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Isotherm Modeling Of Lead (II) Adsorption From Aqueous Solution Using Groundnut Shell As A Low-Cost Adsorbent

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Abstract:*Potentially toxic trace elements such as lead when present in high levels in water, food and soil post serious human health threats all over the world. Adsorption process using different natural materials is among the most effective techniques for removing many heavy metal ions from different types of water sources. In this study, an attempt has been made to investigate the efficiency of groundnut shells for removing lead from aqueous solutions using batch mode technique. The equilibrium data was analyzed using one one-parameter, six two-parameter and two three-parameter adsorption isotherm models. The experimental data fitted well to two-parameter isotherm (Tempkin adsorption isotherm) in comparison to the other adsorption isotherm models analyzed. The correlation coefficient of Tempkin adsorption isotherm was found to be 0.9661 indicating that the groundnut shell could remove about 96.61 % of Pb (II) ions effectively from the aqueous solution.Fourier transform infrared (FT-IR) spectroscopic studies revealed the possible involvement of functional groups, such as hydroxyl, carboxyl, amino and carbonyl group in the biosorption process.*

Keywords: *Adsorption, adsorbent,groundnut shell, isotherm, lead*

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I. Introduction

The excessive release of heavy metals into the natural environment has become a global concern. Heavy metals contamination exist in aqueous wastes due to mining operations, alloy industries, fertilizer manufacturing and storage batteries industries[1]. Lead is a contaminant found in drinking water and inair. Pollution of portable water by lead is a worldwide problem due to its toxic effects on human health and wildlife especially when it forms part of the food chain [2]. The level of lead (II) ions concentration in industrial effluents and wastewaters is about 200–500 mg/L; however, the permissible level according to water quality standards is 0.1–0.05 mg/L [3]. Lead toxicity causes hypertension, nephritis, abdominal pain, constipation, cramps, nausea, behavioral changes, reading problems and development defects[4]. The dangers of heavy metalsin the environment has generated increasing interest and search for novel approaches, which are relatively efficient and low cost to eliminate these harmful metals from aqueous wastes [5]. Adsorption is the most recommended and reliable technique in comparison to other conventional methods (precipitation, electro-coagulation, cementing and exchange of ions on resins) due to its ability to remove metal ions from aqueous solutions [6, 7]. Several agricultural waste materials have been reported for the removal of lead ions using the adsorption technique [8]. Some of these waste materials used as adsorbents include plants seeds [9–11].

In Ghana, 94 % of groundnuts produced come from the Northern part of Ghana and mostly, large quantities of groundnut husks/shells are discarded and burnt, which pollute the environment [12]. The main chemical composition of groundnutsshells were found to be lignocellulose fibers, which comprise hemicellulose, cellulose and lignin [13]. These constituents have great potential to bind heavy metals through replacement of hydrogen ions with metal ions in solution or by donation of an electron pair from these groups to form complexes with metal ions in solution [13].

The linear form of the isotherm models are mostly adopted to determine the isotherm parameters or the most fitted model for the adsorption system due to the mathematical simplicity. In recent times, linear regression analysis has been one of the most applied tools for defining the best fitting adsorption models because it quantifies the distribution of adsorbates, analyzes the adsorption system and verifies the consistency of theoretical assumptions of adsorption isotherm model [14]. The objective of this study was to evaluate the adsorption behavior of Pb (II) ions onto groundnut shell using various types of adsorption isotherm models.

II. Material And Methods

2.1 Preparation of Adsorbent

Groundnut shells were collected from a local groundnut processing center in Navrongo market in the Upper East Region of Ghana. The groundnut shells were washed repeatedly with distilled water to remove dust and any insoluble impurities. The shells were then air-dried under room temperature and subsequently dried in an oven at 105 ^{0}C for 24 hours to constant mass. The shells were ground and sieved to obtained particle size less than 300 µm. The groundnut shells were then used for the experiments without any physical or chemical treatments as an adsorbent [15,16].

2.2 Preparation of adsorbate

All chemicals used for the study were of analytical reagent grade. The stock solution of 1000 mg/L was prepared by dissolving 1.599 g of lead nitrate [Pb $(NO_3)_2$] in 250 mL of distilled water, then 10 mL of concentrated nitric acid (HNO_3) was added and the resulting solution was diluted to the 1,000 mL mark of the volumetric flask using de-ionized water. Working concentrations were prepared from the stock solution by diluting the stock solution with de-ionized water to the required concentrations. The Pb (II) ions concentration were determined spectrophotometrically (Carry 60 UV–Vis Spectrophotometer) by the dithizone method(APHA, 1989).

2.3 Characterisation of the adsorbent

The groundnut shell was characterizedto determine functional groups on its surface using Fourier transform infrared spectrometer (Spectrum Two 94133 series). Thiswas done before and after the metal ions adsorption.

2.4 Equilibrium isotherm studies

The isotherm experiments were carried out using 2.0 g/L of groundnut shell (optimized dose) at initial Pb (II) concentration of 15, 25, 50, 75, and 100 mg/L under room temperature (25 ^{0}C). The solutions were adjusted to pH of 6.0 using 0.1 MNaOH or 0.1 MHCl. The adsorbate-adsorbent solutions were agitated at a constant speed of 120 rpm for equilibrium time of 120 min. The mixtures were filtered and the residual metal ions in the filtrate were analysed using Carry 60 UV-Vis spectrophotometer.
The amount of adsorbate adsorbed at equilibrium and removal efficiency were calculated using equations (1-2).
The amount of adsorbate adsorbed at equilibrium (q_e):

$$q_e = \frac{C_0 - C_e}{m} \times V \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Removal efficiency (RE):

$$RE = \frac{(C_0 - C_e)}{C_0} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where, q_e represents the equilibrium mass of adsorbed substance per unit mass of adsorbent (mg/g),C_0 is the initial metal ion concentration (mg/L), C_e is the equilibrium metal ion concentration (mg/L), V is the volume of solution (mL) and m is the mass of the adsorbent (g).

III. Results and Discussion

3.1 Characterization of groundnut shell

The FT-IR spectra of groundnut shell before and after the adsorption of Pb (II) ions from the aqueous solution are presented in Figs. 1 and 2 respectively. The main constituents found in agricultural wastes that are responsible for heavy metals adsorption include hemicellulose, simple sugars, lignin, proteins, lipids and starch having a variety of functional groups [17]. Functional groups present in these constituents include carbonyl, acetamido, phenolic, amido, carboxyl, amino, alcohols, esters and sulphydryl and it is these groups which possess affinity for complexation with metals[13]. The hydroxyl (OH), amine (NH), carbonyl (C=O) and carboxylic (COOH) groups are the most important sorption sites [18]. From Fig. 1, the broad peak at 3322.39 cm^{-1} was an indicator of -OH and –NH groups. The stretching of the -OH groups bound to methyl radicals presented a signal between 2921.43 and 2168.90 cm^{-1}. The peaks located at 1727.51 and 1628.70 cm^{-1} are characteristics of carbonyl group stretching vibrations from aldehydes and ketones. The peak at 1508.99 $cm^{-1}$is associated with the stretching vibration in aromatic rings. The peaks observed at 1024.22 and 912.29 cm^{-1} are due to C-O and C-H bonds respectively. In Fig. 1 (raw sample), it was observed that three subsequent peaks (2168.9, 2103.93 and 2050.79 cm^{-1}) which corresponded to C≡C stretching vibrations present in the raw sample were not found after using the sample to adsorbPb (II) ions from the aqueous solution. After the adsorption of Pb (II) ions [Fig. 2], it was observed that the peaks at 3322.39 and 1628.70 cm^{-1} became narrowed (3319.01 and 1621.91 cm^{-1} respectively); however, peaks at 1727.51 and 1024.22 cm^{-1} broadened (1729.34 and 1026.94 cm^{-1} respectively). The presence of –OH group, coupled with carbonyl group confirmed the presence of carboxylic acid groups in the groundnut shell [18]. The broadening at peaks 1727.51 and1024.22

cm^{-1} indicated the participation of C=O and C-O groups in the adsorption of Pb (II) ions. Similar spectra were obtained for bio sorption studies of metal ions using baobab fruit shells biomass [19].

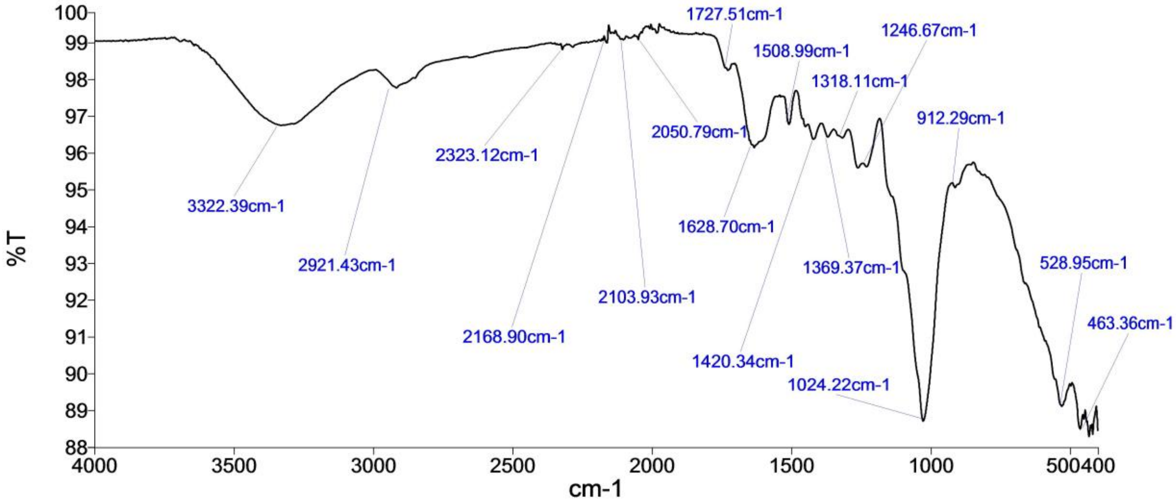

Figure 1: FT-IR spectra of groundnut shell without treatment with Pb (II) ions

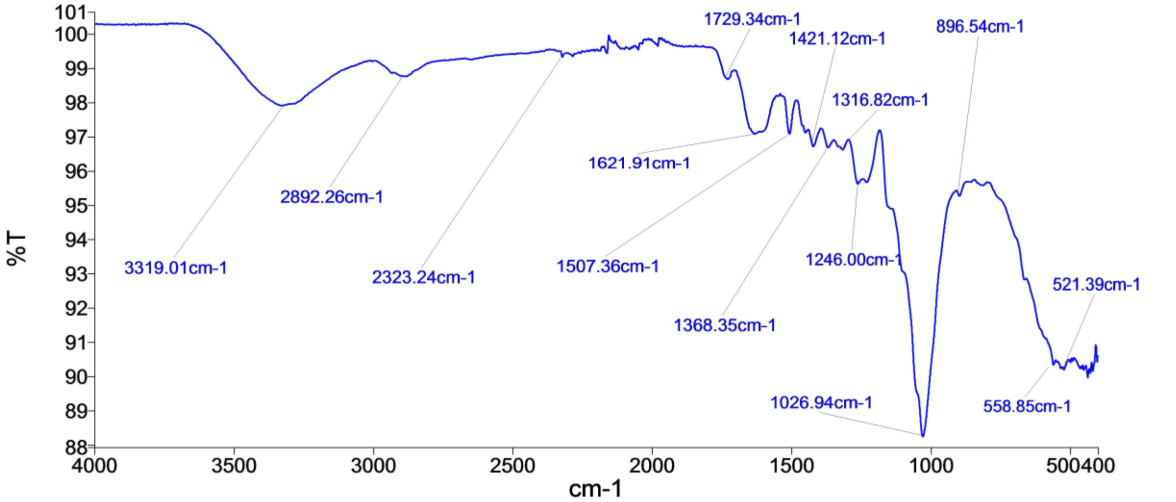

Figure 2: FT-IR spectra of groundnut shell after treatment with Pb (II) ions

3.2 Adsorption Isotherm studies

Adsorption isotherms provide information on how adsorption system proceeds and indicate how efficiently a given adsorbent interacts with the adsorbate. The ability of groundnut shell to adsorb Pb (II) ions from aqueous solution was analzsed and evaluated from the shape of the adsorption isotherm plots. In this study, equilibrium isotherm data were applied to one one-parameter (Henry), six two-parameter (Langmuir, Freundlich, Dubinin-Radushkevich, Tempkin, Harkin-Jura and Elovich) and two three- parameters (Redlich-Peterson and Jossens) adsorption models and the results of their linear regressions were used to find the model with the best fit. The linear form of the various isotherm models are presented in Table 1 while, their correlation coefficients (R^2) and constants are presented in Table 2.

Table 1: Adsorption isotherm models and their linear forms

Isotherm	Non-Linear Form	Linear Form	Plot	Constants obtained from plot
Henry		$q_e = K_{HE} C_e$	q_e vs C_e	K_{HE}
Langmuir	$q_e = q_m K_L \frac{C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	$\frac{C_e}{q_e}$ vs C_e	q_m and K_L
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$\log q_e$ vs $\log C_e$	K_F and n
Dubinin-Radushkevich	$q_e = q_s \exp(-K_{DR} \mathcal{E}^2)$	$\ln q_e = \ln q_s - K_{DR} \mathcal{E}^2$ $\mathcal{E} = RT \ln(1 + \frac{1}{C_e})$	$\ln (q_e)$ vs ε^2	K_{DR} and q_s
Tempkin	$q_e = \frac{RT}{b} \ln A C_e$	$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e$ or $q_e = B \ln A + B \ln C_e$ Where $B = \frac{RT}{b}$	q_e vs $\ln(C_e)$	A and b
Harkin-Jura		$\frac{1}{{q_e}^2} = \frac{B}{A} - \left(\frac{1}{A}\right) \log C_e$	$\frac{1}{{q_e}^2}$ vs $\log C_e$	A and B
Elovich		$\ln\left(\frac{q_e}{C_e}\right) = \ln K_e q_m - \frac{q_e}{q_m}$	$\ln\left(\frac{q_e}{C_e}\right)$ vs q_e	K_e and q_m
Redlich-Peterson	$q_e = \frac{A C_e}{1 + B C_e^{\beta}}$	$\ln\left(\frac{C_e}{q_e}\right) = \beta \ln C_e - \ln A$	$\ln\left(\frac{C_e}{q_e}\right)$ vs $\ln C_e$	A and β
Jossens	$C_e = \frac{q_e}{H} \exp(F q_e^p)$	$\ln\left(\frac{C_e}{q_e}\right) = -\ln(H) + F q_e^p$	$\ln\left(\frac{C_e}{q_e}\right)$ vs q_e	H and F

In Table 2, it was found that the equilibrium data fitted the one-parameter isotherm model (Henry) with correlation coefficient (R^2) of 0.8510. The value of K_{HE} (0.610 L/g) was relatively high which confirmed the fitness of the Henry adsorption isotherm model.

The analysis of the two-parameter adsorption isotherm models showed that the Langmuir isotherm described the adsorption of Pb (II) ions unto groundnut shell from the aqueous solution as indicated by the high correlation coefficient (R^2) of 0.9554. The R_L value was between 0 and 1, which indicated the favorability of the adsorption process under the studied conditions. The Langmuir monolayer adsorption capacity (q_m) value was found to be 42.640 mg/g indicating high adsorption capacity of the groundnut shell. The value of K_L (0.062 L/mg) was relatively high implying high surface energy in the process and consequently high bonding between metal ions and the groundnut shell. It was observed that the Freundlich isotherm also conformed to the experimental data with correlation coefficient of 0.9098. The value of n was found to be 1.632 which indicated that the groundnut shell have a heterogeneous surface since the value satisfied the heterogeneity condition, $1 < n < 10$. While the value of $\frac{1}{n}$ was below unity indicating chemisorption process [20–22], the value of K_F was found to be 0.358 mg/g implying that there was low uptake of the metal ions unto the adsorbent surface. The correlation coefficient (0.9171) obtained from Dubinin-Radushkevich isotherm plot showed a good fitness of the equilibrium data to the model. From the Dubinin-Radushkevich constant (K_{DR}), $3.0 \times 10^{-6} \text{mol}^2/\text{kJ}^2$ the mean sorption energy was calculated as 408.24 J/mol which suggested physisorption process. The experimental data fitted well to Tempkin isotherm with good correlation coefficient(R^2) of 0.9661 indicating that Pb (II) ions adsorption occurred because the heat of adsorption of all ions in the layer decreases linearly because of increased surface coverage [23]. The calculatedvalues of the intensity of sorption, A and the heat of sorption, b further indicated that the data best fit the Tempkin isotherm which imply chemisorption process. The Elovich and Harkin-Jura isotherms fitted less as indicated by the low correlation coefficients of 0.6630 and 0.6901 respectively. The low values of q_m and K_e of the Elovich isotherm and Harkin-Jura constants (A and B) confimed the inability of the experimental data to fit well to these isotherm models.

From the three-parameter isotherm models analyzed, the experimental data fitted the Redlich-Peterson isotherm better than that of theJossens isotherm with correlation coefficients of 0.8010 and 0.6630 respectively. The relative high values of β and A; and Jossens constants (H and F) showed the agreement of the data to Redlich-Peterson and Jossens adsorption isotherm models respectively.

From all the isotherm models analyzed, it was observed that the equilibrium data fitted well toTempkin modelindicating that the sorption of Pb (II) ions onto the groundnut shell was due to chemisorption. Temkin isotherm model was applied by[24]to confirmed that the adsorption of cadmiumions onto nanozero- valent iron particles followed a chemisorption process.

Table 2: Henry, Langmuir, Freundlich, Dubinin–Radushkevich, Temkin, Harkin-Jura, Elovich, Redlich-Peterson and Jossens Isotherm constants and correlation coefficients (R^2) for the adsorption of Pb (II) ions unto groundnut shell

Henry		Langmuir				Freundlich			
K_{HE} (L/g)	R^2	q_m (mg/g)	K_L (L/mg)	R_L	R^2	K_F (mg/g)	n	$\frac{1}{n}$	R^2
0.061	0.8510	42.64	0.062	0.295	0.9554	0.358	1.632	0.613	0.9098

Dubinin- Radushkevich (R-P)				Tempkin				Harkin-Jura		
K_{DR} (mol^2/kJ^2)	q_s (mg/g)	R^2	E (J/mol)	A (L/mg)	b (J/mol)	B	R^2	A	B	R^2
3×10^{-6}	2.520	0.9171	408.24	0.6920	2890.14	0.942	0.9661	0.482	1.458	0.6901

Elovich			Redlich-Peterson			Jossens		
K_e (L/g)	q_m (mg/g)	R^2	A	β	R^2	H	F	R^2
0.102	2.723	0.6630	0.358	0.387	0.8010	3.601	0.637	0.6630

IV.Conclusion

It has been established that the groundnut shell has an acceptable adsorption capacity toward the Pb (II) ions. The Tempkin adsorption isotherm model was found to have the highest correlation coefficient (R^2) and hence, the best fit which showed that the groundnut shell could remove about 96.61 % of Pb (II) ions from the aqueous solution.FT-IR analysis confirmed the role of surface functional groups present on the groundnut shell in the biosorption process.

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