

Effect of Metal Ion Concentration on the Biosorption of Al^{3+} and Cr^{6+} by Almond Tree (*Terminalia catappa* L.) Leaves

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Abstract

The influence of initial metal ion concentration of the batch sorption of Al^{3+} and Cr^{6+} onto a low-cost biosorbent was investigated. The experimental results were analysed in terms of Langmuir and Freundlich isotherms. According to the evaluation using Langmuir equation, the monolayer sorption capacity obtained were 1.12mg/g and 2.67mg/g for Al^{3+} and Cr^{6+} respectively. The data further showed that sorption of the two metals onto the biomass increased with increase in initial metal ion concentration. The thermodynamic assessment of the metal ion – almond tree (*Terminalia catappa* L. biomass system indicates the feasibility and spontaneous nature of the process. ΔG° was evaluated as ranging from -4.56 to - 6.64 KJ mol⁻¹ and -4.03 to -6.10 KJ mol⁻¹ for Al^{3+} and Cr^{6+} sorption respectively. The order of magnitude of the ΔG° values indicates an ion exchange physiosorption process.

Keywords: Adsorption, Almond tree, Heavy metals removal, Phytoremediation, water treatment.

INTRODUCTION

Environment protection must require the use of natural products instead of chemicals to minimize pollution. Thus, this investigation studies the use of a non-useful plant material as naturally occurring biosorbents for the removal of Aluminium and chromium ions in aqueous solution.

The presence of Al^{3+} & Cr^{6+} and other heavy metals in the environment has become a major threat to plant, animal and human life due to their bio accumulating tendency and toxicity and therefore must be removed from municipal and industrial effluents before discharge (Horsfall & Spiff 2005). It is therefore necessary that there are technologies for controlling the concentrations of these metals in aqueous discharge/effluents.

Physico-chemical methods such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery filtration, ion exchange and membrane technologies have been widely used to remove heavy metal ions from industrial waste water. These processes may be ineffective or expensive, especially when the heavy metal ions are in solutions containing in the order of 1 – 100 mg dissolved heavy metal ions (Volesky, 1990a). Biological methods such as biosorption/bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods (Kapoor & Viraraghavan, 1995).

As such, it is necessary to search for alternative adsorbents, which are low-cost, often naturally occurring biodegradable products that have good adsorbent properties and low value to the inhabitants. A range of products has been examined. These include pillared clay (Vinod and Anirudhan, 2001), sago waste (Quek et al, 1998), cassava waste (Abia et al, 2003), banana pith (Low et al, 1995), peanut skins (Randall et al, 1974), medicago sativa (Alfalfa) Gardea-Torrestey et al, 1998) and sphagnum moss peat (Ho et al, 1995) just to mention a few.

Although the biological method has many advantages compared to the conventional treatment methods (Kuyucak, 1990) the biological materials need to have characteristics suitable for process applications: hardness, porosity, particle size, density and resistance to a broad spectrum of variable solution parameters such as temperature, pH and solvent content (Volesky 1990a). The biological materials have several limitations on the aspects of application compared to conventional methods.

The adsorbent used in the present study is almond tree (*Terminalia catappa* L.). The almond tree (*Terminalia catappa* L) has been known for its usefulness in the medical world. The gainful use of this medicinal tree which produces edible fruits will also bring about practical exploitation that would encourage local farmers. In addition, the anticipated use of the biomass from this tree as a biosorbent for trace metals in water and waste effluents will solve environmental problems. The principal aim of the present work is to assess the potential use of the biomass of *Terminalia catappa* L. as a novel biosorbent for the sorption of valuable and toxic metal ions from aqueous media.

The purpose of this paper is to report the effect of initial metal ion concentration and thermodynamics on the sorption of Al^{3+} and Cr^{6+} ions from aqueous effluents by *Terminalia catappa* L. biomass.

MATERIALS AND METHODS

Materials

The almond tree (*Terminalia Catappa* L.) leaves was collected from Akarai-Ekiti, Akarai-Obode, Aboh in Ndokwa East Local Government Area of Delta State. The almond tree leaves were collected with clean polythene bags and then air-dried for one week under normal sunlight conditions. The dried almond tree leaves

mg/l) remaining in solution at equilibrium.

The linear form of the Langmuir model is given in equation 4

$$\frac{C_e}{q_e} = \frac{1}{X_m K_L} + \frac{C_e}{X_m} \quad -4$$

The capacity of the biomass can be obtained if a plot of C_e/q_e against C_e is made.

The second model is Freundlich model which can be written as in equation 5. The mathematical equation is given as:

$$\frac{X}{m} = K C_e^{1/n} \quad -5$$

Where: X is the mass of metal ion adsorbed (mg), m is the mass of biomass used (g), C_e is the concentration of metal ion at equilibrium, n is the adsorption intensity and K is the adsorption constant.

The linear form of equation 5 takes the form (eqn 6)

$$\ln \frac{X}{m} = \ln K + \frac{1}{n} \ln C_e \quad -6$$

A plot of $\ln \frac{X}{m}$ against $\ln C_e$, will give a straight line which will confirm the Freundlich Isotherm.

The data in Table 1 gives some physical characteristics of the almond tree leaves biomass. These characteristics play some important role in the adsorption process of metal ions onto the biomass. The low value of the apparent density (1.17 ± 0.06 , g/cm³) is an indication of the ease of suspension of the biomass in aqueous solution, which is an essential factor in the interaction between metal ion in solution and a coagulation ligand. Apparent density closer to unity indicates higher contact between sorbate and sorbent. The porosity and pore volume are important factor in characterizing the macrostructure properties of the biomass. The porosity and pore volume of the almond tree leaves biomass are $43.3 \pm 0.08\%$ and 0.79 cm³/g.

Table 1: Some physical characteristics of the biomass

Parameters	Values
Apparent density, g/cm ³	1.17±0.06
Porosity %	43.3±0.08
Pore volume, cm ³ /g	0.79
Ash content, %	12.3±0.11

The data showed that, as the initial metal-ion concentration increases, the capacity of the biomass for the metal ions also increases. The data presented in figure 2 showed stable increase in the biomass capacity as the initial metal ion concentrations increases. At 40mg/l 79.8% Al³⁺ and 88.2% Cr⁶⁺ were removed.

These differential removal characteristics may be ascribed to differences in ionic radii of the metal ions are 0.05Å for Al³⁺, 0.52Å for Cr⁶⁺, respectively. Thus the smaller the ionic radius, the greater the tendency of the ion to be captured by the biomass. This leads to an increase in the ability of smaller ions to migrate faster to the surface active sites, of the biomass for sorption.

Table 2: Capacity of biomass for metal ions at various metal ion concentrations

Concentration	Al ³⁺	Cr ⁶⁺
10	0.80	0.086
20	0.150	0.171
30	0.232	0.263
40	0.319	0.353
50	0.381	0.437

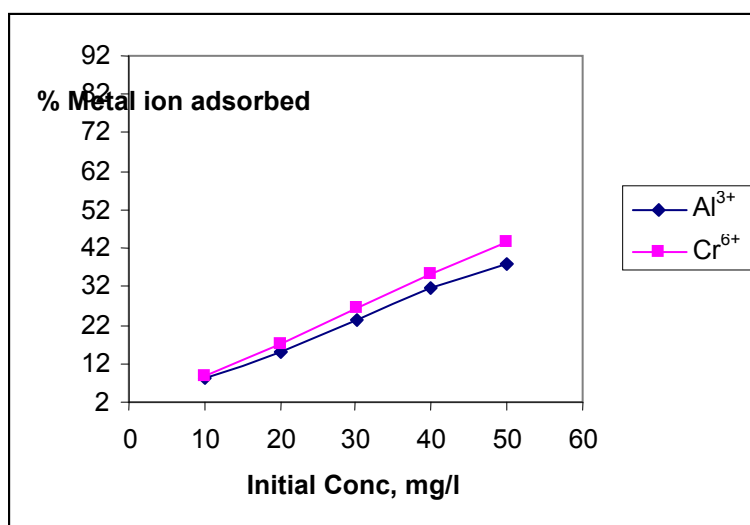


Fig 1: Graphical representation of capacity of metal ion concentrations at different metal ion concentrations

SORPTION EQUILIBRIUM

Sorption equilibria provide fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation. To facilitate the estimation of the sorption capacities, experimental data from various initial concentration experiments were fitted to the Langmuir and Freundlich equilibrium adsorption Isotherms. Table 3 shows the data linearized to fit the Langmuir equation. The plots of specific sorption (C_e/q_e) against equilibrium concentration (C_e) gave the linear – Isotherm parameters q_{max} and K_L (Table 3) the R^2 values suggested that the Langmuir Isotherm provides a good model of the sorption system. The sorption capacity, q_{max} , which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage, showed that the almond tree waste biomass has a higher mass capacity for the two heavy metal ions. The adsorption coefficient, K_L , which is related to the apparent energy of sorption, was greater for Al^{3+} than Cr^{6+} . This could mean that the energy of adsorption is not very favourable for Cr^{6+} sorption, hence not all binding sites may be available for Al^{3+} binding due to its large ionic radius.

The linear Freundlich Isotherms for the sorption of the two metals onto almond tree waste biomass are presented in the table below. Examination of the plot reveals that the Freundlich Isotherm is also an appropriate model for the sorption of Al^{3+} and Cr^{6+} .

Based on the R^2 values, the linear form of the Freundlich Isotherms appears to be an excellent model for the sorption. The Freundlich data fitting better than those of Langmuir. The K_f value of Cr^{6+} is also greater than that of Al^{3+} suggesting that Cr^{6+} has a greater adsorption tendency towards almond tree waste biomass than Al^{3+} . Again, the smaller ionic radius of Al^{3+} and Cr^{6+} might be responsible for their higher adsorptivity. It has been reported, Okiemen et al, (1987) that, the smaller an ion, the greater its affinity towards active groups on biomaterials. The Freundlich equation parameter $1/n$, which is a measure of the adsorption intensity, exceeds 0.95 for both metals.

Table 3: Linearized data for Langmuir and Fruendlich equations

Metal ions	Langmuir			Frudedlich		
	KL	Xm	R2	KF	1/n	R2
AlIII	2.37×10^{-2}	36.25	0.94	1.45×10^{-2}	1.14	0.98
CrVI	1.51×10^{-1}	17.47	0.91	7.5×10^{-3}	0.97	0.95

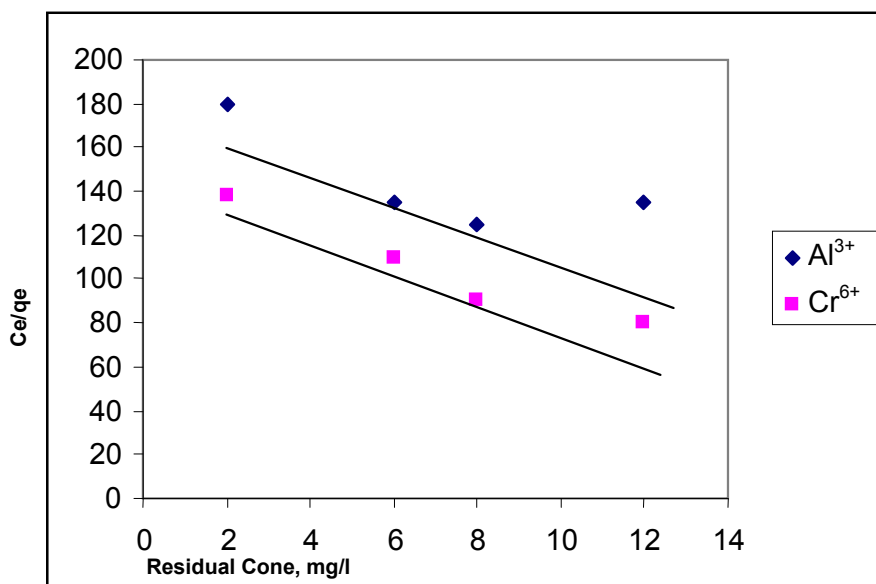


Fig 2: plots of specific sorption (ce/qe) against equilibrium concentration

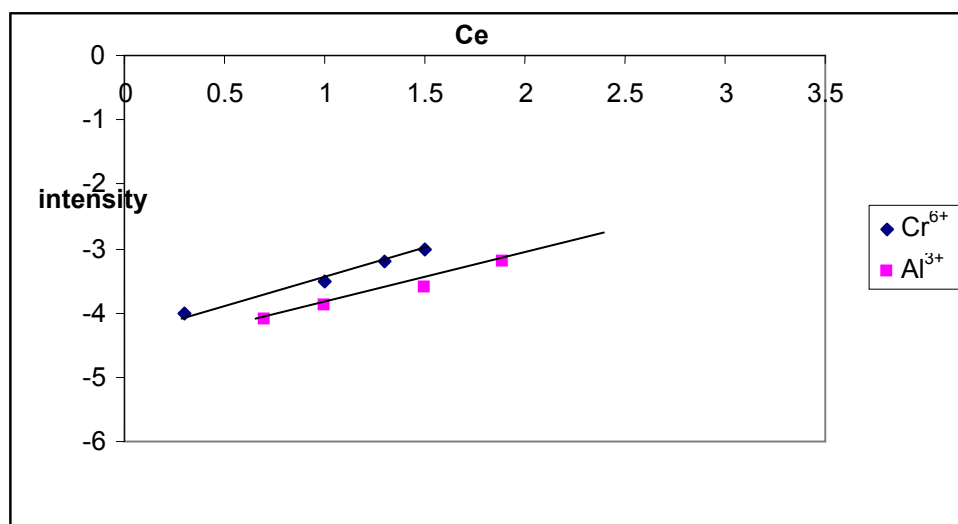


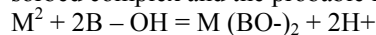
Fig 3: Plots of intensity against equilibrium metal ion concentration

Table 4: Distribution ratios, D, and apparent Gibbs free energy ΔG_{ads}° (KJ mol^{-1}) of the metal ions between the Terminalia catappa L. and aqueous phase

Co (mM)	Al ³⁺		Cr ⁶⁺	
	D	ΔG_{ads}°	D	ΔG_{ads}°
1.0	0.53	-6.10	0.45	-6.10
2.0	0.53	-5.16	0.48	-4.66
3.0	0.57	-4.56	0.52	-4.004
4.0	0.68	-5.01	0.63	-4.56
5.0	0.69	-5.57	0.64	-4.01
6.0	0.80	-5.58	0.72	-4.47
7.0	0.85	-6.07	0.74	-4.34
8.0	0.87	-6.15	0.76	-4.28
9.0	0.90	-6.60	0.80	-4.57
10.0	0.91	-6.63	0.89	-6.07

The relativeness of the biomass in removing the metal ions from aqueous solution was again evaluated in terms of the distribution coefficient, D, which can be defined as the ratio of the metal ion concentration in the adsorbent Mn+Sol. Table 4 shows the value of D for a range of metal ion concentrations. The results show that the concentration of metal ions at the sorbent-water interface is higher than the concentration in the continuous aqueous phase. This suggests that the biomass is effective in the removal of metal ions from aqueous systems.

This indicates that two (2) molecules of biomass were associated with metals. Hence the composition of the sorbed complex and the probable mechanism may be given as follows:



The sorption occurs by an ion-exchange mechanism.

The thermodynamics of the exchange process depends on the number of water molecules (n) replaced by the metal ions. Since the most probable value of n is 2, the apparent Gibbs free energy of the adsorption processes (ΔG°_{ads}) corresponding to Al^{3+} and Cr^{6+} ion on the biomass are evaluated using the Bockris – Swinkel's adsorption isotherm equation as reported by Rudresh and Mayanna (1977) with n = 2 and θ – values. The equation is expressed as:

$$G^{\circ}_{ads} = -2.303RT \log \left[\frac{55.4\theta}{C_o(1-\theta)} \times \frac{\theta + n(1-\theta)^{n-1}}{n^n} \right]$$

Where C_o is the initial concentration of Cr^{6+} ion in the solution. The values of ΔG°_{ads} were then evaluated with n = 2 at various initial metal ion concentrations.

The negative values of ΔG° indicate the spontaneous adsorption nature of Cr^{6+} ion by the Terminalia catappa L. adsorbents and suggest strong adsorption of Cr^{6+} ions on the biomass surface. In general, it is of note that up to – 20 KJ mol⁻¹ are consistent with electrostatic interaction between charged molecules and surface indicative of physisorption while more negative than –40 KJ mol⁻¹ involve chemisorption. The order of magnitude of the values indicates a physical mechanism for the adsorption of metal ions on to the Terminalia catappa L. biomass.

CONCLUSION

In conclusion, the data has shown that, the uptake of Al^{3+} and Cr^{6+} ions on to Almond tree biomass is feasible and spontaneous in nature. The metal ions binding capacity of the biomass was shown as a function of initial metal ion concentrations. The equilibrium data fitted the Freundlich isotherm model, more than that of the Langmuir isotherm model.

The maximum loading capacity of the tree waste for the two heavy metals are 36.25 mg/g (Al^{3+}) and 17.47 mg/g (Cr^{6+}) respectively.

The data showed that, almond tree (Terminalia catappa L.) leaves is a successful biosorbent for treating heavy metal contaminated wastewater and may serve as an alternative adsorbent to conventional means.

Hence, not only is almond tree leaves readily available, it also has the potential for metal removal and recovery from contaminated waters. This process will be environmental friendly and convert the non-useful plant into an economic crop for local farmers. It may also provide an affordable technology for small and medium-scale industries in Nigeria.

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