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Isotherm and Thermodynamic studies on the biosorption of Pb(II), Ni(II) and Cd(II) ions from aqueous solution onto *Newbouldia leavis* (*Bignonaesia*) pod powder.

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Abstract

Anthropogenic activities may have posed a serious threat to the environment due to the release of heavy metal into the environment. In this study, the adsorption behaviour of *Newbouldia leavis* as regards Pb(II), Ni(II) and Cd(II) ions from wastewater has been studied. A series of experiments were conducted in a batch system to assess the effects of the system variables such as of pH, temperature and initial metal concentrations in solution ranging from 10 to 50 mg/L. The experiment showed that the solution pH strongly influenced the adsorptive capacity of the adsorbent as maximum adsorption occurred at pH 4 for Pb(II) ions and pH 6 for both Ni(II) and Cd(II) ions. For the isotherms models applied for sorption studies, Freundlich best described the data properly. The maximum adsorption capacity of Pb(II), Cd(II) and Ni(II) are 0.0042 mg/g, 0.178 mg/g and 0.552 mg/g respectively. The negative value of ΔG^0 indicates the feasibility and spontaneous nature of the process. The negative value of ΔH^0: -50707.09, -8804.53 and -7234.01 for Pb(II), Cd(II) and Ni(II) ions respectively confirms the exothermic nature of adsorption. Moreover, the negative value of ΔS^0: -51197.6, -62.79 and -209.18 for Ni(II), Cd(II) and Pb(II) ions respectively suggests the decreased randomness at the solid-solution interface during adsorption process. According to the equilibrium studies, the selectivity sequence can be given as $Ni^{2+} > Cd^{2+} > Pb^{2+}$. These results show that *Newbouldia leavis* holds great potential to remove cationic heavy metal species from industrial wastewater.

Key Words: Heavy metal, *Newbouldia leavis*, biosorption, Equilibrium, Thermodynamics.

INTRODUCTION

Due to increasing awareness about the environment and stringent environmental regulations, wastewater treatment has always been a key aspect of research [1]. Water is a vital component for the economic prosperity of any country. In coming years, the economic importance of water is expected to grow with the global economic growth, industrial development and urbanization. Industrial wastewater contains the variety of inorganic compounds which are characterized as toxic, carcinogenic and mutagenic which when persist in the environment have the potential to cause adverse effect on man and its environment [2]. The heavy metals present in the industrial waste water such as lead, cadmium, chromium, nickel and zinc are the most toxic and perilous materials among the other toxic materials from the chemical and allied industries [3]. The heavy metals present in the wastewater is persistent and non degradable in nature. Moreover, they are soluble in aquatic environment and thus can be easily absorbed by living cells. Thus, by entering the food chain, they can be bio-accumulated and biomagnified in higher tropic levels also [4]. The heavy metals, if absorbed above the permissible levels, could lead to serious health disorders [5]. The maximum concentration limit standards for Pb, Cd and Ni are 0.006 mg/L, 0.01 mg/L and 0.20 mg/L respectively as established by Babel and Kurniawan, 2003 [6]. Cadmium causes lung damage, and may cause cancer from long-term exposure [7], Nickel causes dermatitis, nausea, chronic asthma, coughing, human carcinogen [2] while Lead damage the foetal brain, diseases of the kidneys, circulatory system and nervous system [8]. Hence, there is burning need for the removal of heavy metal from the wastewater. Treatment of heavy metals containing industrial effluent becomes quite necessary before being discharged into the environment. Various technologies that are currently used for the removal of heavy metals are evaporation, ion exchange, precipitation, membrane filtration, and adsorption [9].

However, these methods are ineffective, costly and require high energy input. Moreover, they are associated with generation of toxic sludge, disposal of which renders it expensive and non eco friendly in nature. Among all these technology adsorption process appears to be more favourable technology as it is low cost, require low maintenance, economical and is energy efficient. Adsorption is known to be an effective method for reducing the concentration of pollutants such as organic compounds, metal ions and dissolved dye in wastewater. Recent studies on adsorption have drawn the attention to waste materials produced by agricultural process. Such materials are calopo seed pod [10], pilinut seed [11], orchid Malabar [12], monkey bread [13] and okro stem [14] among others while *newbouldia leavis* is currently under study.

Materials and methods

Preparation of the adsorbent:

The adsorbent, *newbouldia leavis* 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 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 2 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.

Results and discussion

Batch adsorption experiments

All the reagents used were of analytical grades and were used without further purification. De-ionized water was used in the preparation of all sample solutions. Batch adsorption studies of Ni(II), Cd(II) and Pb(II) ions onto *newbouldia leavis* were investigated as a function of temperature, dosage and initial metal ion concentration variation. The effects of dosage, initial metal ion concentration variation and temperature on the adsorption of the metal ions were studied at a temperature 30 ^{o}C and at a fixed metal ion concentration of 50 mg/L. The isotherm studies were investigated by studying the influence of initial metal ion concentrations on the equilibrium sorption of the metal ions by *newbouldia leavis*. 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 0.4 g (180 µm) while maintaining temperature and pH at 30 ^{o}C and 6.0 respectively. The flasks were agitated intermittently for 2 hr and at the end of the contact time, the mixture filtered and the residual concentrations determined using (Perkin Elmer Analysit 200) Atomic Absorption Spectrophometer AAS. Also dosage studies were investigated by studying the influence of different mass of the adsorbent on the equilibrium sorption of the metal ions. It involves introducing different adsorbent doses of 0.05g, 0.10g, 0.15g, 0.20g and 0.25g each into different 250 ml Erlenmeyer flasks containing 20 mL of metal ion concentration of 50 mg/L while maintaining constant temperature and pH at 30 ^{o}C and 6.0 respectively. The flasks were agitated for intermittently for 2 hr and at the end of the contact time, the mixture filtered and the residual concentrations determined using AAS. The procedure was carried out for temperature studies but at various temperatures of 303 K , 313 K, 323 K, 333 K and 343 K while pH 6.0, concentration 50 mg/L, mass 0.05 g and volume of 20 mL are kept constant. The agitation time remains 2 hr after which the mixture was filtered and residual concentration determined using AAS. 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. The percentage adsorption of the metal ions by the adsorbent was evaluated using the relation:

% R = $(Co-Ce) \times 100$ (1)

While the adsorption capacity, qt (mg/g) at different times was done using mass balance equation: qt = $(Co-Ct)\ v/m$ (2)

Where % R = percentage of the metal ion adsorbed, Co = initial metal ion concentration in mg/L, Ct = residual metal ion concentration in solution (mg/L), V = volume of metal ion solution used in dm^3 and m = the dry mass of the adsorbent in g.

Results and discussion

FT-IR Result: The surface functional groups of the loaded and unloaded biosorbents were detected by Fourier Transform Infrared (FT-IR System 1600 Model, PerkinElmer, USA) spectroscope. The spectra were recorded from 4000-400 cm^{-1} using a KBr disc technique. The FTIR spectra of *Newbouldia leavis* pod powder before adsorption and after adsorption are shown in Fig.1 and Fig.2 respectively. For *Newbouldia leavis* pod, there are broad and strong bands from 2500 to 3600 cm^{-1}, which indicates the presence of carboxylic acid (RCOOH), alcohol (ROH) and amino (RNH_2) groups. This is consistent with the peaks at 1052.48 and 1156.4 cm^{-1} due to alcoholic C-O and C-N bending vibration [15]. The bands at 2924.8 cm^{-1} can be assigned to C-H stretching of the methylene group [16]. The peaks located at 1400-1600 cm^{-1} are assigned to aromatic skeletal vibrations. The band at 1274.4 cm^{-1} is assigned to phenolic hydroxyl group in lignin. The broad peak at 580.10 cm^{-1} and 1384.59 $cm^{-1}$are assigned to the bending and deformation modes of C-H group. Comparing Fig.1 and 2, we observed that some peaks are shifted or disappeared and new peaks detected. These changes in the spectrum suggest the possible involvement of those functional groups in the adsorption process. The peak at 1156.4 cm^{-1} that represented C-N bending vibration had shifted to 1159.3 cm^{-1} after adsorption. All the findings from FT-IR spectra led to a conclusion that O and N-containing groups are the main adsorption sites for the heavy metal ions.

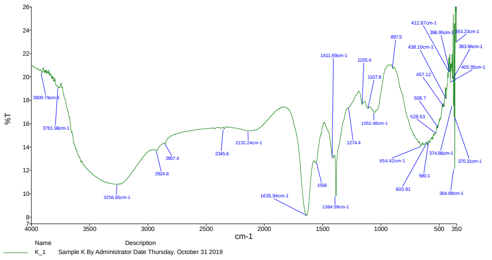

Figure-1: FTIR spectrum of Newbouldia leavis before adsorption.

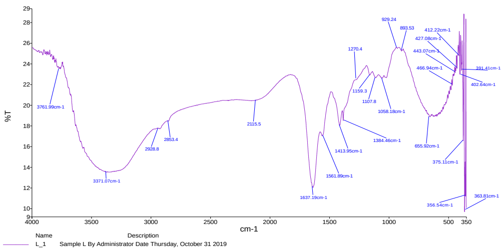

Figure-2: FTIR spectrum of Newbouldia leavis after adsorption.

Effects of pH variation

The pH of the solution affects the surface change of the adsorbent, as well as the degree of the ionization and speciation of the different pollutants. A change in pH affects the adsorptive process through the dissociation of functional groups on the adsorbent surface active sites. In this work, the effect of pH was studied and the results obtained are presented in Fig.3. The figure revealed that the maximum uptake for Ni(II) (8.18mg/g) and Cd(II) (8.3mg/g) occur at pH 6 while Pb (II) (8.28mg/g) occurs at pH 4. This is because at lower pH values, larger quantity of proton jostles with the metal cations for the biomass surface. At pH values greater than 6.0 biosorption studies for Cd(II) and Ni(II) could not be performed due to the precipitation of Cd(II) and Ni(II) ions as hydroxides, but at pH greater than 4.0 for Pb(II). A similar result was determined by Aksu *et al*.[17].

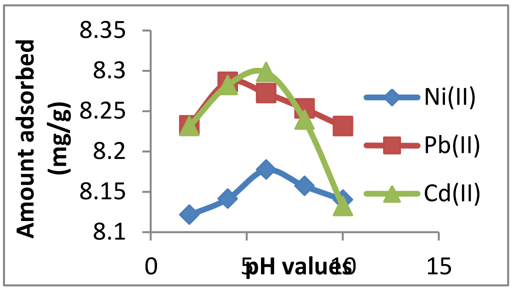

Fig.3: Effect of pH on the adsorption of metal ions onto *Newbouidia leavis*.

Effect of initial metal ion concentration

The initial concentration provides important driving force to overcome all mass transfer resistance of all molecules between the aqueous and solid phases [18].

Fig. 4 shows that the variation of equilibrium sorption capacity diminishes the resistance and makes more contact between metal ions and adsorbent. Availability of metal ions in the vicinity of the adsorbent also increases while increasing the concentration, which results in the high percentage removal of metal ions at higher concentration [10].

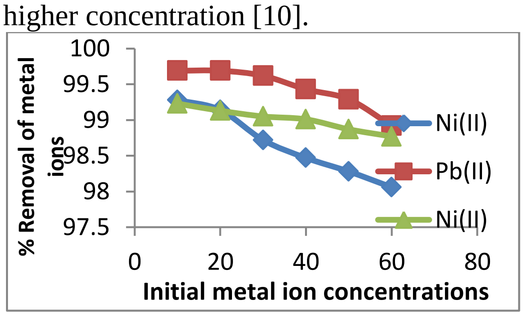

Fig.4: Effect of initial concentration on the adsorption capacity of *Newbouidia Leavis*.

Effect of temperature.

The influence of temperature on the equilibrium adsorption capacity of the adsorbent for the metal ions was determined as presented in Fig. 5. The figure obtained suggests that adsorption decreased with increase in temperature [19]. Houwing and Salomon in1965 [20] had stated that physisorption usually decreases with increase in temperature while chemisorptions increased. The decrease in adsorption capacity for Cd(II) and Pb(II) suggest Physisorption while Ni(II) is a combination of Physisorption and chemisorptions. Increasing temperature could cause any of these; destructing some active sites on the adsorbent due to weakening of the bond or attractive forces [21].

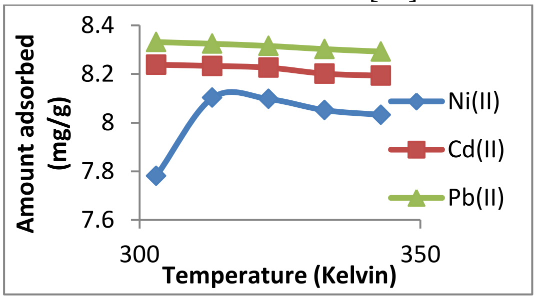

Fig. 5: Effect of temperature on the adsorption metal ions onto *Newbouidia Leavis*.

Freundlich isotherms

The Freundlich [22] isotherms can be used for description of adsorption and heterogeneous surfaces with non-uniform distribution of adsorption heat. 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 linearised form of the Freundlich equation is as:

$\ln qe = \ln K_F + \frac{1}{n} \ln Ce$ (3)

where K_F is an empirical constant related to the sorption capacity of the adsorbent (Lmg^{-1}) and constant n is a constant indicative of the intensity of the adsorption and varies with the surface heterogeneity and affinity. The values of K_F and n can be calculated by plotting ln qe versus ln Ce as shown in Fig.6 and constants presented in Table 1. The K_F values suggests the adsorption trend as Ni(II) > Pb(II) > Cd(II). The n < 0 values suggest unfavourable adsorption process.

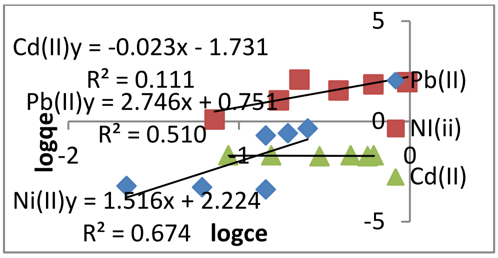

Fig. 6: Effect of Freundlich on the adsorption of metal ions onto *Newbouldia leavis*.

Table 1: Freundlich isotherm constants and correlation (R^2) for sorption of Ni(II), Cd(II), Pb(II) ions by Newbouldia Leavis.

Constants	Ni(II)	Pb(II)	Cd(II)
K_F (L/g)	167.5	5.64	-1.731
N	0.659	0.364	-43.478
R^2	0.674	0.510	0.111

Langmuir isotherm

This isotherm describes adsorbate-adsorbent systems in which the extent of adsorbate coverage is limited to one molecular layer. The isotherm was originally by Langmuir [23]. The Langmuir model assumed that each adsorbate molecule occupies only one site, surface is homogenous, single molecule occupies a single surface site. The linear form of Langmuir isotherm equation is given as:

$$\frac{Ce}{Qo} = \frac{1}{QoKL} + \frac{Ce}{Qo} \quad (4)$$

Where: Qo and K_L is Langmuir constant related to the monolayer adsorption capacity of the adsorbent (mg/g) it is the maximum amount adsorbed and the rate of adsorption (L/mg), respectively from Fig.7. The dimensionless parameter (R_L) is presented in equation 5,

R_L = 1/ 1+ kLCo (5)

If $R_L > 1$ unfavourable adsorption, RL= 1 linear adsorption, 0<RL<1 favourable adsorption and $R_L=0$ irreversible adsorption. The Langmuir constants are shown in table 2. The data suggests the adsorption of Ni(II) and Cd(II) are favourable while that of Pb(II) is unfavourable.

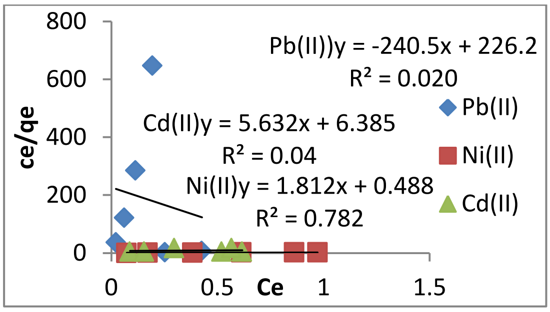

Fig.7: The Langmuir isotherm plot for the adsorption of the metal ions onto *Newbouldia Leavis*

Table 2:The Langmuir isotherm constants for the adsorption and correlation (R^2) for sorption of metal ions by *Newbouldia Leavis*.

Constants	Ni(II)	Pb(II)	Cd(II)
B(L/mg)	3.712	-1.063	0.999
Q_0(mg/g)	0.552	-0.00416	0.178
RL	0.005	1.263	0.0196
R^2	0.782	0.020	0.04

Thermodynamic of adsorption Study

In order to study the feasibility of the process, the thermodynamic parameters such as Gibbs free energy ($\Delta G, kJ/mol$), enthalpy (($\Delta H, kJ/mol$)), and enthropy (($\Delta S, J/k\,mol$)), were obtained from these equations:

$$K = \frac{C_{ad}}{C_e} \qquad (6)$$

$$\ln(K) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (7)$$

where ΔS, ΔH and ΔS are change in activated free energy, activated enthalpy and activated entropy of activation respectively, where R is gas constant (8.314J/K. mol). The value of ΔH^0 and ΔS^0 are calculated from the slope and intercepts of the linear plot of $\ln\frac{k}{T}$ Vs $\frac{1}{T}$ are shown in figure 8. The free energy of specific adsorption ΔG^0 (kJmol^{-1}) is calculated from the following expression:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (8)$$

The negative value of ΔG^0 (table 3) indicates the feasibility of the process and its spontaneous nature. The negative value of ΔH^0 for the system confirms the exothermic nature of adsorption. Similar result was reported for the adsorption of heavy metal ions by pilinut seed [11]. The negative value of ΔS^0 observed for the adsorption of metal ion molecules suggested the decreased 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 increased in the entropy. The negative 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 adsorption of Aluminium [24].

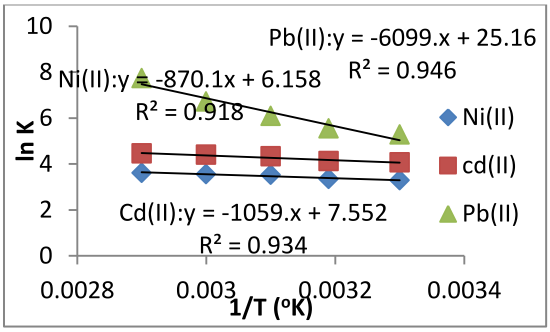

Fig. 8: van't Hoff plot for the adsorption of metal ions onto Newbouldia Leavis at temperature 300K, 313K, 323K, 333K and 343K

Table 2: Thermodynamic values as calculated from van't Hoff plots at T = 303 -343 K

	Temperature (K)	Ni(II)	Cd(II)	Pb(II)
ΔH(J/mol)		-15863.11	-11855.76	-5070.09
ΔS(J/mol)		-51197.6	-62.79	-209.18
ΔG(KJ/mol)	303	-350.23	-7169.16	-68451.24
ΔG(KJ/mol)	313	-161.65	-7797.56	-70543.43
ΔG(KJ/mol)	323	-18117.91	-29085.7	-72635.18
ΔG(KJ/mol)	333	-170488.0	-29713.6	-74726.99
ΔG(KJ/mol)	343	-33423.91	-9681.21	-76818.49

Conclusion

In this study, Newbouldia leavis pod was used for the adsorption of aqueous solution containing Ni (II), Cd (II), and Pb (II) ions. Batch experiment showed that the solution pH strongly influenced the adsorptive capacity of the adsorbent as the solution pH increased the adsorption capacity of the metal ions increased .However greatest adsorption was observed at pH 6.0 for Ni(II) and Cd(II) but pH 4.0 for Pb(II) ions. Metal uptake increased as the initial concentration of the metal increased. The adsorbent successfully removed the metal ions from the solution. This study suggests that Newbouidia leavis pod could be used as an inexpensive and highly efficient adsorption agent for the removal of heavy ions from aqueous solution.

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