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Isotherm and Thermodynamic studies on Biosorption of Metal (II) Ions from Aqueous Solution using *Calopogonium muconoides* (Calopo) Seed Pod

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ABSTRACT

The potential of *Calopogonium muconoides* seed pods for adsorption of Pb(II), Ni(II) and Cd(II) ions from aqueous solution was investigated in a batch adsorption mode. Various physicochemical parameters such as pH, dosage, concentration and temperature were studied. The adsorbent studied exhibits high efficiency for the metal ions adsorption. The equilibrium adsorption data fitted into the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The coefficients of determination of the four models were high with Dubinin-Radushkevich providing best data description for the adsorption of the metal ion onto activated *Calopogonium muconoides* seed pod powder. The maximum adsorption capacity of Ni(II), Pb(II), and Cd(II) are 43.103 mg/g, 42.373 mg/g and 32.33 mg/g respectively. Also these heavy metal ions showed maximum adsorption at pH 6. Different thermodynamic parameters, including Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for the adsorption process have also been evaluated. The negative value of ΔG indicates the feasibility and spontaneous nature of the process. The positive value of ΔH for the system confirms the endothermic nature of adsorption. The positive value of ΔS observed for the adsorption of metal ion molecules suggested the increased randomness at the solid-solution interface during adsorption process. These results indicated that the biosorbent studied was found to be a promising alternative for the adsorption of Pb(II), Ni(II) and Cd(II) ions from aqueous solution. The affinity of the adsorbent for the metal ions also follows the trend Ni(II) > Pb(II) >Cd(II). Therefore, *Calopogonium muconoides* is a promising adsorbent for adsorption of Ni(II), Pb(II) and Cd(II) ions.

Keywords: Biosorption, *Calopogonium muconoides*, Equilibrium, Metal (II) ions, Thermodynamics

INTRODUCTION

Discharge from industry contains various organic and inorganic pollutants. Among these pollutants are heavy metals which can be toxic and/or carcinogenic and which are harmful to humans and other living species (Renge *et al.*, 2012). The heavy metals of most concern from various industries include Lead (Pb), Zinc (Zn), Copper (Cu), Arsenic (As), Cadmium (Cd), Chromium (Cr), Nickel (Ni) and Mercury (Hg) (Mehdipour *et al.*, 2015). They originate from sources such as metal complex, dyes, pesticides, fertilizers, fixing agents (which are added to dyes to improve dye adsorption onto the fibres), mordant's, pigments and bleaching agents (Rao *et al.*, 2010).

Cadmium has no essential biological function and is extremely toxic to humans due to its accumulation in the kidney and the liver. Cadmium accumulates in the human body affecting negatively several organs: liver, kidney, lung, bones, placenta, brain and the central nervous system (Castro & Méndez., 2008; ATSDR, 1993). Nickel in human is carcinogenic in nature and causes kidney and lung problems, gastrointestinal distress, skin dermatitis and pulmonary fibrosis (Borba *et al.*, 2006)**.** Similarly, lead is harmful to human health and can damage kidney, liver, reproductive system and brain functions. Developing central nervous systems of children may be affected, leading to hyperactivity, irritability, headaches, and learning and concentration difficulties (Davies, 1995).

Various conventional treatment technologies employed for the removal of heavy metals include chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultrafiltration, electrodialysis and adsorption (Fu and Wang, 2011). Among these methods, adsorption is the most efficient as the other techniques have inherent limitations such as the generation of a large amount of sludge, low efficiency, sensitive operating conditions and costly disposal. For these reasons, adsorption technology has gained a wider application due to its inherent low cost, simplicity, versatility, robustness and ability to easily regenerate spent adsorbent (Gottipati and Mushra, 2012)

Low cost adsorbents derived from agricultural by-products and industrial solid wastes could be used to remove recalcitrant wastes from synthetic wastewater. A number of agricultural wastes like, hazelnut shells, orange peels, maize cobs, peanut shells, soybean hulls, jack fruit, soybean hulls in natural or modified forms has been explored and significant removal efficiency was reported (Dhiraj *et al*., 2008).

This study seeks to propose a mechanism for the adsorption through thermodynamics and isotherm models of agricultural by product *Calopogonium muconoides* (Calopo) seed pod powder in the removal of heavy metal ions from aqueous medium.

MATERIALS AND METHODS

Materials

All the reagents used were of analytical grades from Merck and were used without further purification. Double de-ionized water was used in the preparation of all sample solutions. Stock solutions of 1000 mg/L of each of the metal ions Cd(II), Pb(II) and Ni(II) used for the adsorption study were prepared from the salt of the individual ions. From the stock solutions, various working concentrations of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/Land 50 mg/L of each of the metal ions were prepared by serial dilution.

Preparation of the Adsorbent

The biomass, *Calopogonium muconoides* seed pod was obtained at Michael Okpara University of Agriculture, Umudike, Abia state Nigeria. The pods were carefully removed, washed with de-ionized water, dried and crushed with a blender. The crushed samples were sieved through to obtain 180 µm mesh size. The sieved samples were soaked in 0.3 M HNO_3, stirred for 30 min and left undisturbed for 24 h. They were then filtered through Whatman no. 41 filter paper and rinsed thoroughly with de-ionized water and sundried for 2 h. The adsorbent was kept in an oven at 105 ºC for 1 h and finally stored in a tight plastic container. The treatment of the adsorbent with 0.3 M HNO_3 helps in the removal of debris or soluble biomolecules that might interact with the metal ions during sorption (Onwu *et al*., 2014).

Adsorption Experiments

Batch adsorption studies of Ni(II), Cd(II) and Pb(II) ions onto *Calopogonium muconoides* seed pod were investigated as a function of dosage, initial metal ion concentrations and temperature at a temperature of 30 ^oC and metal ion concentration of 50 mg/L. The pH of the solutions was adjusted to 2, 4, 6, 7 and 8 using 0.1 M HCl or 0.1 M NaOH solutions as the case may be. Exactly 50 mL of each metal ion solution of different pH were introduced into 250 mL Erlenmeyer flasks containing 0.05 g of the adsorbent. The mixture was agitated intermittently for 1 h in a thermostated shaker and then filtered. The metal ion content of each filtrate was finally determined using Atomic Absorption Spectrophotometer (Perkin Elmer Analysit 200) (Toreb-Motaedi *et al.,* 2010).

Effect of Initial Metal Ion Concentration on the study

The isotherm studies were investigated by studying the influence of initial metal ion concentrations on the equilibrium sorption of the metal ions by *Calopogonium muconoides* seed pod. It involves introducing 50 mL of various concentrations (10, 20, 30, 40 and 50 mg/L) of the metal ions into 250 mL Erlenmeyer flasks containing 0.05 g of the adsorbent of particle size 180 µm while maintaining temperature and pH at 30 ^oC and 6.0 respectively. The flasks were agitated intermittently for 1 hr and at the end of the contact time, the mixture filtered and the residual concentrations determined using AAS (Longzhe *et al*., 2010).

Effect of Adsorbent Dosage on the study

The effect of dosage on equilibrium adsorption of the Pb(II), Cd(II) and Ni(II) ions by the adsorbent was carried out by introducing different adsorbent doses of 0.05 g, 0.10 g, 0.15 g, 0.20 g, and 0.25 g into each 20 mL metal ion solutions of concentration 50 mg/L ions into 250 mL Erlenmeyer flasks containing the different masses of the adsorbent while maintaining temperature and pH at 30 ^oC and 6.0 respectively. The flasks were agitated intermittently for 1 h and at the end of the contact time, the mixture filtered and the residual concentrations determined using Atomic AAS (Chaouch *et al*., 2013).

Effect of Temperature on the study

The procedure was carried out for temperature studies but at various temperatures of 303 K , 313 K , 323 K, 333 K and 343 K under the same working conditions. The procedure was carried out in triplicates and mean residual concentration of each metal ion taken. The amount adsorbed (mg/g) was calculated from the average residual metal ions in solution after adsorption (Vijaya *et al.,* 2008).

DATA ANALYSIS

The amounts of Ni(II), Cd(II) and Pb(II) ions adsorbed by the adsorbents during the batch adsorption studies were determined using a simplified mass balance equation (1);

$$q_e = C_o - C_e \text{ x } \frac{V}{m} \quad (1)$$

The percentage adsorption of the metal ions by the adsorbent was evaluated using equation (2);

$$\% \text{ R} = \frac{C_o - C_e}{Co} \; x \; \frac{100}{1} \quad (2)$$

Where % R = percentage of the metal ion adsorbed, q_e is equilibrium sorption capacity (mg/g), C_o and

C_e are the initial and equilibrium or residual concentration of metal ions in mg/L, V is the volume of adsorbate solution in L and m is the dry mass of the adsorbent in g.
(Dermibas *et al.*, 2004).

RESULTS AND DISCUSSION

Effect of Adsorbent

The effect of dosage on Ni(II), Cd(II), Pb(II) ions removal was studied by varying the adsorbent dose (0.05 g, 0.10 g, 0.15 g, 0.20 g, 0.25 g and 0.30 g) at 50 mg/L metal ions concentration , constant equilibrium time and 30 ^{o}C temperature. It can be seen that adsorbent dose is another important parameter that determines the percentage removal of metal ions from aqueous solutions. From Figure 1, the % removals of metal ions decrease with increase in the adsorbent dosage. This may be attributed to the aggregation of adsorbent particles at a high dosage, which reduces the total surface area of the adsorbent and results in an increase in the diffusions path length (Shukla *et al.*, 2002).

However, the decrease in adsorption capacity with increase in adsorbent dose is due to the smaller availability of the exchangeable sites or surface area at higher concentration of the biosorbent. This trend implies that at constant initial metal ion concentration, it is expected that the amount of adsorbent may decrease with biosorbent dose if the mass of the adsorbent used is not enough to adsorb all the metal ions. As the biosorbent dose increases, it reaches a point when the masses of biosorbent used is in excess of the initial concentration, hence there will be no appreciable decrease in the amount of adsorbent. Similar result was reported by Abole- Ghani and Henfy (2007).

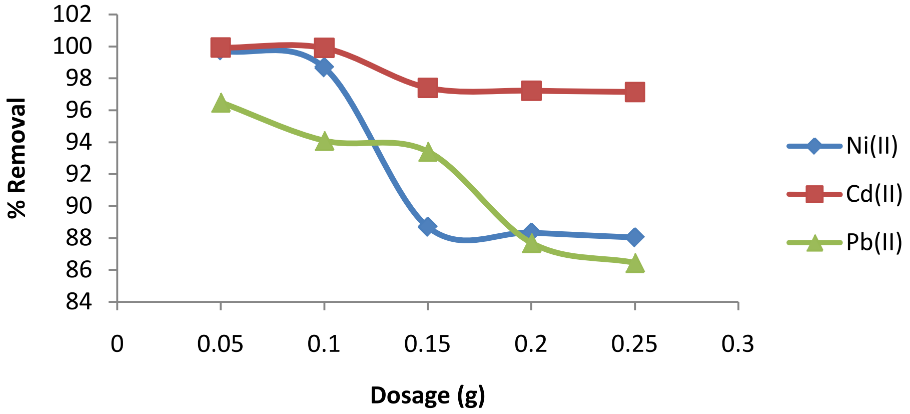

Figure 1: Effect of adsorbent dose on the adsorption of metal ions onto *Calopogonium muconoides* seed pods

Effect of Initial Metal ion Concentration

The rate of sorption of metal ions was determined by contacting (10, 20, 30, 40 and 50 mg/L) of the metal ion solution (pH 6.0) with 0.05 g/L of the adsorbent for contact time of 1 hr, the adsorption capacities (qe) are given in Figure 2. The adsorption quantity increased with an increase in the initial concentration until 50 mg/L concentration where equilibrium was reached. At that saturation point, the rate of adsorption becomes equal to the rate of desorption at 100 mg/L and above. However, the increase in the initial metal ion concentration caused an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass at a high initial metal concentration (Salleh *et al.*, 2011). In other words, the residual concentration of metal ions will be higher for higher initial metal ion concentrations. However, under lower concentrations, the ratio of the initial number of metal ions to the available adsorption sites is low, hence, the fractional adsorption does not dependent on the initial concentration accordingly (Hayati and Mahmoodu, 2012).

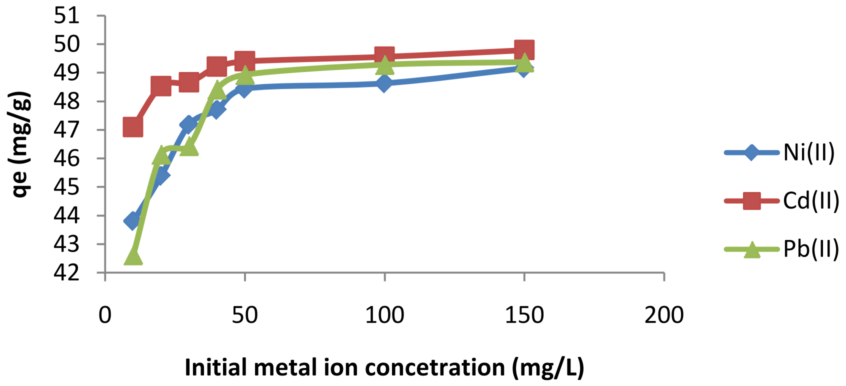

Figure 2: Effect of initial metal ions on the adsorption of metal ions onto *Calopogonium muconoides* seed pods

Equilibrium Isotherm Modelling.

Adsorption properties and equilibrium parameters, commonly known as adsorption Isotherms, describe how the adsorbate interacts with adsorbents and comprehensive understanding of the nature of interaction. Isotherm helps to provide information about the optimum use of adsorbents. There are several isotherm equations available for analyzing experimental sorption equilibrium parameters. In this study, the various adsorption processes were evaluated using the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models.

Langmuir Isotherm Model

Langmuir (1918) proposed a theory to describe the adsorption of gas molecules onto metal surface. The Langmuir adsorption isotherm has found successful application to many other real sorption processes of monolayer adsorption. Langmuir's model of adsorption depends on the adsorption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. It is assumed that once a metal ion occupies a site, no further adsorption can take place at the site. Moreover, the Langmuir equation is based on the assumption of a structurally homogenous adsorbent where all sorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the adsorbate. Therefore, a saturation value reached beyond which no further sorption can take place. The saturated or monolayer capacity can be represented by the expression:

$$\frac{Ce}{qe} = \frac{1}{Qob} + \frac{Ce}{Qo} \qquad 3$$

Where Q_o is a constant which signifies the adsorption of the monolayer capacity of the adsorbent (mg g^{-1}). b is the Langmuir constant related to the adsorption energy (dm^3 mg^{-1}).

The plot of Ce/qe vs Ce gives a straight line with a linear regression coefficient of 0.9979, 0.9988 and 0.8187 for Pb(II), Ni(II) and Cd(II) ions respectively. From the intercept and slope of such plot, constants Q_o and b were evaluated. A dimensionless equilibrium parameter, R_L can express the essential characteristics of Langmuir isotherm:

$$R_L = \frac{1}{1+bCo} \qquad 4$$

The value of R_L indicate the type of Isotherm to be either irreversible ($R_L = 0$) favourable ($0 < R_L < 1$); linear ($R_L = 1$); or unfavourable ($R_L > 1$). In the present study, the value of R_L as shown in the Table 1 are unfavourable adsorption isotherm to Pb(II), Ni(II) and Cd(II) ions. However, the correlation coefficients values suggest that Langmuir isotherm could interpret the experimental data.

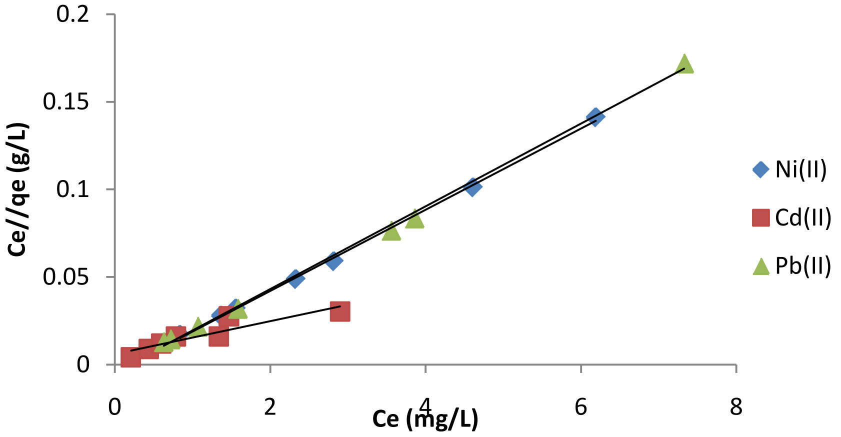

Figure 3: Langmuir isotherm plot of Ce/qe vs Ce for the adsorption of the metal ions onto *Calopogonium muconoides* seed pods

Freundlich Isotherm Model

The Freundlich (Freundlich 1906) equation encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. This isotherm is another form of Langmuir approach for adsorption on an "amorphous" surface. The Freundlich equation predicts that the metal ion concentration on the adsorbent will increase so long as there is an increase in the metal ion concentration in the liquid. The empirical equation employed by Freundlich to describe heterogeneous system, in which it is characterized by the heterogeneity factor 1/n can be written:

$$qe = K_F C_e^{1/2} \qquad 5$$

The linearised form is:

$$log\ qe = log\ K_F + \frac{1}{n}\ log\ Ce \qquad 6$$

where K_F the Freundlich constant (L/g) and 1/n the heterogeneity factor were determined from a plot of log Ce vs log qe (Figure 4). The Freundlich constants are presented in Table 1. Where qe is solid phase sorbate concentration in equilibrium (mg/g), Ce is liquid phase sorbate concentration in equilibrium (mg/L). The values of n are greater than 1.0 indicating the adsorption metal ions on the *Calopogonium muconoides* seed pods is favourable. There is a remarkable difference in the correlation coefficient between Freundlich and Langmuir models. The adsorption data did not fit well for Freundlich models as is in Langmuir models.

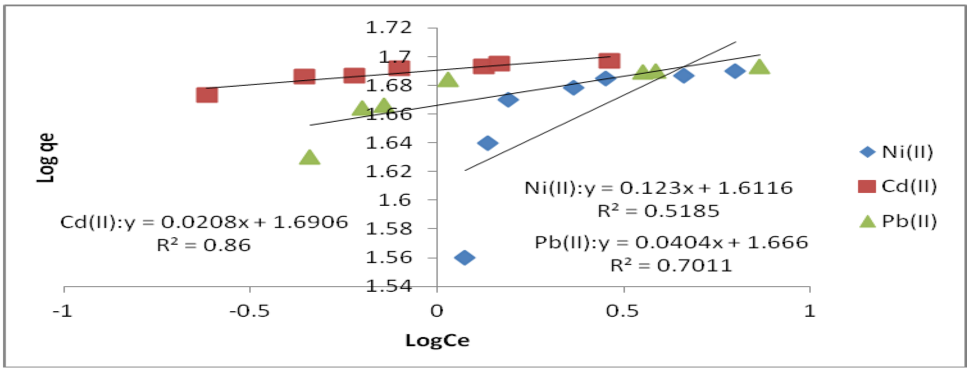

Figure 4: Freundlich isotherm plot for the adsorption of the metal ions onto *Calopogonium muconoides* seed pods

Dubinin-Radushkevich (D-R) Isotherm Model

The Dubinin-Radushkevich (D-R) isotherm model describes the adsorption on a single uniform pore. The D-R model was applied to the equilibrium data to assess the nature of the adsorption process, i.e.; whether it is physical or chemical adsorption. The Dubinin-Radushkevich isotherm is generally expressed as follows (Subha and Namasivayam, 2009):

$$qe = q_D\ e^{-}\ B_D \varepsilon^2 \qquad 7$$

The linear form of D-R isotherm equation is represented as:

$$ln\ qe = In\ q_D - B\varepsilon^2 \qquad 8$$

$$\text{Where } \varepsilon = RT\ In\ (1+\frac{C0}{Ce}) \qquad 9$$

Where q_D is the theoretical saturation capacity (mol/g), B is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2), E is the Polanyi, R = 8.314 (J/mol/k) is the gas constant and T (K) is the absolute temperature. The D-R constants q_o and B were calculated from the linear plot of *In*qe versus ε^2 Figure 4 and their constants presented in table 1. The constant B gives an idea about the mean free energy E (KJ/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the following relationship;

$$E = \frac{1}{\sqrt{2B}} \qquad 10$$

The adsorption process is physisorption when the energy of activation is 5 to 40 kJ/mol and chemisorptions when the energy of activation is 40 to 800 kJ/mol (Chen and Chen, 2009). From Table 1, it was suggested that the adsorption of the metal ions by the adsorbent is chemisorption in nature. Therefore, D-R isotherm could not as much describe the experimental data as Langmuir isotherm judging by their variations in correlation coefficients.

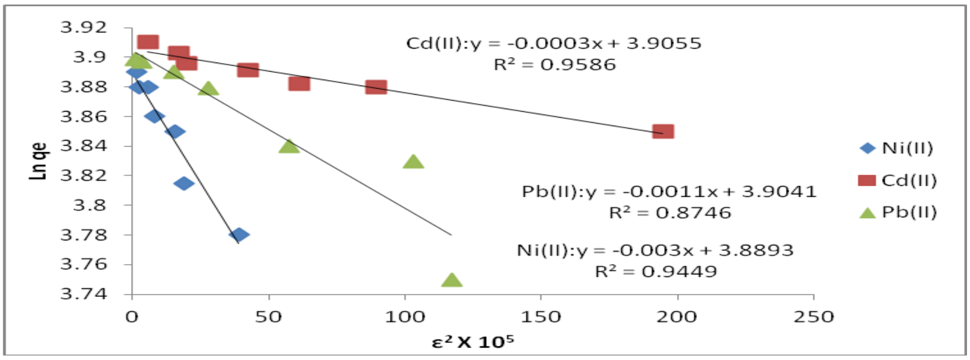

Figure 5: Dubinin-Radushkevich isotherm plot for the adsorption of the metal ions onto *Calopogonium muconoides* seed pods

Temkin Isotherm Model

Temkin adsorption isotherm was used to evaluate the adsorption potential of the metal ions for Muconoides seed pods. The derivation of the Temkin isotherm assumes that the fall in heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been applied in the following form (Wang and Qin, 2005).

$$q_e = RT/b\ln(AC_e) \qquad 11$$

The Temkin isotherm equation (11) can be simplified to the following equation:

$$q_e = \beta\ \ln \propto + \beta\ In\ C_e \qquad 12$$

The adsorption data were analyzed according to the linear form of the Temkin isotherm equation 12. A plot of q_e vs In C_e gives a straight line as shown in Figure 5 with a slope of β and intercept of β ln $\propto$. The parameters $\propto$ and β are presented in Table 1, Where β = (RT)/b, T is the absolute temperature in Kelvin and R is the universal gas constant 8.314 (J/mol/k). The constant b is related to the heat of adsorption (Akkaya and Ozer, 2005). The data shows that the Temkin isotherm did not fit well with Ni(II), Pb(II) and Cd(II) ions adsorption for the *Calopogonium muconoides* seed pods. The correlation coefficient R^2 obtained from Temkin model as shown in Table 1 depicts non applicability of this model in the explanation of these adsorption processes.

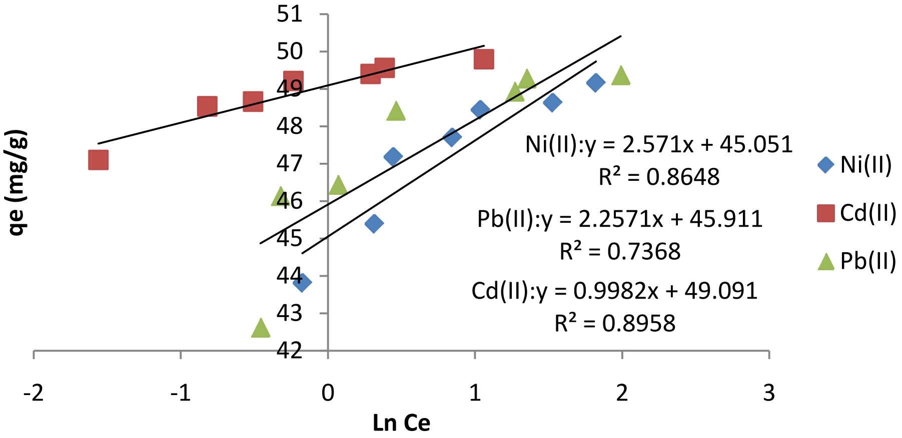

Figure 6: Temkin isotherm plot for the adsorption of the metal ions onto *Calopogonium muconoides* seed pods

Effect of Temperature on the Adsorption Process

The influence of temperature on the equilibrium adsorption capacity for the metal ions by the adsorbents was studied at 30 ^{0}C, 40 ^{0}C, 50 ^{0}C, 60 ^{0}C, 70 ^{0}C and 80 ^{0}C. From Figure 7, it is observed that adsorption decreased as the temperature increased. Houwing and Salomon (1965) had stated that physisorption usually decreases with increase in temperature while chemisorptions increases as the temperature is increased suggesting that the bonding of the metal ions to the adsorbents in our study could be physical adsorption. The decrease in adsorption capacity with increasing temperature for the adsorption of the metal ions onto *Calopogonium muconoides* seed pods could have resulted from any of the following: increase in the relative escaping tendency (desorption) of the metal ions from the adsorbent phase to the bulk phase, deactivating the adsorbent surface, or destructing some sites on the adsorbent phase due to weakening of the bond (Meena *et al.*, 2005) or due to the weakening of attractive forces between the active sites of the sorbents and the adsorbate species and also between the adjacent molecules of the sorbed phase (Ahmet and Mustafa, 2008). This weakening of attractive forces may have caused the adsorbate (metal ions) to detach from the adsorbent surface into the solution phase. The plots for variation of temperature with sorption capacity, qe are shown in Figure 7.

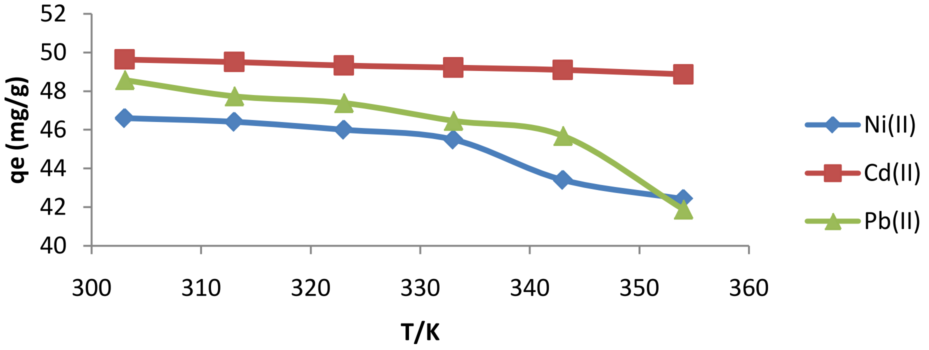

Figure 7: Plot of sorption capacity (qe) vs temperature for adsorption of the metal ions onto *Calopogonium Muconoides* seed pod

Thermodynamics of Adsorption

Thermodynamic parameters like ΔG, ΔS, and ΔH were calculated from van't Hoff theory derivation (equation 13) plot:

$$InK = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R} \qquad 13$$

Where K is rate constant, the value of ΔH and ΔS are calculated from the slope and intercepts of the linear plot of InK Vs $\frac{1}{T}$ are shown in Figure 8.

The free energy of specific adsorption ΔG (kJmol^{-1}) is calculated from the following expression:

$$\Delta G = \Delta H - T\Delta S \qquad 14$$

The negative value of ΔG (Table 2) indicates the feasibility of the process and its spontaneous nature. If adsorption takes place spontaneously then the free energy diminishes during the process so that ΔG° must have a negative value. The positive value of ΔH for the system confirms the endothermic nature of adsorption. The positive value of ΔS observed for the adsorption of metal ion molecules suggested the increased randomness at the solid-solution interface during adsorption process. The metal ions in the aqueous media are hydrated. When the metal ion molecule get adsorbed on the adsorbent surface, the water molecules previously hydrogen bonded to the metal ion molecules get released and dispersed in the solution, this results in an increased in the entropy.

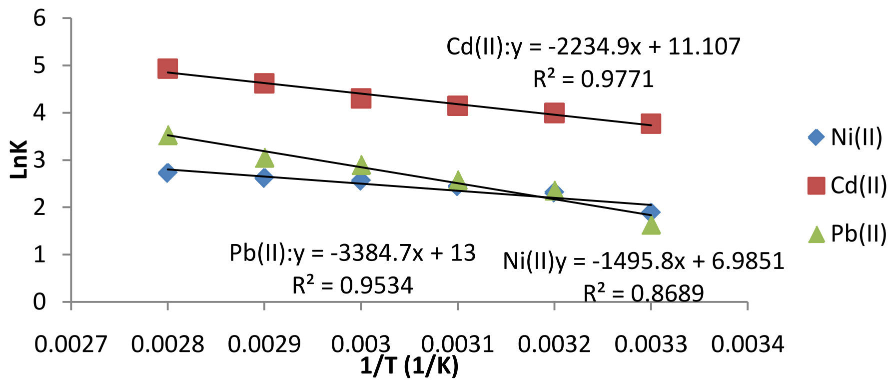

Figure 8: van't Hoff plot for the adsorption of metal ions onto *Calopogonium muconoides* at varying temperatures

Table 1: Isotherm model parameters for metal (II) ions adsorbed on the surface of *Calopogonium muconoides* at 303K

Isotherm models	Parameters	Pb(II)	Cd(II)	Ni(II)
Langmuir	q_m (mgg^{-1})	42.37	106.383	43.103
	K_L (Lmg^{-1})	-5.76	1.5666	-5.395
	R_L	-114.12	32.332	-106.9
	R^2	0.9979	0.8187	0.9988
Freundlich	K_F	46.344	49.045	40.888
	n	8.130	24.752	48.076
	R^2	0.5185	0.7011	0.86
Temkin	β_T (Jmol^{-1})	2.2571	0.9982	2.2571
	α_T(Lg^{-1})	4 x 10^7	7 x 10^8	62 x10^{-21}
	b_T(Jmol^{-1}K^{-1})	2312	2523	979
	R^2	0.7368	0.8958	0.8648
D-R Isotherm	k_D (mgg^{-1})	49.605	49.6749	48.876
	B_D(mol^{2}kJ^{-2})	0.0011	0.0003	0.003
	E_n (kJmol^{-1})	21.320	40.833	12.910
	R^2	0.8746	0.9386	0.9449

Table 2: Thermodynamic Parameters for Sorption of the Metal Ions onto *Calopogonium muconoides* at varying temperatures

Metal ions	ΔH (kJ/mol)	ΔS (kJ/mol)	-ΔG (kJ/mol)						R^2
			303 K	313 K	323 K	333 K	343 K	353 K	
Ni(II)	12.4361	0.05807	16.3604	3.7411	6.3219	6.9026	7.4833	8.0641	0.8689
Cd(II)	18.5809	0.09234	9.3992	10.3224	11.2458	12.1692	13.0929	14.0163	0.9971
Pb(II)	28.1404	0.10808	4.6085	5.6892	6.7700	7.8509	8.9317	10.0125	0.9534

CONCLUSION

This study aimed to propose a mechanism for the adsorption through thermodynamics and isotherm models. The experimental data was tested with different Isotherm models. The influences of metal ions temperature and dosage were examined. Langmuir Isotherm model with correlation-coefficient (R^2 of 0.9979, 0.9988 and 0.8187 for Pb(II), Ni(II) and Cd(II) respectively proved to be the best fit than other Isotherm model evaluated. Thermodynamics parameters such as ΔG, ΔS and ΔH were evaluated in the study. The negative value of ΔG indicates the feasibility and spontaneous process. The positive value of ΔH for the system contains the endothermic nature of the adsorption process. And the positive value of ΔS, suggests increased randomness at the solid – solution interface during the adsorption process. Thus, calopo seed pod is a promising adsorbent for the removal of Cd(II), Ni (II) and Pb(II) ions in aqueous solution.

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