

# Kinetic, Isothermal, and Thermodynamic Studies of the Biosorption of Ni(II) and Cr(III) from Aqueous Solutions by *Talinum triangulare* (Water Leaf).

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## ABSTRACT

The ability of *Talinum triangulare* (water leaf) to remove Ni (II) and Cr (III) from aqueous solutions through biosorption was investigated in batch experiments. pH dependence study of the biosorption process revealed that the best pH for Ni (II) and Cr (III) were 6 and 5, respectively. Kinetic experiments revealed that 0.3mM of nickel and chromium solutions attained equilibrium within 10 and 30 min respectively. The biosorption of metal ions exhibited pseudo-second-order kinetics. The adsorption data for Cr (III) fit well to the Langmuir isotherm model with R<sup>2</sup> value of 0.937. The reverse is the case with Ni (II) ion whose R<sup>2</sup> value showed a better fit with Freundlich isotherms. Maximum adsorption capacities for an initial metal ion concentration of 0.3 mM calculated from the Langmuir isotherm were 40 mg/g and 333.33 mg/g for chromium and nickel, respectively. Thermodynamic studies revealed that sorption of both metal ions onto *Talinum triangulare* were spontaneous. Change in enthalpy,  $\Delta H$ , values obtained were -13.03 and 18.71KJ/mol for Cr (III) and Ni (II), respectively. Corresponding change in entropy,  $\Delta S$  were -42.59 and 63.63 JK<sup>-1</sup>mol<sup>-1</sup>. These studies showed that *Talinum triangulare* is a viable biomass for the removal of Cr (III) and Ni (II) ions from aqueous solutions. The biosorption is spontaneous and further suggests that *Talinum triangulare* will be good for phyto-remediation.

(Keywords: biosorption, *Talinum triangulare*, pseudo-second-order, adsorption isotherms)

## INTRODUCTION

Heavy metal pollution in aquatic environment has become a source of great concern

(Rangsayatorn, 2004; Reed, 1998). This fear has been heightened in recent times due to advancements in technology (Sarin et al., 2006). Therefore the need to remove or at least reduce heavy metals to meet regulatory standards has become necessary (Matheickal and Yu, 1999).

Conventional methods for heavy metals removal from aqueous solutions include chemical precipitation, electrolytic recovery, ion exchange/chelation and solvent extraction/liquid membrane separation (Sarin et al., 2006; Rorrer, 1998). These methods are becoming undesirable due to their short comings which include high cost, limited tolerance to pH change, incomplete removal of metals, moderate or no metal selectivity (Eccles, 1999; Yan and Viraraghavan, 2001).

These disadvantages have therefore prompted the demand for economical alternative means to conventional processes for the removal of metals (Volesky, 1990). The new technology is based on the utilization of low cost biological materials as adsorbent of heavy metals in a process called biosorption (Gadd, 1992; Ahalya, 2003). This new technology is based on metal binding capacities of various biological materials (Volesky, 1986; Babarinde et al., 2008).

Wastewater containing nickel originates from the metal-processing industries, steel foundries, aircraft and motor vehicle industries, printing, and chemical industries (Eckenfelder, 1989; Williams and Edyvean, 1997). Whereas, chromium is generally found in electroplating and metal finishing industrial effluents, sewage and wastewater treatment plant discharge, and cooling water that often contains chromate additive (Manahan, 1991; Yun et al, 2001).

Although nickel is not considered to be toxic at low levels, like other pollutant metals, it accumulates in the food chain and once adsorbed into the body cannot be easily excreted (Williams and Edyvean, 1997). For chromium, the main oxidation states found in aquatic environment are the trivalent state and hexavalent oxidation state, which is more toxic (Evangelou, 1998). Trivalent chromium, Cr(III), is an essential element required for normal carbohydrate and lipid metabolism (Mertz, 1993). However as a toxin, it has been found to have mutagenic (Cheng and Dixon, 1998), carcinogenic (Shumilla et al., 1999) and teratogenic effects (Asmatullah et al., 1998).

Over the past few decades, many researchers have examined various biomaterials such as dead biomass of macro-algae (Axtell et al., 2003; Gupta et al., 2001), seaweed (Park et al., 2005; Yun et al., 2001; Williams and Edyvean, 1997), agricultural waste biomass (Zafar et al., 2006) and industrial waste biomass (Selvaraj et al., 2003) for the removal of chromium and nickel from aqueous solutions or wastewater. Some of these biomaterials have shown a good performance as adsorbents for chromium and nickel removal.

This study involves the use of *Talinum triangulare* (water leaf) to remove chromium (III) and nickel (II) from aqueous solutions containing these metals. Water leaf is a multi-ethnic weed common throughout the humid tropics. It has been documented for several countries in West and Central Africa (Fontem & Schippers, 2004).

The plant grows in abundance, in most cases it becomes a waste as it rot away when not used. It often grows as weed on land and as a result, alternative use for it has to be sought. Due to its high water content (90.8 g per 100 g of edible leaf) (Fontem & Schippers 2004), it is speculated that the plant would have the ability to biosorb heavy metals, which means that it could be grown on heavily polluted soil with the hope of absorbing water containing the toxic metal(s).

Investigations of the effects of pH, agitation time, biosorbent dose, and initial metal ion concentration on the biosorption of chromium (III) and nickel (II) ions by *Talinum triangulare* are therefore the objective of this study. The kinetics, equilibrium modeling, and the thermodynamics of the biosorption system are also investigated.

## MATERIALS AND METHODS

**Biosorbent:** The leaves of *Talinum triangulare* used for the experiments were collected from a farm within the campus of The University of Ibadan, Ibadan, Nigeria. The leaves were first washed in running tap water to remove debris and then rinsed with de-ionized water. The fresh leaves were oven dried and the dried samples were pulverized and subsequently sieved to about 150 sieve mesh size. The biosorbent obtained was then stored in an air tight polythene bag.

**Biosorption Experiments:** Batch studies carried out include, pH dependence, biosorbent dose dependence, time dependence and concentration dependence studies. All the batch studies except biosorbent dose study were carried out to yield a biosorbent-metal ion solution concentration of approximately 2 mg/ml, that is, 30 mg of biosorbent suspended in 15 mL of metal ion solution. These suspensions were shaken in a 250 mL plastic bottle on an electrical shaker at 200 rpm. Atomic Absorption Spectrometer (Thermo S Series) was employed in the analyses of the resulting supernatants obtained from centrifugation of the agitated metal ion suspension. Each experiment was done in duplicate.

Effect of pH on metal uptake was investigated by carrying out the study at different pHs (i.e., pH 2, 3, 4, 5, and 6) and at the temperature of 28°C. Concentrated solutions of nitric acid and sodium hydroxide were used to adjust the pH of the metal ion solutions. The metal solutions containing the biosorbent were thereafter agitated at 200 rpm for 2 hours.

Influence of biosorbent dosage was investigated using an initial metal ion concentration,  $C_0$  of 0.3 mM. Biosorbent masses used for the study were 10, 30, 50, 70, 90, and 110 g. The study was carried out at the temperature of 28°C and at the optimum pH values earlier determined for each metal. The agitation time for this experiment was set at 2 hours.

Effect of agitation time was studied by varying the agitation time. Time intervals chosen for the biosorption of chromium ion were 5, 10, 20, 30, 60, and 120 minutes. For the  $Ni^{2+}$  ion, time intervals chosen were 2, 6, 10, 20, 30, 60, and

120 minutes. The time dependent study was carried out at the temperature of 28°C.

The effect of initial metal concentration on biosorption was determined by using the pre-determined optimal pH, biosorbent dose and equilibration time for each metal ion at 25°C. Initial metal ion concentrations,  $C_o$  used for each metal were 0.1 mM, 0.3 mM, 0.5 mM, 0.75 mM, 1.0 mM, and 2.0 mM.

The thermodynamic studies were investigated by carrying out batch study at the optimal conditions and at different temperatures. The temperatures chosen for study were 15°C, 25°C, 37°C, and 50°C.

**Calculation of Metal Uptake:** The following relationship was used to determine the metal uptake by the biosorbent.

$$q = \frac{(C_o - C_e)V}{M_s} \dots\dots\dots(1)$$

where, q = quantity of metal adsorbed after equilibrium in mg/g;  $C_o$ = initial metal ion concentration after equilibrium in mg/ L;  $C_e$ = concentration of metal left after equilibrium in mg/ L; V= volume of metal ion solution in liters;  $M_s$ = mass of biomass used in gram.

The percentage metal uptake was also determined by the following equation:

$$X\% = 1 - \frac{C_o}{C_e} \times 100\% \dots\dots\dots(2)$$

where, X% = percentage metal removed.

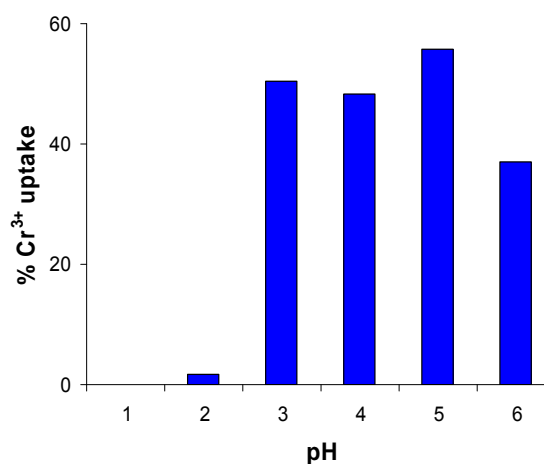
## RESULTS AND DISCUSSION

**Effect of pH:** It has been reported that pH affects the biosorption of metal ion from solution (Yin et al, 1999). The effects of pH on the percentage metal uptake by *Talinum triangulare* are shown in Figures 1 and 2.

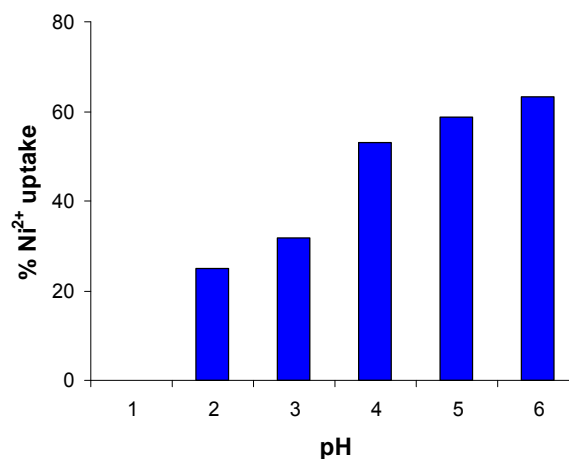
Biosorption of Cr (III) ion solution gave the best percentage removal of 55.67% at pH 5. The experiment was not performed beyond pH 6 because at higher pH, precipitation may occur and this may therefore interfere with the

biosorption process (Parvathi et al., 2006; Mahamadi et al., 2007). The least quantity of the metal ion removed occurred at pH 2. Eneida et al. (2002) have also reported a pH 5 for Cr (III) adsorption by *Sargassum* sp. biomass.

For the biosorption of nickel, gradual increase in pH resulted in an increase in the amount of Ni (II) ion removed from the solution by *Talinum triangulare*. pH 6 was observed as the optimum pH for the highest removal of Ni (II) ions from the aqueous solution as illustrated in Figure 2. pH 6 has also been reported for sorption of Ni (II) ions by protonated rice bran (Zafar et al., 2006).



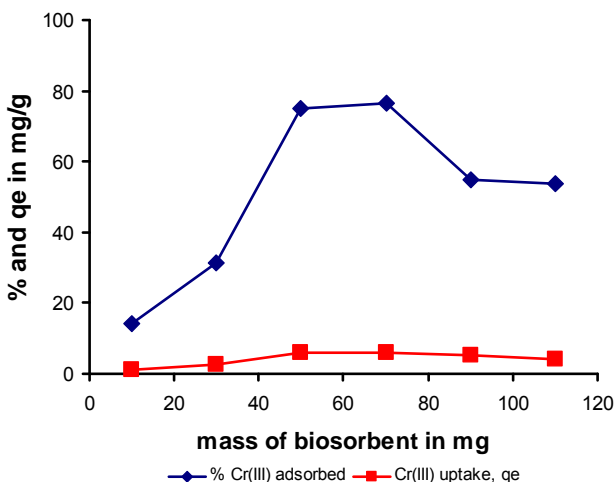
**Figure 1:** pH Dependent Profile of the Biosorption of Chromium by *Talinum triangulare* using 30 mg Biomass Dose, 120 minute Agitation Time, 0.3 mM Initial Metal Ion Concentration, and 28°C.



**Figure 2:** pH Dependent Profile of the Biosorption of Nickel on *Talinum triangulare* using 30 mg Biomass Dose, 120 minute Agitation Time, 0.3 mM Initial Metal Ion Concentration, and 28°C.

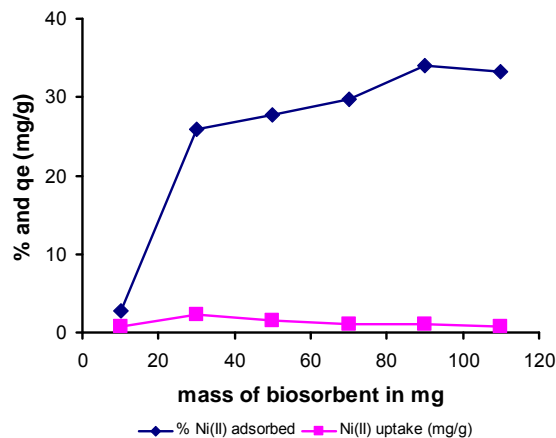
**Effect of Biosorbent Dose:** The relevant parameters used in this study are both the percentage metal removed (%) and amount of metal uptake,  $q_e$ . Figure 3, shows that the amount of Cr (III) ion removed,  $q_e$ , increased with biosorbent dose up to a dosing mass of 50 g and subsequently decreased. Whereas the percentage of Cr (III) removed increased with dosing mass up to 70 g and then decreased thereafter. A decrease in  $q_e$  with increase in mass could be linked to limited available binding sites (De Rome & Gadd, 1987).

Figure 4 shows the result of the study of the effect of mass dose of *Talinum triangulare* on the biosorption of Ni (II) ion. Like it is for Cr (III), the adsorption capacity of nickel increased from 0.72 to 2.28 mg/g for a mass increase from 10 g to 30 g. It subsequently decreased with increasing mass dose. This is similar to the result obtained from the study of biosorption of nickel by protonated rice bran (Zafar et al., 2006). On the other hand, the percentage nickel removed increased with mass dose from 2.74 % to 33.97 %. A decrease was only noticed for a dosing mass of 110 g.



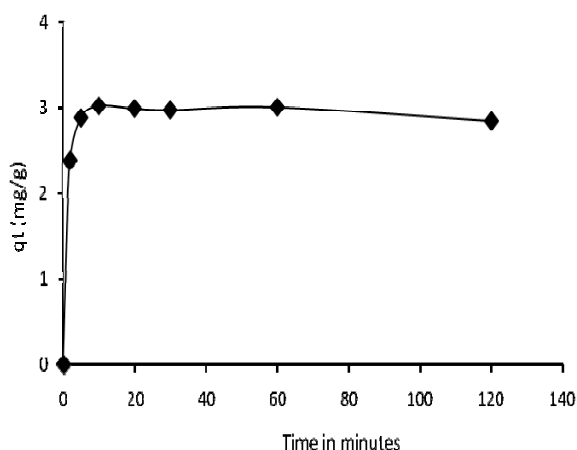
**Figure 3:** Effect of Biosorbent Dose on Biosorption of Cr (III) ion by *Talinum triangulare* using pH 5, 120 Minutes Agitation Time, 28° C, and 0.3 mM Initial Metal Concentration.

**Effect of Agitation Time:** For an initial metal ion concentration of 0.3 mM, it was observed that rapid metal uptake occurred within the first 10 minutes for Ni(II) ion (Figure 5).

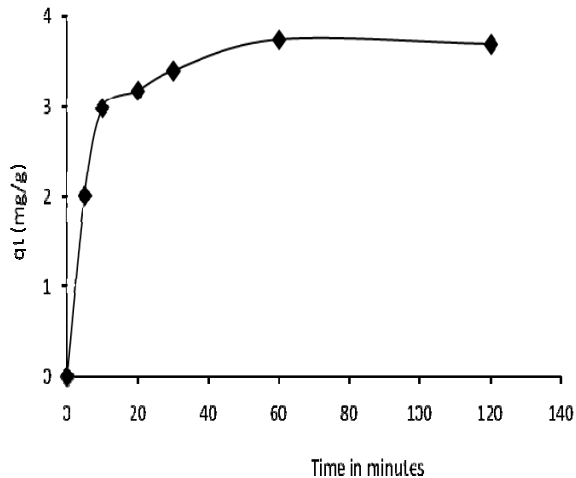


**Figure 4:** Effect of Biosorbent Dose on Biosorption of Ni (II) ion by *Talinum triangulare* using pH 6, 120 Minute Agitation Time, 28° C, and 0.3 mM Initial Metal Concentration.

For Cr (III) ion, metal uptake increased with increase in agitation time up to 60 min., after which equilibrium was attained (Figure 6). This study shows that the kinetics of chromium biosorption was faster than that of nickel. The observed fast biosorption kinetics for chromium is consistent with biosorption of metal involving non-energy mediated reactions, where metal removal from solutions is due to purely physico-chemical interaction between biomass and metal solution (Aksu, Z. 2001). This fast metal uptake from solution indicates that binding might have resulted from interactions with functional groups on the cell wall of the biosorbent rather than diffusion through the cell wall of the biomass.



**Figure 5:** Time Dependent Study of the Biosorption of Nickel by *Talinum triangulare* using 30 mg Biomass Dose, 28° C, 0.3 mM Initial Metal Concentration and pH 6.



**Figure 6:** Time Dependent Study of the Sorption of Chromium *Talinum triangulare* using 30 mg Biomass Dose, 28° C, 0.3 mM Initial Metal Concentration and pH 5.

**Kinetic Study Profiles:** In order to evaluate the kinetics of the sorption process data from the time study were fitted into the pseudo-first order and pseudo-second order models. Kinetic sorption of heavy metals from wastewater has been studied using mostly pseudo-first-order (Langergren, 1898) and pseudo-second-order (Ho and McKay, 2000) models.

**Pseudo-First-Order (Langergren, 1898) Model:**

The rate law is shown below:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \dots\dots\dots (3)$$

Where,  $q_e$  and  $q_t$  represent adsorption in mg/g at equilibrium and time,  $t$ , respectively. Integrating this expression between the boundary condition of  $t=0, t = t$  and  $q_t = 0, q_t = q_e$ , we obtain the linearized form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \dots\dots\dots (4)$$

where,  $k_1$  is the rate constant of pseudo-first order biosorption;  $q_e$  is the metal uptake in mg/g at equilibrium; and  $q_t$  is the metal uptake in mg/g at time,  $t$ .

A plot of  $\log(q_e - q_t)$  against  $t$  was made and values of  $k_1$  and  $q_e$  were obtained from the slope and intercept, respectively.

$q_e$  is pre-estimated by making a plot of  $q_t$  against time,  $t$ , which gives a parabolic curve whose  $q_t$  value plateau to  $q_e$  at infinite time  $t$ .

**Pseudo-Second-Order Model:** Its' rate law is shown below:

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

where,  $k_2$  is the rate constant of pseudo-second order biosorption.

On integrating between the boundary condition of  $t = 0, t = t$  and  $q_t = 0, q_t = q_e$ , we obtain the following expression:

$$\frac{q_t}{q_e(q_e - q_t)} = k_2 t \dots\dots\dots (6)$$

On linearizing, we have:

$$t/q_t = \left(\frac{1}{k_2 q_e^2}\right) + \left(t/q_e\right) \dots\dots\dots (7)$$

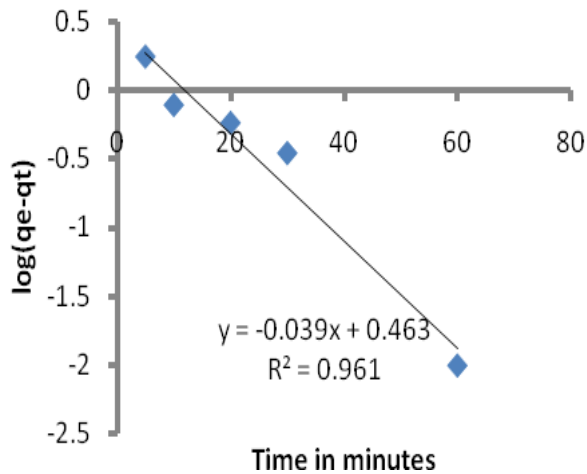
A plot of  $(t/q_t)$  against  $t$  gives  $(1/q_e)$  as slope and  $(1/k_2 q_e^2)$  as intercept from which  $k_2$  can be obtained. Both models are tested for suitability using their correlation of coefficient,  $R^2$  (Ho and McKay, 2000).

Figures 7 to 10 show the linear plots of pseudo-first and pseudo second order kinetics for the biosorption of Cr (III) and Ni(II) by *Talinum triangulare*. The values of the parameters,  $k_1, k_2$  and  $q_e$  obtained for pseudo-first and pseudo-second-order kinetics are presented in Table 1 and Table 2, respectively.

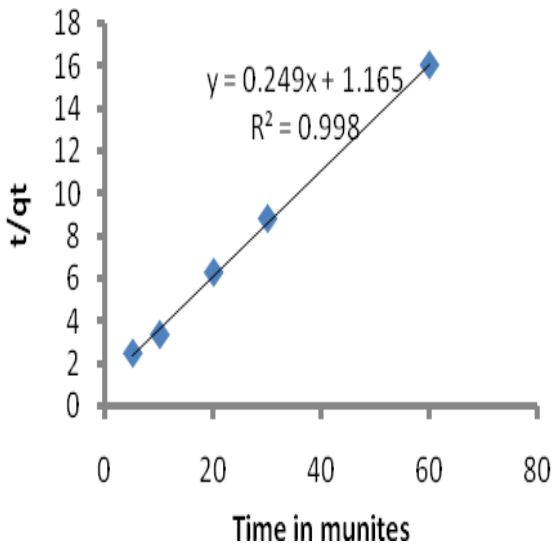
From the plots, it can be observed that chromium fits both the pseudo-first-order and pseudo-second order models with correlation coefficient ( $R^2$ ) of 0.998 and 0.961 respectively. The pseudo-second-order and the pseudo-first-order best fits kinetics for Ni(II) gave  $R^2$  value of 0.999 and 0.975, respectively.

From Table 2, the estimated values of  $q_e$  (calculated) are close to the  $q_e$  (experimental). All these point to the fact that second order kinetic best explain the observed rate, which means that the biosorption of the metal ions involves two species - the metal

ion and the biomass, and that the biosorption is the rate-limiting step (Wallace et al. 2003).

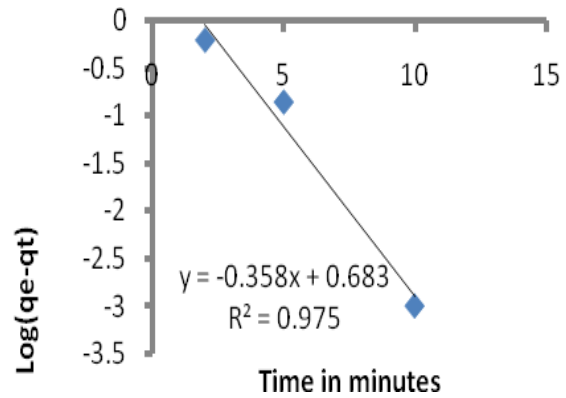


**Figure 7:** Pseudo-First-Order Graph for Sorption of Cr (III) ions by *Talinum triangulare*.

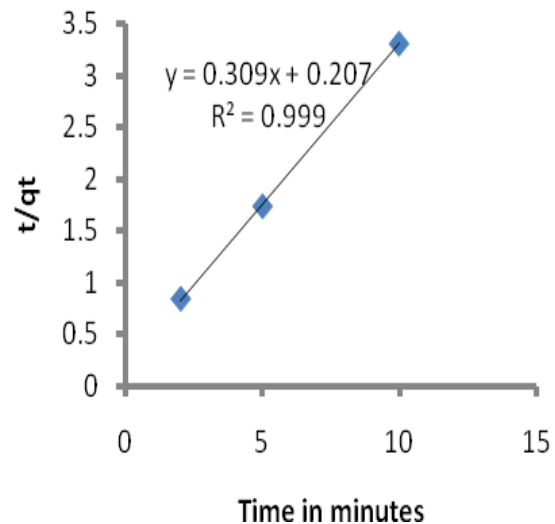


**Figure 8:** Pseudo-Second-Order Graph for Sorption of Cr (III) ions by *Talinum triangulare*.

**Thermodynamic Studies:** Thermodynamic studies were done by carrying out equilibrium studies at various temperatures to obtain corresponding values of  $C_a$  and  $C_e$  (Mckay and Ho, 1999).



**Figure 9:** Pseudo-First Order Graph for Sorption of Ni (II) ions by *Talinum triangulare*.



**Figure 10:** Pseudo-Second-Order Graph for Sorption of Ni (II) ions by *Talinum triangulare*.

From these values, equilibrium constant,  $K$  is calculated using the relationship:

$$K = \frac{C_a}{C_e} \dots\dots\dots (8)$$

where,  $C_a$  represents adsorption in mg/L at equilibrium;  $C_e$  is the equilibrium concentration of the metal in mg/L;  $K$  represents the thermodynamic equilibrium constant (Sarin et al., 2006).

**Table 1:** Pseudo-First-Order Constants for the Biosorption of Cr (III) and Ni (II) by *Talinum triangulare*.

Metal	$K_1$	$q_e(\text{calc})$	$q_e(\text{expt})$	$R^2$
Cr	0.090	2.90	3.75	0.961
Ni	0.824	4.82	3.02	0.975

**Table 2:** Pseudo-Second-Order Constants for the Biosorption of Cr (III) and Ni (II) by *Talinum triangulare*.

Metal	$K_2$	$q_e(\text{calc})$	$q_e(\text{expt})$	$R^2$
Cr	0.053	4.02	3.75	0.998
Ni	0.460	3.24	3.02	0.999

The Gibb's free energy  $\Delta G$  is related to the thermodynamic equilibrium constant by the following:

$$\Delta G = -RT \ln K \dots \dots \dots (9)$$

where,  $\Delta G$  is the Gibb's free energy in J/mole; R is the ideal gas constant whose value is  $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ; K represents the thermodynamic equilibrium constant; T is temperature in Kelvin.

In thermodynamics, the Gibb's free energy is related to the enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) at constant temperature by the following van't Hoff equations:

$$\ln K = -\left(\frac{\Delta G}{RT}\right) + \left(\frac{\Delta S}{T}\right) \dots \dots \dots (10)$$

$$\log K = -\left(\frac{\Delta H}{2.303RT}\right) + \left(\frac{\Delta S}{2.303T}\right) \dots \dots \dots (11)$$

where,  $\Delta H$  stands for enthalpy change in J/mol;  $\Delta S$  represents entropy change in  $\text{Jmol}^{-1}\text{K}^{-1}$ ;

The values of  $\Delta H$  and  $\Delta S$  are obtained from the slopes and intercepts, respectively, of the plot of  $\log K$  against  $1/T$  (Mckay and Ho, 1999).

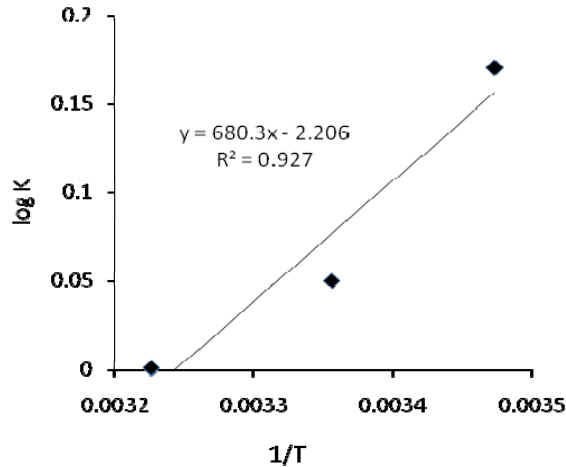
The results of the thermodynamic studies of the biosorption process are presented in Tables 3 and in Figures 11 and 12.

Cr (III) gave negative values for  $\Delta H$  and  $\Delta S$ . A negative enthalpy ( $\Delta H$ ) indicates that the adsorption process is exothermic. For chromium,  $\Delta G$  decreases in magnitude from -938.55 through -75.89 to -7.72 J/mol for the temperatures 288 K, 298 K and 310 K. The decrease in adsorption with rise in temperature may be due to weakening of adsorptive forces between the active sites of adsorbent and adsorbate species and also between the adjacent molecules of the adsorbed phase (Pandey et al., 1986). A negative change in entropy,  $\Delta S$ , indicates that the biosorption is stable, as there is increase in orderliness of the system, which is at the aqueous metal ion- solid biosorbent interface.

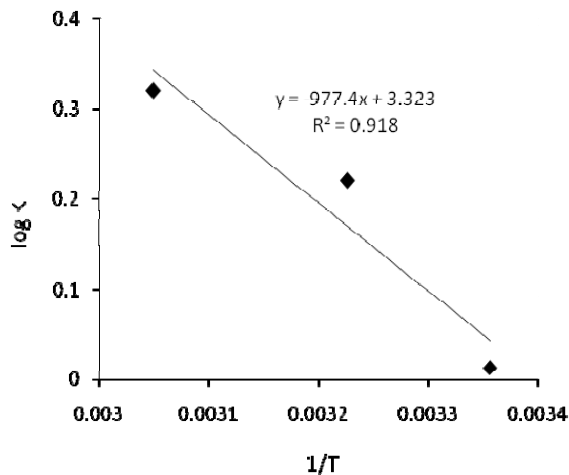
For nickel biosorption, an opposite trend was observed. Positive values of entropy ( $\Delta S$ ) and enthalpy ( $\Delta H$ ) were noticed. The change in Gibb's free energy,  $\Delta G$ , for nickel increase in magnitude for the temperature range 298 K, 310 K and 323 K (Table 3).

In general, negative values of  $\Delta G$  show the feasibility and spontaneous nature of the sorption of Cr (III) and Ni (II), on *Talinum triangulare*. A positive  $\Delta H$  indicates endothermic reaction. A positive change in entropy is an indication of increase in randomness at the solid-liquid interface during the adsorption of nickel and cadmium (Koby, 2003).

**Effect of Initial Metal-Ion Concentration:** As illustrated in Figure 13, the result of the study of the effect of initial metal ion concentration on the biosorption of Cr(III) and Ni(II) indicated that sorption capacity increased with increase in initial metal ion concentration for both metals on the biomass. This sorption characteristic indicated that surface saturation was dependent on the initial metal ion concentrations. At low concentrations, adsorption sites took up the available metal more quickly. However, at higher concentrations, metal needed to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate (Zafar et al., 2006).



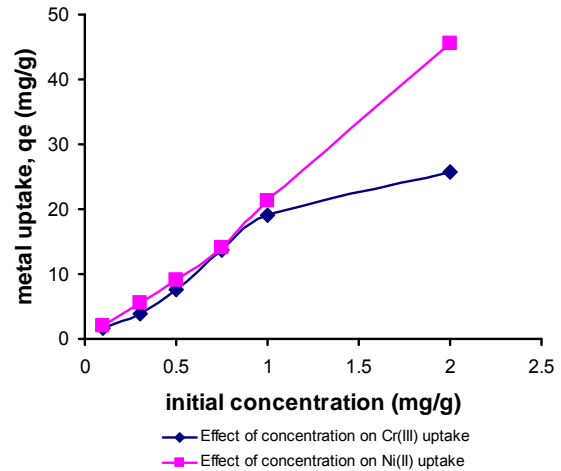
**Figure 11:** Thermodynamic Profile of Sorption of Cr (III) Ions by *Talinum triangulare* at 30 mg Dose, pH 5, 60 Minute Agitation Time, and 0.3 mM Initial Metal Ion Concentration.



**Figure 12:** Thermodynamic Profile of Sorption of Ni (II) Ions by *Talinum triangulare* at 30 mg Dose, pH 6, 10 Minute Agitation Time, and 0.3 mM Initial Metal Ion Concentration.

**Equilibrium Modeling:** The equilibrium of the biosorption process is often described by fitting the experimental points with models which are used to represent the equilibrium adsorption isotherm (Gadd, et al., 1988).

The simplest forms of these terms are Langmuir and Freundlich isotherms. Both isotherms are described based on physical interactions of adsorption and desorption. Other models are more empirical in form, only formulated to give a fitting for experimental data (Muhamad, 1998).



**Figure 13:** Effect of Chromium and Nickel Concentration on Biosorption by *Talinum triangulare*.

**Langmuir Model:** It is represented by the expression below (Langmuir, 1918);

$$q_e = \frac{(q_{\max} K_L C_e)}{1 + K_L C_e} \dots \dots \dots (12)$$

where,  $C_e$  is the equilibrium solute concentration in the fluid (mg/L or mM);  $K_L$  represents Langmuir equilibrium adsorption constant ( $L/mg$  or  $mM^{-1}$ );  $q_{\max}$  is the Langmuir maximum metal uptake in (mg/g);  $q_e$  is metal uptake in (mg/g)

The linearized form of Equation (12) is:

$$\frac{1}{q_e} = \frac{1}{q_{\max} K_L} \left( \frac{1}{C_e} \right) + \frac{1}{q_{\max}} \dots \dots \dots (13)$$

A plot of  $1/q_e$  against  $1/C_e$  gives a straight line plot with a slope of  $(1/q_{\max} K_L)$  and an intercept of  $1/q_{\max}$ . Langmuir model essentially describes monolayer kind of adsorption. Its advantages hinge on the availability of interpretable parameters. However it is limited in application and can only be applied to monolayer type adsorption (Langmuir, 1918).

**Freundlich Model:** Freundlich model is also an empirical equation like Langmuir model. It is used to estimate the adsorption intensity of sorbent towards the adsorbate and is given by the equation (Freundlich, 1907):



$$q_e = K_F C_e^{1/n} \dots \dots \dots (14)$$

where,  $q_e$  is metal uptake in (mg/g);  $C_e$  is the equilibrium solute concentration in the fluid (mg/L or mM);  $n$  represents Freundlich constant (dimensionless). It is related to adsorption intensity;  $K_F$  is Freundlich adsorption constant related to adsorption capacity.

Linearizing Equation (14) we obtain Equation (15) below:

$$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log K_F \dots \dots \dots (15)$$

A plot of  $\log q_e$  against  $\log C_e$  gives a straight line graph with  $(1/n)$  as slope and  $\log K_F$  as intercept.

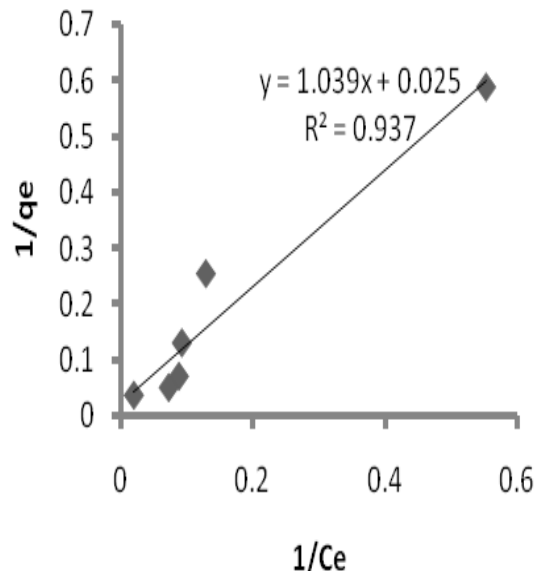
The corresponding constants and coefficients of correlation ( $R^2$ ) associated with each linearized models of Langmuir and Freundlich adsorption isotherms at 25°C for each of Cr (III) and Ni (II) ions are presented in Table 4.

Figures 14 to 17 show the graphs of the linearized Langmuir and Freundlich adsorption isotherms at 25°C.

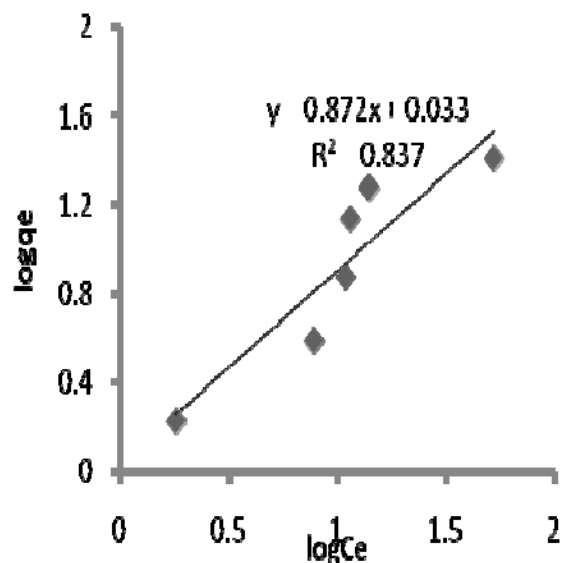
The result showed that Langmuir isotherm fits Cr (III) ion biosorption by *Talinum triangulare*. Although both models are suitable to describe the biosorption of Ni (II) ion, the biosorption process fits the Freundlich adsorption isotherm better than the Langmuir isotherm.

Metal	$q_m$ (mg/g)	$K_L$ (L/g)	$R^2$	$K_f$	$n$	$R^2$
Ni (II)	333.3	0.003	0.989	1.005	1.073	0.995
Cr (III)	40.00	0.024	0.937	1.079	1.147	0.837

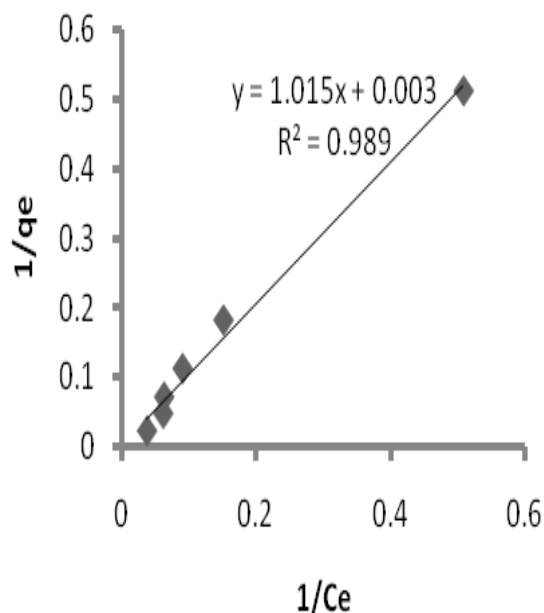
**Table 4:** Langmuir and Freundlich Adsorption Constants Associated with the Adsorption of Ni (II) and Cr (III) by *Talinum triangulare* at 25°C.



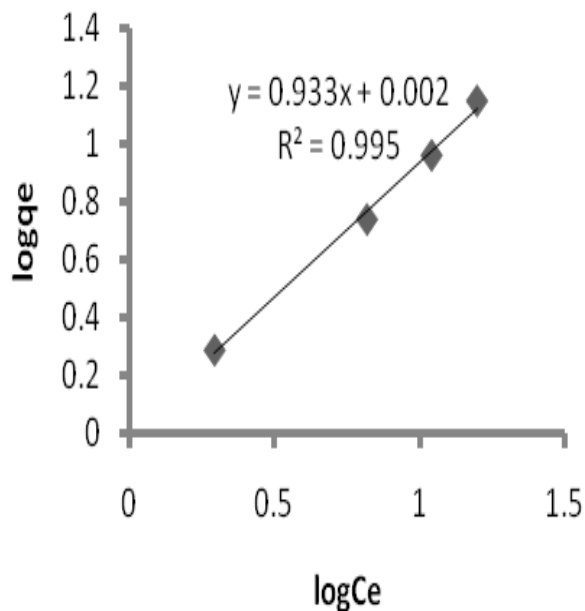
**Figure 14:** Langmuir Isotherm for Sorption of Cr (III) ions by *Talinum triangulare*.



**Figure 15:** Freundlich Isotherm for Sorption of Cr (III) ions by *Talinum triangulare*.



**Figure 16:** Langmuir Isotherm for Sorption of Ni (II) ions by *Talinum triangulare*.



**Figure 17:** Freundlich Isotherm for Sorption of Ni (II) ions by *Talinum triangulare*.

## CONCLUSIONS

This study showed that dried leaves of *Talinum triangulare* can efficiently remove both chromium and nickel ions from aqueous solution. It also showed that the biosorption process was pH, time, biomass dosage and concentration dependent.

Comparing the kinetics of the two metal ions, the binding of Cr (III) ion to *Talinum triangulare* occurs within 10 min. of contact, which means the kinetics of the reaction was very fast compared to that of Ni (II) in which the adsorption equilibrium was not reached until after 60 min.

Both pseudo-first-order and pseudo-second-order models are suitable to describe the kinetics of the reaction. However the kinetics of the biosorption process for the two metals can be better described by pseudo-second-order model.

The negative values of  $\Delta G$  for the two metal ions show that the biosorption process is feasible and spontaneous. Enthalpy change for chromium biosorption is exothermic while that of nickel biosorption is endothermic. Biosorption equilibrium data for chromium fit well to Langmuir model, while those of nickel fit well to Freundlich model.

**Table 3:** Thermodynamic Parameters for the Biosorption of  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$  by *Talinum triangulare*.

Metal ion	$\Delta H^\circ$ ( $\text{kJmol}^{-1}$ )	$\Delta S^\circ$ ( $\text{kJK}^{-1}\text{mol}^{-1}$ )	$\Delta G^\circ$ ( $\text{kJmol}^{-1}$ )			
			$T_1=288\text{K}$	$T_2=298\text{K}$	$T_3=310\text{K}$	$T_4=323\text{K}$
$\text{Cr}^{3+}$	-13.03	-42.59	-938.55	-34.38	-7.72	-1146.00
$\text{Ni}^{2+}$	18.71	63.63	-1389.07	-74.18	-1315.93	-1985.23

In general, this study shows that *Talinum triangulare* will be a good biosorbent for the removal of chromium and nickel from wastewater.

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