Studies on the effect of pH on the sorption of Al^{3+} and Cr^{6+} Ions from aqueous solutions by Almond Tree (*Terminalia catappa L.*) Biomass

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Abstract

Environmental protection requires the use of natural products instead of chemicals to minimize pollution. This investigation studies the use of a non-useful plant material as naturally occurring biosorbents for the removal of cationic pollutants in wastewater. The effect of pH on the sorption of Al^{3+} and Cr^{6+} ion unto Terminalia catappa biomass was investigated. The experimental results have been analysed in terms of Langmuir and Freundlich isotherms. The data showed that the maximum pH (pH max) for efficient sorption of Al^{3+} was 4.0 (85.5 mg/g) and for Cr^{6+} 2.0 (82.6 mg/g). Evaluation using Langmuir equation gave the monolayer sorption capacity as 1.12mg/g and 2.67mg/g at the respective pHmax for Al^{3+} and Cr^{6+}. The thermodynamic assessment of the metal ion – Terminalia catappa L. biomass system indicates the feasibility and spontaneous nature of the process.

Keywords: adsorption, heavy metal removal, almond tree, phytoremediation, water treatment.

Introduction

The conventional technologies for effluent treatment are not economically feasible for small-scale industries prevalent in developing economies due to huge capital investment. It is therefore necessary to search for alternative adsorbents which are low cost, often naturally occurring products that have good sorbent properties and no value to the people.

The presence of Al^{3+} and 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. Resultantly, it is necessary that there are technologies for controlling the concentrations of these metals in aqueous emissions.

A range of products has been examined. Few of these include pillared clay[1], sago waste[2], cassava waste[3], banana pith[4], Medicago sativa[5], wilt cocoyam[6], and spagnum moss peat[7].

The adsorbent used in this study is almond tree biomass. The almond tree belongs to the family called combretaceae (Combretum family). The botanical name of the tropical almond tree is *Terminalia catappa L.* The almond tree (*Terminalia catappa L.*) has been known for its usefulness in the medical world. The use of the biomass as a biosorbent for trace metals in water and waste effluents is expected to solve environmental problems.

The equilibrium distribution of metal ions between the sorbent and the solution is important in determining the maximum sorption capacity. Two sorption models, (the Langmuir and Freundlich) will be used to assess the different isotherms and their ability to correlate experimental data. The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. The Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the biomass. The major aim of the present work is to investigate the potential use of the biomass of almond tree (*Terminalia catappa* L.) as a novel biosorbent for the sorption of valuable and toxic metal ions from aqueous media.

This paper reports the effect of pH on the ability of the biomass of the almond tree (*Terminalia catappa* L.) to remove Al^{3+} and Cr^{6+} ions from single metal ion solutions. The effect of varying initial pH and equilibrium sorption on the potential ability of the *Terminalia catappa* L. in removing these two metal ions from solution was investigated.

Material and Methods

Collection and preparation of sample (biosorbent) investigated: The almond tree (*Terminalia Catappa L.*) leaves were collected from Akarai-Etiti, Akarai-Obodo and 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 5g biomass in excess 0.03M HNO_3 for 25 hours, followed by washing thoroughly with deionized water. The washing process continued until the filtrate gave a negative EDTA (Ethylenediaminetetraacetic acid) test for heavy metal ions. The test was carried out by the addition of 5 drops of 0.001M 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 $65^{o}C$ to constant weight.

Characterization of the Biomass: 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 $500^{o}C$ 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[6]:

$$\% \text{ Ash} = \frac{M_a}{M_s} \times 100 \quad (1)$$

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^{III} from $Al(NO_3)_3 \cdot 9H_2O$ and Cr^{VI} 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.

Measurement: pH was measured using X74081 Toptronic pH meter (Vetrerie ed Apparecchiature Per Laboratori Chmici, Milano, Italy). The metal ion concentrations were measured using Buck Scientific Flame Atomic Absorption Spectrometer (FAAS) model 300A, Germany). The samples were read in duplicates. The analytical wavelengths used for the metals studied were: 309.3 nm and 358.2nm for Aluminium and Chromium respectively. Analytical grade standards were used to calibrate the instrument response. The correlation coefficient for calibration curve was about 98.6.

The batch experiments were performed in duplicates and the mean (or the slope and intercept) were computed for each set of values.

Experimental Procedure: Adsorption isotherm studies: Effect of pH: The pH solutions ranging from 2.0 to 8.0 was studied, the solution were adjusted to the required pH values by adding a solution of In HCl or 1m NaOH. All the flasks were reacted on a shaker for one hour. The suspensions were filtered using No. 45 Whatman filter paper and then centrifuge at 2800rpm for five minutes in order to remove all traces of cloudiness. The metal ions investigated were determined using FAAS model 300A.

Data Evaluation: 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

$$q_e = \frac{v}{m}(C_0 - C_e) \quad (2)$$

where
q_e = 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

$$q_r = \frac{q_m K_l C_e}{1 + K_L C_e} \quad (3)$$

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

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

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 Fruendlich 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)

In $\dfrac{X}{m} = 1nK + \dfrac{1}{n}InC_e$ (6)

A plot of $1n \dfrac{x}{m}$ against $1nC_e$, will give a straight line which will confirm the Freudlich Isotherm.

Results and Discussions

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.

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

Table-2
The pH dependent data for sorption of Al(III) and Cr(VI)

pH	Al^{3+}	Cr^{6+}
2	0.081	0.083
4	0.086	0.076
6	0.071	0.063
8	0.063	0.059

Effect of pH: Most plant materials are made up of complex organic residues such as lignin and cellulose that contain several types of polar functional groups. These groups can be involved in chemical bonding and may be responsible for the typical cation-exchange characteristics of most biomaterials.

The pH of the aqueous medium affects the surface charge of the adsorbent, the degree of ionization, and the species of the adsorbate[5].

The pH dependence data for the sorption of the two metals under investigation are presented on figure 1. The data revealed that, at pH 2.0, there was significant removal of the metal ions by the almond tree waste biomass; 85.5% for Al^{3+} and 82.6% for Cr^{6+}. However, when the pH was raised to 4.0, there was a large increase in the amount of metal ion removed. At pH 4.0, the biomass removed 85.5% Al^{3+} and 76.1 Cr^{6+}. Above pH 4.0, a gradual decrease in the amount of metal ions removed by the almond tree waste biomass was observed.

A close look at the metal ions investigated a pH 2 favours Cr^{6+} removal with a percentage of up to 82.6% while a pH 4 favours Al^{3+} as shown in figure 1.

The overall trend observed in the pH-dependent sorption behaviour suggests that metal uptake occurs through ion-exchange. Our results, thus, indicate that binding follows an ion-exchange mechanism that involves electrostatic interaction between the negatively charged groups in the walls of the biomass and the metallic cations. At low pH, the surface of the adsorbent would closely be associated with hydroxonium ions (H_3O^+) that hinder the access of the metal ions to the surface functional groups, consequently decreasing the percentage of ion removal at low pH[4].
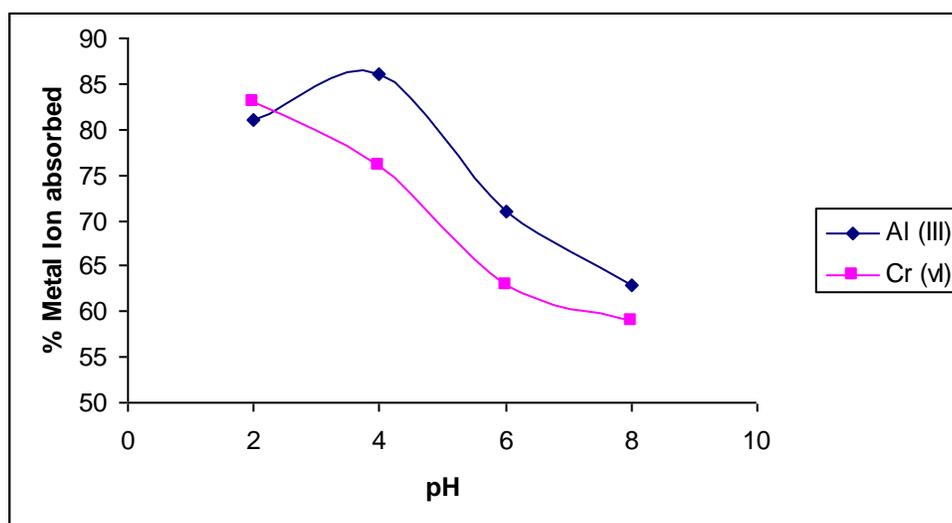

Figure -1
Graphical representation of the pH dependent data for sorption of Al(III) and Cr(VI)

Table-3
The values of experimental results as analysed in terms of Langmuir and Fruedlich isotherms

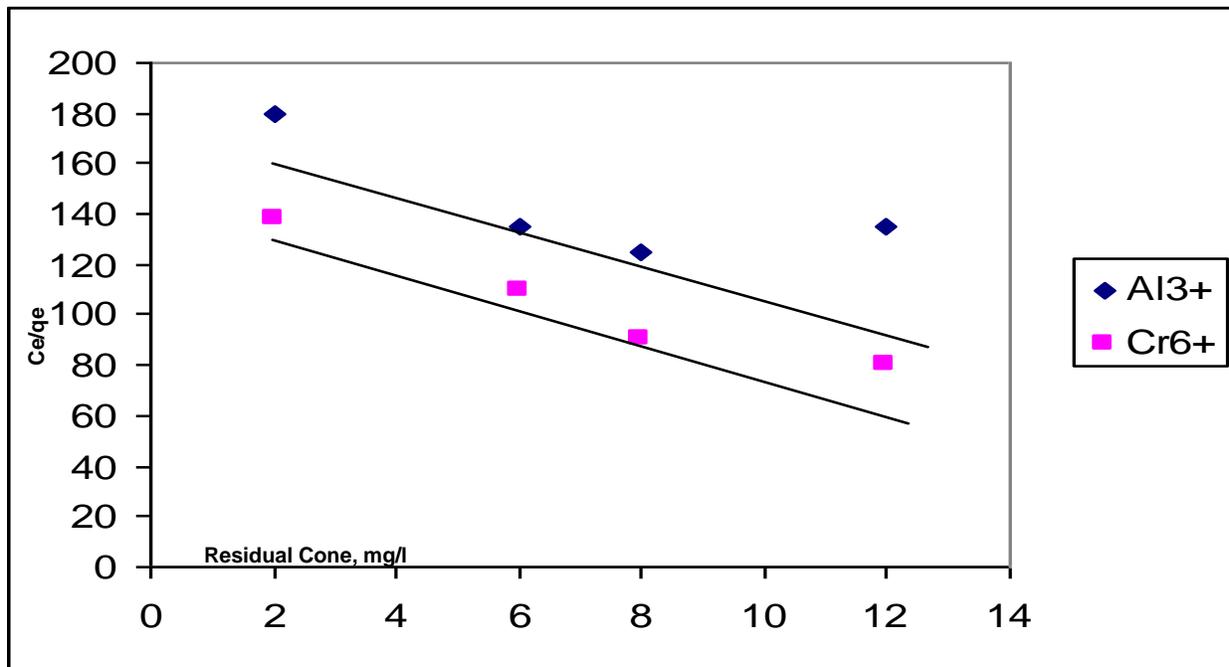| Metal ions	Langmuir			Fruedlich		
	KL	**Xm**	**R2**	**KF**	**1/n**	**R2**
A1III	2.37×10^{-2}	36.25	0.94	1.45×10^{-2}	1.14	0.98
CrVI	1.51×10^{-1}	17.47	0.91	7.5×10^{-3}	0.97	0.95

Figure -2
Graphical representation of the analytical results in terms of Langmuir and Fruedlich isotherms
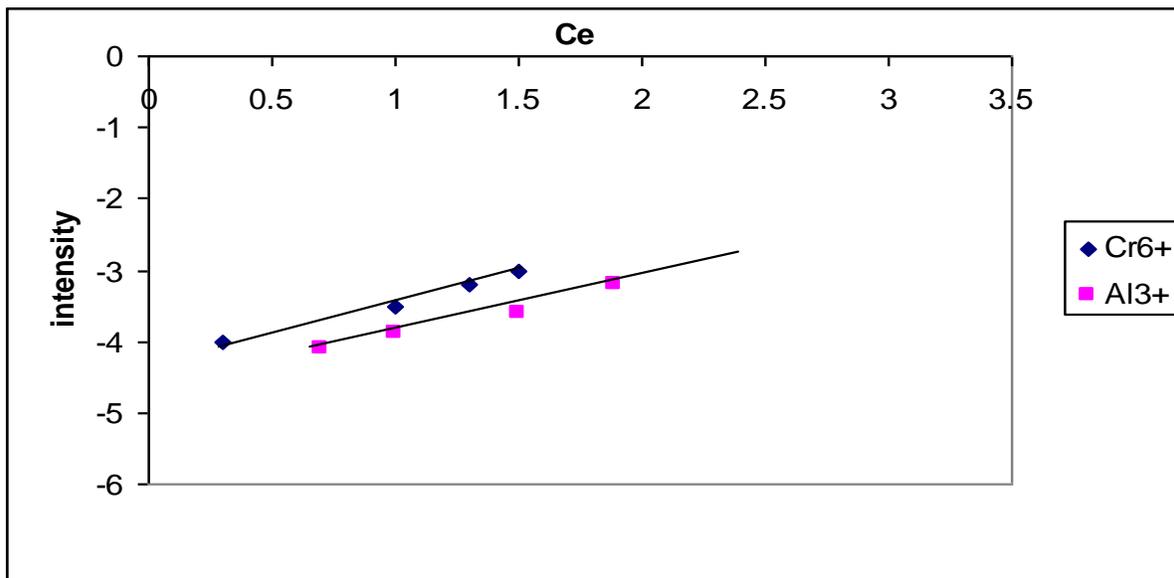

Figure-3
Graphical representation of the equilibrium metal ion concentrations against intensity

Surface of the adsorbent, would be closely associated with hydroxonium ions (H_3O^+) which hinder the access of the metal ions to the surface functional groups. Consequently, the percentage of metal ion removal may decrease at low pH.

Sorption Equilibrium: The applicability of sorption processes as a unit operation can be evaluated using isotherm models. The equilibrium sorption data obtained were analysed in terms of the Langmuir and Freundlich equations. The data linearised to fit the Langmuir equation and presents the constants derived by regression analysis for the equation. A comparison of the Langmuir sorption capacity at various initial pH was made by plotting q_{max} (mg/g) against pH_{in}. The results confirmed that at pH 2 and 4, the sorption of Al^{3+} and Cr^{6+} on Terminalia catappa L. biomass was much less than at pH 6 and above, indicating that the Terminalia catappa L. biomass was much less effective sorbent at lower pH values. Hence, lowering the pH may aid the regeneration and recycling of spent biomass. The R^2 values suggested that the Langmuir isotherm provides a good model of the sorption system. The sorption coefficient, K_L, which is related to the apparent energy of sorption, was greater for Al^{3+} than for Cr^{6+} at all pH_{in}. The high values of K_L for Al^{3+} and Cr^{6+} at pH 2 and 4 respectively, indicate that the energy sorption is more favourable at these pH maxima than other pH values.

The linear Freundlich isotherm plots for the sorption of the two metals (Al^{3+} and Cr^{6+}) onto the Terminalia catappa L. biomass are presented. Examination of the plot suggests that the Freundlich isotherm is also an appropriate model for the sorption study of Al^{3+} and Cr^{6+}. Table below shows the linear Freundlich sorption isotherm constants and the coefficients of determination (R^2). Values of I/n for Al^{3+} and Cr^{6+} were found to be less than unity at all pH respectively, indicating that significant sorption could take place at these initial pH values. Confirmation of the pH_{max} was made by plotting the Freundlich equation parameter, I/n, which is a measure of the sorption intensity against pH_{in}. The plot further confirmed that, the pH maxima for the sorption of Al^{3+} and Cr^{6+} onto Terminalia catappa L. biomass are 2.0 and 4.0 respectively. Based on the coefficient of determination (R^2) values, the linear form of the Freundlich isotherm appears to produce a reasonable model for the sorption of the two metals, with Al^{3+} fitting the data better than Cr^{6+}. The K-values suggests that Al^{3+} has greater sorption tendency towards the Terminalia catappa L. biomass in neutral solutions. However, for Cr^{6+} the greater affinity towards active groups on the biomaterials was observed at pH 4.0.

Conclusion

In conclusion, the data has shown that, the sorption process of Al^{3+} and Cr^{6+} ions on to Terminalia catappa L. biomass is feasible and spontaneous in nature. The metal ions binding capacity of the biomass was shown as a function of initial pH of the aqueous solution. The equilibrium data fitted the Langmuir and Freundhich isotherms very well. The two models confirmed that maximum sorption capacity onto the biomass occurred at

pH 2.0 for Al^{3+} and pH 4.0 for Cr^{6+}. Thus efficient removal of the two metal ions in an effluent using *Terminalia catappa L.* biomass may require pH adjustment between 4.0 and 2.0. The equilibrium sorption of the two metal ions at their PH_{max} was determined from the Langmuir equation and found to be 85.50 mg/g and 82.60 mg/g for Al^{3+} and Cr^{6+} respectively. The data showed that, Terminalia catappa L. is a successful biosorbent for treating heavy metal contaminated wastewater and may serve as an alternative adsorbent to conventional means. Hence, not only is Terminalia catappa L. readily available, it also has the potential for metal removal and recovery from contaminated waters. This process will be environment 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. The pH study is particularly important for determining the ligands that may be involved in the reaction for optimization in the design of sorption process units.

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