



Isotherms and Thermodynamic studies on biosorption of Co(II), Cu(II), Ni(II) and Cd(II) ions from aqueous solution using carbonized biosorbent derived from Pilinut (*Canarium Ovatum*) seed

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Abstract The potential of Pilinut (*Canarium Ovatum*) seed in adsorbing Co(II), Cu(II), Ni(II) and Cd(II) ions from aqueous solution was investigated in a batch adsorption process. Various physicochemical parameters such as adsorbent dosage, initial metal ion concentration and temperature were investigated in the study. The adsorbent employed exhibited high efficiency in the removal of the metal ions from the solutions. The equilibrium adsorption data were described by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The coefficients of determination (R^2 values) of the four models were all high with Dubinin-Radushkevich providing best description for the experimental adsorption data. The maximum adsorption capacities of Cd(II), Co(II), Ni(II) and Cu(II) ions were found to be 58.82 mg/g, 18.18 mg/g, 17.24 mg/g and 13.51 mg/g respectively at the study temperature of 303 K. Different thermodynamic parameters, viz; Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) were evaluated. The negative values of ΔG_{ads} indicate the feasibility of the process while the positive values of ΔH_{ads} confirm the endothermic nature of the adsorption process. The positive values of ΔS_{ads} observed suggest increased randomness at the solid-solution interface. These results indicate that the biosorbent studied could be a promising alternative for the adsorption of Co(II), Cu(II), Ni(II) and Cd(II) ions from aqueous solution. The trend of the heavy metal adsorption follows thus: Cd(II) > Co(II) > Ni(II) > Cu(II), indicating that the biosorbent has high affinity for Cd(II).

Keywords Adsorption isotherms, Adsorption thermodynamics, Biosorbent, *Canarium ovatum*, Metal ions

Introduction

Heavy metal pollution is a pervasive and extremely serious environmental concern. The industrial and domestic wastewaters are responsible for introducing different toxic heavy metals into the environment and negatively impacting on the health of the people. The high level of heavy metal pollution in many developing countries is largely attributed to low environmental consciousness and also the desire for excess economic benefits [1]. With regards to effective environmental protection, heavy metals are considered as priority pollutants due to their important industrial roles and widespread presence in various waters or industrial effluents, and also their accumulation through the food chain, which results in toxic or inhibitory effects on living things [2, 3]. Hence, proper management of global environment is increasingly becoming an important issue.

Heavy metals may gain entry into water bodies such as rivers and lakes, through natural and anthropogenic sources. They could also be introduced through wet and dry fallouts of atmospheric particulate matters derived from the natural sources, such as the dust from weathering of rock and soil or from anthropogenic activities, including the combustion of fossil fuels and the processing of metals.

Several conventional techniques such as chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-precipitation have been employed in the heavy metals removal from solutions. But they are



not very suitable especially when very low concentrations of metals are involved and are also not cost effective [4, 5]. In addition, some of these conventional methods involve generating secondary pollutants, which will require further treatments. Biosorbents have therefore emerged as one of the potential cost effective alternatives for adsorption of heavy metals from solutions. Plants, algae, fungi are some of the biosorbents which have been found capable of removing heavy metals from aqueous solution by adsorption [6-8]. Low cost agricultural waste and by-products such as *Orchid malabar* [9], sugarcane bagasse [10], sawdust [11], coconut husk [12] *etc.* have been applied in the removal of heavy metals from aqueous solutions. The biosorbents bind with heavy metal ions thereby forming metal complexes or chelates due to the presence of functional groups such as hydroxyl, amino, carboxyl, phosphate, sulphhydryl, sulfate, thioether, carbonyl, amide, imidazole *etc.* on their surfaces [13]. In some cases, chemical treatments on the biosorbents using various kinds of modifying agents such as thioglycolic acid, EDTA, tartaric acid, NaOH *etc.* increase the number of these functional groups and further enhance the removal of the metal ions [14, 15].

Since cost is an important parameter for comparing sorbent materials, there is therefore the need for employing different biomass to assess their efficiency in the removal of toxic metals from aqueous environment. The need for an urgent exploration of all possible sources of agro-based inexpensive adsorbents should be investigated and their feasibility for the removal of heavy metals should be studied in detail. The objective of this study is therefore to contribute in the search for less expensive adsorbent and its utilization possibilities in the adsorption of some heavy metals. The present study involves the applications of carbonized Pilinut (*Canarium ovatum*) seed in the removal of Co(II), Cu(II), Ni(II) and Cd(II) ions from aqueous medium. The biosorbent was chosen because of its cheap, non-toxic and commercially available quantity.

Materials and Methods

Preparation of the Adsorbent

The adsorbent carbonized pilinut (*Canarium Ovatum*) seed was obtained at Michael Okpara University of Agriculture, Umudike, Abia State Nigeria. It was dried, carbonized in a limited supply of oxygen according to the method reported in Odoemelam *et al.*, 2015 [16] and crushed in the mill. The sample was sieved through 0.40 mm mesh. The sample retained after sieving was used for the sorption process.

Chemical Activation of the Adsorbent

The sieved pilinut seed samples with particle size 0.40 mm were soaked in 0.3 M HNO₃ for 24 h. It was then filtered with Whatman No.41 filter paper and rinsed thoroughly with deionized water until a pH 7.0 was obtained. The rinsed adsorbent was kept in an oven at 100 °C for 12 h and finally stored in an air tight plastic container. The treatment of the adsorbent with 0.3 M HNO₃ helps to oxidize the adhering organic materials and to remove any debris or soluble bio-molecules that might interact with the metal ions during adsorption.

Preparation of metal ion solutions

All the reagents used were of analytical grade and were used without further purification. De-ionized water was used in the preparation of all sample solutions. Stock solutions of 1000 mg/L of each of nickel, cobalt, cadmium and copper were prepared from their salts, NiSO₄.6H₂O, Co(NO₃)₂, CdSO₄.8H₂O and CuSO₄.7H₂O, respectively. This was done by dissolving appropriate amount of each salt in 1000 cm³ of de-ionized water, and made up to the mark of volumetric flask. From the stock solutions of 1000 mg/L, working concentrations of 10 to 50 mg/L of each of the metal ions were prepared by serial dilution. The initial concentration of 50 mg/L of each of the metal ion solutions was used for investigation of the effects of adsorbent dose, pH and temperature on the adsorption study. The effect of metal ion concentration was also investigated using different concentrations of 10, 20, 30, 40 and 50 mg/L of each of the metal ions under study.

Batch Adsorption Experiments

Equilibrium sorption of Co(II), Cu(II), Ni(II) and Cd(II) ions onto the carbonized pilinut (*Canarium ovatum*) adsorbent was studied as a function of temperature, dosage and initial metal ion concentration. The effects of dosage and temperature on the adsorption of the metal ions were studied at a temperature 30 °C and at a fixed initial metal ion concentration of 50 mg/L.

The isotherm studies were investigated by studying the influence of initial metal ion concentration on the equilibrium sorption of the metal ions by the adsorbent. It was done by introducing 50 ml of various



concentrations (10, 20, 30, 40 and 50 mg/L) of each of the metal ions into 250 ml Erlenmeyer flasks containing 0.4 g of the adsorbent of particle size 0.40 mm while maintaining temperature and pH at 30 °C and 6.0 respectively. The flasks were agitated intermittently for 2 h and at the end of the contact time, the mixture was filtered and the residual metal ion concentrations determined using Atomic Absorption Spectrophotometer.

The effect of adsorbent dosage on the sorption studies was investigated by introducing different adsorbent masses of 0.05 g, 0.10 g, 0.15 g, 0.20 g and 0.25 g into 250 mL Erlenmeyer flask containing 50 ml of 50 mg/L of each of the metal ion solutions. The temperature and pH of the solutions were maintained at 30 °C and 6.0 respectively. The flasks were agitated intermittently for 2 h and at the end of the contact time, the mixture was filtered and the residual metal ion concentrations determined using Atomic Absorption Spectrophotometer (Perkin Elmer Analytist 200). The procedure was carried out for temperature studies by conducting the adsorption study at varying temperatures of 303 K, 313 K, 323 K, 333 K and 343 K at a pH, initial metal ion concentration, adsorbent mass and volume of solution of 6.0, 50 mg/L, 0.4 g and 50 ml respectively. The equilibrium agitation time was maintained at 2 h and after which the mixture was filtered and residual concentration determined with AAS (Perkin Elmer Analytist 200).

Data Analysis

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

$$q_e = (C_o - C_e) V/m \quad (1)$$

where q_e is the equilibrium sorption capacity (mg/g), C_o and C_e are the initial and equilibrium or residual concentrations of the 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.

Results and Discussion

Effect of adsorbent mass on the sorption process

The effect of adsorbent dosage on the sorption of Ni(II), Cd(II), Co(II) and Cu(II) ions from solution is shown in Figure 1. It can be seen from the plots that the amount of metal ions adsorbed per unit mass of the adsorbent decreased with increasing adsorbent dosage. This can be explained from the fact that the active sites of the adsorbent are effectively utilized at low adsorbent dosage at a constant concentration of the metal ions and these sites become unsaturated at higher adsorbent dose due to availability of exchangeable sites at higher adsorbent concentration. This observation could also be interpreted to result from aggregation of the adsorbent particles at a high dosage, which will reduce the total surface area of the adsorbent and ultimately results in an increase in the diffusions path length, and a similar results had been obtained by earlier researchers [17, 18]. This trend implies that at constant initial metal ion concentration, it is expected that the amount adsorbed may decrease with biosorbent dose since the amount of the metal ions are not sufficient to saturate the exchangeable (active) sites on the biosorbent. This shows that as the biosorbent dose increases, it reaches a point where the masses of biosorbent used are in excess of the initial metal ion concentration, hence there will be no appreciable decrease in the amount of adsorbent and similar result has been reported [19].

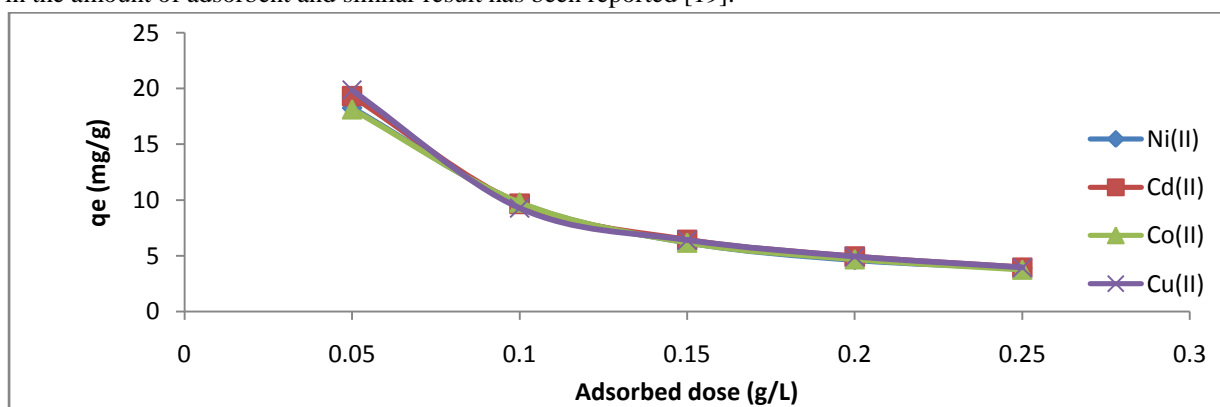


Figure 1: Effect of adsorption dose on the adsorption of metal ions onto carbonized *Pilnut (Canarium ovatum)* seed



Equilibrium Isotherm Modelling

Equilibrium adsorption isotherms describe how the adsorbates interact with the adsorbents and ultimately give a comprehensive understanding of the nature of interaction existing between them. In order to optimize the design of an adsorption system to remove metal ions from solutions, it is essential to establish the most appropriate correlation for the equilibrium data. There are several isotherm equations available for analyzing experimental sorption equilibrium data and in this study, the Langmuir, Freundlich, Dubini-Radushkevich and Temkin Isotherm models were employed.

Langmuir Isotherm model

The Langmuir Isotherm is based on the assumption that the surface of an adsorbent is structurally homogenous and that the sorption sites are identical and energetically equivalent. It further predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. Theoretically, the adsorbent has a finite capacity for the adsorbate and therefore attains a saturation value, beyond which no further sorption can take place. The Langmuir isotherm model can be represented by the expression:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)$$

Where Q_0 is a constant which signifies the maximum adsorption capacity corresponding to the monolayer coverage on the adsorbent (mg/g), b is the Langmuir constant relating to the adsorption energy. The plots of C_e/q_e vs C_e gave straight lines for the obtained equilibrium adsorption data as shown in Figure 2. From the slope and intercept of the plots, the Langmuir constants Q_0 and b were evaluated. An essential characteristics of the Langmuir isotherm is expressed by a dimensionless equilibrium parameter, R_L as shown in equation. (3)

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

The values of R_L express the type of Isotherm obtained to be either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$); linear ($R_L = 1$) or unfavorable ($R_L > 1$). In the present study, the values of R_L were less than 0.5 indicating the Langmuir adsorption Isotherm to be favorable in the adsorption of the metal ions under study.

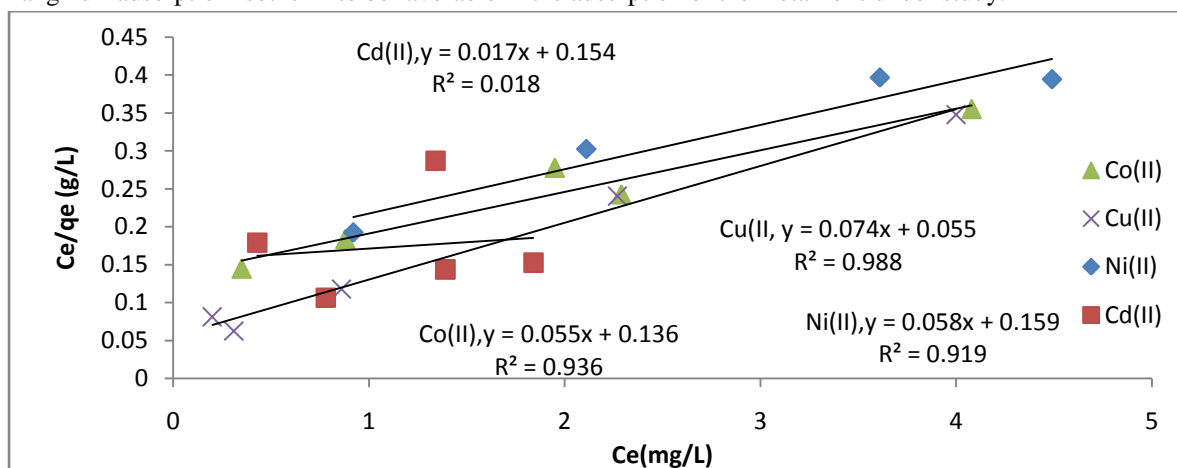


Figure 2: The Langmuir isotherm plots for the adsorption of the metal ions onto carbonized Pilinut (*Canarium ovatum*) seed

Table 1: Langmuir Isotherm constants and correlation coefficients (R^2 values) for sorption of Ni (II), Co(II), Cu(II) and Cd(II) ions by the carbonized pilinut seed

Constants	Metal ions			
	Ni (II)	Cu (II)	Co (II)	Cd (II)
b (L/mg)	0.3647	1.3454	0.4044	0.1104
Q₀ (mg/g)	17.241	13.514	18.182	58.824
R_L	0.0519	0.0146	0.0471	0.153
R²	0.919	0.988	0.936	0.018

Freundlich Isotherm model

The Freundlich Isotherm explains the heterogeneity of a surface and the exponential distribution of sites and their energies on the surface. The Freundlich Isotherm further describes reversible adsorption and the likelihood of formation of multilayer. The linearized Freundlich isotherm is expressed as:



$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

Where K_F is the Freundlich constant and $1/n$ is a constant expressing the heterogeneity factor and both constants were determined from the intercept and slope of the linear plots respectively (Fig. 3) and are presented in Table 2. The values of n obtained from the study were all greater than 1.0 but less than 10, indicating that the adsorption of the metal ions on the carbonized Pilinut (*Canarium ovatum*) seed is favorable. The correlation coefficients (R^2 values) obtained showed that the adsorption data fitted reasonably well into the Freundlich equation.

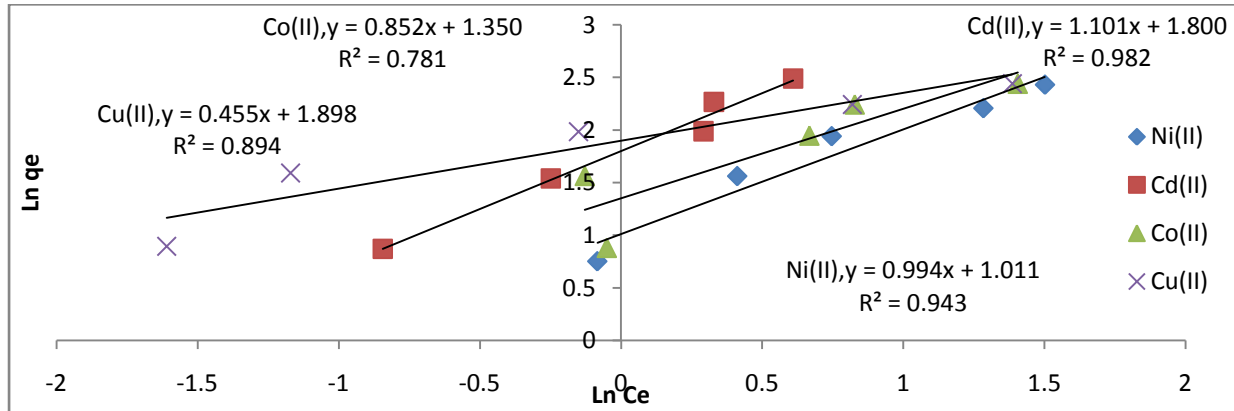


Figure 3: Freundlich isotherm plots for the adsorption of the metal ions onto carbonized Pilinut adsorbent

Table 2: Freundlich Isotherm constants for sorption of Ni(II), Co(II), Cu(II) and Cd(II) ions by carbonized pilinut seed

Constants	Metal ions			
	Ni(II)	Co(II)	Cu(II)	Cd(II)
K_F	2.7483	3.8574	6.6725	6.0496
n	1.0060	1.173	2.1978	0.908
R^2	0.943	0.781	0.894	0.982

Dubinin-Radushkevich Isotherm model

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 linearized Dubinin-Radushkevich isotherm is generally expressed as follows [20]:

$$\ln q_e = \ln q_D - \beta \varepsilon^2 \quad (5)$$

The Polanyi potential ε is expressed as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (6)$$

Where q_D is the theoretical saturation capacity (mg/g), β is a constant relating to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2), $R = 8.314(\text{J}/\text{mol}/\text{k})$ is the gas constant and T (K) is the absolute temperature. The D-R constants, q_D and β were calculated from the intercept and slope of the linear plots of $\ln q_e$ versus ε^2 (Figure 4) and the results presented in table 3. The constant q_D gives an idea of the mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate as it is transferred to the surface of the solid from infinity distance in the solution and can be calculated from the following relationship:

$$E = \frac{1}{\sqrt{2\beta}} \quad (7)$$

The value of E obtained gives an indication of the likely mode of the adsorption process with the adsorption process being described as physisorption when the value of E is within the range of 1.0 to 8.0 kJ/mol and chemisorption when the value of E is within 9.0 to 16 kJ/mol [21]. From table 3, it could be suggested that the adsorption of the metal ions by the adsorbent follows physisorption mechanism. D-R isotherm describes the experimental data well because of the good correlation coefficients (R^2) obtained.



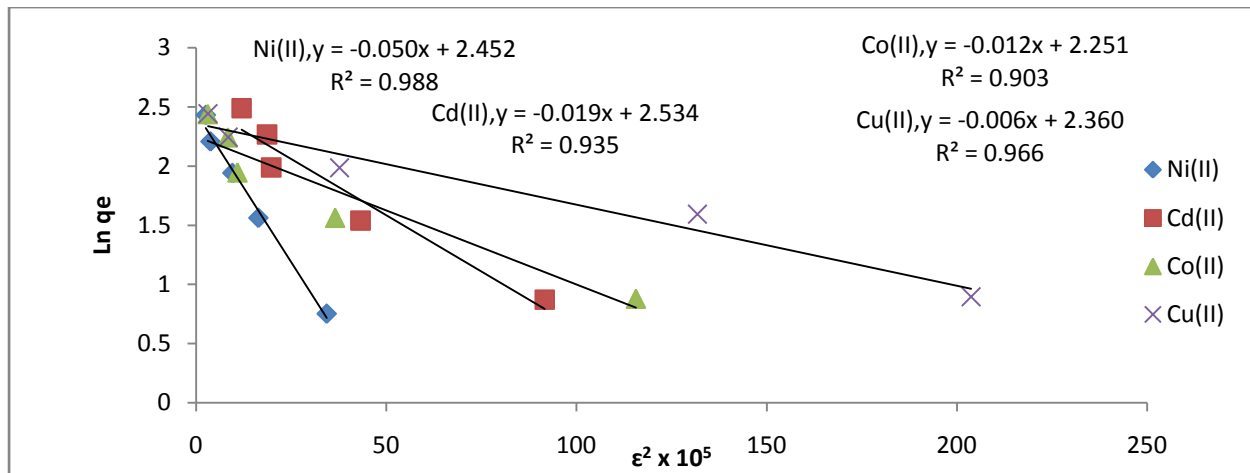


Figure 4: Dubinin-Radushkevich isotherm for the adsorption of the metal ions onto the Pilinut (*Canarium ovatum*)

Table 3: Dubinin-Radushkevich Isotherm constants for sorption of Ni(II), Co(II), Cu(II) and Cd(II) ions by carbonized pilinut seed

Constants	Metal ions			
	Ni (11)	Cu (11)	Co (11)	Cd (11)
q_n (mgg^{-1})	11.611	10.590	9.497	12.603
β ($\text{mol}^2\text{KJ}^{-2}$)	0.050	0.006	0.012	0.019
E_n (KJ mol^{-1})	3.162	8.129	6.455	5.130
R^2	0.988	0.966	0.903	0.935

Tempkin Isotherm model

Tempkin adsorption isotherm was used to evaluate the adsorption potential of the metal ions for carbonized pilinut (*Canarium ovatum*). 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 Linearized Temkin isotherm has commonly been expressed in the following form [22, 23].

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad (8)$$

Where $\beta = (RT)/b$, T is the absolute temperature in Kelvin and R is the universal gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$). The constant b is related to the heat of adsorption [24, 25]. A plot of q_e versus $\ln C_e$ gives a straight line as shown in figure 5 with a slope of β and intercept of $\beta \ln \alpha$. The parameters, α and β were evaluated and presented in table 4. Examination of the isotherm curve shows that the Temkin isotherm fitted the experimental equilibrium adsorption data well. The correlation coefficient (R^2 values) obtained from Temkin model were high and comparable to those of Langmuir and Freundlich equations, indicating that the Temkin model gave good a good description to the adsorption of Cu(II), Co(II), Ni(II) and Cd(II) ions onto the carbonized Pilinut (*Canarium ovatum*).

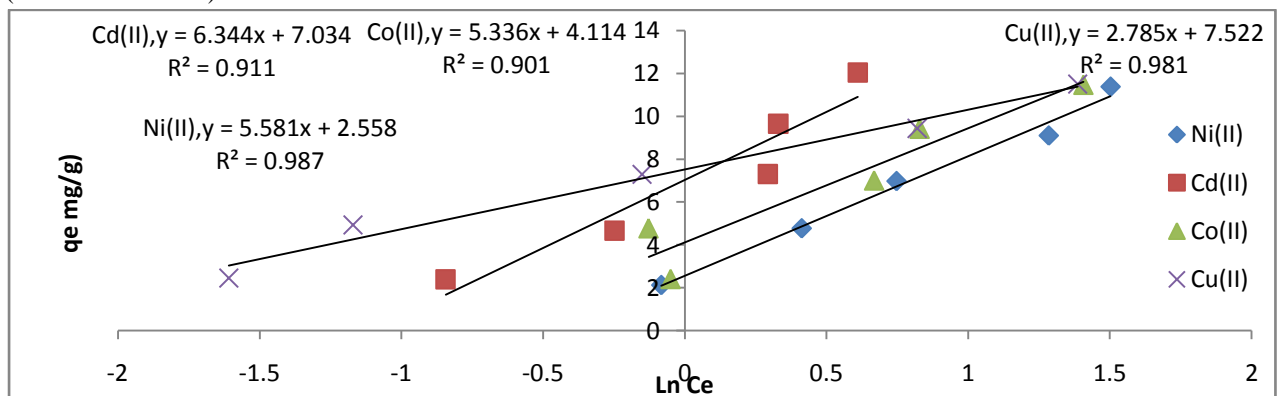


Figure 5: Temkin isotherm for the adsorption of the metal ions onto Pilinut (*Canarium ovatum*)



Table 4: Tempkin Isotherm constants for sorption of Ni(II), Co(II), Cu(II) and Cd(II) ions by carbonized pilinut seed

Constants	Metal ions			
	Ni (II)	Co (II)	Cu (II)	Cd (II)
α (Lg^{-1})	1.5813	2.1617	14.8916	3.0304
β (mg L^{-1})	5.581	5.336	2.785	6.344
b	0.00221	0.0021	0.0011	0.0025
R²	0.987	0.901	0.981	0.911

Effect of temperature on the adsorption process

The influence of temperature on the equilibrium adsorption of the metal ions by the adsorbent was studied at temperatures 30, 40, 50, 60 and 70 °C, at 50 mg/L initial metal ion concentration and pH 6. Results showed that the amount of metal ions adsorbed decreased as the temperature increased as shown in Figure 6. The decrease in amount of the metal ions adsorbed with increasing temperature by Pilinut (*Canarium ovatum*) could have resulted from either the desorption of the metal ions from the adsorbent phase into the bulk phase, due to the increased temperature [26] 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 [27]. This decrease in the amount adsorbed with increasing temperature may suggest that physisorption is the likely mode of bonding of the metal ions to the adsorbent in our study.

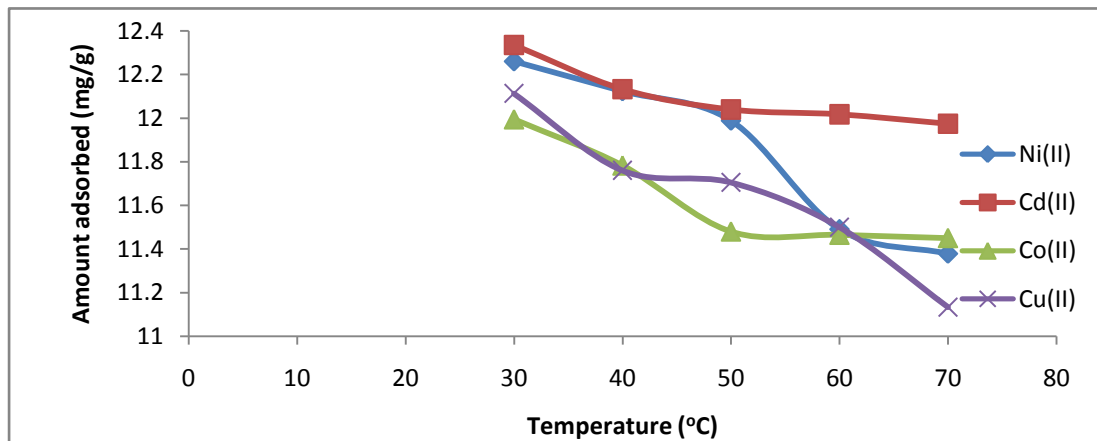


Figure 6: Plot of sorption capacity (q_e) vs temperature for adsorption of the metal ions onto Pilinut (*Canarium ovatum*)

Thermodynamic Study

The various thermodynamic parameters for the adsorption process were evaluated to estimate the feasibility and the likely mode of bonding of the metal ions onto the adsorbent. The activation energy was calculated by using the Arrhenius relation.

$$k = A \exp(-E_a/RT) \quad (9)$$

The Gibbs free energy of adsorption, ΔG (kJ/mol), enthalpy of adsorption, ΔH (kJ/mol), and entropy of adsorption, ΔS (J/k mol) were obtained from the following relations:

$$K = \frac{C_{ad}}{C_e} \quad (10)$$

$$\ln\left(\frac{K}{T}\right) = \left(\ln\frac{R}{N_A h} + \frac{\Delta S^\#}{R}\right) - \frac{\Delta H^\#}{RT} \quad (11)$$

Where R is the gas constant, N_A is Avogadro's number, A is Arrhenius or pre-exponential factor and h is the Planck's constant.

In calculating the activation energies for the adsorption of the metal ions onto carbonized Pilinut (*Canarium ovatum*), the linearized Arrhenius equation was used.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (12)$$



A plot of $\ln k$ versus $1/T$ produced straight lines with slope $-\frac{E_a}{R}$ and the intercept equal to $\ln A$. It should be noted that if the value E_a is greater than 6 kJ mol^{-1} , it reveals the chemical mechanism of the binding of the sorbate (chemisorption). If E_a is smaller than 4 kJ mol^{-1} , sorption takes place as a result of weaker physical interactions.

Figure 7 shows Arrhenius plot for the adsorption of metal ions onto carbonized pilinut (*Canarium ovatum*) seed and the values of the E_a calculated through slope of the lines on the plots and results shown in table 5. The activation energy values obtained are 24.51, 22.77, 35.20, and 16.07 J/mol for Cu(II), Cd(II), Ni(II), and Co(II) ions respectively. The magnitude of activation energy may give us an idea about the type of sorption. In this study, the low values of the activation energies confirm that the nature of adsorption of these metal ions by Pilinut (*Canarium ovatum*) is physisorption [28].

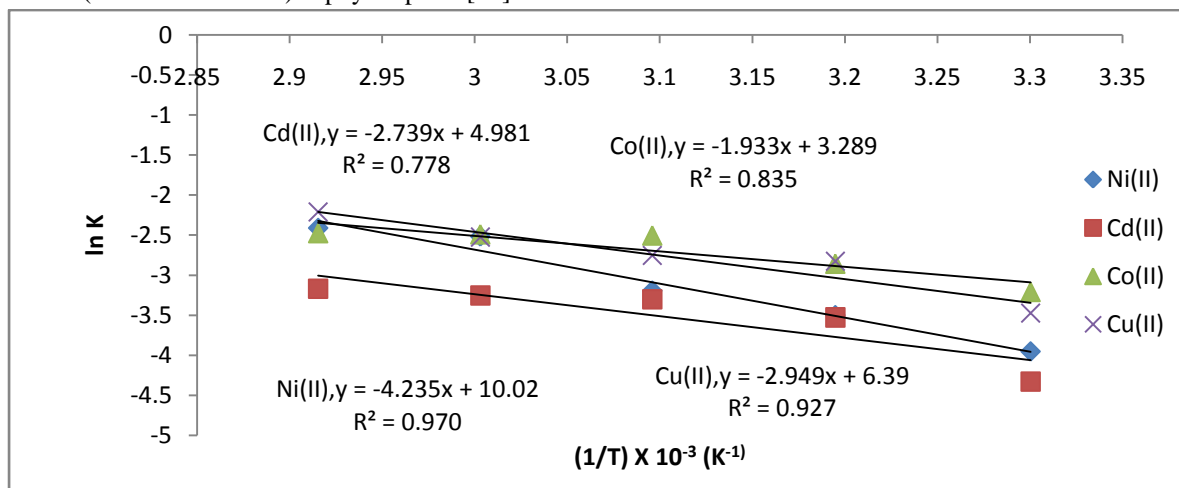


Figure 7: Arrhenius plot for the adsorption of metal ions onto carbonized Pilinut (*Canarium ovatum*)

Table 5: Activation energies for the Arrhenius plots

Metal ions	Cu	Co	Cu	Cd
E_a (J/mol)	24.5179	16.0709	35.2094	22.7720
A	595.8565	26.8160	22471.42992	145.61992

The various thermodynamic parameters viz; ΔH , ΔS , and ΔG of adsorption were calculated from transition state theory derivation (equation 11).

The values of ΔH^0 and ΔS^0 were calculated from the slope and intercepts of the linear plots of $\ln \frac{k}{T}$ Vs $\frac{1}{T}$ are shown in figure 8. The free energy of specific adsorption ΔG^0 (kJ mol^{-1}) is calculated from the following expression:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

The negative values of ΔG^0 (table 6) 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^0 must have a negative value. The positive value of ΔH^0 for the system confirms the endothermic nature of adsorption. Similar result was reported for the adsorption of Crystal Violet by *Citrullus Lanatus Rind* [29].

The positive value of ΔS^0 observed for the adsorption of the metal ions suggested the increased randomness at the solid-solution interface during adsorption process. The metal ion molecules 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 increase in the entropy. The positive values of entropy changes also reflect good affinity of the metal ion towards the adsorbent. The entropy changes in the present study are in excellent agreement with previous study on the adsorption of methylene on Wheat shell [30] and aluminium [31].



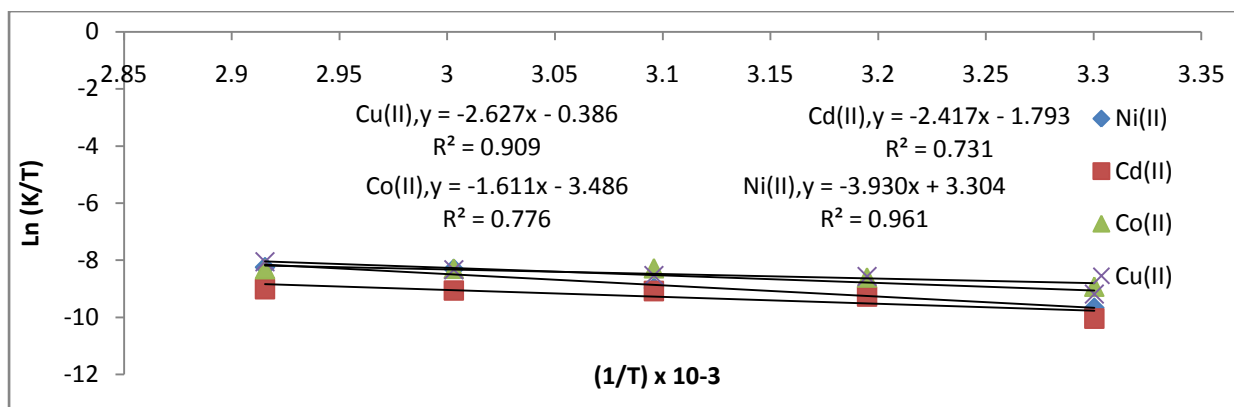


Figure 8: Transition state plot for the adsorption of metal ions onto carbonized Pilinut (*Canarium ovatum*) seed

Table 6: Thermodynamic values as calculated from the transition state plots at T = 303K

Metal ions	ΔH (J/mol)	ΔS (J/mol)	ΔG (KJ/mol)
Ni (II)	32.67402	465.0929	-140.8904
Cd (II)	20.0949	422.7165	-128.0630
Co (II)	13.3938	408.6612	-123.8109
Cu (II)	21.840	434.414	-131.605

Table 7: Thermodynamic values as calculated from the transition state plots at T = 313K

Metal ions	ΔH (J/mol)	ΔS (J/mol)	ΔG (KJ/mol)
Ni (II)	32.67402	465.0929	-145.5414
Cd (II)	20.0949	422.7165	-132.2901
Co (II)	13.3938	408.6612	-127.8756
Cu (II)	21.840	434.414	-131.949

Table 8: Thermodynamic values as calculated from the transition state plots at T = 323K

Metal ions	ΔH (J/mol)	ΔS (J/mol)	ΔG (KJ/mol)
Ni (II)	32.67402	465.0929	-150.1923
Cd (II)	20.0949	422.7165	-136.5173
Co (II)	13.3938	408.6612	-131.9841
Cu (II)	21.840	434.414	-140.2938

Table 9: Thermodynamic values as calculated from the transition state plots at T = 333K

Metal ions	ΔH (J/mol)	ΔS (J/mol)	ΔG (KJ/mol)
Ni (II)	32.67402	465.0929	-154.8432
Cd (II)	20.0949	422.7165	-140.7444
Co (II)	13.3938	408.6612	-136.0708
Cu (II)	21.840	434.414	-144.6380

Table 10: Thermodynamic values as calculated from the transition state plots at T = 313K

Metal ions	ΔH (J/mol)	ΔS (J/mol)	ΔG (KJ/mol)
Ni (II)	32.67402	465.0929	-159.4942
Cd (II)	20.0949	422.7165	-144.9716
Co (II)	13.3938	408.6612	-140.1578
Cu (II)	21.840	434.414	-148.982

Conclusion

The study investigates the potential of carbonized Pilinut (*Canarium ovatum*) seed in removing four heavy metal ions: Co(II), Cd(II), Ni(II), Cu(II) from aqueous solutions. The influences of metal ions concentration, temperature and dosage were examined. The equilibrium experimental data were tested with four different isotherm models; the Langmuir, Freundlich, Dubinin-Radushkevich and Tempkin isotherms. The experimental adsorption data were best described by the Dubinin-Radushkevich isotherm model. Assessment of the maximum amount of metal ions adsorbed onto the adsorbent showed that Cd(II) ions were best adsorbed onto the adsorbent among the four metal ions studied. The metal removal by the adsorbent was found to follow the trend: Cd(II) > Co(II) > Ni(II) > Cu (II)..



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