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SORPTION EQUILIBRIUM, KINETICS AND THERMODYNAMIC STUDIES OF Pb (II), Ni (II) AND Co (II) IONS ADSORPTION IN AQUEOUS SOLUTION BY SWEET DATTOCK (*Detarium microcarpum*) SHELL

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Abstract: Chemically activated *Detarium microcarpum* shell was used as an adsorbent to remove Pb (II), Ni (II) and Co (II) ions from aqueous solution by batch adsorption technique. Batch adsorption experiments were performed as a function of pH, contact time, initial metal ion concentrations and temperature. The residual concentra tions were determined using Atomic Absorption Spectrophotometer (AAS). The optimum pH required for maximum adsorption was found to be 5.0 for Co (II) ion, 6.0 for Pb (II) and Ni (II) ion respectively. Equilibrium times of 60 minutes were attained for Ni (II) and Co (II) ions and 90 minutes for Pb (II) ions. The amount of metal ions adsorbed by the substrate increased with increase in initial metal ion concentration. The equilibrium data correlated well with Freundlich and Dubinin-Radushkevich (D-R) adsorption model. The trend of adsorption isotherm was Freundlich > Dubinin –Radushkevich (D-R) > Langmuir adsorption isotherm. Adsorption kinetics data were modeled using the pseudo-first and pseudo-second order models. The results indicated that pseudo-second order model best described adsorption kinetic data. The thermodynamic parameters (standard Gibbs Free energy (ΔG^o), standard Enthalpy (ΔH^o) and standard Entropy (ΔS^o)) showed that the adsorption process of the metal ions was feasible, non-spontaneous, endothermic and decreased randomness at the sorbent-sorbate interface. The biosorption study showed that *Detarium microcarpum* shell could be a viable alternative to commercial activated carbon in the removal of potentially toxic elements from aqueous solution.

Keywords: Sorption, equilibrium, kinetics, *Detarium microcarpum* shell, lead, nickel, cobalt.

Introduction

The rates at which potential toxic elements are being discharged into the environment due to advancement in technology have been on the increase. Toxic metals posed a major threat to the environment and public health due to their acute toxicity and bioaccumulation, not biodegradable in living organism, even at low concentration (Hanna *et al*., 2010; Renuga *et al*., 2010). Pb (II), Ni (II) and Co (II) ions have high solubility in the aquatic environment and thus can be absorbed by living organisms (Gonen & Serin, 2012), and if these metal ions are ingested beyond permitted concentration, they cause serious health disorder (Dadhaniya *et al*., 2009). As a result of this, increasing attention is therefore being paid on the development of know-how for their discharge into water bodies and natural streams.

A number of technologies have been developed over the years to remove toxic metals from waste water; such as reduction followed by electrochemical precipitation, chemical precipitation, chemical oxidation-reduction, ultra filtration, ion-exchange, reverse osmosis, solvent extraction, electro dialysis, electrochemical coagulation, evaporation, (Regina *et al*., 2008; Ahmadpour *et al*.,2009). Most of these methods suffered much drawback due to high capital and operational cost and generation of residual metal sludge after treatment (Demirbas *et al*., 2008; Gupta *et al*., 2010). These disadvantages, together with the need for more economical and effective methods of metal recovery/removal from waste water, have resulted into the development of alternate separation technique to include biosorption. Biosorption process has distinct advantages over other conventional methods, which include reusability of biomaterial, low operational cost, local availability, technical feasibility and engineering applicability (Wanna *et al*., 2009). In recent years, many biosorbents of agricultural base have been utilized for toxic metal removal; these include Pomelo peel (Wanna *et al*., 2009), Duck weed (Dhabab, 2011), Almond green hull (Sahranavard *et al*., 2011), Banana leaf (Babarinde *et al*., 2012), Coconut leaf (Babarinde *et al*., 2012), Orange peel (Gonen and Serin, 2012).

The sorbent material considered in this work was *Detarium microcarpum* shell, otherwise called Sweet dattock, which is arainforest and savannah tree of tropical Africa shrubby tree of 8-10m high, having twisted trunk and wide spreading crooked branches belonging to the subfamily *Caesalpinioideae*. It is widely distributed geographically in tropical western Africa countries such as Senegal, Sudan and Nigeria (Mann, 2003). It is called by various names among the tribes in Nigeria. For instance, the Yorubas referred to it as Ogbogbo, the Nupes called it Gungorochi, while the Hausas and Igbos name it Taura and Ofo, respectively. *Detarium microcarpum* as an agricultural product provides essential benefits to humans. In spite of these benefits, large quantities of the waste generated are disposed improperly. Disposal by burning generate CO_2 that depletes the ozone layer, and other forms of environmental pollution. These provide pressing need of harnessing these low value wastes by converting it into a useful adsorbent that can remove toxic metals from wastewater, thereby helpful in the search for cheaper and eco-friendly adsorbent materials in waste water remediation. This study therefore was conducted to remove Pb (II), Ni (II) and Co (II) ions using *Detarium microcarpum* shell from aqueous solution.

Materials and Methods

Sample collection and preparation

Detarium microcarpum fruits were purchased from different locations at Maitunbi within Minna metropolis, Niger state in Nigeria, during the month of March, 2012. The pericarps were removed and de-shelled, then the edible part and the shell was washed off, sun dried for days, and then grounded to powder form with mortar and pestle (Musah *et al*., 2016).

Sample pretreatment

The powdered biomass was defatted by soaking in 500 cm^3 of hexane for 15 hours after which it was washed with distilled deionized water till the color of the washing water was clear, later sun dried. The modification process was done by adding 0.5M of oxalic acid so as to open-up the micropores of the adsorbent thereby making them ready for sorption. This chemical activation was done for 24 hours and the mixture properly stirred. The adsorbent was then filtered and rinsed with deionized water. The rinsed adsorbent was later air dried for 12 hours and re-crushed using porcelain mortar and pestle to obtain a finer particle size, which was creened through 250 µm mesh size and store in airtight bottles (Musah *et al.*, 2016).

Preparation of aqueous solution

$Co(NO_3).6H_2O$, $NiCl_2.6H_2O$ and $Pb(NO_3)_2$ were supplied by Sigma Aldrich and used without further purification. Aqueous solution containing Co(II), Ni(II) and Pb(II) ions were prepared by dissolving 4.9 g, 4.03 g and 1.6 g analytical grades of $Co(NO_3).6H_2O$, $NiCl_2.6H_2O$ and $Pb(NO_3)_2$ respectively in 1000 cm^3distilled de-ionized water to give a concentration of 1000 ppm. 100 ppm was further prepared from 1000 ppm stock solution by serial dilution and were used for each experiment.

Sorption experiment

Effect of pH on adsorption

The effect of pH on adsorption was studied using an initial concentration of 5 mg/L; the pH range chosen for this experiment were pH 1 to 8. The pH of the solution was adjusted using 0.1M HCl or 0.1M NaOH. 0.5 g of the pretreated powdered sample was added to 50 cm^3 of aqueous solution. The mixtures in the conical flask were corked and shaken on a rotatory shaker for 2 hours at room temperature, after which the mixtures were filtered using Whatman filter paper, then stored in a sample bottle prior to analysis. The final concentration of the metal ion in the solution was determined by atomic absorption spectrometer (Perkin Elmer Analyst 200).

Effect of contact time on adsorption

The effect of contact time was studied using an initial concentration of 5 mg/L. The time interval chosen for this experiment were 30, 60, 90, 120, 150 and 180 min. 0.5 g of the pretreated powdered sample was mixed with 50 cm^3 of the prepared aqueous solution in a conical flask, well corked and the mixture shaken on a rotatory shaker at 250 rpm. At the end of each contact time period, the mixture was filtered using Whatman filter paper and the residual fraction was stored in sample bottles and refrigerated prior to analysis. The residual concentration of the metal ion in the filtrate was determined by atomic absorption spectrometer (Perkin Elmer Analyst 200).

Effect of initial metal ion concentration

The effect of initial metal ion concentrations was studied using various concentrations of 20, 40, 60, 80, 100 mg/L. 0.5 g of the pretreated powered sample was added to 50 cm^3 of aqueous solution in a conical flask. The resultant solution with the adsorbent in the conical flask were well corked and shaken on a rotatory shaker for 60 and 90 minutes for each metal ion after which it was filtered using a Whatman filter paper and the residual concentration of the metal ion in the filtrate was determined using an atomic absorption spectrophotometer (Perkin Elmer Analyst 200).

Effect of temperature on adsorption

The effect of temperature on adsorption was studied using an initial concentration of 5 mg/L. The temperature range was between 30^oC - 70^oC at interval of $10^o C$ using a water bath. 0.5 g of the pretreated powered sample was added to 50 cm^3 of aqueous solution in a 100 cm^3 beaker. The desired temperature was adjusted on the water bath and the beaker containing the mixture was clamped on a retort stand and was partly immersed in the heated water, other experimental conditions were noted such as pH and contact time. The solution was stirred continuously using a stirring rod after which it was filtered using a Whatman filter paper (0.45 µm) and the residual concentration of the metal ion in the filtrate was determined using an atomic absorption spectrophotometer (Perkin Elmer Analyst 200).

Determination of adsorbed metal contents

The percentage of metal removed by the adsorbent was computed using the equation.

$$Adsorption(E), \% = \frac{Ci - Ce}{Ce} \times 100$$

Where: C_i and C_e is the initial and equilibrium concentration of metal ion mg/l, E is the % removal.Adsorption capacity was calculated by using the mass balance equation for the adsorbent

$$Qe = \frac{(Ci - Ce)V}{W}$$

Where Q_e is the adsorption capacity (mg/g), V; is the volume of metal ion solution W; is the weight of the adsorbent (g)

Adsorption isotherm

In order to establish the equilibrium adsorptive behavior of the adsorbent, it is necessary to understand the equation state between the two phases that made up the adsorption system. Base on this, three kinds of several isotherms were tested to fit the equilibrium data (Sampranpiboon *et al*, 2014).

The Freunlich model is represented as:

$$Logqe = \frac{1}{n} \log Ce + \log Kf$$

The Langmuir equation:

$$\frac{Ce}{qe} = \frac{Ce}{qmax} + \frac{1}{qmax} b$$

Dubinin- Radushkevich model:

$$lnQe = lnVm - k\varepsilon^2$$

Where:Qe represent the amount of metal ions removed in mg/g

V'm is the D–R adsorption capacity (mg/g); *K*'is the constant related with adsorption energy (mol^2 k/J^2); *ε*, the Polanyi potential, the Polanyi potential (*ε*) can be obtained using the equation below:

$$\varepsilon = RTln\ (1 + \frac{1}{Ce})$$

hence, D-R isotherm equation can be re-expressed as

$$LogQe = \log Vm - KR^2T^2 \log(1 + \frac{1}{Ce})$$

Adsorption kinetic

Several kinetic models are needed to establish the mechanism of adsorption process. In order to investigate the adsorption kinetic of these metal ions on the shell of *Detarium microcarpum*, the Lagergren first order (Lagergren, 1989) and the pseudo second order kinetics models (Ho and Mckay, 1999) were employed.

Lagergren pseudo-first order model which considers that the rate of occupation of the biosorption sites is proportional to the unoccupied sites (Ertugay and Bayhan, 2008)

The expression for the Lagergren pseudo-first order model is (Farouq and Yousef, 2015):

$$\frac{Dqt}{dt} = K1\,(qe - qt)$$

On integration, linearized form of the equation is obtained

$$Log(qe - qt) = \log qe - k1\frac{t}{2.303}$$

Where

k_1 is the Lagergren rate constant for adsorption (min.$^{-1}$)

q_e is the amount of metal adsorbed at equilibrium (mg/g)

q_t is the amount of metal adsorbed at (mg/g) at any time t.

The values of k_1 and q_e were determined from the slope and intercept of the straight line gotten from the plot of t against log (q_e - q_t).

The data was likewise subjected to the pseudo-second order kinetic model. The equation for the pseudo second order model is

$$\frac{Dqt}{dt} = K2(qe - qt)^2$$

Integration and rearrangement gives the below equation

$$\frac{t}{qt} = \frac{1}{k2xqe^2} + \frac{1}{qet}$$

Where: k_2 is equilibrium rate constant of second order kinetics model (g/mg/min)

q_e is the equilibrium capacity

q_t is the biosorption capacity at any time t.

The values of k_2 and q_e was determined from the slope and intercept of the straight line obtained from the plot of t against t/q_t.

Thermodynamics analysis

The temperature effect on the biosorption of Ni (II), Co (II) and Pb (II) ions onto shell of *Detarium microcarpum* helps in evaluating the change in free energy (ΔG˚), enthalpy (ΔH˚) and entropy (ΔS˚). The free energy change was estimated using the relation below as proposed by de la Rosa *et al*., (2008) and Sun *et al*. (2008)

$$\Delta G^o = -RT\ln K_c$$

T (k) denotes the absolute temperature; R is the gas constant (KJ/mol). The equilibrium constant (K_c) was evaluated using the following relationship: $K_c = C_{ad}/ Ce$

Where: C_e and C_{ad} are the equilibrium concentrations of metal ions (mg/L) in solution and on biosorbent, respectively. Enthalpy and entropy were obtained using Van't Hoff equation (Qu *et al.*, 2010; Uluozlu *et al.*, 2010). Having estimated the value of ΔG^o, graph of ΔG^o versus T(k) were plotted (Figure 20 – 22) and the values of ΔH^o and ΔS^o which represent the slope and intercept were obtained from the plots

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

ΔH^o represents the enthalpy change, T is the temperature,

ΔS^o is the change in entropy

Results and Discussion

From Fig. 1, it was observed that Co (II) ions had the maximum adsorption at pH of 5 which decreased later as the pH increased to 8. For Ni (II) ions the highest removal was at pH of 5 then a decrease as pH was increased to 8. Furthermore, Pb (II) ion had maximum removal at pH 6 and then a decrease as the pH was increased.

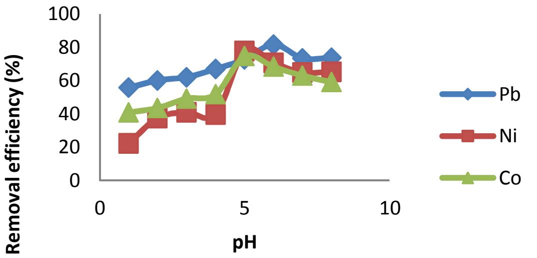

Fig. 1: Effect of pH on adsorption of Pb (II), Ni (II) and Co (II) ions from aqueous solution by *Detarium microcarpum* shell

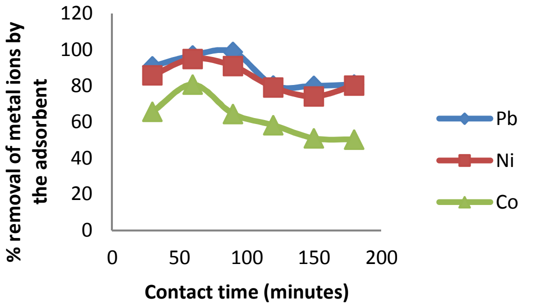

Fig. 2: Effect of variation of contact time on adsorption of Pb (II), Ni (II) and Co (II) ions from aqueous solution by *Detarium microcarpum* shell

From Fig. 2, it was revealed that as the contact time increases from 30 to 180 minutes, the amount of metal ion removed also increases, this trend was consistent between 30,60 and 90 minutes until equilibrium was attained at 60 minutes for Co (II) and Ni (II) ions, while that of Pb(II) ion was at 90 min. Further increase above equilibrium time resulted into desorption.

From Fig. 3, it was also observed that as the initial metal ion concentration increases, the mount of Pb (II), Ni (II) and Co(II) ions adsorbed also increased in the orderCo(II)>Ni(II)>Pb(II) ion.

From Fig. 4, it was revealed that as temperature increases, amount of metal ions adsorbed also increases. At initial temperature of 303K, Pb(II) ions were the least adsorbed, while Co(II) ions were the most adsorbed, at 313K Pb(II) ions became the most adsorbed, at final temperature of 343K Pb(II) ions were the most adsorbed, while Co(II) ions were the least adsorbed.

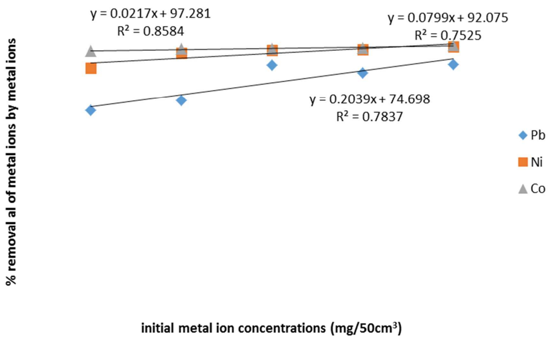

Fig. 3: Effect of variation of initial metal ion concentration on adsorption of Pb(II), Ni(II) and Co(II) ion from aqueous solution by *Detarium microcarpum* shell

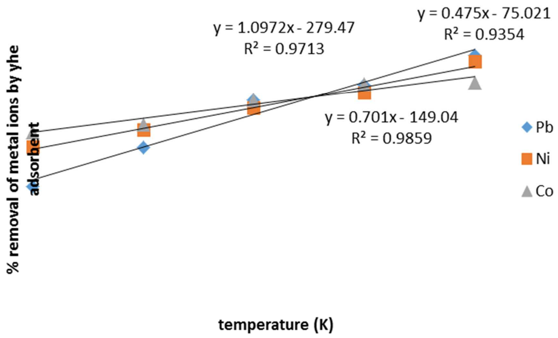

Fig. 4: Effect of variation of temperature on adsorption of Pb (II), Ni (II) and Co (II) ions from aqueous solution by *Detarium microcarpum* shell

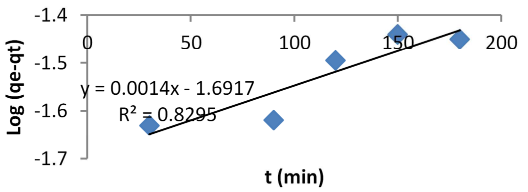

Fig. 5: Pseudo-First order for sorption of Ni (II) ions by the shell of *Detarium microcarpum*

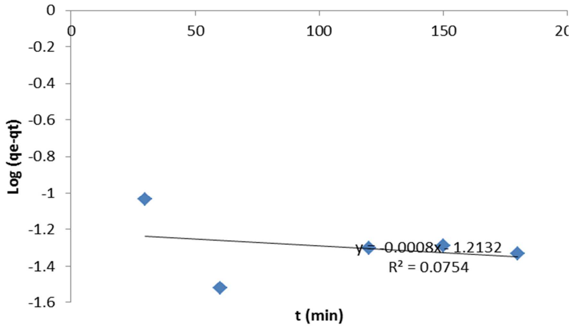

Fig. 6:Pseudo-First order for sorption of Pb (II) ions by the shell of *Detarium microcarpum*

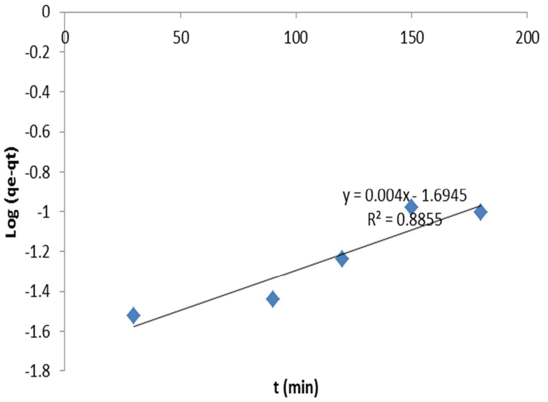

Fig. 7: Pseudo-First order for sorption of Co (II) ions by the shell of *Detarium microcarpum*

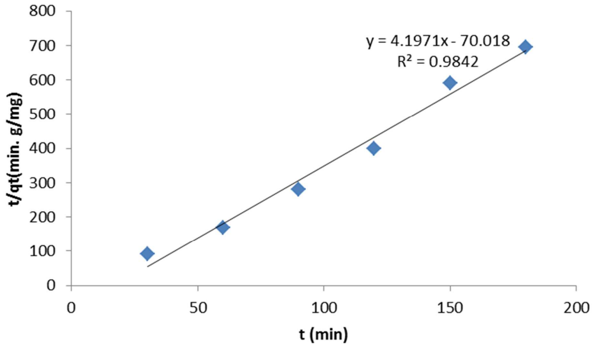

Fig. 8: Pseudo-Second order for sorption of Co (II) ions by the shell of *Detarium microcarpum*

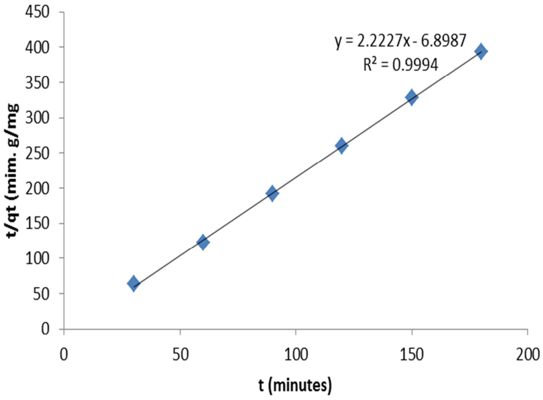

Fig. 9: Pseudo-Second order for sorption of Ni (II) ions by the shell of *Detarium microcarpum*

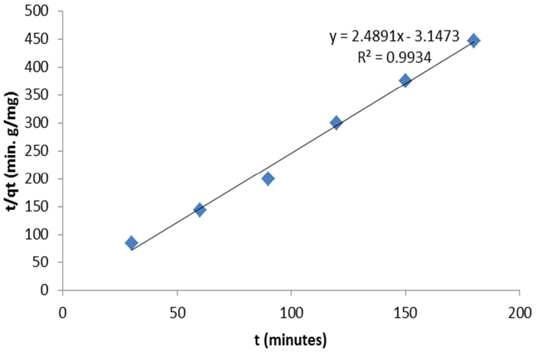

Fig. 10: Pseudo-Second order for sorption of Pb (II) ions by the shell of *Detarium microcarpum*

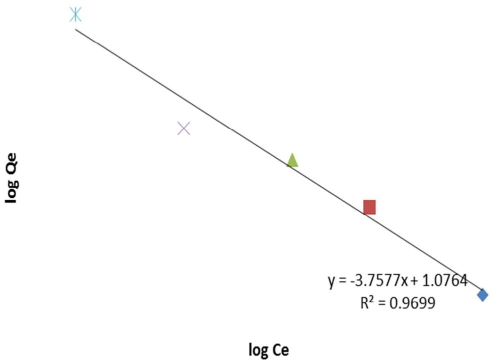

Fig. 11: Freundlich adsorption isotherm plot of Ni (II) ions by the shell of *Detarium microcarpum*

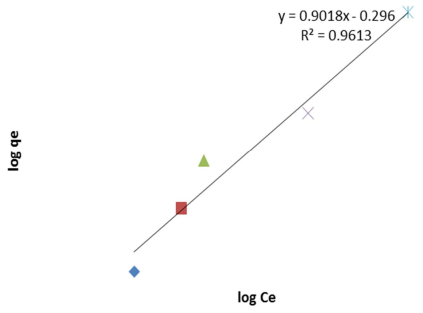

Fig. 12: Freundlich adsorption isotherm plot of Pb (II) ions by the shell of *Detarium microcarpum*

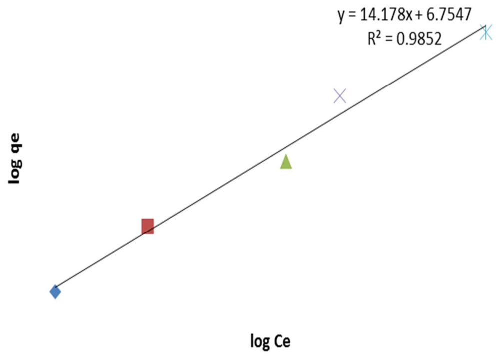

Fig. 13: Freundlich adsorption isotherm plot of Co (II) ions by the shell of *Detarium microcarpum*

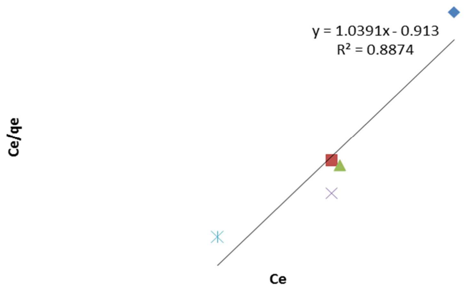

Fig. 14: Langmuir adsorption isotherm plot of Ni (II) ions by the shell of *Detarium microcarpum*

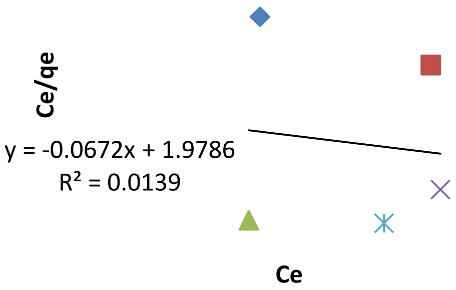

Fig. 15: Langmuir adsorption isotherm plot of Pb (II) ions by the shell of *Detarium microcarpum*

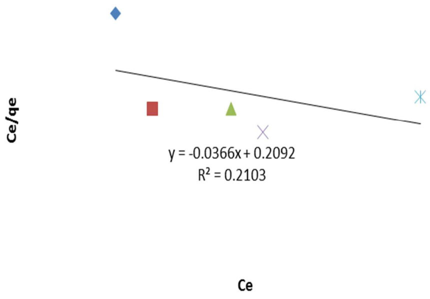

Fig. 16: Langmuir adsorption isotherm plot of Co (II) ions by the shell of *Detarium microcarpum*

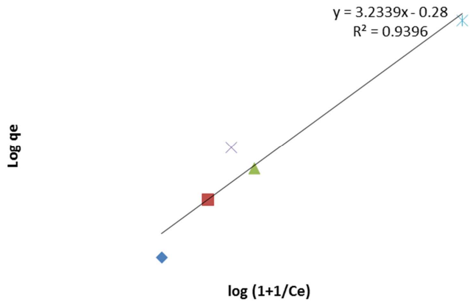

Fig. 17: Dubinin-Radushkevich (D-R) adsorption isotherm plot of Ni (II) ions by the shell of *Detarium microcarpum*

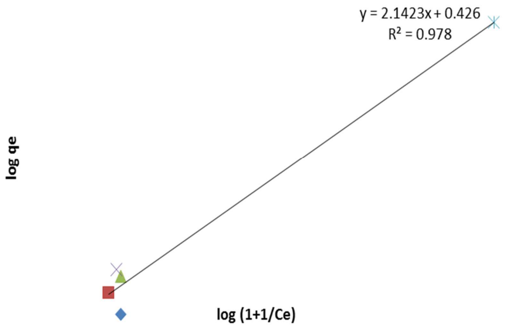

Fig. 18: Dubinin-Radushkevich (D-R) adsorption isotherm plot of Pb (II) ions by the shell of *Detarium microcarpum*

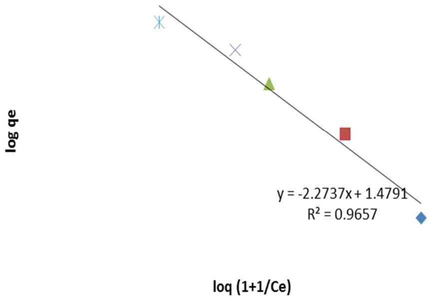

Fig. 19: Dubinin-Radushkevich (D-R) adsorption isotherm plot of Co (II) ions by the shell of *Detarium microcarpum*

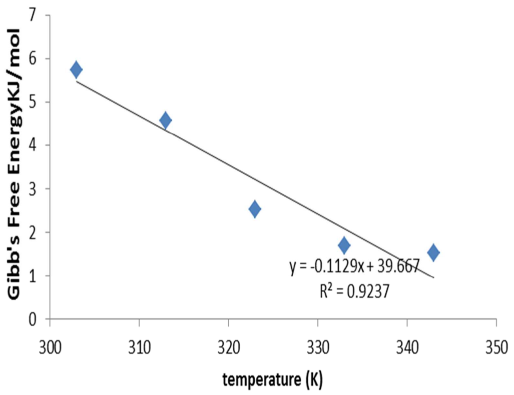

Fig 20: Thermodynamic plot for the biosorption of Pb (II) ionsby the shell of *Detarium microcarpum*

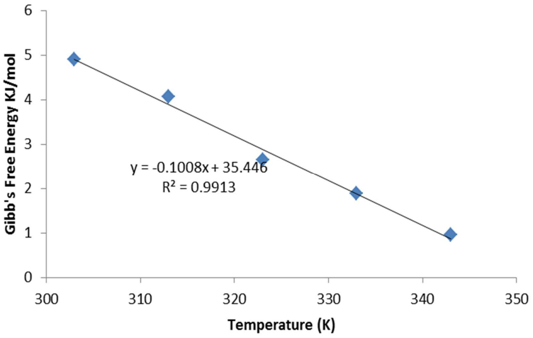

Fig. 21: Thermodynamic plot for the biosorption of Ni (II)by the shell of *Detarium microcarpum*

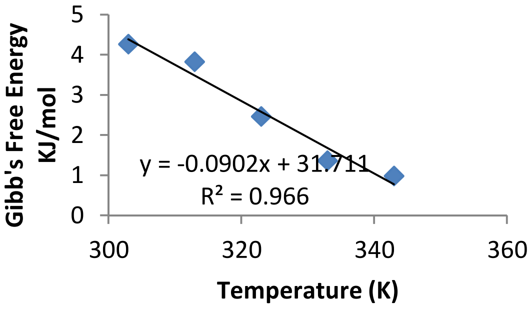

Fig. 22: Thermodynamic plot for the biosorption of Co(II)by the shell of *Detarium microcarpum*

Effect of solution pH on metal ion uptake

The pH of solution has a marked impact on the removal of potentially toxic elements, because it affects the surface charges of the adsorbent, the degree of ionization of the functional groups and speciation of the adsorbate (Flaviane *et al.*, 2010). Also, the level of dissociation of functional groups on the adsorbent surface, solubility of the metal ions and concentration of the counter ions in solution are also affected by pH (Nomanbhay and Palanisamy, 2005). From Fig. 1, adsorption of the metal ion was minimal at low pH (pH 1–3); which could be ascribed to hydrogen ions competing with metal ions for sorption sites, thus, hindering the metal ions from reaching the binding sites of the adsorbent caused by repulsive forces (Nuhoglu and Malkoc, 2009). This means that H^+ ions present favored the preferential adsorption of hydrogen ion compared to the metal ion (Ajmal *et al*., 2000). This is similar to the findings reported by Egila *et al.* (2011), Jimoh *et al.* (2012), Babarinde *et al.* (2012). In contrast, as pH increases the ligands on the adsorbent were fully exposed, more negatively charged surface becomes available thus facilitating greater metal ion uptake. The increase in percentage removal as pH increases implies that ion-exchange process was involved. As pH increases between 7 and 8, the formation of anionic hydroxide complexes or precipitate decreases the concentration of the metal ions, which peradventure reduces the rate of adsorption of metal ions sorbed (Stephen and Sulochana, 2004).

Effect of contact time on metal ion uptake

The result of the effect of contact time on adsorption of Pb (II), Ni (II) and Co (II) ions from aqueous solution is shown in Fig. 2. It was observed that the percentage of metal ions removed by *Detarium microcarpum* increased with increasing contact time. The percentage of metal ions removed was rapid within 60 minutes for Co (II) and Ni (II) ion and 90 minutes for Pb (II) ions. Additional increase in contact time resulted in a decrease in the amount of ions adsorbed, this implies that the binding sites on the adsorbent were exhausted and further shaking resulted in desorption. Similar trend was observed for the biosorption of Pb (II) ion (Babarinde and Babalola, 2010), Co (II) ion (Egila *et al*., 2010), and Ni (II) ion (Nuhoglu and Malkoc, 2009). It is evident that the shell of *Detarium microcarpum* was more efficient and effective for the removal of Pb (II) ions than Ni (II) and Co (II) ions. Although Co (II) and Ni (II) ions reached equilibrium faster than Pb (II), but the percentage of Pb (II) ions bound at every given contact time was more than the percentage removed by Ni (II) and Co (II) ions. This is might be due to the differences in hydrated ionic sizes of the metal ion. More so, this differential adsorption of metal ions could be explained in terms of difference in their ionic radii. The smaller the ionic radius, the greater its tendency to hydrolyze, and of course this led to reduce sorption. This might be the reason why more of Pb (II) ions were adsorbed than Ni (II) and Co (II) ion. This is similar to the previous findings by Hanif *et al.* (2007) and Jimoh *et al*. (2011).

Effect of initial ion concentration

The variation in the amount of metal ion adsorbed with initial metal ion concentration is illustrated in Fig. 3. The percentage removed increases with increase in the initial metal ion concentration which might be due to increase in effective collision between the metal ions and the active sites. The initial faster rate of the removal of each metal ion could be due to the presence of available surface area on the adsorbent (Qadeer and Akhtar, 2005). Furthermore, there was progressive increase in the columbic interactions between the cationic species in water and the adsorbent sites, therefore, more adsorption sites were being covered as the metal ion concentration increased (Laraous *et al*., 2005; Gong *et al*., 2006). The percentage removal followed the order Co (II) >Ni (II) >Pb (II) ions. The difference in the uptake levels of the metal ions could also be explained in terms of the difference in the ionic size and atomic weight of the metal ions, the mode of interactions between the metal ions and the substrate. This order is the same as reported by Egila *et al.* (2011) and comparable to Babarinde *et al*. (2012). The percentage increase in the metal ions removed by the substrate was enhanced as a result of the modification by 0.5M oxalic acid. This was because oxalic acid assists by donating proton which in turn made the biosorbent surface became positively charged and resulted to electrostatic attraction. The higher the electrostatic attraction, the higher the percentage of metal ions sorbed.

Effect of temperature

Temperature has a profound effect on the sorption process. From Fig. 4, it was shown that as temperature increases, the rate of diffusion of metal ions across the external and internal layers of the sorbent particle increases. This in turn led to increase in percentage metal ions removed. At initial temperature of 303 K, Pb(II) ions was the least adsorbed, followed by Ni (II) while Co(II) ions was the most adsorbed. Pb(II) ions became the most adsorbed at 313 K and 343 K respectively and Co(II) ions remained the least adsorbed. Again, the differences in hydrated ionic sizes of the metal ion and ionic radii might be responsible for the observed removal efficiency. This corroborated the findings of Madhavi *et al.* (2011) on the biosorptive removal of Cd^{2+}, Pb^{2+} and Cu^{2+} from aqueous solution using *Cassia augustifolia* bark. It was also observed from Fig. 4 that high temperature favour the biosorption of metal ions suggesting the endothermic nature of the process. This might occurred as consequence of the increase in the number of pores on the adsorbent surface at high temperature as high temperature reduces the thickness of outer surface of the adsorbent and subsequently increases kinetic energy of the adsorbate. This made the metal ions to be easily adsorbed by the sorbent.

Adsorption kinetics modeling

Adsorption efficiency is governed mainly by kinetic study (Gonen and Serin, 2012) and was developed to explain the transport of metals onto various adsorbents. Several of models are needed to establish the adsorption mechanism. For this study, pseudo- first order and the pseudo second order kinetics models were employed to describe the adsorption kinetic of these metal ions onto shell of *Detarium microcarpum*. The coefficient of correlation (R^2) for the experimental point was used as the fitting parameter. Comparing the R^2 values for Pb(II), Co(II) and Ni(II) ion removal as shown in Tables 1 and 2, the pseudo-second order kinetic model gave better R^2 value and the higher the value of R^2, the higher the applicability of the model to the data. The applicability of this model suggests that adsorption of these metal ions on the shell of *Detarium microcarpum* was based on chemical reaction between metal ions and active sites of the adsorbent. Conformation of adsorption process to pseudo-second order kinetic has also been reported by El-Ashtoukhy *et al.* (2008); Babarinde and Babalola (2010); Ejikeme *et al.* (2011); Yusra and Bhatti, (2011) and Babarinde *et al.* (2012).

Table 1: Pseudo-first-order constant for the adsorption of Pb (II), Ni (II) and Co (II) ions by the shell of *Detarium microcarpum*

Metal	$K_{1\,(min^{-1})}$	$Q_{e\,(mg/g)}$	R^2
Pb(II)	0.0008	1.21	0.0754
Ni(II)	0.0014	1.69	0.8295
Co(II)	0.0040	1.69	0.8855

Table 2: Pseudo-Second-order constant for the adsorption of Pb (II), Ni (II) and Co (II) ions by the shell of *Detarium microcarpum*

Metal	K_2 (g/mg/min)	Q_e (mg/g)	R^2
Pb(II)	1169	0.014	0.9934
Ni(II)	21.43	0.144	0.9900
Co(II)	4.00	1.032	0.9842

Adsorption equilibrium

The adsorption equilibrium is established only when the concentration of the sorbate in bulk solution is in dynamic balance with that on the liquid-sorbent interface. The degree of the sorbent affinity for the sorbate determines its distribution between the solid and liquid phases (Meera and Ganesan, 2015; Qaiser *et al.*, 2009). Several models were often employed to interpret the equilibrium data. In this present research, the Freundlich, Dubinin-Radushkevich and Langmuir models were utilized to explain the experimental data. Tables 3 and 5 show that Freundlich and Dubinin-Radushkevich (D-R) isotherm fitted well for the biosorption of the metal ions than Langmuir isotherm (Table 4). This is due to the fact that the correlation coefficient (R^2) of both isotherm were high and showed good linearity than Langmuir isotherm that showed little correlation. Thus, the data of Pb (II), Ni (II) and Co (II) ions adsorption onto the shell of *Detarium microcarpum* might be concluded to perfectly fit to Freundlich and Dubinin-Radushkevich (D-R) isotherm. The isothermal biosorption parameters compare well with those of other biosorbent that was reported by Ejikeme *et al.*, (2011).

Table 3: Freunlich model parameters associated with the adsorption of Pb (II), Ni (II) and Co (II) ions by shell of *Detarium microcarpum*

Metal ion	N	$K_{F(l/g)}$	R^2
Pb(II)	3.37	7.69	0.96
Ni(II)	0.93	5.75	0.97
Co(II)	0.14	1.48	0.99

Table 4: The Langmuir model parameters associated with the adsorption of Pb (II), Ni (II) and Co (II) ions by shell of *Detarium microcarpum*

Metal ions	q_{max} (mg/g)	B (l/mg)	R^2
Pb(II)	14.93	0.130	0.013
Ni(II)	0.96	0.950	0.887
Co(II)	4.78	0.007	0.210

Table 5: Dubinin-Radushkevich (D-R) model parameters associated with the adsorption of Pb (II), Ni (II) and Co (II) ions by shell of *Detarium microcarpum*

Metal ion	V'm	K	R^2
Pb(II)	27.04	0.475	0.95
Ni(II)	1.67	-0.28	0.94
Co(II)	0.36	1.48	0.97

Adsorption Thermodynamic

From Table 6, it was observed that the values of ΔH^o were positive for the biosorption of the three metals ions, suggesting that the adsorption process was endothermic in nature. This was evident by the increase in the percentage of metal ion removed with rise in temperature. The positive values of ΔH^o indicates the presence of an energy barrier in the adsorption process. The positive values of ΔG^o for the three metal ions indicated that the adsorption process was feasible but not spontaneous, while the value of ΔS^o was negative, an indication of decreased randomness at the sorbent-sorbate interface during the adsorption of metal ions onto adsorbent. This was further supported by the findings of Babarinde *et al*. (2009) who reported the biosorption thermodynamics of Pb (II) ions onto *Calyperes erosum*.

Table 6: Thermodynamic parameters for the biosorption of Co (II), Ni (II)and Pb (II) onto shell of *Detarium microcarpum*

Metal ion	ΔH^o (J/mol/K)	ΔS^o (J/mol/K)	ΔG^o (kJ/mol/K)	R^2
Co(II)	0.09	-31.71	9.67	0.96
Ni(II)	0.10	-35.44	10.81	0.99
Pb(II)	0.11	-39.66	12.096	0.92

Conclusion

The following conclusions were drawn from the present study. The optimum pH required for maximum adsorption were found to be 5.0 for Co(II) ion, 6.0 for Pb (II) and Ni (II) ion respectively. Equilibrium times of 60 minutes were attained for Ni (II) and Co (II) ions and 90 minutes for Pb (II) ions. The amount of metal ions adsorbed by the substrate increased with increase in initial metal ion concentration. The kinetics of the biosorption of these metal ions followed a pseudo-second-order model. The adsorption equilibrum fitted well to Freundlich and Dubinin-Radushkevich (D-R) isotherm model. The thermodynamic parameters (ΔG^o, ΔH^o and ΔS^o) showed that the adsorption of Pb(II), Ni(II) and Co(II) ions was not spontaneous but feasible, endothermic and low randomness at the sorbent-sorbate interface. The obtained results in the present study revealed that the shell of *Detarium microcarpum* has high potentials for the removal of the selected potential toxic elements.

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