Technical Paper

Equilibrium Sorption Study of Al^{3+}, Co^{2+} and Ag^{+} in Aqueous Solutions by Fluted Pumpkin (*Telfairia Occidentalis* HOOK f) Waste Biomass

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Abstract

An ensemble of equilibrium sorption techniques was combined to study the influence of ionic radius on the sorption characteristics of Al^{3+}, Co^{2+} and Ag^{+} by fluted pumpkin waste biomass. The experimental results were analyzed in terms of five two-parameter adsorption isotherm equations - the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Flory-Huggins isotherms. According to the evaluation using Langmuir equation, the monolayer sorption capacity obtained was 16.98 mg/g, 10.34 mg/g and 8.03 mg/g for Al^{3+}, Co^{2+} and Ag^{+} respectively. The data further showed that, the Freundlich and Langmuir isotherms described the data appropriable than Temkin, Dubinin-Radushkevich and Flory-Huggins isotherms. The result showed that fluted pumpkin waste could be used for the removal of Al^{3+}, Co^{2+} and Ag^{+} from wastewater and ionic radius influences the rate of metal ion migration to the biomass surface and the adsorption intensity of the metal.

Key words: equilibrium sorption, Flory-Huggins isotherm, fluted pumpkin, wastewater treatment, process biotechnology

Introduction

Fluted Pumpkin (*Telfairia occidentalis*) is a creeping vegetative shrub that spread low across the ground with large lobed leaves, and long twisting tendrils. The genus *Telfairia* (Cucurbitaceae) comprises two species, *T. pedata* and *T. occidentalis*. *T. pedata* is grown in East Africa for its oil and protein-rich seeds while *T. occidentalis* is grown in some parts of West Africa for its nutritious leaves and seeds.[1] After harvesting, the leaves are carefully removed from the stem, which are discarded as waste. A single stem with leaves weighing 1.2 kg produces less than 200 g of leaves leaving over 1 kg stem as wastes. Fluted pumpkin is the largest consumed vegetable in the West African sub-region and therefore creates one of the major agrowaste problems in Nigeria. Preliminary investigations showed that several tons of these wastes are produced daily in market places around the country but are scarcely useful and therefore create environmental nuisance. For this reason, they would be tested as adsorbents for toxic and valuable metals from industrial wastewater.

Due to the bioaccumulating tendency and toxicity of heavy metals in the environment, it has been consistently desired that their levels be considerably reduced in industrial and municipal effluents to meet regulatory standards before final repository in the ecosystem. Techniques presently in existence for removal of heavy metals from wastewater are relatively expensive and non-environment friendly. It is therefore necessary to search for agricultural by-product that is relatively abundant in our environment and transform such material to an adsorbent. Agrowastes are currently receiving attention as raw materials for water pollution control because of their low cost and availability. A range of products has been examined clay,[2] sago waste,[3] cassava waste,[4] banana pith,[5] peanut skin,[6] *Medicago sativa* (Alfalfa)[7] and sphagnum moss peat[8] just to mention a few. These workers have used mostly divalent metal ions. A literature search reveals that no work has been reported on the use of waste from fluted pumpkin (*Telfairia occidentalis* Hook f) as adsorbent for metal removal from aqueous systems. Thus, the purpose of our project is to test the influence of ionic charge on the removal of metal ions from aqueous systems by using metal ions of different charges. An additional goal is to establish the ability of five two-parameter equations - (the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Flory-Huggins isotherms) to model the equilibrium sorption data.

To achieve these goals a batch sorption technique over a wide range of initial metal ion concentrations on the ability of fluted pumpkin waste for the removal of Al^{3+}, Co^{2+} and Ag^{+} from aqueous systems were tested. This information will undoubtedly contribute to the sorption data bank.

Results and discussion

The percent removal of the metal ions from aqueous solution was found to decrease with increase in initial metal ion concentration (Figure 1). This may be due to the fact that at lower concentrations almost all the ions were adsorbed very quickly and further increases in initial metal ion concentrations led to saturation of biomass surface.

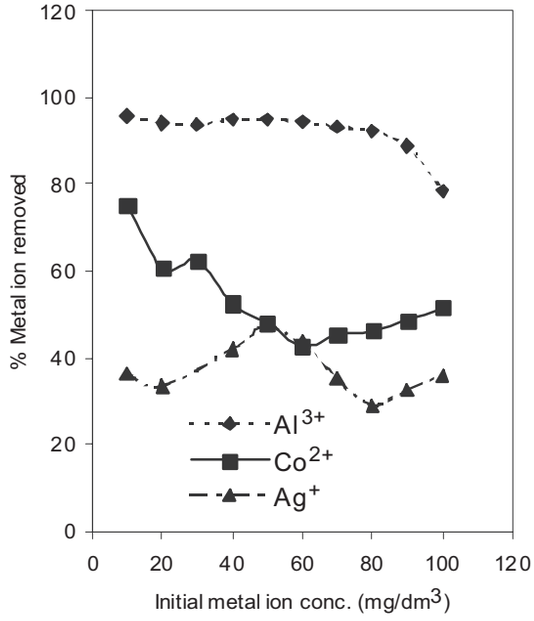

Figure 1. Effect of initial metal ion concentration in the sorption of the three metal ions onto fluted pumpkin waste biomass.

The analysis of experimental results by equilibrium sorption isotherms are important in developing accurate data that could be used for sorption design purposes. The sorption equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of the sorbent.

Langmuir Isotherm

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. The plots of specific sorption (C_e/q_e) against the equilibrium concentration (C_e) for Al^{3+}, Co^{2+} and Ag^+ are shown in Figure 2 and the linear isotherm parameters, q_m, K_L and the coefficient of determinations are presented in Table 1. The sorption capacity, q_m, which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage showed that the fluted pumpkin waste had a mass capacity for Al^{3+} (16.98 mg g^{-1}) than Co^{2+} (10.34 mg g^{-1}) and Ag^+ (8.03 mg g^{-1}). The adsorption coefficient, K_L that is related to the apparent energy of sorption for Ag^+ (6.39×10^{-1}) was greater than that of Co^{2+} (1.86×10^{-1} dm^3g^{-1}) and Al^{3+} (2.22×10^{-2} dm^3g^{-1}). This observation showed that the energy of adsorption is not very favourable to Ag^+ probably due to its large ionic radius; hence not all binding sites may be available to Ag^+. The same capacity order have been reported[9,10] for different metal ion sorption on modified coconut noir and cassava wastes biomass.

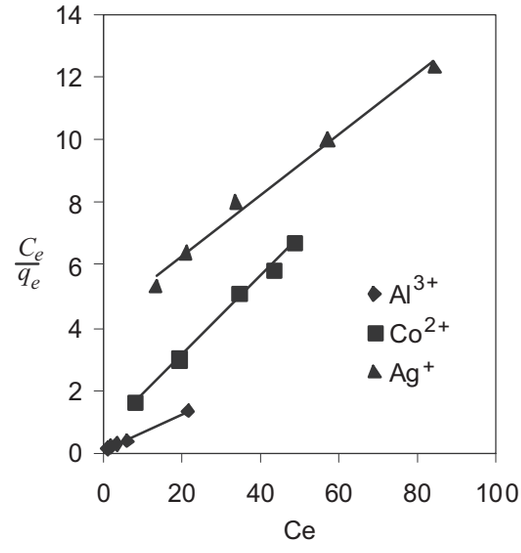

Figure 2. Langmuir equilibrium isoterm model for the sorption of the three metal ions onto fluted pumpkin waste biomass.

The data in Table 1 further indicated that, the effectiveness of fluted pumpkin waste in the sorption of the three metals from aqueous system was $Al^{3+}>Co^{2+}>Ag^+$. This preferential sorption behaviour could be explained in terms of ionic radii of the metal ions (Al^{3+} = 0.52 Å; Co^{2+} = 0.78 Å; Ag^+ = 1.26 Å). The element with smaller ionic radius will compete faster for exchange sites than those of larger ionic radius. The larger the charge of an ion, the smaller, the ionic radius, hence the charge of an ion may influence its ability to sorb on biosorbents. Hydration energy is an important factor in sorption process accounting for the hydrolysis of metal ions, which occurs by the replacement of water liquids in the inner coordination sphere with hydroxo groups. Adsorption may be related to the loss of the entire hydration sphere that precedes hydrolysis. The observed order indicates that Al^{3+} may have greater accessibility to the surface of certain pores than Co^{2+} and Ag^+ due to its small ionic radius.

Furthermore favourability of adsorption of the three metal ions on the fluted pumpkin waste biomass was tested using the essential features of the Langmuir isotherm model, expressed in terms of a dimensionless constant called separation fac-

tor S_F, which is defined by the following relationship.

$$S_F = \frac{1}{1 + K_L C_o} \qquad (1)$$

Where K_L = Langmuir isotherm constant; C_o = initial metal ion concentration.

The separation parameters for the three metals are less than unity indicating that fluted pumpkin waste biomass is an excellent adsorbent for the three metal ions. However, S_F value of $Ag^+ >> Al^{3+}$ and Co^{2+}, indicating that in a mixed metal ion system, Al^{3+} and Co^{2+} will compete for binding sites faster than Ag^+. This observed separation factor indicates that high concentration of Al^{3+}, Co^{2+} and Ag^+ in an effluent may not be a limiting factor in the ability of fluted pumpkin waste to sorb these metal ions.

Table 1. Linear Langmuir isotherm parameters.

Metal ions	q_m mg g^{-1}	K_L dm^3g^{-1}	S_F
Al^{3+}	16.98	2.22×10^{-2}	0.009
Co^{2+}	10.34	1.86×10^{-1}	0.10
Ag^+	8.03	6.39×10^{-1}	0.03

The Langmuir capacities can also be used to compare the efficiency of fluted pumpkin waste biomass with other materials which have been tested as biosorbents for metal ions. Table 2 makes such a comparison and, although several of the metals studied based on a survey of adsorption shows that there is very little or no information in the literature based on Al^{3+}, Co^{2+} and Ag^+ removal by sorption. According to Marulanda and Harcum,[11] *C. caldarium* an algal biomaterial had a capacity of 1.40 mg g^{-1} for Al^{3+}. This value is significantly lower than the capacity of fluted pumpkin waste biomass (16.98 mg g^{-1}) towards Al^{3+}. For Co^{2+}, the effect is not as marked when compared with agro-waste of soybean but much better than cottonseed hulls. While it seems that Ag^+ sorption study is very little. *Medicago sativa* (Alfalfa)[7] has a limited capacity for Al^{3+}, sphagnum moss peat,[8] has been utilized for Co^{2+} and Ag^+. The fluted pumpkin waste has greater capacity than many of the materials tested previously.

Table 2. Comparative Langmuir maximum sorption capacities of Al^{3+}, Co^{2+} and Ag^+.

Metals	Sorbent	X_m (mg g^{-1})	Reference
Ag^{3+}	Fluted pumpkin waste	16.94	This study
	Cyanidium caldarium	1.40	11
	Medicago sativa (Alfalfa)	3.45	7
Co^{2+}	Fluted pumpkin waste	10.34	This study
	Soybean by-product	15.39	12
	Cottonseed hulls	1.77	12
	sphagnum moss peat	8.29	8
Ag^+	Fluted pumpkin waste	8.03	This study
	sphagnum moss peat	7.24	8

Freundlich Isotherm

The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface. The experimental data from the batch sorption study of the three metal ions on fluted pumpkin waste biomass were plotted logarithmically (Figure 3) using the linear Freundlich isotherm equation.

The linear Freundlich isotherm constants for Al^{3+}, Co^{2+} and Ag^+ on fluted pumpkin waste biomass are presented in Table 3. The Freundlich isotherm parameter 1/n measures the adsorption intensity of metal ions on the biomass. Examination of Table 2 showed that the values of 1/n were found to be greater than unity indicating that the isotherms can be characterized by a convex Freundlich isotherm. This implies that significant adsorption may take place even at high metal ion concentration. The high 1/n value of Al^{3+} (1.64) in relation to Co^{2+} (1.01) and Ag^+ (1.04), first indicate the preferential sorption of Al^{3+} than Co^{2+} and Ag^+ probably due to its smaller ionic radius and secondly shows the ability of the fluted pumpkin biomass to remove these three metal ions from solution even at high concentrations.

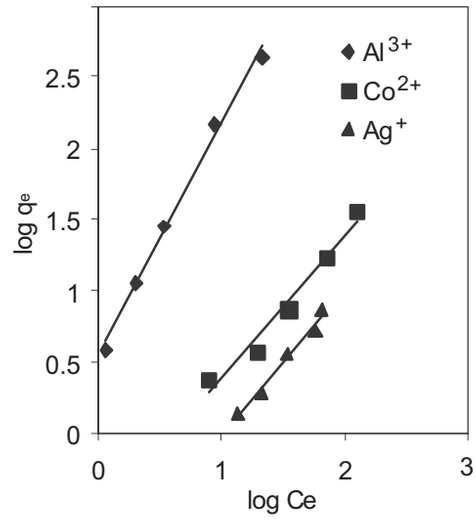

Figure 3. Freundlich equilibrium isoterms model for the sorption of the three metal ions onto fluted pumpkin waste biomass.

The observed differential sorption behaviour is useful in that high Al^{3+} concentrations in an effluent may not limit the ability of fluted pumpkin waste to sorb other metals. The ultimate adsorption capacity K_F, of the adsorbent was calculated from the isothermal linear regression equation. The K_F value of Al^{3+} (4.27) is greater than that of Co^{2+} (3.43) and Ag^+ (1.06), suggesting and confirming that Al^{3+} has greater adsorption tendency towards the fluted pumpkin waste biomass than the other two metals. Again, the ionic radius of the metal ions may be responsible for this observation. Previous studies[8,13,14] have shown that

the smaller the ionic radius, the greater the affinity of cationic species towards binding sites on biomaterials.

Table 3. Freundlich isotherm parameters.

Metal ions	1/n	K_F
Al^{3+}	1.64	4.27
Co^{2+}	1.01	3.43
Ag^{+}	1.04	1.06

Temkin Isotherm

The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. The Temkin isotherm plot for the three metal ions are presented in Figure 4 and the isotherm parameters is given in Table 4.

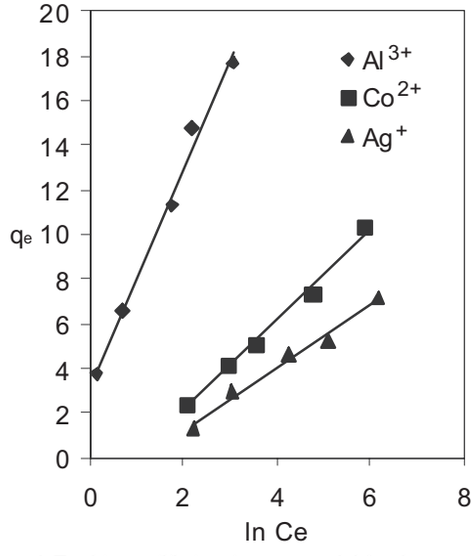

Figure 4. Temkin equilibrium isoterm model for the sorption of the three metal ions onto fluted pumpkin waste biomass.

The Temkin adsorption potential, K_T, of fluted pumpkin waste biomass for Al^{3+}, Co^{2+} and Ag^{+} are 1.90, 1.74 and 1.47 respectively, indicating a lower biomass-metal ion potential for Ag^{+} probably due to its large ionic radius. The Temkin constant, b_T, related to heat of sorption for the three metal ions were 8.96 kJ mol^{-1}, 5.16 kJ mol^{-1} and 5.10 kJ mol^{-1} for Al^{3+}, Co^{2+} and Ag^{+} respectively. It has been reported (Ho et al. 1995) that the typical range of bonding energy for ion-exchange mechanism is 8–16 kJ mol^{-1}. The low values in this study indicates a weak interaction between sorbate and sorbent, supporting an ion-exchange mechanism for the present study.

Table 4. Temkin isotherm parameters.

Metal ions	K_T	b_T kJ mol^{-1}
Al^{3+}	1.90	8.96
Co^{2+}	1.76	5.16
Ag^{+}	1.47	5.10

Dubinin – Radushkevich isotherm

The Dubinin – Radushkevich model was chosen to estimate the characteristic porosity and the apparent free energy of adsorption. The linear regression of the Dubinin-Radushkevich isotherm plot for the sorption of the three metal ions on fluted pumpkin waste biomass are presented in Figure 5, and the isotherm parameters are shown in Table 5.

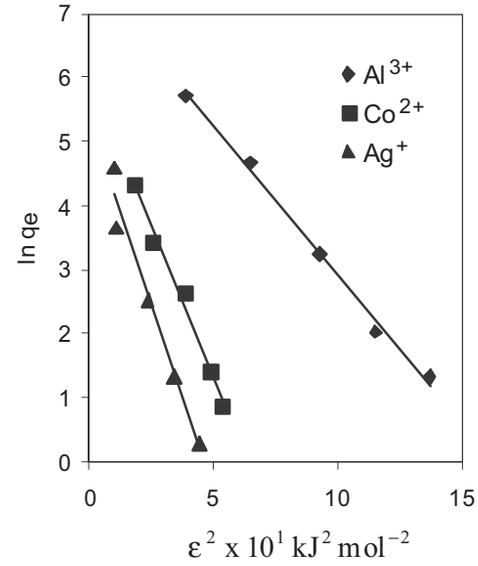

Figure 5. Dubinin-Radushkevich equilibrium isoterm model for the sorption of the three metal ions onto fluted pumpkin waste biomass.

The sorption affinity of the biomass for Al^{3+}, Co^{2+} and Ag^{+} are 7.55 mg g^{-1}, 6.02 mg g^{-1} and 5.32 mg g^{-1} respectively, indicating that the biomass had a greater affinity for Al^{3+}. The porosity factors, K_{DR} for the biomass towards the metal ions were 0.46 (Al^{3+}), 0.95 (Co^{2+}) and 1.54 (Ag^{+}). The porosity factors were found to be less than unity, except that of Ag^{+}, indicating that sorption of Ag^{+} by fluted pumpkin waste biomass may not be significant in a mixed metal ion system such as an industrial effluent probably due to its large size. This implies that the use of fluted pumpkin waste biomass for the removal of Ag^{+} in wastewater may require several numbers of cycles to reduce the concentration of this metal ion to below regulatory levels. The apparent free energies from the Dubinin – Radushkevich model for the sorption process are –0.96 kJ mol^{-1} (Al^{3+}), –1.38 kJ mol^{-1} (Co^{2+}) and –1.52 kJ mol^{-1} (Ag^{+}) respectively. Physisorption processes have adsorption energies less than –40 kJ mol^{-1} and the energy values for the three metal ions sorption on the fluted pumpkin waste biomass indicates that the sorption process is physisorption. The negative values of E_s indicate

that the sorption process is exothermic and that lower solution temperature will favour the sorption process.

Table 5. Dubinin-Radushkevich isotherm parameters.

Metal ions	X_m	K_{DR}	E_s
Al^{3+}	7.95	0.46	–0.96
Co^{2+}	6.02	0.95	–1.38
Ag^{+}	5.32	1.15	–1.52

Flory-Huggins Isotherm

The Flory-Huggins model was chosen in order to account for the degree of surface coverage characteristics of the adsorbate on the adsorbent. The plot of $\log(\theta/C_0)$ versus $\log(1–\theta)$ for the three metal ions was made (Figure 6) and regression lines obtained. The isotherm data (Table 6) showed that, the apparent number, n, of metal ions occupying sorption sites is greater for Al^{3+} (0.671) than that of Co^{2+} (0.571) and Ag^{+} (0.528). The overall coverage processes indicate that over 50% of binding sites on the biomass surface were covered by metal ions during sorption process. The equilibrium constants, K_{FH}, as obtained by the Flory-Huggins isotherm showed that K_{FH} for Al^{3+}, Co^{2+} and Ag^{+} are 1.25, 2.13 and 1.38 respectively.

Furthermore, the equilibrium constants, K_{FH}, obtained from the Flory-Huggins isotherm model were used to compute the Gibbs free energy of spontaneity. The Gibbs free energy of spontaneity is related to equilibrium constant as follows

$$\Delta G^\circ = -RT\ln K_{FH} \qquad (2)$$

where R is universal gas constant 8.324 J/mol, T is absolute temperature (K) and K_{FH} is equilibrium constant from Flory-Huggins isotherm equation.

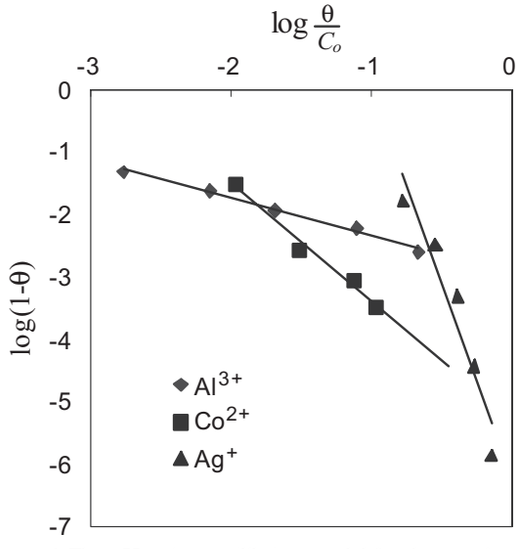

Figure 6. Flory-Huggins equilibrium model for the sorption of the three metal onto fluted pumpkin waste.

The negative values of ΔG° (Table 6) indicate that the sorption process is spontaneous in nature and supports an exothermic reaction. The low energy values obtained using the Flory-Huggins model supports the values from the Dubinin-Raduskevich model.

Table 6. Dubinin-Radushkevich isotherm parameters.

Metal ions	n	K_{FH}	ΔG^o
Al^{3+}	0.67	2.13	–0.56
Co^{2+}	0.57	1.38	–1.91
Ag^{+}	0.53	1.25	–0.81

Coefficients of determination

The regression coefficients of determination, r^2, from the linearization of the five two-parameter isotherm models are listed in Table 7. The r^2 values suggest that the Langmuir and Dubinin-Radushkevich isotherms provide a good model for the sorption of Al^{3+} than Co^{2+} and Ag^{+}. While the Freundlich, Temkin and Flory-Huggins isotherms produce a reasonable fit to the experimental data for Co^{2+} than Al^{3+} and Ag^{+}. Due to the bias resulting from linearization, the internal structure not accessible at first glance of the r^2 values in Table 7 were determined by two-way analysis of variance (ANOVA) without replication ($P<0.5$). This method provides explanation to the relationships (1) between the five two-parameter isotherm models in describing the sorption system and (2) between the three metal ions for binding sites on the fluted pumpkin waste biomass. The summary of the statistical analysis is presented in Table 8a and b. Consideration of the comparative magnitudes of the r^2 values (Table 8a) suggest that the Langmuir isotherm model does provide a better model for the sorption systems and that Co^{2+} experimental data exhibits a better fitting to the five isotherm models. However, the two-way ANOVA results (Table 8b) indicate no significant difference between the five two-parameter isotherm models in describing the sorption process of the three metal ions on fluted pumpkin waste biomass. This indicates that the five two-parameter isotherm models are appropriate in their own merits in describing the potential of fluted pumpkin waste biomass for the removal of Al^{3+}, Co^{2+} and Ag^{+} from aqueous solution. The ANOVA data further showed that metal ion sorption on the biomass may not be too restricted to differences in their ionic radius. Other physical parameters such as hydration energy, ionic mobility, electronegativity and so on may also be a contributing factor. These observations are further confirmed by the overall minimal error (4.44×10^{-4}) from the source of variation from all the r^2 sets for the isotherms.

Table 7. Linear isotherm coefficients of determination (r^2).

Linear isotherm	Metal ions		
	Al^{3+}	Co^{2+}	Ag^{+}
Langmuir	0.9967	0.9903	0.9961
Freundlich	0.9930	0.9970	0.9830
Temkin	0.9898	0.9925	0.9857
Dubini-Radushkevich	0.9949	0.9899	0.9736
Flory-Huggins	0.9712	0.9907	0.9835

Table 8. Two-way analysis of variance (ANOVA) without replication at $\propto = 0.05$.

A. Summary

	Count	Sum	Average	Variance
Langmuir	3	2.9831	0.9944	1.25×10^{-5}
Freundlich	3	2.973	0.9910	5.20×10^{-5}
Temkin	3	2.968	0.9893	1.17×10^{-5}
D - R	3	2.9584	0.9861	1.24×10^{-4}
F - H	3	2.9454	0.982	9.72×10^{-5}
Al^{3+}	5	4.9456	0.989	1.07×10^{-7}
Co^{2+}	5	4.9604	0.992	8.55×10^{-6}
Ag^{+}	5	4.9219	0.984	6.45×10^{-5}

B. ANOVA

Source of variation	Sums of square	Degrees of freedom	Mean sums of square	Calculated F ratio value	Statistical F ratio value
Isotherms	2.76×10^{-4}	4	6.89×10^{-5}	1.24	3.83
Metals	1.51×10^{-4}	2	7.54×10^{-5}	1.36	4.46
Error	4.44×10^{-4}	8	5.55×10^{-5}		
Total	8.7×10^{-4}	14			

Conclusions

A detailed isotherm analysis of experimental data was carried out to determine the best isotherm models for the sets of equilibrium data for three metal ions: Al^{3+}, Co^{2+} and Ag^{+} on fluted pumpkin waste. It was noted that ionic radius has an influence in the magnitude of metal loading on the adsorbent. The experimental results were analyzed using five two-parameter adsorption isotherm models - the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Flory-Huggins isotherms. Evaluating the correlation coefficients from the five isotherm equations using two-way ANOVA at $p<0.05$ for fitting the analytical data showed that the Freundlich and Langmuir isotherms described the data appropriable than Temkin, Dubinin-Radushkevich and Flory-Huggins isotherms. Sorption capacity increases with increase in smaller ionic radius metal ion. The result showed that fluted pumpkin waste could be used for the removal of Al^{3+}, Co^{2+} and Ag^{+} from wastewater. The fluted pumpkin waste is abundantly available but is scarcely useful. A single stem with leaves weighing 1.2 kg produces over 1 kg stem as wastes, which in-turn produced over 320 g of biomass. For this reason, they could be regarded as ecomical adsorbents for toxic and valuable metals from industrial wastewater.

Experimental

Adsorbent. The experiments were conducted with fluted pumpkin waste (*T. occidentalis*) biomass sourced from Nigeria. The waste was washed and then dried at a temperature of 55±5 °C to constant weight and finally screened to particle size of 100-μm before use.

Adsorbent Characterization. The surface characteristics of the fluted pumpkin waste biomass has earlier been characterized for surface area, particle density, pore volume, porosity and surface charge density[10] and found to exhibit characteristics which are favourable for the sorption of divalent metal ions. In order to find out the inherent metal ions of natural origin, metal concentrations in the fluted pumpkin waste biomass was determined by digesting 1.0 mg sample by heating in nitric acid and filtering. The metal ion concentrations were determined by flame atomic absorption spectrometry (FASS). The results are given in Table 9.

Table 9. Mean metal concentrations ($\mu g\ g^{-1}$) in fluted pumpkin waste biomass (results are given as mean of triplicate analyses).

Metal	Conc. ($\mu g\ g^{-1}$)	Metal	($\mu g\ g^{-1}$)
Iron	743.12 ± 1.8	Potassium	<1.0
Aluminium	197.82 ± 1.21	Copper	<1.0
Lead	24.69 ± 0.91	Chromium	<1.0
Cadmium	1.28 ± 0.04	Manganese	26.76 ± 0.01
Nickel	0.89 ± 0.02	Magnesium	107.12 ± 0.97
Zinc	35.33 ± 0.11	Mercury	<1.0
Cobalt	0.87 ± 0.041	Silver	<1.0

Activation and Purification of the biomass. Since the native fluted pumpkin waste contain some metals (Table 9), it is necessary to purify the biomass to completely remove all metals bioaccumulated while growing in the field. 500 g of finely divided biomass was activated and at the same time purified by soaking in excess 0.3M HNO_3 for 24h, after which it was washed thoroughly with deionized water until a pH of 7.1±0.1 was attained and then air-dried. The air-dried activated biomass was then washed with deionized water and re-suspended in 1.0 M hydroxylamine to remove all O-acetyl groups. To remove all other soluble materials, the biomass was washed with deionized water and centrifuged at 3000 × g for five minutes using a Portable Refrigerated test tube centrifuge model

PR - 2 with 20" diameter stainless solid basket 3/4HP 1/60/115 volt motor with temperature indicator, timer and speed controls. The supernatants obtained were discarded and the purified biomass cake obtained dried at room temperature. 1.0 mg of the purified biomass was further digested and analysed for the same metal ions and found to contain less than 1.0 μg g^{-1} in all cases.

Sorption Equilibrium studies. The sorption experiments for the metal systems were carried out as follows. Several standard solutions with concentrations of 10, 20, 30, 40, and 50 mg/L were made from spectroscopic grade standards of Al^{3+}, Co^{2+} and Ag^{+}. The metal solutions made separately were adjusted to pH 5.0 with conc. HCl. Fifty milliliters of each metal ion solution was added to accurately weighed (250 ± 0.01 mg) activated/purified biomass in different flasks and agitated for two hours to ensure that equilibrium was achieved. At the end of the time, the suspension was filtered through Whatman No 45 filter paper and centrifuged at 2800 × g. The supernatants were analyzed for metal ions by flame atomic absorption spectroscopy.

Analysis of Metal Content. The Al^{3+}, Co^{2+} and Ag^{+} content in each experiment were determined with a Buck Scientific Flame Atomic Absorption Spectrometer (FAAS) model 300A. Spectroscopic grade standards were used to calibrate the instrument, which was checked periodically throughout the analysis for instrument's response. The batch experiments were performed in triplicates and the means were computed for each set of values to maintain quality assurance.

Data Evaluation

Calculation of Al^{3+}, Co^{2+} and Ag^{+} Removed By Biomass

The amount of Al^{3+}, Co^{2+} and Ag^{+} removed by the biomass during the series of batch investigations were determined using a mass balance equation expressed as in equation 3.

$$q_e = \frac{v(C_o - C_e)}{m} \qquad (3)$$

where q_e = metal concentration on the biomass (mg/g biomass) at equilibrium, C_e = metal concentration in solution (mg/L) at equilibrium, C_o = initial metal concentration in solution (mg/L), v = volume of initial metal solution used (L), m = mass of biomass used (g).

Equilibrium Sorption

Five two-parameter equations - the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Flory-Huggins isotherms were examined for their ability to model the equilibrium sorption data.

The linear form of the Langmuir equation is usually expressed by

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_e} \qquad (4)$$

where K_L = Langmuir isotherm constant (dm^3 g^{-1}); q_m = Langmuir monolayer sorption capacity (mg g^{-1}). A plot of C_e/q_e against C_e was made to confirm the Langmuir isotherm.

The Freudlich model is represented in equation 4:

$$\log q_e = \log K_F + \frac{1}{n} lon C_e \qquad (5)$$

where q_e = sorption density (mg/g); C_e = conc. Of metal ion in solution at equilibrium mg/dm^3); K_L and 1/n are the Freundlich constants. The value of n indicates the affinity of the sorbent towards the biomass. Plotting log q_e against log C_e was used to test the Freundlich model.

The linear form of the Temkin isotherm model as shown in equation 5 was plotted as q_e against ln C_e.

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \qquad (6)$$

where the $1/b_T$ indicates the adsorption potential of the adsorbent and K_T is the Temkin isotherm constant (dm^3 g^{-1}).

The linear form of the Dubinin-Radushkevich equation is represented by equation 6

$$\ln q_e = \ln X_m - K_{DR}\varepsilon^2 \qquad (7)$$

where K is related to the free energy of sorption and X_m is the Dubinin-Radushkevich isotherm constants related to the degree of sorbate sorption by the biomass surface. The parameter ε is expressed by (equation 7)

$$\varepsilon = RT \ln \frac{C_o}{C_s} \qquad (8)$$

A plot of Inq$_e$ against ε^2 yielding a straight line was made to confirm the model. The mean free energy of adsorption (E_s) from the Dubinin-Radushkevich equation can be computed using the following relationship (equation 8)

$$E_s = (-2K)^{-1/2} \qquad (9)$$

The linear form of the Flory-Huggins equation is represented by

$$\log \frac{\theta}{C_o} = \log K_{FH} + n \log(1 - \theta) \qquad (10)$$

where $\theta = (1 - C_e/C_0)$ is the degree of surface coverage, n is the number of metal ions occupying sorption sites, K_a is the equilibrium constant and C is the equilibrium

concentration. A plot of $\log(\theta/C)$ against $\log(1-\theta)$ yielding a straight line was made to confirm this model.

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Povzetek

Z različnimi metodami smo raziskovali vpliv ionskih radijev na sorpcijo Al^{3+}, Co^{2+} in Ag^{+} ionov na odpadni biomasi iz buč. Eksperimentalne rezultate smo analizirali s pomočjo petih dvo parametrskih enačb: Langmuirjeve, Freundlichove, Temkinove, Dubinin-Radushkevicheve in Flory-Hugginsove izoterme. Dobljena kapaciteta monoplastne adsorpcije znaša po Langmuirjevi adsorpcijski izotermi 16.98 mg/g, 10, 34 mg/g in 8.03 mg/g za Al^{3+}, Co^{2+} in Ag^{+} ion. Ugotovili smo, da Freundlichova in Langmuirjeva izoterma process adsorpcije opišeta bolje kot Temkinova, Dubinin-Radushkevicheva in Flory-Hugginsova izoterma. Rezultati kažejo, da ionski radij vpliva na hitrost migracije kovinskega iona k površini biomase ter s tem na intenziteto adsosrpcije ter, da so bučni odpadki uporabni za odstranjevanje Al^{3+}, Co^{2+} in Ag^{+} ionov iz odpadnih vod.