Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **3(11),** 1-6, November **(2013)** *Res. J. Chem. Sci.*

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

Enemose Edith A.[1], Osakwe S.A.[1*] and Horsfall, Michael Jnr.[2]
[1]Department of Chemistry, Delta State University, Abraka, Delta State, NIGERIA
[2]Department of Chemistry, University of Portharcourt, River State, NIGERIA

Available online at: www.isca.in, www.isca.me
Received 20th January 2012, revised 25th June 2012, accepted 17th August 2013

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^o 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^o 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. 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[1]. Biological methods such as biosorption/ bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods[2].

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[3], sago waste[4], cassava waste[5], banana pith[6], peanut skins, medicago sativa (Alfalfa) Gardea-Torrestey et al[7] and sphagnum[8] moss peat just to mention a few.

Although the biological method has many advantages compared to the conventional treatment methods 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. 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.

Material 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 were initially crushed to smaller size with mortar and pestle and further ground using a food processor (Magimix Cuisine System 5000) to 90-µm size to obtain a fine biomass which was then stored in clean, air tight plastic container and ready for use.

Biosorbent activation: The purpose of activation is to increase the porosity and open more pores in the biomass. The finely divided biomass was activated by soaking 5 g biomass in excess 0.03 $MHNO_3$ for 25 hours, followed by washing thoroughly with deionized water. The washing process continued until the filtrate gave a negative EDTA (Ethylene diamine tetraacetic acid) test for heavy metal ions. The test was carried out by the addition of 5 drops of 0.001 M EDTA solution and 2 ml of NH_3/NH_4Cl buffer to 5 ml of the washing water filtrate. The appearance of blue color of the EDTA solution indicates the absence of metal ions. The filtered biomass was then oven-dried at 65°C to constant weight.

The finely divided biomass was characterized for apparent density and porosity were determined by mercury intrusion porosimeter (Micrometrics model-9310) and specific gravity bottle respectively. Pore volume was estimated as the inverse of reaction of particle density (Horsfall et al, 2005), while the ash content was determined using the ignition method by burning 1.0g of biomass sample (placed in a thoroughly washed crucible) in a furnace which was pre-heated to 500°C for 3 hours. The crucible was removed and cooled in a desiccator and reweighed until a constant weight was obtained. The percentage ash content was calculated using the formula:

$$\%\ \text{Ash} = \frac{M_a}{M_s} X 100$$

Where M_a = mass of ash (g) and M_s = mass of sample used (g)

Preparation of Metal Solutions: The aqueous solutions of the metal ions used were prepared by using analytical grade reagents provided by Fluka (Switzerland). Individual stock metal ion solution of 1000mg/l concentration of Al^{3+} from $Al(NO_3)_3.9H_2O$ and Cr^{6+} from $K_2Cr_2O_7$ were prepared. Serial dilutions were made with double distilled water from these stock solutions. In order to prevent the formation of metal hydroxide and allow all metal ion to be solution, the stock solutions were acidified with HNO_3 to $4<pH<6$.

Batch Sorption Experiment: The Batch experimental procedure to determine the effect of metal ion concentration is described below. An equilibrium contact time of 2 h was used for metal ion-Terminalia Catappa L. A 10 mg of the biomass samples was weighed and place din pre-cleaned test tubes in triplicates. Several metal ion solutions with standard concentrations of 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 nM were made from HPLC – analytical grade standards of Al^{3+} from $Al(NO_3)_3$ and Cr^{6+} from $K_2Cr_2O_7$. The two sets of metal solutions made separately were adjusted to pH 5.0 with concentrated HCl. 2 mL of each metal solution were added to each tube containing the biomass and equilibrated for 2 h by shaking at 29°C. The supernatants were analysed for Al^{3+} and Cr^{6+} using flame atomic absorption spectrometer model 300A.

Results and Discussion

The amount of metal ion taken by the biomass was calculated using a mass balance equation which has been previously used by other researches in evaluating the amount of metal ion adsorbed by the Almond tree leaves biomass. The mass balanced equation is given as

$$q_e = \frac{v}{m}(C_0 - C_e)$$

where: qe = amount of metal ion removed by the almond tree waste biomass (mg/g), m = Mass of almond tree waste biomass used (g), v = Volume of initial ion solution used (ml)[1] Co = initial metal ion concentration (mg/l), Ce = Equilibrium metal ion concentration (mg/l).

Adsorption Isotherms: Two of the most sorption models were used to fit the experimental data. The Langmuir model which assumes that equilibrium is attained when a monolayer of the adsorbate molecules saturates the adsorbent. This model can be presented as in equation 3.

$$q_r = \frac{q_m K_l C_e}{1 + K_L C_e} \tag{3}$$

Where X_m and K are the Langmuir constants and specifically Xm is the monolayer and sorption capacity of the biomass q_e is the concentration of metal ion on the biomass (mg/g) at equilibrium and C_e as the concentration (in mg/l) remaining in solution at equilibrium.

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

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

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

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

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 equation 6.

$$\text{In}\ \frac{X}{m} = 1\text{nK} + \frac{1}{n}\text{InC}_e \quad (6)$$

A plot of 1n $\frac{X}{m}$ against 1nC$_e$, will give a straight line which will confirm the Freudlich 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/cm^3) 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 ± 0.08% and 0.79 cm^3/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% Al^{3+} and 88.2% Cr^{6+} were removed.

These differential removal characteristics may be ascribed to differences in ionic radii of the metal ions are 0.05Å for Al^{3+}, 0.52Å for Cr^{6+}, 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.

Sorption Equilibrium: Sorption equilibra 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 (Ce/qe) against equilibrium concentration (Ce) 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.

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

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[9], 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**			**Fruedlich**		
	KL	**Xm**	**R2**	**KF**	**1/n**	**R2**
A1III	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

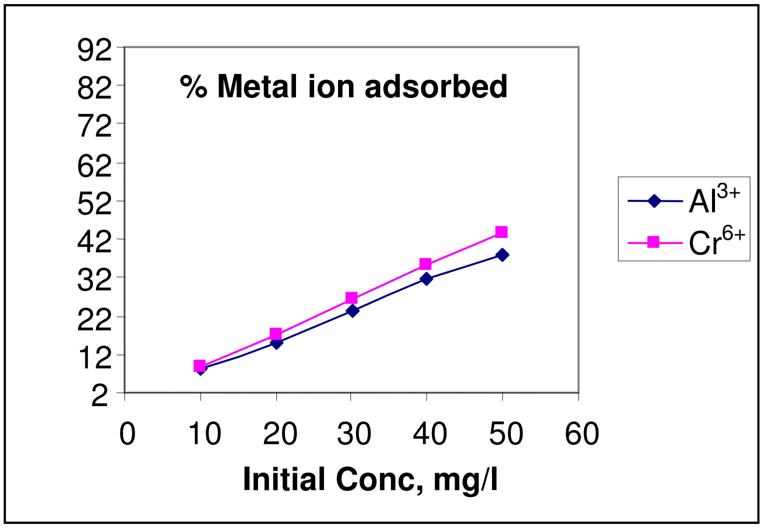

Figure-1
Graphical representation of capacity of metal ion concentrations at different metal ion concentrations

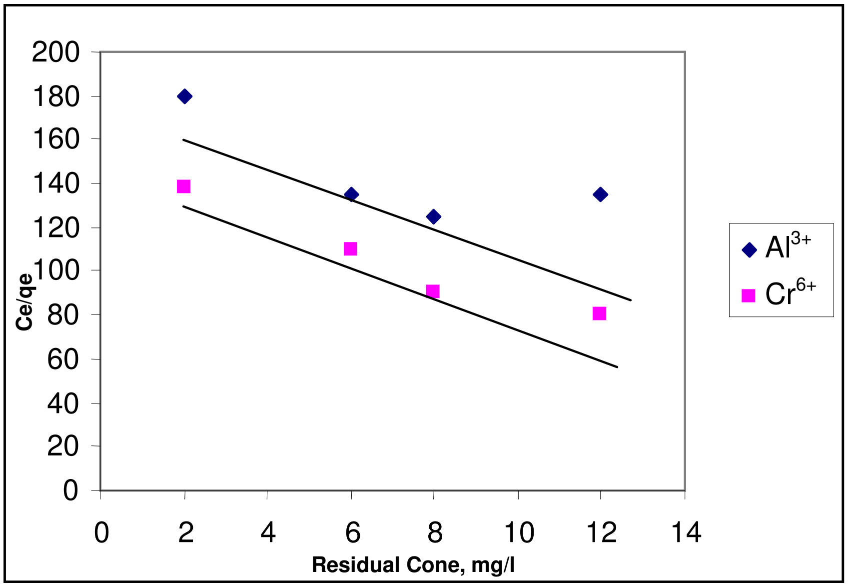

Figure-2
Plots of specific sorption (ce/qe) against equilibrium concentration

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

Co (mM)	Al^{3+}		Cr^{6+}	
	D	ΔG^o_{ads}	D	ΔG^o_{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

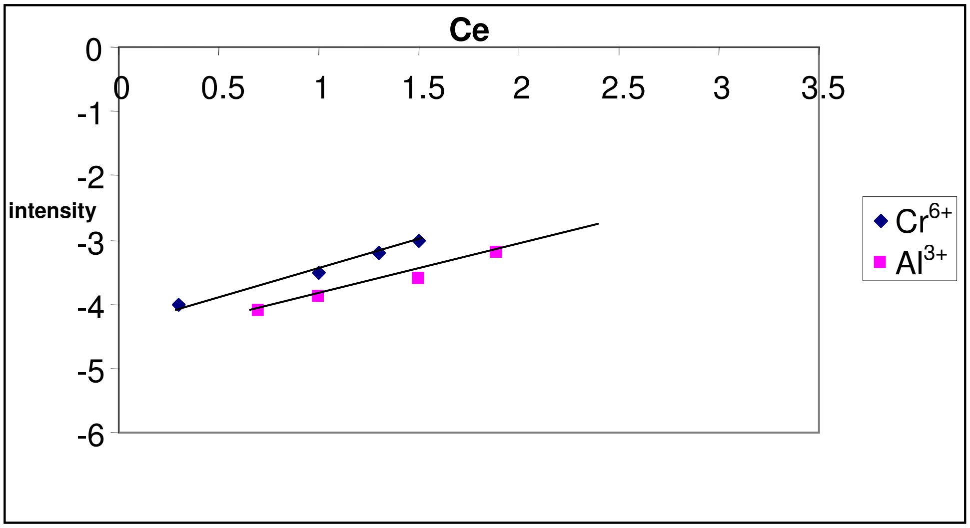

Figure-3
Plots of intensity against equilibrium metal ion concentration

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:

$M^2 + 2B - OH = M\ (BO\text{-})_2 + 2H+$

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^o_{ads}) corresponding to Al^{3+} and Cr^{6+} ion on the biomass are evaluated using the Bockris – Swinkel's adsorption isotherm equation as reported y Rudresh and Mayanna with n = 2 and θ – values. The equation is expressed as:

$$G^o{}_{ads} = -2.303RT\log\left[\frac{55.4\theta}{C_o(1-\theta)} \times \frac{\theta + n(1-0)^{n-1}}{n^n}\right]$$

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

The negative values of ΔG^o 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 physiosorption 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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