

Evaluation of Biosorptive Capacity of Banana (*Musa paradisiaca*) Stalk for Lead(II) Removal from Aqueous Solution

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Abstract

Raw Banana Stalk (RBS), Acid Activated Banana Stalk (AABS) and Base Activated Banana Stalk (BABS) prepared from banana stalk were used as biosorbents to remove Lead(II) from aqueous solution. The biosorbents were characterised using proximate analysis and Fourier Transform Infrared (FTIR) spectroscopy. Pb(II) of 1000 mg/L concentration was prepared from Pb(NO₃)₂ salt and other concentrations were obtained from this stock through serial dilution. Effects of adsorbent dose, temperature, initial metal concentration, contact time and pH on the percentage Pb(II) removal were evaluated. The Pb(II) concentrations in the solutions were analysed using Atomic Absorption Spectrophotometer. Kinetic, isotherm and thermodynamic parameters were determined. FTIR spectroscopy showed that RBS, AABS and BABS are rich in carboxyl, hydroxyl and phenolic functional groups. At an equilibrium time of 180 minutes, the percentage Pb(II) removal was 63.97%, 96.13% and 66.90% for RBS, AABS and BABS, respectively. Pseudo-second order kinetics best described the process with R^2 (0.95, 0.98, 0.97) for RBS, AABS and BABS, respectively. Langmuir isotherm (AABS) has the maximum adsorption capacity (q_{max}) of 13.53 mg/g and R^2 (0.99). Thermodynamic parameters obtained were ΔG^0 (-18.75 kJ/mol), ΔH^0 (12.63 kJ/mol), ΔS^0 (0.05 kJ/mol·K) and E_a (4.37 kJ/mol). Banana stalk has viable characteristics for preparing biosorbents. Acid activated banana biosorbent is more efficient for removal of lead ions from its aqueous solution.

Keywords

Biosorption, Isotherm, Banana Stalk, Kinetics, Lead(II)

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1. Introduction

Lead is one of the heavy metals that are often found in industrial wastewater and its discharge into the environment poses serious threat due to its toxicity to aquatic and terrestrial lives [1] [2]. It is a group IV element on the periodic table which is remarkably highly resistant to corrosion in most acid and naturally occur as element buried in the earth crust in insoluble and biologically inoffensive forms [3]. Enhanced industrialization such as manufacturing of storage batteries, television tube, printing, paints, pigments, photographic materials, gasoline additives, matches and explosives brought about lead bearing wastewater [4]-[7].

Exposure to Lead is widely recognized as a major risk factor for several human diseases once it goes beyond the World Health Organisation (WHO) maximum permissible limit ($3 - 10 \mu\text{g}\cdot\text{L}^{-1}$) in drinking water [8]-[12]. It forms complexes with oxo-groups in enzymes to affect virtually all steps in the process of haemoglobin synthesis and porphyrin metabolism [13]. Other problems associated with toxic levels of lead exposure are encephalopathy, seizures and mental retardation, anemia and nephropathy [14] [15]. Hence, lead must be removed as much as possible from industrial effluents to prevent environmental hazard from its discharge.

Adsorption technology has been widely preferred to other traditional methods such as coagulation, flocculation, filtration, ozonation or sedimentation in the removal of pollutants from wastewater [16]-[18]. In this technology, activated carbons are commonly used adsorbent due to their high adsorption capacity, a result of their high surface area and surface reactivity but their regeneration is, however, difficult and expensive [19] [20].

Quest for effective and economical technologies have brought about biosorption. It is based on metal binding capacities of various biological materials mainly composed of cellulose, hemicelluloses and lignin that make them effective adsorbents for a wide range of pollutants due to the presence of functional groups such as hydroxyl, carboxyl, methoxyl and phenols [21]-[25]. Recent studies have shown that heavy metals can be removed using plant materials such as empty palm oil fruit bunch [26], sour soup seeds [27], modified cassava fibre [28], coconut shell [29], duck weed [30], sago waste [31], African spinach stalk [32], palm fruit fibre [33], hop [34], orange peels [35]-[37] and spent tea leaves [18] [38].

Banana Stalks (BS) are generated in large amount as waste product after the consumption of banana and these constitute environmental menace due to the fact that they are left to decompose being of non-economic importance [39]. However, BS is a rich lignocellulosic agricultural waste whose previous application has been limited to the production of activated carbon for malachite green dye removal [40] and not yet applied to Pb(II) removal [41]-[48]. The present study investigated the adsorptive capacity of BS as a low-cost adsorbent for the biosorption of Lead(II) from aqueous solution. The effects of physical parameters such as initial concentration, pH, and temperature and biosorbent dosage on the biosorption process have been investigated. In addition, the biosorption equilibrium isotherms, kinetics and thermodynamic parameters have been determined.

2. Materials and Method

2.1. Preparation and Characterization of Adsorbent

Banana Stalks were first sundried, cut into small pieces and washed with distilled water to remove dirt particles. BS pieces were then dried in the oven at 100°C for 24 hours to constant weight before being grounded and screened to $300 - 425 \mu\text{m}$ mesh particle size. It was then stored as Raw Banana Stalk (RBS). RBS of 200 g was soaked with 1 M H_3PO_4 in ratio 1:1, kept in the oven for 24 hours at 80°C for activation and stored as Acid Activated Banana Stalk (AABS). Similarly, Base Activated Banana Stalk (BABS) was prepared by soaking another 200 g of the RBS in 0.1 M KOH for 24 hours at 80°C in an oven and stored as BABS. The Proximate analysis of the biosorbents was carried out to know the percentage compositions of its constituents. Fourier Transform Infrared (FTIR) spectroscopic analysis was performed on RBS, AABS and BABS using FTIR spectroscope (FTIR-2000, Perkin-Elmer). The spectra were measured from 4000 to 400 cm^{-1} .

2.2. Preparation of Simulated Wastewater

Simulated wastewater samples containing Pb(II) was prepared from $\text{Pb}(\text{NO}_3)_2$ of $1000 \text{ mg}\cdot\text{L}^{-1}$ stock solutions. Reagents used were of analytical grade and deionized water was used in solution preparation. Other concentrations ($20 - 100 \text{ mg/L}$) were obtained from this stock solution by serial dilution. Fresh dilutions were used for each experiment. The concentration of Pb(II) in simulated wastewater was analysed by Atomic Absorption Spectrophotometer (model PyeUnicam SP-9 Cambridge, UK).

2.3. Batch Biosorption Equilibrium Studies

Batch equilibrium tests were carried out on the adsorption of Pb(II) on RBS. The effect of initial metal ion concentration, contact time, temperature, solution pH and adsorbent dose were investigated. Sample solutions were withdrawn at time interval and equilibrium to determine residual concentrations. Solutions were filtered prior to analysis in order to minimise the interference of the RBS. For equilibrium studies, the experiment was carried out for 360 minutes to ensure that equilibrium was reached. The linear Beer-Lambert relationship between absorbance and concentration with the calibration curve was established by plotting the graph of absorbance versus concentration of the lead solution. The concentration of lead solution before and after adsorption was determined using an Atomic Absorption Spectrophotometer (model Pye Unicam SP-9 Cambridge, UK). This experiment was done in turns for AABS and BABS.

The adsorbed phase concentration (q_t , in mg/g) at time (t) was calculated using Equation (1)

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

where, C_o and C_t are the initial and the final lead concentration (mg/L), respectively; V is the water sample volume (L); and m is the mass of adsorbent used (g).

The biosorption at equilibrium, q_e (mg/g), was calculated according to Equation (2)

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

where, C_o and C_e are the initial and the final (equilibrium) lead concentration (mg/L) respectively; V is the water sample volume (L); and m is the mass of adsorbent used (g). The percentage of lead ion removal was calculated using Equation (3):

$$\text{Removal (\%)} = \frac{C_o - C_t}{C_o} \times 100\% \quad (3)$$

2.4. Effects of Adsorption Conditions

RBS of 1 g was measured into a 125 ml Erlenmeyer flask with 100 ml of 100 mg/l of Pb(II) solution with pH of 7 monitored using a pH meter (model CD70 WPA) and controlled with 0.1 M NaOH and 0.1 M HCl. The flask was agitated at 30°C at a constant 125 rpm using the Thermostatic water bath shaker, the sorption experiment carried out for sufficient time of 360 minutes. The supernatant was filtered using Watman Filter Paper and Lead(II) concentration was analysed using Atomic Absorption Spectrophotometer (AAS). The effect of contact time (30, 60, 90, 120, 150, 180, 210, 240, 300, 360 minutes), biosorbent dose (0.2, 0.4, 0.6, 0.8, 1.0, 1.5 and 2.0 g), initial metal ion concentration (20, 40, 60, 80, 100 and 120 mg/L), pH (4, 6 and 8) and temperature (30, 40 and 50°C) were evaluated during the study. During the experiment, the particular parameter considered was varied while the other four were kept constant variously for RBS, BABS and AABS biosorbents.

3. Results and Discussion

3.1. Characterisation of Biosorbent

The result of proximate analysis carried out on the biosorbent samples are as presented in **Table 1**. It revealed that the AABS, BABS and RBS are rich in crude fibre of 67.69%, 62.07% and 58.47%, respectively. This rich crude fibre comprise of lignin, cellulose and hemicellulose content. Lignin is a compound rich with functional groups, such as carbonyl, ether and hydroxyl [21] [41] and has been used for metals adsorption by some researchers [40] [49]. The implication of this is that the presence of the active site presupposes that banana stalks are good biosorbents. The FTIR spectra characteristics for the three biosorbents are as shown on **Table 2** while main spectra are on **Figure 1**. The analysis revealed that the biosorbents are rich in hydroxyl, carboxyl and the phenolic groups which indicates that RBS, AABS and BABS are viable for the adsorption of Pb(II) onto the biosorbents.

3.2. Effect of Initial Concentration and Contact Time

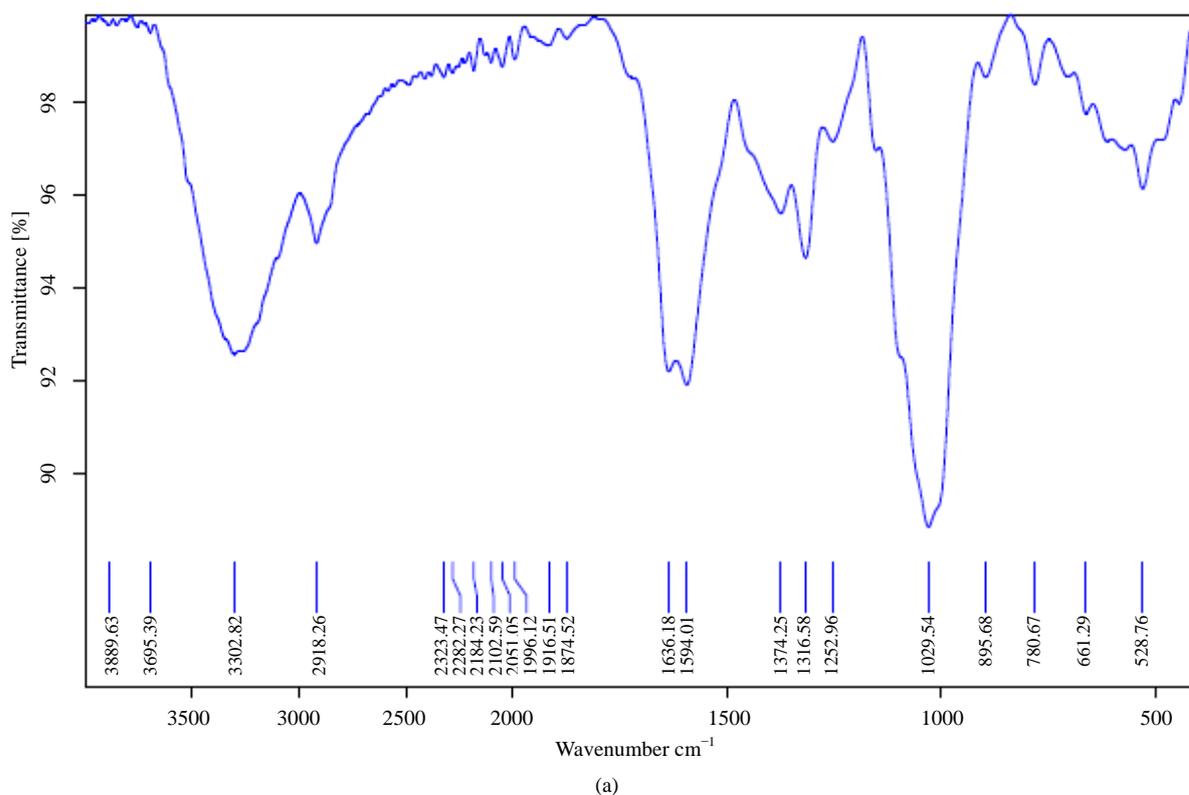
The rate of biosorption is a function of the initial concentration and contact time of the sorbate and these makes them important factors for effective biosorption. **Figure 2** shows the effect of contact time on Pb(II) adsorption onto RBS, BABS and AABS. It was found that the adsorption of Pb(II) by the three banana stalks increased with contact time until equilibrium was reached at around 180 minutes. The biosorption process was rapid initially

Table 1. Proximate analysis of banana stalks.

Sample	Moisture content (%)	Ash content (%)	Crude fibre (%)	Protein (%)	Carbohydrate (%)
AABS	10.38	5.52	67.69	6.29	10.12
BABS	10.88	5.93	62.07	7.93	13.26
RBS	12.19	7.40	58.47	8.58	14.10

Table 2. FTIR spectra characteristics for RBS, BABS and AABS.

IR peak	Band wave number (cm ⁻¹)			Assigned functional group
	RBS	BABS	AABS	
1	3889.63	3287.10	3327.12	O-H stretching vibration of alcohol or carbonyl acid
2	2918.26	2920.86	2918.94	C-H stretching vibration of alkane
3	2184.23	2541.21	2209.05	C-H stretching of alkyne
4	1916.51			C-O stretching vibration of alkene and ketones
5	1636.18	1604.94	1628.34	C-H stretching of alkene
6	1029.54	897.33	660.63	CH bending vibration of C-H ₂ and C-H ₃ (finger print region)



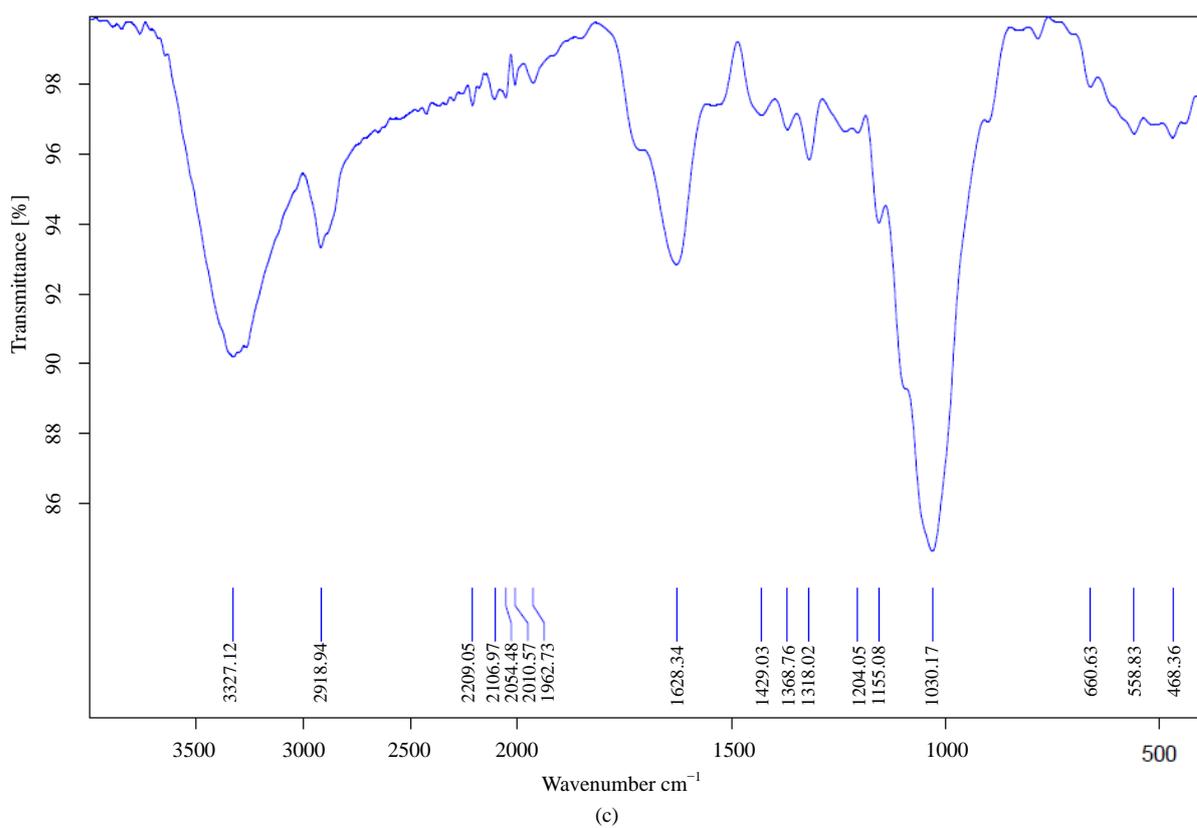
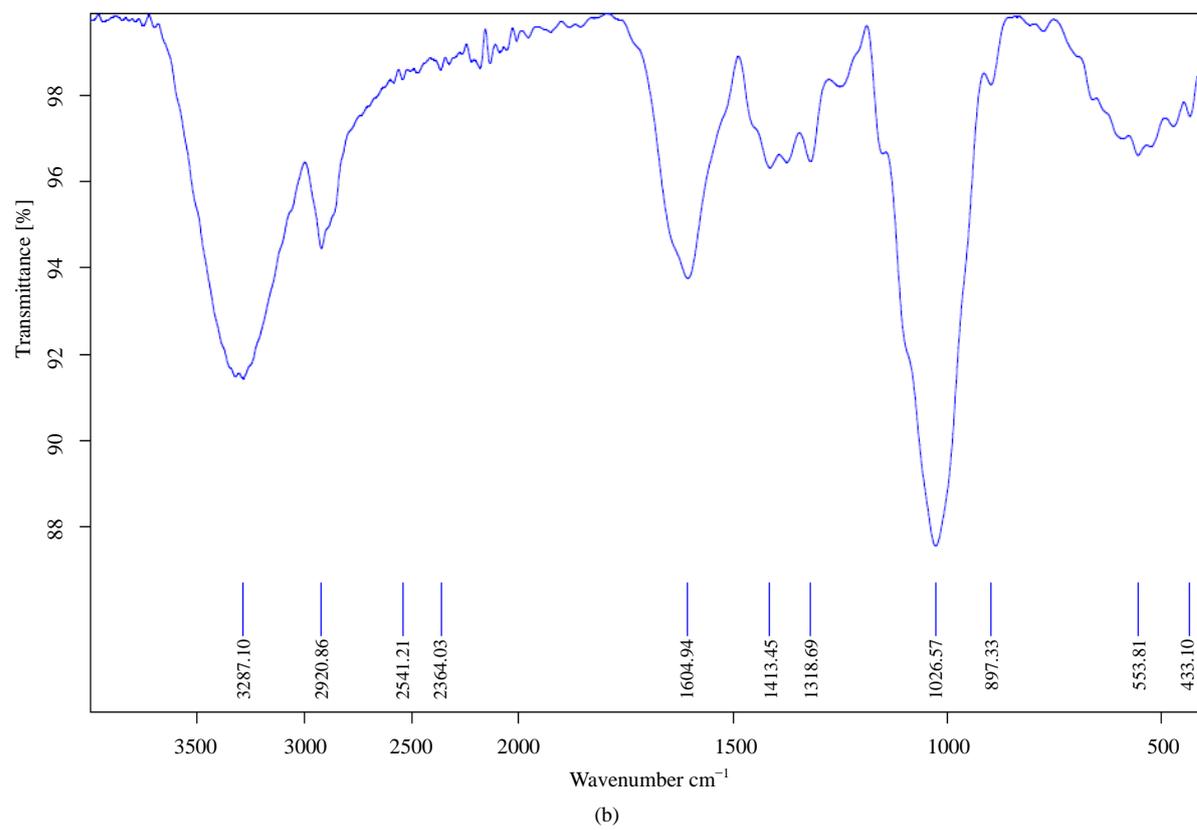


Figure 1. FTIR Spectroscopy for the biosorbents, (a) RBS; (b) BABS; (c) AABS.

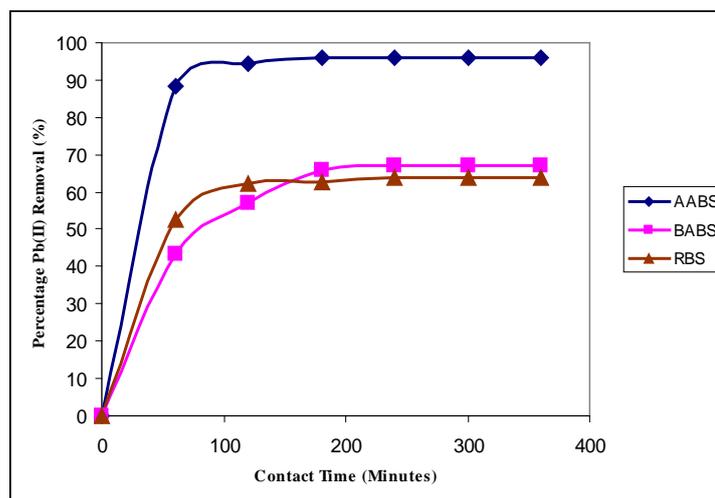


Figure 2. Effect of contact time on the percentage removal of Lead(II).

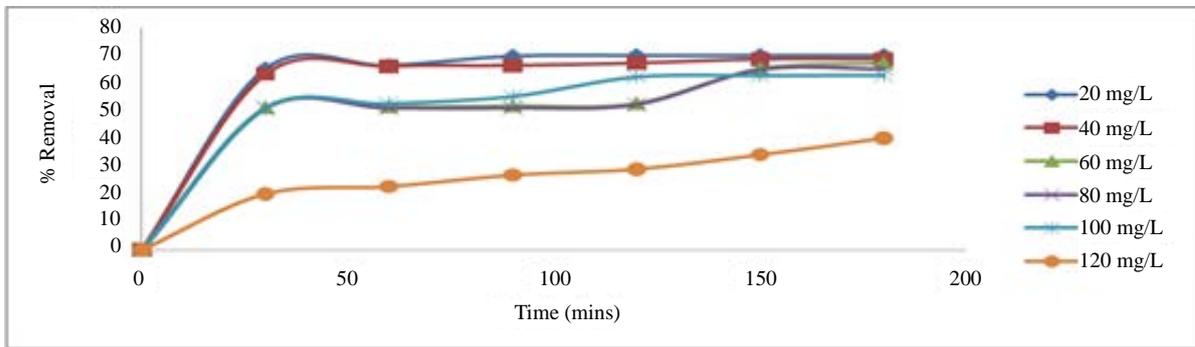
due to increased availability of active binding site on the biosorbent surface and this is controlled by diffusion process from the bulk to the surface. However, during the last stages, biosorption is likely to be attachment-controlled process due to reduction in the available active sites. AABS has 96.00% removal at equilibrium, followed by BABS (66.90%) while RBS had the least percentage removal and adsorptive capacity even beyond 180 minutes of 63.9% and $6.39 \text{ mg} \cdot \text{g}^{-1}$, respectively. **Figure 3** reveals that, at lower concentrations of $20 - 40 \text{ mg} \cdot \text{L}^{-1}$, biosorption was completed at about 60 minutes while at higher concentration, the biosorption process became constant at 180 mins as observed in **Figures 3(a)-3(c)**, respectively. At lower concentrations, all metal ions present in the solution interacted with binding sites and then facilitated about 70.1% on RBS (**Figure 3(a)**) 74.6% on BABS (**Figure 3(b)**) with 93% Pb(II) removal on AABS (**Figure 3(c)**). At higher concentrations between $80 - 120 \text{ mg} \cdot \text{L}^{-1}$, more Pb(II) is left unabsorbed in the solution due to the saturation of binding sites. This may be due to the increase in the number of ions competing for available binding sites on the three Banana Stalks considered in this study. This result is similar to other researcher findings [18] [50].

3.3. Effect of Adsorbent Dose

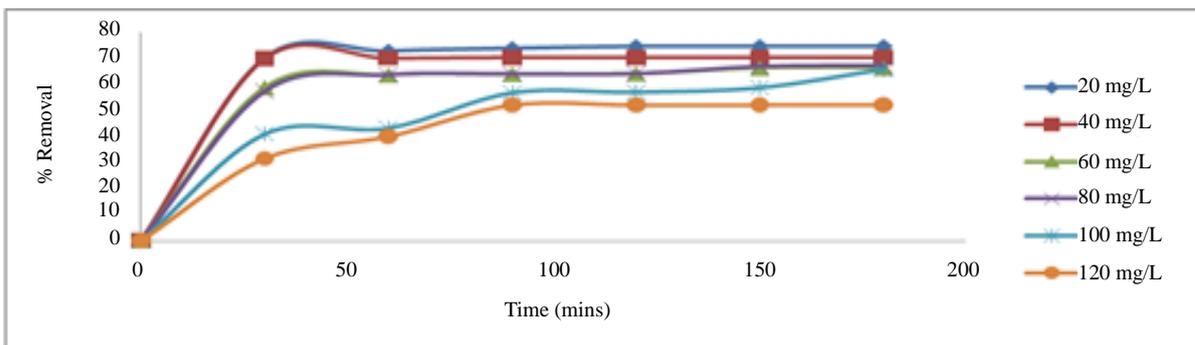
Varying adsorbent dosage of 0.2 to 2.0 g were used to test for the effect of adsorbent dose on the biosorption process keeping the initial lead concentration at $100 \text{ mg} \cdot \text{L}^{-1}$, while all other parameters were kept constant. It was observed as shown on **Figure 4** that, when the adsorbent dose was increased from 0.2 g to 2.0 g, the percentage adsorption generally increased from 30.2% to 97.3%, but the amount adsorbed per unit mass of adsorbent decreased considerably. The increase in the adsorption percentage or decrease in unit adsorption with increased dose of the biosorbent is due to the increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the adsorption sites which is in agreement with previous researcher [33]. When the adsorbent added is beyond 0.6 g, the decrease in lead ion adsorption is not very prominent which is perhaps due to the formation of adsorbent agglomerates reducing available surface area and blocking some of the adsorption sites. Maximum adsorption capacity of lead ions was observed with adsorbent dose of 0.6 g with adsorption capacity of $15.8 \text{ mg} \cdot \text{g}^{-1}$ and thereafter, a slow increase in the percentage removal was seen reaching a constant value with respect to adsorbent dosage.

3.4. Effect of pH

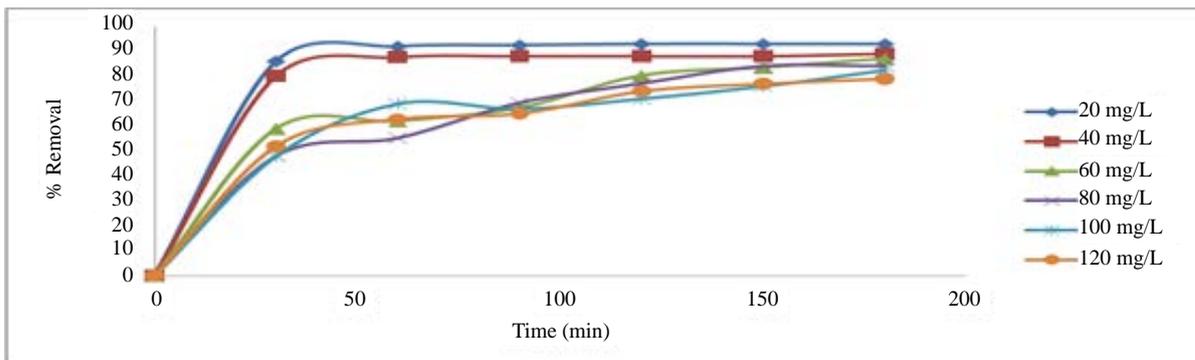
Surface charges on the adsorbent and degree of ionization of the sorbate are affected by the pH of the solution and this makes pH an important factor in adsorptive studies. **Figure 5** reveals that, the adsorptive capacity was best at pH 8 with 89% removal of the lead ion. This is because biosorption is low at strong acidic medium (pH 2 - 4) because the surface charge on the biosorbents is positive, thus, Pb(II) is not favourable attached because of electrostatic repulsion between the RBS, BABS and AABS surfaces and the positively charged Pb(II). At higher pH, uptake increased because more metal binding sites could be exposed and carried negative charges, with



(a)



(b)



(c)

Figure 3. Effect of different initial lead concentration on the percentage removal of Pb(II) on Raw banana stalk biosorbent, (a) RBS; (b) BABS; (c) AABS.

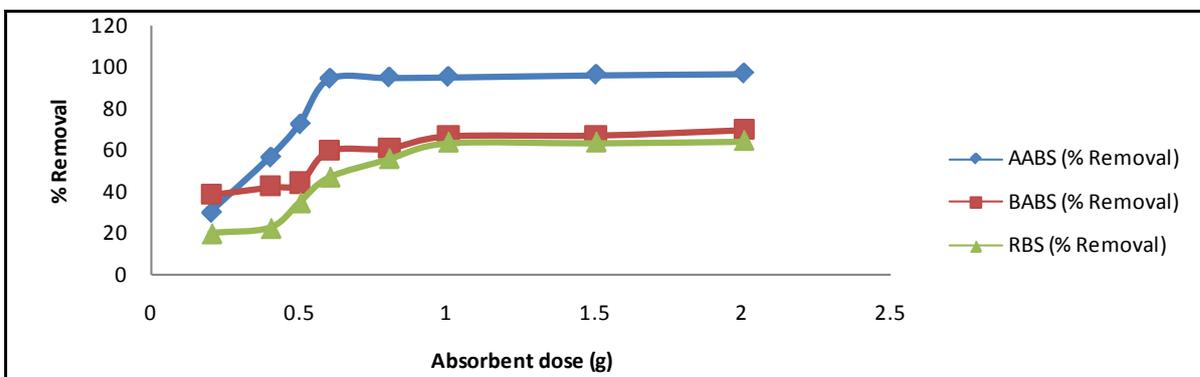


Figure 4. Effect of adsorbent dose on the percentage removal of Pb(II) removal using different biosorbents.

subsequent attraction of the positively charged metal ions with the biosorbent surface and this agreed with Bello *et al.* [40] on the adsorptive features of banana stalk-based activated carbon for malachite green dye removal. Experiments were carried out with the pH values of up to 8 due to the fact that metal precipitation appeared at higher pH values and interfered with the accumulation or biosorbent deterioration which was in agreement with the result obtained by Puranik and Paknikar [51].

3.5. Effect of Temperature

The percentage Pb(II) removal decreased with increased temperature for AABS as shown on **Figure 6** while BABS and RBS followed a reverse trend. AABS highest percentage removal was at 30°C (82.4%) and declined with increasing temperature. The reverse in the trend of result obtained for AABS compared with the other two may be due to the fact that at increased temperature, AABS surface for adsorption has acquire the maximum energy for adsorption while RBS and BABS had not. A similar result, in which adsorptive capacity is inversely proportional to temperature was obtained by Paresch *et al.* [52] using a biosorbent. Lower temperature of 30°C also favoured the Biosorption of Lead(II) and Nickel(II) using Pigeon peas hulls waste by Ramana *et al.* [53].

3.6. Adsorption Kinetics for Biosorption

3.6.1. The Pseudo-First-Order Kinetics Model

The pseudo-first-order kinetics equation is expressed as Equation (4) according to Lagergren [54]

$$\ln(q_e - q_t) = q_e - k_1 t \quad (4)$$

where q_e and q_t are the adsorption capacities at equilibrium (mg/g) and time t , respectively. K_1 is the rate constant for Pseudo-first-order adsorption (min^{-1}). Plots of $\ln(q_e - q_t)$ against t at various temperatures resulted in linear graphs with negative slopes k_1 and q_e values were calculated as intercepts. All the values as well as their correlation coefficient (R^2) are as shown on **Table 3** for biosorbents. Though values of R^2 were high but high SSE and the various disparity between the values of $q_{e\text{ cal}}$ and $q_{e\text{ exp}}$ is an indication that the biosorption of Pb(II) unto AABS, BABS and RBS do not follow the pseudo-first-order kinetics.

3.6.2. The Pseudo-Second-Order Kinetics Model

The pseudo-second-order kinetics equation is expressed as Equation (5) according to Ho and Mckay [55]

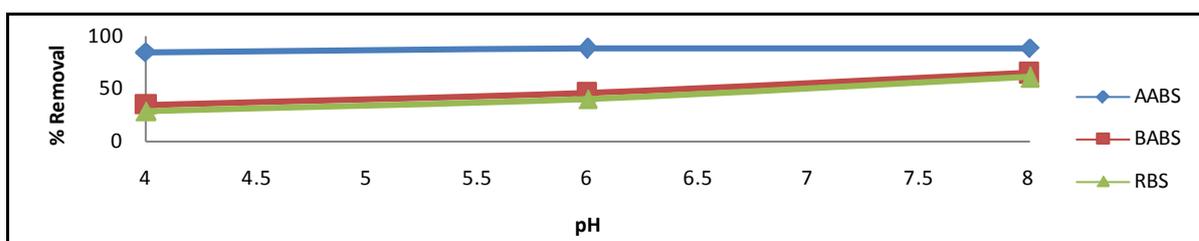


Figure 5. Effect of pH on the percentage removal of Lead(II) using biosorbents.

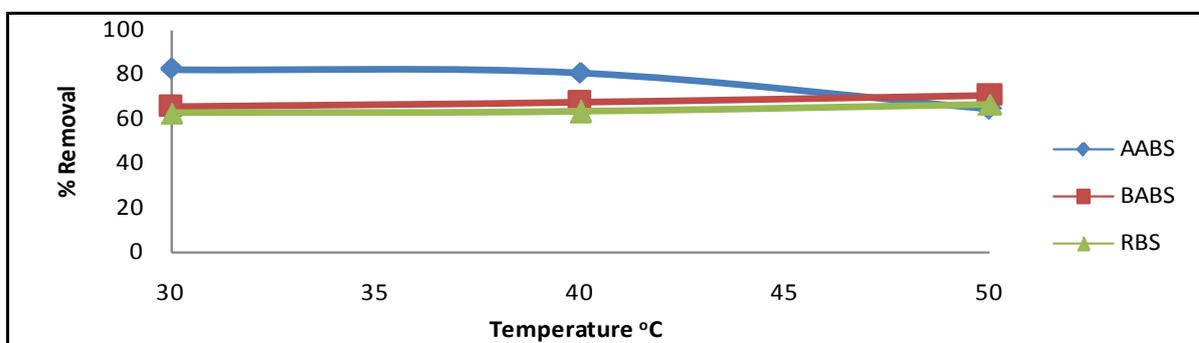


Figure 6. Effect of temperature on the percentage removal of Pb(II) using different banana stalk biosorbents.

Table 3. Pseudo-first-order and pseudo-second-order kinetic parameters and correlation coefficients obtained for the bio-sorption of Pb(II).

Adsorbents	T(°C)	Pseudo-first-order					Pseudo-second-order				
		$q_e(\text{exp})$ (mg·L ⁻¹)	k_1 (min ⁻¹)	$q_e(\text{cal})$ (mg·L ⁻¹)	R^2	SSE	k_2 (g·mg ⁻¹ ·min ⁻¹)	$q_e(\text{cal})$ (mg·L ⁻¹)	R^2	SSE	
AABS	30	9.967	0.0091	7.184	0.969	1.14	0.0013	9.950	0.999	0.01	
	40	9.338	0.0105	11.413	0.855	0.85	0.0011	10.468	0.992	0.46	
	50	9.232	0.0114	2.436	0.684	2.77	0.0010	10.136	0.983	0.36	
BABS	30	3.756	0.0056	8.602	0.864	1.98	0.0489	2.749	1.000	0.41	
	40	8.042	0.0059	6.181	0.884	0.76	0.0261	8.117	0.999	0.03	
	50	8.052	0.0091	8.355	0.932	0.10	0.0067	8.389	0.997	0.10	
RBS	30	8.968	0.0069	8.737	0.887	0.08	0.0012	10.460	0.968	0.60	
	40	9.011	0.0056	7.448	0.862	0.64	0.0066	9.259	0.998	0.10	
	50	2.352	0.0118	1.553	0.841	0.33	0.0010	4.730	0.957	0.96	

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (5)$$

where k_2 is the rate constant of pseudo-second-order adsorption (g·mg⁻¹·min⁻¹). For the boundary conditions $t = 0$ to $t = t$ and $q_e = q_t$ the integrated form of the equation becomes

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (6)$$

Rearranging this equation, we have a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

A plot of t/q versus t was made and q_e and k_2 value was estimated from the slopes and intercepts of the plot. The Sum of Error Square (SSE%) was also used to evaluate the difference between the $q_{e(\text{exp})}$ and $q_{e(\text{cal})}$, giving as

$$\text{SSE} = \frac{\sqrt{\sum (q_{\text{exp}} - q_{\text{cal}})^2}}{N} \quad (8)$$

where, N is the number of experiments.

The R^2 values were as high as 0.99 and the sum of square error was lower when compared to that of pseudo-first-order as there was good agreement between the $q_{e \text{ cal}}$ and $q_{e \text{ exp}}$ of the pseudo-second-order kinetics as shown on **Table 3**. Therefore the biosorption of Pb(II) onto AABS, BABS and RBS follows a pseudo-second-order kinetics.

3.7. Adsorption Isotherms AABS

3.7.1. Langmuir Isotherm Model

Langmuir isotherm is based on the monolayer sorption of Pb(II) on the surface of carbon sites and is represented linearly by the following equation [56]:

$$\frac{C_e}{q_e} = \frac{1}{q_o K_L} + \frac{C_e}{q_o} \quad (10)$$

where C_e (mg/L) and q_e (mg/g) are the concentration of Pb(II) solution (mg/L) and the amount of adsorbed lead at equilibrium, respectively, q_{\max} or q_o and K_L are Langmuir constants related to sorption capacity (mg/g) and the energy of sorption (L/mg) respectively.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter R_L which confirms the favourability of the adsorption process. Given as,

$$R_L = \frac{1}{1 + bC_o} \quad (11)$$

where b is the Langmuir constant and C_o is the highest Pb(II) concentration (mg/L).

The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($0 < R_L < 1$). The values of R_L reported in **Table 4** obtained at various temperatures were < 1 , indicating that the adsorption of Pb(II) onto AABS is favourable. The value of q_o obtained was compared with those of other adsorbents used for Pb(II) removal from aqueous solution and the present study gave the best as shown on **Table 5**.

3.7.2. Freundlich Isotherm Model

Freundlich isotherm describes the heterogeneous surface energies by multilayer sorption and is expressed by the following equation [57]:

$$q_e = K_F C_e^{1/n} \quad (12)$$

Table 4. Comparison of the Isotherms for the adsorption of lead onto AABS at different temperatures.

Models	Temperature (K)		
	303	318	333
Langmuir isotherm			
Q_o (mg·g ⁻¹)	13.53	16.50	18.12
K_L (L·mg ⁻¹)	0.083	0.49	1.08
R^2	0.98	0.99	0.99
R_L	0.099	0.095	0.090
Freundlich isotherm			
K_f	1.49	1.04	0.62
N	1.69	1.44	1.66
R^2	0.99	0.99	0.90
Temkin isotherm			
B	2.74	3.16	2.04
A	1.04	0.63	0.40
B	0.92	0.82	1.32
R^2	0.96	0.97	0.86
D-R isotherm			
Q_o (mg·g ⁻¹)	6.85	42.20	5.16
β (mol ² ·J ⁻²) × 10 ⁻⁶	0.80	0.24	6.01
R^2	0.79	0.91	0.83
E (kJ·mol ⁻¹)	0.79	1.58	0.28

Table 5. Comparison of adsorption capacities of various adsorbents for Pb(II).

Adsorbent	Adsorptive capacity (Q_e in $\text{mg}\cdot\text{g}^{-1}$)	Reference
Saracaindica leaf powder	1.19	Goyal et al. [60]
Bentolite	7.56	Mishra and Patel [61]
Activated carbon	6.68	Mishra and Patel [61]
Fly ash	4.98	Mishra and Patel [61]
Kaolin	4.50	Mishra and Patel [61]
Banana stalk	13.53	This study

Linearised as,

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (13)$$

where K_F and n are the Freundlich constants incorporating the factors affecting the adsorption capacity and the degree of non-linearity between the solute concentration in the solution and the amount adsorbed at equilibrium respectively. Plots of $\log q_e$ versus $\log C_e$ gave linear graphs with high to R^2 . Comparing the R^2 values of the two isotherms (Table 4), the adsorption fits the Langmuir model better. Value of $n > 1$ indicates that the adsorption is favourable.

3.7.3. Temkin Isotherm Model

Temkin isotherm based on the ions sorption heat, which is due to the sorbate and adsorbent interactions, is given by Temkin and Pyzhev [58]

$$q_e = B \ln A + B \ln C_e \quad (14)$$

where:

$$B = \frac{RT}{b} \quad (15)$$

where C_e is the concentration of sorbate at equilibrium ($\text{mg}\cdot\text{L}^{-1}$), q_e is the quantity of sorbate bioadsorbed at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), A is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy and constant B is related to the heat of sorption. T is the temperature (K), and R is the ideal gas constant ($8.314 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). The values of A , B and b are given in Table 4, the lower value of b being $1.32 \text{ kJ}\cdot\text{mol}^{-1}$ ($< 8 \text{ kJ}\cdot\text{mol}^{-1}$) indicates that the interaction between lead ions and AABS can be expressed as a physisorption process.

3.7.4. Dubinin-Radushkevich Isotherm (D-R) Model

The Dubinin-Radushkevich (D-R) model was used to estimate the characteristic porosity of the AABS and the apparent energy of adsorption. The non-linear form of the D-R isotherm equation is given in Equation (16) according to Dubinin-Radushkevich [59]:

$$q_e = q_o e^{-\beta \varepsilon^2} \quad (16)$$

The equation is linearised by taking the logarithm on both sides of equation and is expressed as,

$$\ln q_e = \ln q_o - \beta \varepsilon^2 \quad (17)$$

where q_e is the heavy metal amount that is adsorbed per unit mass of AABS in $\text{mg}\cdot\text{g}^{-1}$; q_o is the maximum adsorption capacity in $\text{mg}\cdot\text{g}^{-1}$; β is the free energy of sorption per mole of the sorbate as it migrates to the surface of AABS from an infinite distance in the solution in $\text{mol}^2\cdot\text{kJ}^{-2}$, and ε is the Polanyi potential. The Polanyi potential (ε) can be given as:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (18)$$

where R is the gas constant in $\text{kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and T is the absolute temperature in K . A plot of $\ln q_e$ versus ε^2 gave a linear plot (not shown) from which β and q_o are obtained from the slopes and the intercepts respectively (Table 4). Similarly, the β value obtained was then used to estimate the mean free energy of adsorption E which is calculated by,

$$E = \sqrt{\frac{1}{2\beta}} \quad (19)$$

The values of E were found to be in the range $0.29 - 1.58 \text{ kJ}\cdot\text{mol}^{-1}$ over the range of temperatures used in this study. Because $E < 8 \text{ kJ}\cdot\text{mol}^{-1}$, it suggests that the biosorption of lead ion onto AABS is physically controlled.

3.8. Thermodynamics Studies for AABS

Thermodynamic parameters; standard free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were calculated using the following equation:

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H^0}{RT} \quad (20)$$

$$\Delta G^0 = -RT \ln K_L \quad (21)$$

where K_L is the Langmuir constant (L/mol), T is the temperature in K and R is the gas constant ($\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). A plot of $\ln K_L$ against $1/T$ gave linear plot from which ΔH^0 and ΔS^0 values were obtained from the slope and intercept respectively. From the pseudo-second-order rate constant, k_2 (Table 3), the activation energy E_a for the adsorption of Pb(II) onto AABS could be determined using equation

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (22)$$

where k_2 is the biosorption rate constant, A is the Arrhenius constant, E_a is the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$). By plotting $\ln k_2$ versus $1/T$, E_a can be obtained from the slope of the linear plot and is presented in Table 6. The negative free energy values at various temperature as shown on Table 6 indicates that the adsorption of Pb(II) onto AABS is spontaneous and thermodynamically favoured. In addition, the range of values between 0 to $-20 \text{ kJ}\cdot\text{mol}^{-1}$ further confirms that the adsorption process is a physisorption process. The positive value of ΔH^0 obtained shows that the process is endothermic in nature and its range of values ($2.1 - 20.9 \text{ kJ}\cdot\text{mol}^{-1}$) implies that the process is physically controlled. The values of ΔS^0 is positive indicating that there was randomness at the solid-liquid interface during the adsorption of the Pb(II) onto AABS.

4. Conclusion

The biosorption experiment carried out using banana stalk (*Musa paradisiaca*) was found suitable for the adsorption of Pb(II). Considering the three modified banana stalk (AABS, BABS and RBS) used in this study, AABS was established to be the best adsorbent of Pb(II) with 96.76% metal removal. The operational parameter (Adsorbent dose, temperature, initial metal ion concentration, time and pH) had varied effects on the percentage Pb(II) removal. It was found out that Pseudo-second order kinetic model was suitable for the adsorption of

Table 6. Thermodynamic parameters for the biosorption of Pb(II) by AABS.

T ($^{\circ}\text{C}$)	ΔG^0 ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔH^0 ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS^0 ($\text{kJ}\cdot\text{mol}^{-1}$)	E_a ($\text{kJ}\cdot\text{mol}^{-1}$)
30	-18.75	12.63	0.049	4.365
40	-24.02			
50	-26.00			

Pb(II). Four adsorption Isotherms (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) were tested and confirmed suitable to describe the nature of the adsorption process of Pb(II) removal from aqueous solution, but Langmuir Isotherm was the best. The thermodynamics studies showed that ΔG^0 values were negative indicating that the process of Pb(II) adsorption onto AABS was spontaneous and the positive ΔH^0 and ΔS^0 suggests that the biosorption process is an endothermic reaction.

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