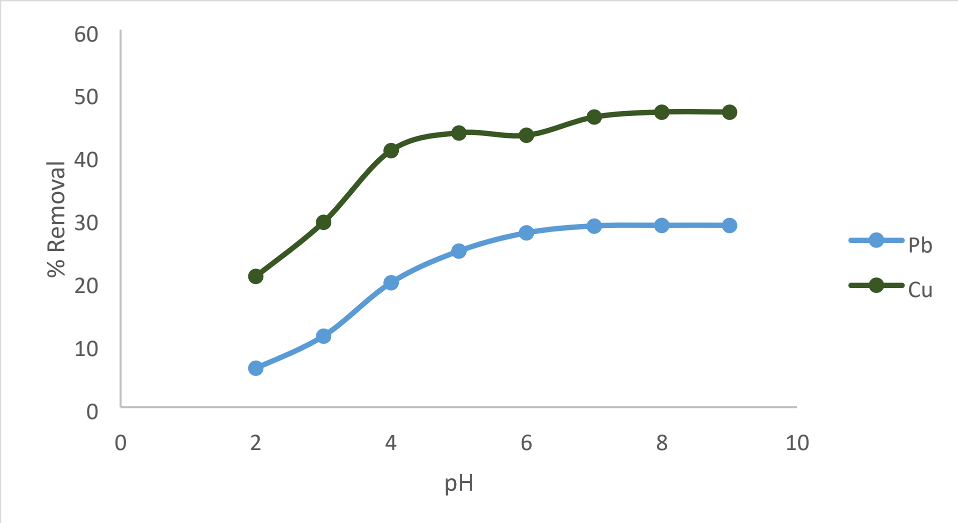

Fig. 4 Effect of pH of the solution on Cu^{2+}& Pb^{2+} adsorption Initial metal concentration

As the initial concentration of metal ions increases, the removal percentage decreases for a fixed adsorbent dose and contact time. This behaviour can be explained by limited active site on the adsorbent surface.

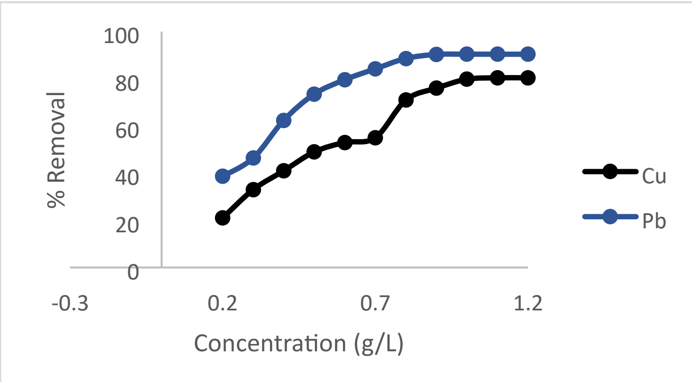

Fig. 5 Effect of initial concentration

The Cu^{2+} and Pb^{2+} adsorption efficiency of treated macadamia biochar is displayed in Figure 5. As adsorbent concentrations increase, so did macadamia's adsorption capabilities. At doses of 0.2–1.2 g/L, the Pb^{2+} adsorption efficiency significantly increased. Before achieving the maximum of 90.4% of Pb^{2+} removal at the adsorbent concentration of 1 g/L, it progressively increases with dose. Cu^{2+} adsorption efficiencies likewise showed similar tendencies, increasing with increasing adsorbent concentrations and peaking at 79.8% at an adsorbent concentration of 1 g/L.

Effect of biosorbent dose

The amount of adsorbent in the aqueous solution has an impact on the adsorption process. It is evident that the adsorption process is significantly impacted by the biosorbent dosage parameter. The ideal dosage of TAC must be ascertained in order to get optimal biosorption capability. As a result, various concentrations of TAC have been employed, ranging from 0.25 to 1 g of solution with concentrations of heavy metals ranging from 0.2 to 1.2 g/L at a temperature maintained at 25°C. Figure 6 illustrates how adsorbent dosage affects the removal of heavy metals. Clearly, when the sorbent dosage of TAC increased, so did the adsorption.

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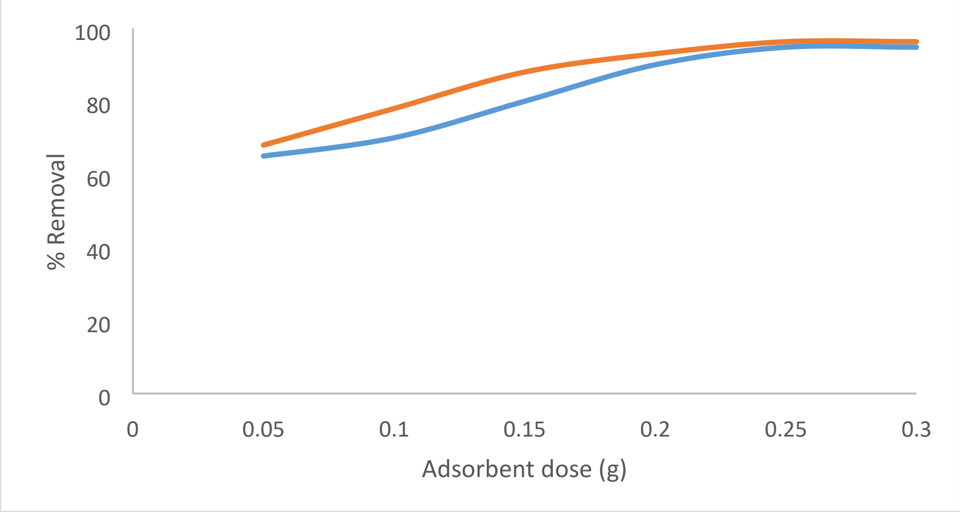

Fig. 6 Effect of adsorbent dosage Kinetic study

The kinetic studies and modelling of the experimental data are presented in Figure 7 and certain parameters are shown in Table 1. From the correlation coefficient obtained as presented in Table 1 for the pseudo-first-order and pseudo-second order models, it is verified that both models fit well to the experimental data. The pseudosecond-order model proposed by Ho *et al*. (1996) assumes that the process occurs by chemical adsorption involving the participation of valence forces or electron exchange between the metal and the biosorbent, while the pseudo-first-order model assumes the occurrence of the adsorption by physisorption [19].

In this study, the highest correlation coefficient was obtained for the kinetic model of pseudo-second-order, which is the model that best adapts to the experimental data. A preliminary comparison related to adsorption velocity (q_e) between the calculated and experimental values can be performed to prove the best fit, since the values calculated by the kinetic model of pseudo-second-order are closer to those obtained experimentally.

Table 1. Obtained parameters of kinetics models for adsorption on macadamia

Ion	**Pseudo-first-order**			**Pseudo-second-order**		
	k_1	q_e	R^2	k_2	q_e	R^2
Pb	0.0045	6.855	0.2556	0.0989	14.1336	0.9999
Cu	-0.0146	3.19	-0.944	7.22×10^{-3}	0.781	0.962

The biosorption rate constant obtained by the pseudo-2nd order has a higher sorption rate for Pb^{2+}, while the Cu^{2+} has lower rate.

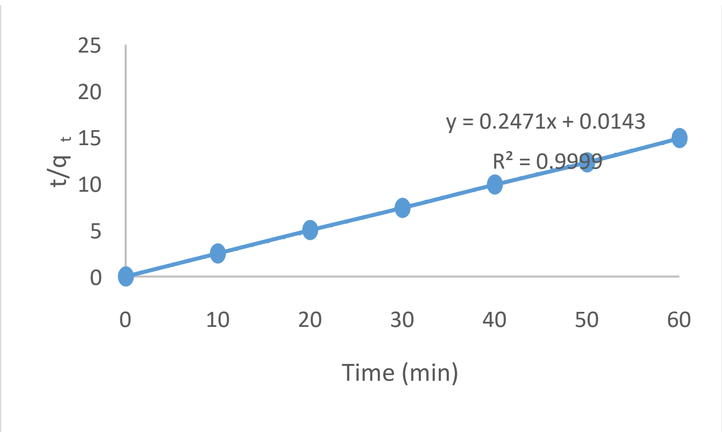

Fig.7 Pseudo-second order for sorption of Pb^{2+} ions by macadamia.

Summary of the adsorption isotherm models for the composites

Table 2. Parameters of the mathematical models of Langmuir and Freundlich for the adsorption of Cu^{2+} and Pb^{2+} ions on macadamia

Ion	**Langmuir**					**Freundlich**			
	k_L	q_m	k^f	R^2	n	K_d	q_s	q_m	R^2
Pb	0.3459	33.18	0.75	0.948	0.94	-0.00002	2.7284	17.79	0.9991
Cu	0.089	3.191	0.12	0.961	0.95	4.876	4.86	8.86	0.89

These adsorption isotherm models indicate that the adsorption process occurs in a multilayer heterogeneous surface. Hence, it was concluded that the data fitted best in Freundlich model largely because of the diversity of adsorption sites on the macadamia

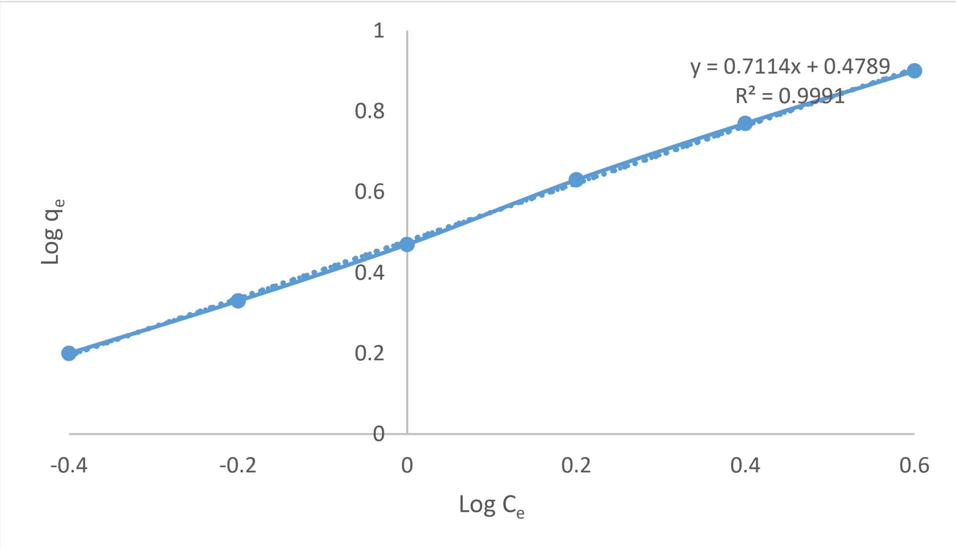

Fig. 8 Linearized biosorption isotherms of Freundlich.

Thermodynamic studies on biosorption of Cu^{2+} and Pb^{2+} ions

The obtained thermodynamic parameters were computed from a plot of *ln* b against 1/T using the derived thermodynamic equilibrium constant. Equation (6) was used to determine the entropy, enthalpy, and Gibbs free energy for the adsorption process for Pb^{2+} at various temperatures. The sorption process was endothermic because the macadamia's capacity to absorb Pb^{2+} increased with temperature. Table 3 provides the thermodynamic parameters. Positive values of ΔH° indicate that lead ion adsorption on macadamia is endothermic. In this investigation, positive ΔG° values were obtained. Because of the activated complex that the cationic sorbate forms with the biosorbent, it has been proposed that a positive value for ΔG° is quite typical when an ion-exchange mechanism applies in the biosorption of cationic sorbate [20]. An increase in randomness during the biosorption process was shown by the positive value of ΔS◦ [21].

Table 3. Thermodynamic parameters for the Pb^{2+} biosorption process

Temp (K)	ΔG° (KJ/mol)	ΔH°(KJ/mol)	ΔS° (J/mol)
298	3.46		
303	3.32		
313	3.04	11.52	26.79
323	2.77		

CONCLUSION

Cu^{2+} and Pb^{2+} were adsorbed from aqueous solution using acid treated macadamia nutshell The obtained results showed that macadamia nutshell biosorbent was a very effective biosorbent in the removal of Cu^{2+} and Pb^{2+} ions from water. FTIR and SEM were applied to assess diverse functional groups responsible for adsorption and morphology. The FTIR confirmed various functional groups such as amine/amide, carbonyl, hydroxyl and carboxylic that could be responsible for selective recovery of heavy metal ions. The biosorption process was pH, contact time, dosage and metal ion concentration dependent. SEM depicted porous morphology that might be responsible for retention of precious metal ions. The optimal conditions for recovery of the heavy metal ions obtained from the study were: pH 5; 60 minutes' agitation time. Biosorption of Cu^{2+} and Pb^{2+} ions solutions obeyed Langmuir and Freundlich isotherms. R_L value from Langmuir and n from Freundlich isotherms show that biosorption of Cu^{2+} and Pb^{2+} ions solutions on treated macadamia is favourable.

The endothermic nature of the biosorption process was validated by thermodynamic investigations; when an ionexchange mechanism is involved in the biosorption of cationic sorbate, a positive value for $\Delta G°$ is frequently observed. The chemisorption of Cu^{2+} and Pb^{2+} ion solutions on treated macadamia nutshell is confirmed by the kinetics analysis of sorption, which shows that the pseudo second-order model offers a better correlation of the sorption data than the pseudo first-order model. The obtained results of this investigation indicated that the modified adsorbent was able to remove heavy metals ions.

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Conflict Of Interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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