Equilibrium sorption of divalent metal ions onto groundnut (*Arachis hypogaea*) shell: kinetics, isotherm and thermodynamics

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A R T I C L E   I N F O

A B S T R A C T

The equilibrium, kinetics, and thermodynamics of the biosorption of Pb(II), Cd(II) and Zn(II) onto groundnut (*Arachis hypogaea*) shell were investigated under various physicochemical parameters. Optimisation studies were carried out using batch biosorption studies. The extent of the metal ion biosorption increased with increase in solution pH, initial metal ion concentration, dosage of biosorbent and contact time but decreased with the temperature of the system. The biosorption of each of the metal ions was found to be pH-dependent. Kinetic study showed that the metal ions biosorption process followed the pseudo-second-order kinetic model. The sorption of each metal ion was analysed with Freundlich and Langmuir isotherm models, in each case, the equilibrium data were better represented by Freundlich isotherm model. Thermodynamically, parameters such as standard Gibbs free energy ($\Delta G°$), standard enthalpy ($\Delta H°$), standard entropy ($\Delta S°$) and the activation energy (A) were calculated. The biosorption of each metal ion was spontaneous and the order of spontaneity of the biosorption process being Cd(II) > Zn(II) > Pb(II). Similarly, change in entropy was observed for each and the order of disorder is Cd(II) > Zn(II) > Pb(II).

Capsule Summary: Groundnut shell was investigated for the sorption of Pb(II), Cd(II) and Zn(II), process variables were optimized, sorption data was subjected to kinetic and isotherm models and thermodynamic studies were also performed. Results showed that groundnut shell has high efficiency in the sorption of Pb(II), Cd(II) and Zn(II) and could possibly be used for treating wastewater containing these metal ions.

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INTRODUCTION

Heavy metal pollution in aquatic environment has become a source of great concern. In natural aquatic ecosystems, metals occur in low concentrations but in recent times, the occurrence of metals in excess of natural loads has become a problem of increasing concern. This situation has arisen as a result of industrialization and urbanization (Hanan et al., 2010). The increased industrialization results in the release of varied types and amounts of industrial wastes into the environment. These industrial wastes consist of several classes of pollutants including heavy metals. Apart from industrial activities, other sources of heavy metals into the environment include untreated domestic effluents, agricultural wastes, discharge from sewage treatment works,

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urban storm-water run-off, leaching of metals from garbage and solid wastes dump (Bilal et al., 2014; Iqbal et al., 2013; Iqbal and Bhatti, 2014, 2015; Iqbal and Khera, 2015; Iqbal and Nisar, 2015; Manzoor et al., 2013; Qureshi et al., 2015; Ullah et al., 2013).

Heavy metals are important source of pollution not just because they are toxic above a relatively low concentration but also because they are persistent, remaining in the environment long after the source of pollution has been removed that is, they do not biodegrade into harmless end product. Biosorption, a process whereby certain types of inactive, dead biomass may bind and concentrate heavy metals from aqueous solutions is considered an alternative technology for removal of toxic heavy metals from waste water and industrial effluents (Kaewsam and Yu, 2001; Romero-Gonzalez et al., 2001; Yu et al., 2001; Al-Subu, 2002; Sekhar et al., 2004; Naja et al., 2005; Saeed et al., 2005; Wankasi et al., 2005; Doyurum and Celik, 2006; Deng et al., 2007; Uluozolu et al., 2007, 2008, 2010; Babarinde *et al.*, 2008; Qaiser et al., 2009; Opeolu et al., 2010). The main advantage of using biosorption technology is the cost effectiveness of the biosorbents, since they may be derived from various cheap and abundantly available biological raw materials. Other advantages include competitive performance, heavy metal selectivity, no sludge generation, reusability of biomaterial, improve selectivity of specific metals of interest and short operation time (Babarinde et al., 2009; Sari et al., 2007). In this study, groundnut shell was investigated as a biosorbent for the uptake of Pb(II), Cd(II) and Zn(II) from solution.

Groundnut (*Arachis hypogaea*) is a plant that is grown across the world for its high nutritional value. It is widely use as meal and snacks because of its high protein content. However, the shell is unutilized, thereby becoming environmental nuisance. It is found to contain abundant functional groups such as hydroxyl, amine and carboxyl groups which contain lone pairs of electrons needed for biosorption of cationic pollutants in solution. It was on this basis that this readily available agricultural waste was investigated for its potential in treating effluent containing Pb(II), Cd(II) and Zn(II). Previous studies on groundnut biomass include evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution (Brown et al., 2000) and the removal of heavy metals from solution using groundnut husk (Okieimen et al., 1991). Other studies include biosorption of Pb(II) and Cr(VI) on groundnut hull (Qaiser et al., 2009), the use of activated carbon prepared from groundnut shell for the sorption of malachite green dyes (Malik et al., 2007). We have recently investigated the biosorption of Ni(II), Cr(III) and Co(II) with groundnut shell (Babarinde et al., 2012) and found the sorbent very effective hence the need to extend the study to other metal ions that contaminate the environment. Therefore, in present investigation, groundnut shell efficiency for the adsorption Pb(II), Cd(II) and Zn(II) was evaluated.

MATERIAL AND METHODS

Preparation of biosorbent

Groundnut (*Arachis hypogaea*) was obtained from Kuje market, Abuja, Nigeria. The shells were properly rinsed with water, sun dried immediately and kept dry in an air tight polythene bag until time of usage.

Preparation of solution

All chemicals (BDH, England) used in this study were of analytical reagent grade and were used without further purification. Standard solutions of Pb(II), Cd(II) and Zn(II) used for the study were prepared from $Pb(NO_3)_2$, $3CdSO_4.8H_2O$ and $Zn(NO_3)_2.6H_2O$, respectively. The working solutions with different concentrations of the metal ions were prepared by appropriate dilutions of the stock solution prior to their use with distilled water. The initial pH of the solution was adjusted accordingly with a pH meter (Horiba F-11) to between 1.0 and 6.0. Thermostated water bath (AdvantecLB240) was used as the medium for the process. The concentration before and after biosorption of each metal ion was determined using a Perkin-Elmer Analyst 700 flame atomic absorption spectrophotometer.

Characterization of biomass

Fourier transform infrared (FT-IR) spectra of dried unloaded biomass and metal loaded biomass were recorded at 400 to 4000 cm^{-1} using a Shimadzu FT-IR model 8400S spectrophotometer.

Biosorption experiments

Batch equilibrium biosorption studies were carried out by contacting 0.5 g of the groundnut shell with 25 ml of the metal ion solution under different conditions for a period of time in a boiling tube. The biosorption studies were conducted at 28°C using thermostated water bath (AdvantecLB240) to determine the effect of pH, biomass dosage, contact time, initial metal ion concentration and temperature on the biosorption. The initial pH of the solution was adjusted accordingly with a pH meter (Horiba F-11). The amount of metal ion biosorbed from solution was determined by difference and the mean value was calculated.

Effect of pH on biosorption

The effect of pH on the biosorption of the metal ion was carried out within the range that would not be influenced by the metal precipitated. This was done by mixing 0.5 g of groundnut shell with 25 ml of 100 mgL^{-1} metal ion solution in a boiling tube within the pH range of 1-6. pH of each solution was adjusted to the desired value by drop wise addition of 0.1 M HNO_3/0.1 M NaOH. The boiling tubes containing the mixture were maintained in a water bath for 2 h.
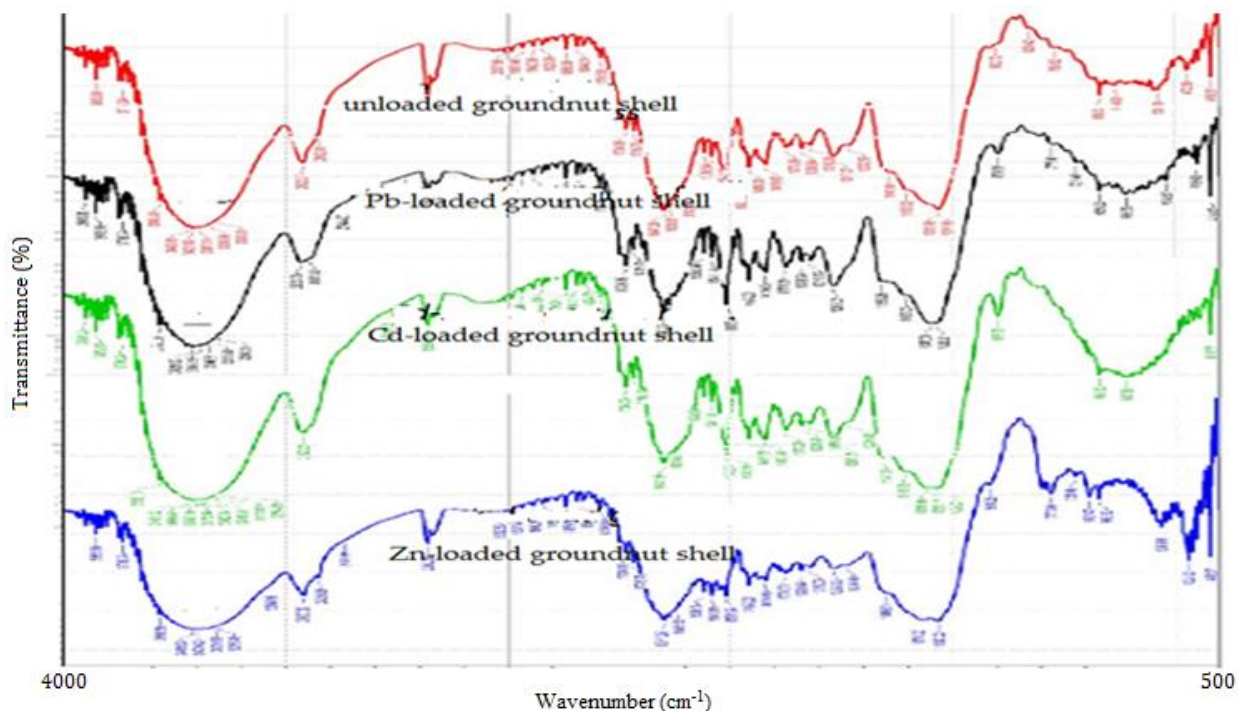
Fig. 1: FT-IR-spectra of the free and metal-bound groundnut (*Arachis hypogaea*) shell

The biomass was removed from the solution by decantation. The residual metal ion concentration in the solution was analyzed. The optimum pH was determined as the pH with the highest biosorption of each metal ion.

Effect of biosorbent dosage

Effect of biosorbent dosage was investigated using an initial metal ion concentration of 100 mgL^{-1}. Biosorbent masses used for the study were within the range 0.1 – 2 g. The study was carried out at the temperature of 28°C and at pH 5. The contact time for this experiment was 2 h.

Effect of contact time on biosorption

The biosorption of the metal ions by groundnut shell was studied at various time intervals (0 -300 min) and at a concentration of 100 mg/L. This was done by contacting 2 g of groundnut shell with 25 ml of 100 mgL^{-1} of metal ion solution in a boiling tube at pH 5 and temperature of 28°C. The shell was left in the solution for different periods of time. The solution in the boiling tube was decanted at different time intervals from the first to the last tube. Each aliquot was analysed for residual metal ion concentration using atomic absorption spectrophotometer. The amount of metal ions biosorbed was calculated for each sample.

Effect of initial concentration on biosorption

Batch biosorption study of metal ion was carried out using a concentration range of 10 to 100 mgL^{-1}. This was done by introducing 2 g of the groundnut shell into 25ml metal ion solution in the boiling tubes employed at pH 5. The tubes were maintained in a thermostated water bath maintained at 28°C for 2 h. The groundnut shell was removed from the solution by decantation and the concentration of residual metal ion in each solution was determined.

Effect of temperature on biosorption

The batch biosorption process was studied at different temperatures of 20 to 50°C in order to investigate the effect of temperature on the biosorption process. This was done by contacting 2 g of groundnut shell with 25 ml of 100 mgL^{-1} of metal ion solution at the pH 5. The biosorption of metal ion may involve chemical bond formation and ion exchange since the temperature is a main parameter affecting them.

Statistical analysis

The curve fittings of the data obtained were performed using Microcal Origin 6.0 software.

RESULTS AND DISCUSSION

FT-IR studies groundnut shell

The FT-IR spectra of dried unloaded, Pb-loaded, Cd-loaded and Zn-loaded groundnut shell were taken with FT-IR

spectrophotometer. The spectra give information on the nature of possible interactions between the functional groups of groundnut shell biomass and the metal ions as presented in Figures 1. The IR spectra pattern of the biomass showed distinct and sharp absorptions indicative of the existence of the –OH, -NH, and -C-O- groups. These bands are due to the functional groups of groundnut shell that participated in the biosorption of Pb(II), Cd(II) and Zn(II). On comparison, there are clear band shifts and decrease in intensity of bands as reported in Tables 1. The FT-IR spectra of the groundnut shell biomass indicated slight changes in the absorption peak frequencies due to the fact that the binding of the metal ions causes reduction in absorption frequencies. These shifts in absorbance observed imply that there were metal binding processes taking place on the active sites of the biomass. Analysis of the FT-IR spectra showed the presence of ionizable functional groups which are able to interact with cations (Pradhan *et al.*, 2007; Bueno *et al.*, 2008; Sun *et al.*, 2008; Ertugay and Bayhan, 2008; Uluozlu *et al.*, 2008). This implies that these functional groups would serve in the removal of positively charged ions from solution.

Effect of solution pH on metal ion biosorption

The pH of the solution has been established to be a vital parameter in biosorption process (Sun et al., 2008; Babarinde et al., 2009). The net charge of the sorbate and that of the sorbent are dependent on the pH of the solution. At low pH, the metal ion uptake is inhibited by net positive charge on the sorbent and the competition between the metal ions and hydrogen ions in solution. The experiments were not conducted above pH 5.0 to avoid possible precipitation of hydroxide, especially with Pb(II). As the pH increases, the negative charge density on biomass increases as a result of deprotonation of the metal binding sites on the shell, consequently, the biosorption of the metal ions increases. The biosorption capacity increased with increasing pH and the effect of pH was in the order Pb(II) > Zn(II) > Cd(II). A similar order has been reported for the sorption of Pb(II), Cu(II) and Cd(II) by brewery biomass (Kim *et al.,* 2005). This effect of pH on the biosorption capacity can be explained as the result of competition of the hydronium ions and metal ions for the available binding sites. Figure 2 shows the variation of the metal ion biosorbed on groundnut shell at various solution pH values. In each case, the biosorption increased steadily as the pH increased from pH 1. The increase in biosorption with increase in pH implies that ion-exchange process is involved. The reaction involved the biosorption of metal ion (represented as M^{x+} for a metal ion) from the liquid phase to the solid phase, the biosorbent with lone pair of electrons (represented as Ä), and can be considered as a reversible reaction with an equilibrium being made between the two phases as schematically shown in Equation 1 for a divalent metal ion in the solution.
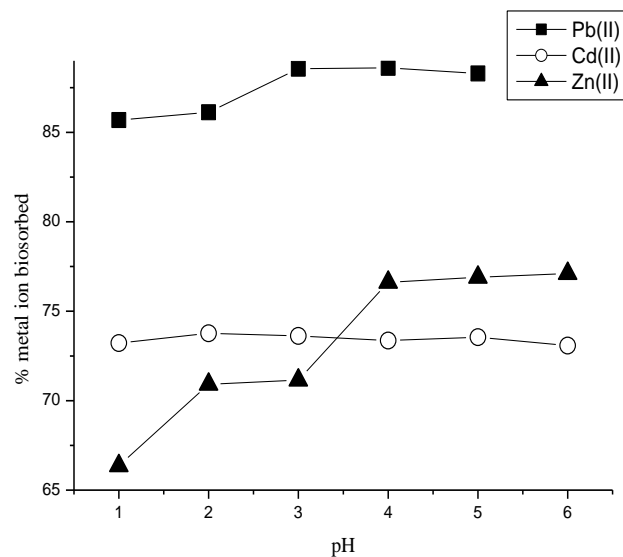
$$\ddot{A} + M^{2+} \rightleftharpoons A\text{-}M \tag{1}$$

Fig. 2: pH-dependence profile of the biosorption of Pb(II), Cd(II), and Zn(II) by groundnut (*Arachis hypogaea*) shell at 28°C, 100 mgL^{-1}
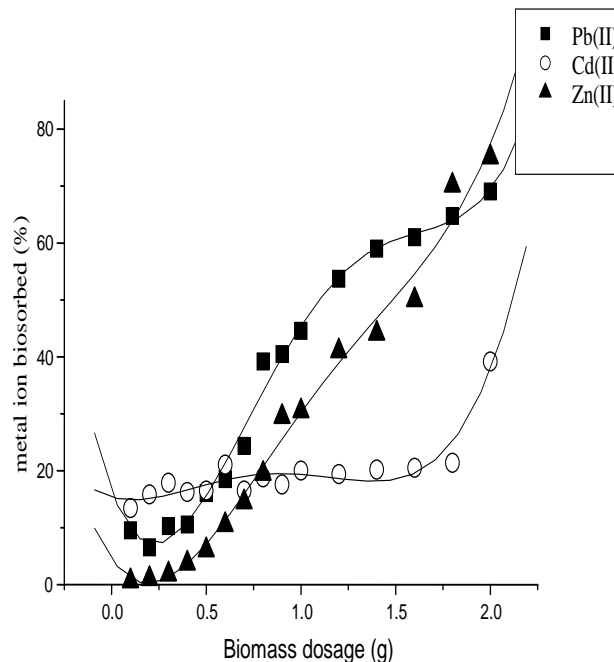

Fig. 3: Effect of biomass dosage on the biosorption of Pb(II), Cd(II) and Zn(II) by groundnut (*Arachis hypogaea*) shell at 28°C, 100 mgL^{-1}, pH 5

The reversibility of the biosorption process is observed when the metal-bound biomass is treated with dilute HNO$_3$ which is a desorption process. It was observed in each case that optimum pH was obtained at pH 5, this was then used as the

optimum pH for subsequent studies in the investigation of the effect of other physicochemical parameters.

Effect of biomass dosage on biosorption

The effect of the biomass dosage on the biosorption of the metal ions was investigated. The results are presented in Figure 3. The results show that biosorption of each metal ion increased with increase in biomass dosage, which implies that more active site were available for the biosorption of each metal ion. Consequently, the biomass dosage of 2g was used for subsequent studies. The general trend of increase in metal ion biosorbed with increase in biomass dosage indicates an increase in uptake due to more binding sites on the biomass available for biosorption. Such trend has been reported for other biosorbents (Babarinde et al., 2009).

Biosorption kinetics

The results of the effect of contact time on the biosorption of the metal ions are presented in Figure 4. In each case it is observed that biosorption increased with increase in contact time until saturation occurred. The optimum time of 2 h was used for subsequent studies in the investigation of the effect of other physicochemical parameters.

Figure 4 illustrates the dynamic biosorption process of the metal ions on groundnut shell. It is observed that the biosorptive quantities of the metal ions on groundnut shell increased with increasing contact time. In each case, bipahsic kinetics is observed: an initial rapid stage (fast phase) where biosorption is fast and contributes to equilibrium uptake and a second stage (slow phase) whose contribution to the metal ion biosorption is relatively smaller. The fast phase is the instantaneous biosorption stage, it is assumed to be caused by external biosorption of metal ion to the shell surface. The second phase is a gradual biosorption stage, which is diffusion rate controlled. Finally, the biosorption sites are used up, the uptake of the metal ion reached equilibrium.

This phase mechanism has been suggested to involve two diffusion processes, external and internal, respectively (Wu et al., 2010). The biosorption of each of the metal ions achieves equilibrium within 2 h, although, their rates of uptake are different. This might be due to the differences in hydrated ionic sizes of the metal ions (Kielland, 1937; Babarinde et al., 2012).

The data obtained from the study on the effect of time on biosorption was subjected to kinetic models in order to establish the mechanism of the biosorption process. Several kinetic models are needed to establish the mechanism of a biosorption process (Okasha and Ibrahim, 2010). In order to investigate the kinetics of the biosorption of these metal ions on groundnut shell, pseudo-first-order and pseudo-second-order kinetic models were employed. One of such models is the Lagergren pseudo-first-order model which considers that the rate of occupation of the biosorption sites is proportional to the number of the unoccupied sites (Ertugay and Bayhan, 2008):

$$rate = -\frac{d[A]}{dt} = k\,[A]^n \tag{2}$$

Which can also be written as

$$\frac{d}{dt}q_t = k_1(q_e - q_t) \tag{3}$$

Integrating between the limits $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, we obtain

$$\log\left[\frac{q_e}{(q_e - q_t)}\right] = \frac{k_1}{2.303}t \tag{4}$$

This can be rearranged to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{5}$$

Where, k_1 is the Lagergren rate constant of the biosorption (min^{-1}); q_e and q_t are the amounts of metal ions sorbed (mg g^{-1}) at equilibrium and at time t, respectively. The plot of Log(q_e-q_t) versus t for the biosorption of metal ions on the biomass at initial concentration of 100 mgL^{-1} should give a straight line for a process that follows first-order kinetic model. The data was equally subjected to the pseudo-second-order kinetic model. The pseudo-second-order kinetic model is represented in Eq. 6.

$$\frac{d}{d_t}q_t = k_2(q_e - q_t)^2 \tag{6}$$

On integrating between boundary conditions, we have

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{7}$$

On rearrangement, we have

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

Where k_2 is the equilibrium rate constant of pseudo-second-order biosorption process (g mg^{-1} min^{-1}). In the metal ions under study, the straight line plots of t versus t/q_t show better fitness of experimental data with the second-order kinetic model than that of the pseudo-first-order kinetics as presented in Figure 5.

The correlation coefficient were found to be higher for the pseudo-second-order kinetic model in each case it was above 0.99 as reported in Tables 2. The pseudo-second-order kinetic model is therefore better to predict the dynamic biosorption of Pb(II), Cd(II) and Zn(II) onto groundnut shell.

Biosorption isotherms

The biosorption data were analysed with Freundlich and Langmuir isotherms. In each case, the Feundlich isotherm better represents the biosorption process as indicated by the values of the correlation coefficient.

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Table 1: FT-IR spectra characteristics of groundnut shell before and after biosorption of Pb(II), Cd(II) and Zn(II) for 2 h

Metal ion	Absorption bands (cm^{-1})			Assignment
	Initial	final	difference	
Pb(II)	1031.95	1035.81	+3.86	alcohol & carboxyl stretching
Cd(II)	1031.95	1031.81	-0.14	alcohol &carboxyl stretching
Zn(II)	1031.95	1030.02	-1.93	alcohol &carboxyl stretching
Pb(II)	1647.26	1653.05	+5.79	Stretching –C=O
Cd(II)	1844.01	1824.72	+19.29	C=O stretching
Pb(II)	3336.96	3319.6	+17.36	bonded OH, -NH stretching
Cd(II)	3336.96	3313.82	+23.14	bonded OH, -NH stretching
Zn(II)	3336.96	3309.96	-27	bonded OH, -NH stretching

Table 2: Parameters of the pseudo second-order kinetic model for the biosorption of Pb(II), Cd(II) and Zn(II) by groundnut shell

Metal ion	k_2(g.mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2	S.D.
Pb(II)	7.4336	94.07	0.9998	0.0121
Cd(II)	0.0773	104.71	0.9947	0.0558
Zn(II)	4.7218	86.13	0.9921	0.1088

Table 3: Freundlich isotherm parameters for the biosorption of Pb(II), Cd(II) and Zn(II) by groundnut shell

Metal ion	1/n	K_f	R^2	S.D.
Pb(II)	1	0.1349	1	7.0159x10^{-14}
Cd(II)	13.89	1.42x10^{-25}	0,9905	0.05944
Zn(II)	18.9	3.28x10^{-34}	0.9987	0.01533

Table 4: Thermodynamic parameters for biosorption of Pb(II), Cd(II) and Zn(II) by groundnut shell

Metal ion	ΔH^o(kJ mol^{-1})	ΔS^o(J mol^{-1}K^{-1})	A(kJ mol^{-1})@298K	A(kJ mol^{-1})@308 K
Pb(II)	-30.89	-96.98	-28.41	-28.33
Cd(II)	-8.42	-16.35	-5.95	-5.96
Zn(II)	-18.02	-51.45	-15.54	-15.46

Figure 6 illustrates the Freundlich isotherm for the biosorption of Pb(II), Cd(II) and Zn(II) onto groundnut shell. The equilibrium biosorption increases with increase in metal ion concentration. The Freundlich and Langmuir isotherms were employed to calculate the biosorption capacity. The Freundlich isotherm is an empirical equation describing adsorption onto a heterogenous surface. The Freundlich isotherm is expressed in Eq. 9.

$$\log \Gamma = \frac{1}{n} \log C_e + \log K_f \qquad (9)$$

Where, K_f and $\frac{1}{n}$ are the Freundlich constants related to the biosorption capacity and biosorption intensity of the biosorbent, respectively. The linear form of the Langmuir equation is expressed as shown in Eq. 10.
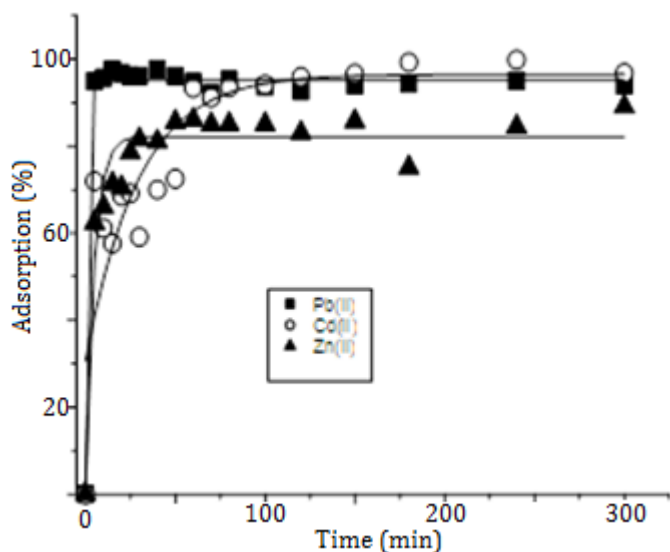
Fig. 4: Time course for the biosorption of Pb(II), Cd(II) and Zn(II) by groundnut shell at 28°C, 100 mgL-1, pH 5
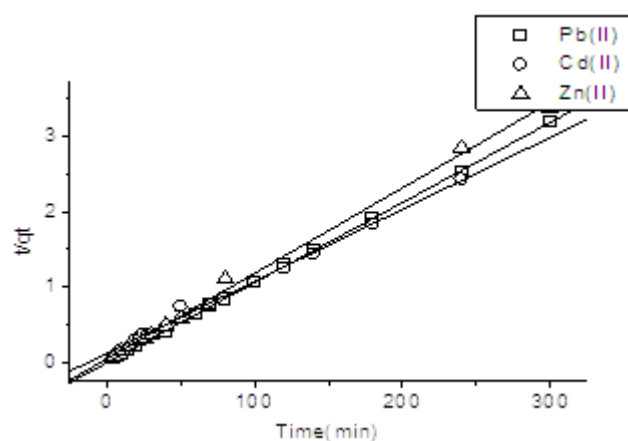

Fig. 6: Freundlich isotherm plot for biosorption of Pb(II), Cd(II) and Zn(II) by groundnut shell at 28°C, pH 5

Fig. 5: The pseudo-second-order kinetic plot for the biosorption of Pb(II), Cd(II) and Zn(II) by groundnut shell at 28°C, 100 mgL-1, pH 5

Fig. 7: Effect of initial concentration on biosorption of Pb(II), Cd(II) and Zn(II) on groundnut shell at 28°C, pH 5

$$\frac{1}{\Gamma} = \frac{1}{b_m}\frac{1}{C_e} + \frac{1}{\Gamma_m}$$

(10)

Where, Γ, Γ_m and b_m are the Langmuir parameters.

Biosorption efficiency

The result of the study on the effect of initial metal ion concentration on biosorption efficiency is as shown in Figure 7. The plots show that the biosorption efficiency of the biomass increases with increase in the initial metal ion concentration for all the metal ions which might be due to increase in effective collision between the metal ions and the
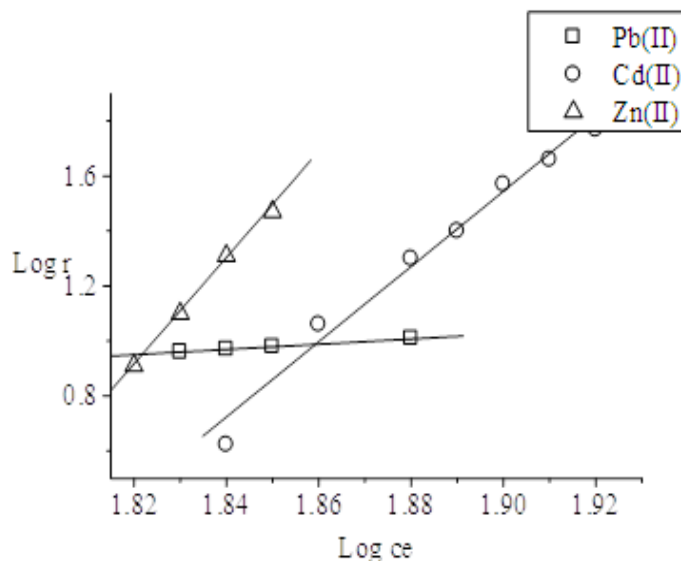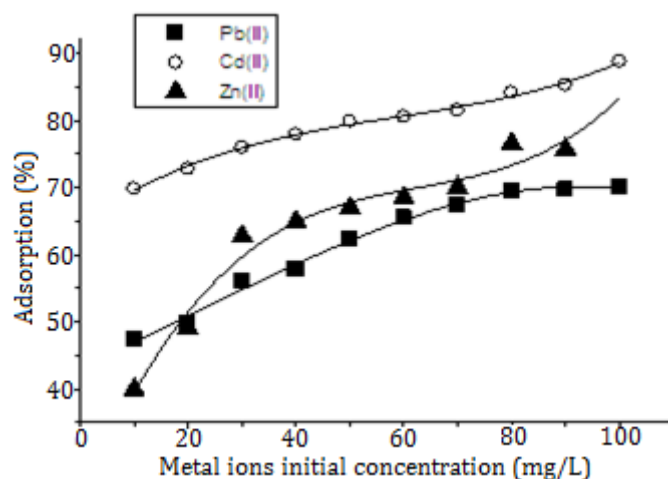
active sites. The biosorption efficiency (E) for each metal ion was calculated as shown in Eq. 11.

$$E = 100\left(\frac{C_i - C_e}{C_i}\right)$$

(11)

Where, C_i and C_e are the initial and the equilibrium metal ion concentration (mgL-1), respectively.

Thermodynamic treatment of the biosorption process

Thermodynamic parameters ($\Delta G°$, $\Delta H°$, $\Delta S°$) associated with the biosorption process were calculated using equations 12-15. The variation of temperature affects the biosorption of

metal ions onto solid surfaces of biomass since the biosorption process is a reversible one. The nature of each side of the equilibrium determines the effect that temperature has on the position of equilibrium. The side that is endothermic is favoured by increase in temperature, while the contrary holds for the exothermic side. The corresponding free energy change was calculated from the relation (Sun et al., 2008; Karthik and Meenakshi, 2014):

$$\Delta G^\circ = -RT \ln K_c \qquad (12)$$

Where, T is the absolute temperature, (K) and R is the universal gas constant (8.314 Jmol^{-1} K^{-1}). The biosorpion distribution coefficient (equilibrium constant), K_c, was calculated from the relationship shown in Eq. 13.

$$K_c = \frac{C_a}{C_e} \qquad (13)$$

Where, C_e and C_a are the equilibrium concentrations of metal ions (mgL^{-1}) in solution and on biosorbent, respectively. Consequently, the thermodynamic behaviour of the biosorption of Pb(II), Cd(II) and Zn(II) onto groundnut shell was evaluated through the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). The change in free energy is related to other thermodynamic properties (Eq. 14)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (14)$$

The biosorption distribution coefficient can be expressed in terms of ΔH and ΔS as a function of temperature (Eq. 15).

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (15)$$

Where, T is the absolute temperature (K); R is the gas constant (8.314 Jmol^{-1}K^{-1}). ΔH° is the standard enthalpy change (Jmol^{-1}) and ΔS° is the standard entropy change (Jmol^{-1}K^{-1}) were calculated from the slope and intercept of the linear plot of ΔG° versus T, respectively. The plots shown in Figure 8 are linear over the entire range of temperature investigated. The negative values of ΔG° indicate spontaneity of each biosorption process.

The thermodynamic parameters (free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°)) for the biosorption of the metal ions were calculated as stated above are presented in Table 5. In general, the change of standard free energy for physiosorption is in the range of −20 to 0 kJ mol^{-1} and for chemisorption varies between −80 and −400 kJmol^{-1} (Vimonses et al., 2009; Sen et al., 2011). In the present study, the overall ΔG° has values ranging from −4.0 to 0 kJmol^{-1}. These results correspond to a spontaneous physical adsorption of the metal ions, indicating that this system does not gain energy from external resource (Vimonses et al.,

2009; Arias and Sen, 2009). The increase in ΔG° with increase in temperature indicates less efficient biosorption at higher temperature.

The negative values of ΔH° for the biosorption of the three metal ions suggest an exothermic nature of each biosorption process. This is also supported by the decrease in the value of biosorption capacity of the biosorbent with rise in temperature. Similarly, the ΔS° values are negative indicating decrease in randomness during the biosorption process for these three metal ions. These negative values of ΔS° observed for the biosorption of these metal ions showed a decrease in randomness at the solid/solution interface during each biosorption process (Vimonses et al., 2009). Furthermore, the magnitude of activation energy (A) gives an idea about the type of adsorption which is mainly diffusion controlled process (not diffusivity of solute through micropore wall surface of a particle) or chemical reaction processes (Abd EI-Latif et al., 2010). Energies of activation, A, below 42 kJmol^{-1} indicate diffusion-controlled processes, and higher values give chemical reaction-based processes. Therefore, energy of activation, A, has been calculated as per the following relation (Eq. 17).

$$A = \Delta H^\circ + RT \qquad (17)$$

The values of A at two different temperatures are presented in Table 5. In this study, the activation energy (A) values were less than 42 kJmol^{-1} indicating diffusion-controlled adsorption processes.
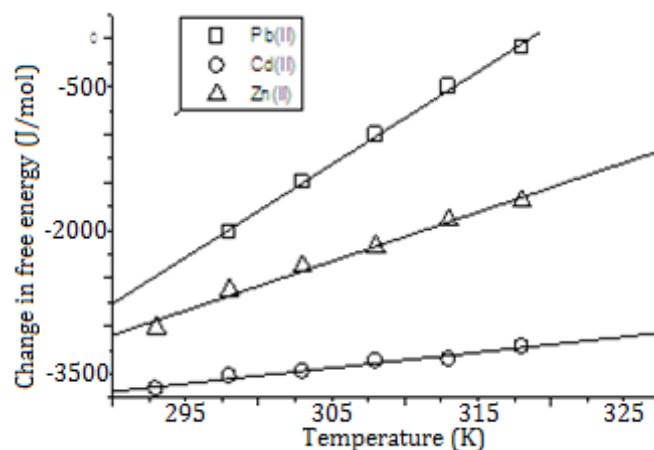

Fig. 8: Thermodynamic plots for biosorption of Pb(II), Cd(II) and Zn(II) by groundnut shell

CONCLUSIONS

The biosorption of Pb (II), Cd(II) and Zn(II) by groundnut shell under various conditions was studied in this work . The pH has much effect on the biosorption of these metal ions from aqueous solutions. The rate of the biosorption of these metal ions followed pseudo-second-order kinetics. The

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sorption isotherms of these metal ions onto the biosorbent are well described by Freundlich isotherm models. The thermodynamic study showed that the biosorption of each of Pb(II), Cd(II) and Zn(II) was spontaneous. This study shows that groundnut (Arachis hypogaea) shell has high potential for treating industrial effluents containing Pb(II), Cd(II) and Zn(II).

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