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Research Article



Removal of zinc (II) ions using peanut hulls (*Arachis hypogaea* Linn.) from aqueous solutions in a batch system

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Abstract

The present investigation revealed that peanut hulls (*Arachis hypogaea* Linn.) can be an inexpensive, excellent biosorbent for the removal of zinc (II) ions from aqueous solutions. FTIR analysis of biosorbent confirmed that hydroxyl, carbonyl and carboxyl group, so that the cell wall surface of the biosorbent that may interact with the zinc (II) ions. The SEM represents a porous structure with large surface area. The optimal parameters such as solution pH, biosorbent dose, initial zinc (II) ions concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of zinc (II) ions onto peanut hulls (*Arachis hypogaea* Linn.). The maximum zinc (II) ion loading capacity (q_m) of peanut hulls (*Arachis hypogaea* Linn.) was found to be 14.492 mg g⁻¹ with perfect fit to Langmuir isotherm model and follows pseudo-second order kinetics. The thermodynamic study confirmed that reaction of biosorption of zinc (II) ions onto peanut hulls (*Arachis hypogaea* Linn.) is spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that peanut hulls (*Arachis hypogaea* Linn.) has considerable biosorption capacity, available in abundant, non-hazardous agro material could be used as an effective indigenous material for treatment of wastewater stream containing zinc (II) ions.

Keywords: zinc (II) ions, *Arachis hypogaea* Linn, FTIR, SEM, adsorption isotherm, adsorption kinetics, thermodynamic study.

Introduction

Pollution is a addition of unwanted and undesirable foreign matter to environment as a result of enormous industrial development and modernization. The discharge of untreated solid, liquid and gaseous wastes that contaminate the physiological and ecological environment is the greatest threat to mankind. Waste water contaminated with heavy metals is one of the most common environmental problems due to their toxicity. Zinc finds its way into water bodies through effluents from smelters, mining, processing plants, paints and pigments, pesticides and galvanizing units. Trace concentration of zinc are important for the physiological function of living tissue and regulate

many biochemical process. However trace amount of free zinc ions can cause heavy damage to the environment and kill organisms. When zinc is present in the wastewater beyond the permissible limits of concentration, it can have severe toxicological effects on both human and aquatic ecosystems (Norton, et al. 2004).

The threshold limiting value of zinc in drinking water is 5 mg/L and in public sewage, inland surface water and marine water it is 15 mg/L (Drinking water specifications, IS-10500, 1991). Ingestion of more than 2 g/L causes toxic symptoms like fever, diarrhea, and gastrointestinal tract irritation etc in humans.

Hence, it is of prime importance to prevent the accumulation of zinc from exceeding its threshold concentration. Zinc stands at 74th rank with a score of 932.89 points in the series of toxic heavy metals, as per Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) 2007. Earlier, it was demarcated that zinc (II) ion toxicity adversely affects gastrointestinal system but the latest research suggests that the toxicity of zinc is also involved in circulatory, neurological and renal damages. The effluents discharged from various metallurgical units contain zinc in range of 0.14 mg/L –130 mg/L.

United States Environmental Protection Agency (USEPA) and World Health Organization (WHO 2008) have demarcated the permissible limit of zinc in wastewater and potable water as 5 mg/L and 3 mg/L respectively. Hence, the removal of zinc (II) ions becomes mandatory before the discharge of industrial effluents containing zinc in main water stream.

Treatment of industrial effluent with sorbents of biological origin is simple, comparatively inexpensive and friendly to the environment. Biosorption is a powerful, most efficient and cost effective technique which is based on the principle of metal binding capacities of various biological materials, which is very useful method for removal of metal pollutant from wastewater (Ahalya et al., 2003; Maind et al., 2012; Maind et al., 2013; Maind et al., 2013, Bhalerao, 2011). The biosorption is a process that utilizes low-cost biosorbents to sequester toxic heavy metals (Kratochvil and Volesky, 1998). Biosorption has distinct advantages over expensive clean up technologies in industrial sector. Biosorption have advantages which include: re-usability of biomaterial, low operating cost, and selectivity for specific metal, short operation time and no chemical sludge (Mungasavalli, et al. 2007).

In the recent years many biosorbents materials of agricultural based have been utilized for heavy metal biosorption. Recently, several studies on the removal of zinc from effluents using low cost agricultural materials have been reported. In most cases, zinc uptake capacities are quite low and biosorbents are susceptible to degradation at low pH acid regeneration. Now, the most popular removal material are biosorbents whereby zinc can exchange prefer with other ions such as H⁺, Na⁺, Ca⁺.

Several investigations have been carried out to identify suitable and relatively cheap biosorbents that are capable of removing significant quantities of heavy metals ions. Among the various resources in biological waste, both dead and live biomass, exhibit particularly interesting metal-binding capacities. The use of dead biomass eliminates the problem of toxicity and the economics aspects of nutrient supply and culture maintenance (Pino et al., 2006). Successful metal biosorption has been reported by a variety of biological materials including *Erythrina variegata* orientalis leaf (Venkateswarlu, et al., 2008), *Cedrus deodara* sawdust (Mishra, et al., 2011), *Asperigillus niger* (Mungasavalli, et al., 2007; Yun-gun, et al., 2006), *Eriobotrya japonica* (Loquat bark) (Salem, et al., 2012), *Eichornia crassipes* (Water Hyacinth) (Verma, et al., 2005), *Thiobacillus ferrooxidans* (Celaya, 2000); Corn cobs (Maind, et al., 2013), Moss (Maind, et al., 2012), Papaya wood (Asma, et al., 2005), Waste Tea leaves (Ahluwalia and Goya, 2005), sea urchin test (John Babu D., Et al., 2014), Banana and Orange Peel Waste (Annadurai, et al., 2003). Many low cost biosorbents have been intensively examined for their abilities to be applied in biosorption of zinc (II) ions (Verma, 2005; Venkateswarlu, 2008; Celaya, 2000; Mishra, et al., 2011; Salem, et al., 2012) ions from aqueous solutions.

In the present research work, peanut hulls (*Arachis hypogaea* Linn.) belongs to family Leguminaceae and sub family Papilionaceae are an agro-industrial waste material and these material have the potential to sequester heavy metals from solutions. The chemical characterization of peanut hulls (*Arachis hypogaea* Linn.) showed a high cellulose (44.8%) and lignin (36.1%) content, which favours biosorption of heavy metals cations (Oliveira, 2010). The present research will be conducted to utilize peanut hulls (*Arachis hypogaea* Linn.) for the biosorption of zinc (II) ions from aqueous solutions in a batch system. The study will extend with the objective for estimation and calculation of various parameters affecting the biosorption of metals: such as solution pH, biosorbent dose, initial zinc (II) ions concentration, contact time and temperature. Adsorption isotherms (Langmuir, Freundlich, Dubinin-kaganer-Redushkevich (DKR) and Temkin) and kinetics models (pseudo-first-order, pseudo-second-order, Elovich and intraparticle rate diffusion) was employed to understand the probable adsorption mechanism. Thermodynamic studies was

also carried out to estimate the standard Gibbs free energy change (G^0), standard enthalpy change (H^0) and standard entropy change (S^0).

Materials and Methods

Chemicals and reagents

All the chemicals and reagents used were of analytical reagent (AR) grade. Double distilled water was used for all experimental work including the preparation of metal solutions. The desired pH of the metal ion solution was adjusted with the help of dilute hydrochloric acid and sodium hydroxide.

Preparation of zinc (II) stock solution

The stock solution of 1000 ppm of zinc (II) ions was prepared by dissolving 0.1g zinc metal in 100 ml of double distilled water and further desired test solutions of zinc (II) were prepared using appropriate subsequent dilutions of the stock solution.

Preparation of biosorbent

The peanut hulls (*Arachis hypogaea* Linn.) was collected locally and washed with several times with distilled water to remove the surface adhered particles, dirt, other unwanted material & water soluble impurities and water was squeezed out. The washed biosorbent was then dried at 50°C overnight and grounded in a mechanical grinder to form a powder. The powder was sieved and a size fraction in the range of 100-200 µm will be used in all the experiments. This powder was soaked (20 g/l) in 0.1 M nitric acid for 1 hour. The mixture was filtered and the powder residue was washed with distilled water, several times to remove any acid contents. This filtered biomass was first dried at room temperature and then dried in an oven at 105°C for 1-2 hrs. For further use, the dried biomass was stored in air tight plastic bottle to protect it from moisture.

Experimental protocol

The static (batch) method was employed at temperature (30°C) to examine the biosorption of zinc (II) ions by biosorbents. The method was used to determine the biosorption capacity, stability of adsorbent and optimum biosorption conditions. The parameters were studied by combining adsorbent with solution of zinc (II) ions in 250 ml reagent bottle. The

reagent bottles were placed on a shaker with a constant speed and left to equilibrate. The samples were collected at predefined time intervals, centrifuged, the content was separated from the adsorbents by filtration, using Whatmann filter paper and amount of zinc (II) ions in the supernatant/filtrate solutions was determined using digital UV-visible spectrophotometer (EQUIP-TRONICS, model no. Eq-820). The following equation was used to compute the percentage biosorption (% Ad) of zinc (II) ions by the biosorbent,

$$\% \text{ Ad} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

where C_i and C_e are the initial concentrations and equilibrium concentrations of the zinc (II) ions in mg/L.

The equilibrium zinc (II) ions adsorptive quantity was determined by the following equation:

$$q_e = \frac{(C_i - C_e)}{w} \times V \quad (2)$$

where q_e (mg metal per g dry biosorbent) is the amount of zinc (II) ions adsorbed, V (in liter) is the solution volume and w (in gram) is the amount of dry biosorbent used.

Estimation of zinc (II) ions concentration

A 0.002 % w/v solution of dithizone was prepared in CCl_4 . Known volume of sample solutions containing zinc (II) ions, were pipette out into 250 ml separating funnel, add 5 ml of acetate buffer (pH 5) and shake with two portions of 25 ml of 0.002 % H_2Dz until the green CCl_4 layer no longer changes the colour. Each shaking should not less than 2 minutes. Wash out free dithizone from CCl_4 layer with dilute ammonia (1 drop of conc. NH_3 solution in 25 ml of water). Dilute the pink solution of zinc dithizonate ($\text{Zn}(\text{HDz})_2$) with CCl_4 in a 25 ml standard flask and mix well. Zinc (II) ions concentration was estimated by measuring intensity of the pink colour, Zn-dithizonate complex using a UV-visible spectrophotometer. The absorbance was measured against reagent blank at wavelength 538-nm. A linear plot for standard zinc (II) ions solution was obtained indicating adherence to the Beers Lamberts law in the concentration range studies and amount of zinc (II) ions was estimated. The amount determined was a mean of triplicate sample analysis with standard deviation less than 5 %.

The blank solution i.e. solution containing biomass without zinc (II) ion was tested and results shows that no any appreciable signal of intensity at wavelength 538-nm obtained.

Results and Discussion

Characterization of biosorbent by Fourier Transform Infrared (FTIR) analysis

The Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups present in the biosorbent. The biosorbent samples were examined using FTIR spectrometer (model:FT/IR-4100typeA) within range of 400-4000 cm^{-1} . All analysis was performed using KBr as back ground material. In order to form pellets, 0.02 g of biomass was mixed with 0.3 g KBr and pressed by applying pressure. To investigate the functional groups of biosorbent and metal loaded with biosorbent, a FTIR analysis was carried out and the spectra are shown in Fig.1. (a and

b). As seen in the figure unloaded biomass displays a number of absorption peaks, reflecting the complex nature of biosorbent. The broad peak at 3422 cm^{-1} is the indicator of -OH and -NH groups. The stretching of the -OH groups bound to methyl groups presented in the signal at 2924 cm^{-1} . The peaks at 2366 cm^{-1} and 2345 cm^{-1} are stretching peaks. The peaks located at 1735 cm^{-1} and 1637 cm^{-1} are characteristics of carbonyl group. The presence of -OH group along with carbonyl group confirms the presence of carboxyl acid groups in the biosorbent. The peak at 1508 cm^{-1} is associated with the stretching in aromatic rings. The peaks observed at 1066 cm^{-1} are due to C-H and C-O bonds. The -OH, NH, carbonyl and carboxyl groups are important sorption sites. As compared to simple biosorbent, biosorbent loaded with zinc (II) ions, the broadening of -OH peak at 3422 cm^{-1} and carbonyl group peak at 1637 cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of zinc (II) ions.

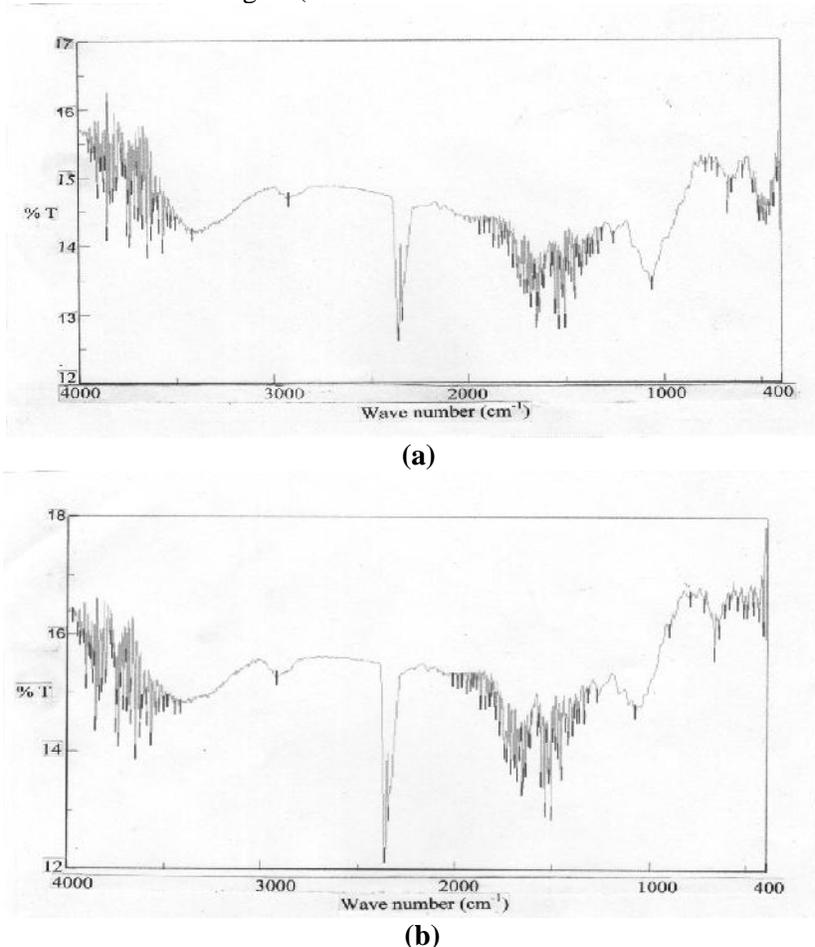


Fig.1. FTIR spectra (a) biosorbent peanut hulls (*Arachis hypogaea* Linn.) unloaded with zinc (II) ions (b) biosorbent peanut hulls(*Arachis hypogaea* Linn.) loaded with zinc (II) ions

Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis

The surface morphology of peanut hulls (*Arachis hypogaea* Linn.) was examined using Scanning Electron Microscope (SEM), before and after adsorption and the corresponding SEM micro graphs

were obtained accelerating voltage of 10.0 kv at 15000x for before and 1500x for after adsorption magnification and are presented in Fig. 2(a and b). At such magnification, the peanut hulls (*Arachis hypogaea* Linn.) particles showed rough areas of within which micro pores were clearly identified.

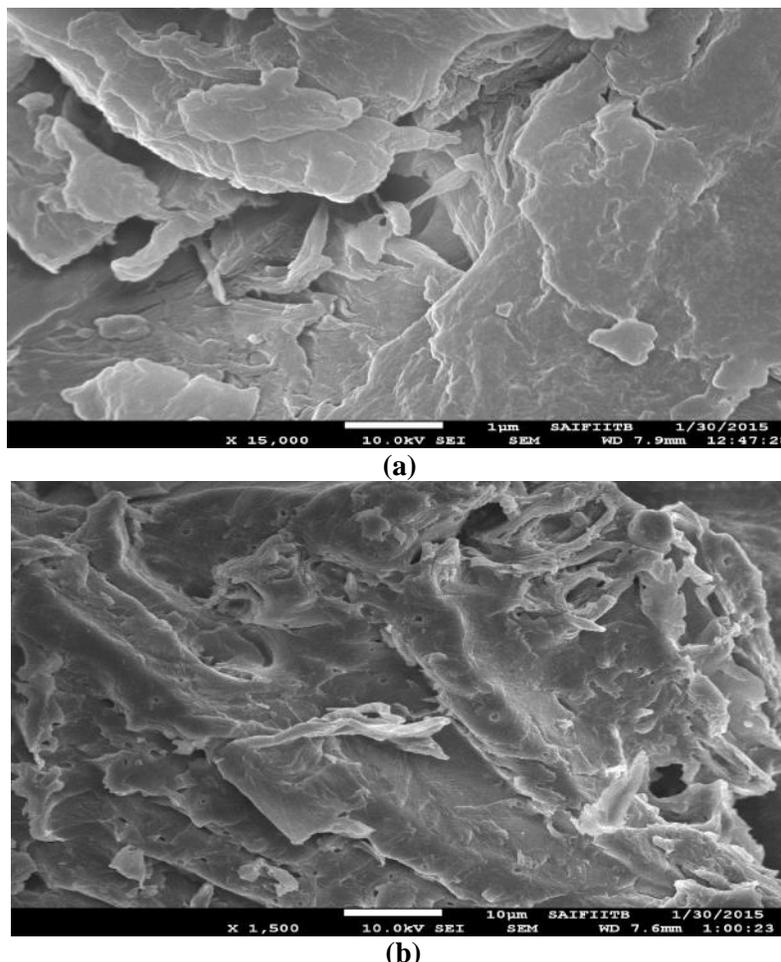


Fig.2.SEM Analysis (a) biosorbent peanut hulls (*Arachis hypogaea* Linn.) unloaded with zinc (II) ions (b) biosorbent peanut hulls (*Arachis hypogaea* Linn.) loaded with zinc (II) ions

Effect of pH

pH is considered as a very important parameter in biosorption process. The functional groups responsible for binding of metal ions in the biosorbent, affected by pH. It also affects the competition of metal ions that gets adsorb to active sites of biosorbent. pH influences the chemical structure of the zinc (II) ions in aqueous solution, hence influencing its bio-availability. The sorption capacity of the zinc (II) ions depends on the pH of the biosorption medium, which influences electrostatic binding of zinc (II) ions to

corresponding functional groups. The optimization of pH was done by varying the pH in the range of 2-10 for zinc (II) ions and pH trend observed in this case is shown in Fig. 3. It was found that percent biosorption increased by increasing pH and at pH 6 the biosorption process was maximum with 71.91 % and then decreases till pH 10. The lesser biosorption at lower pH was due to lesser surface sites are available for sorption. pH 6 was chosen for all further biosorption studies.

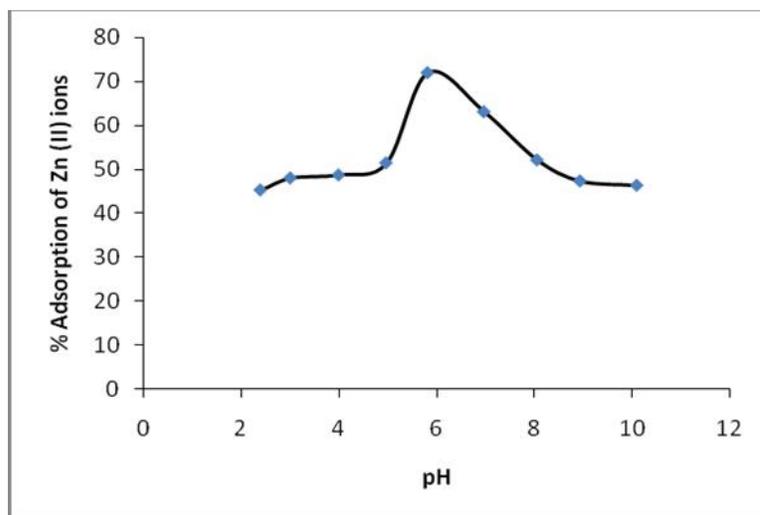


Fig.3. Effect of pH on zinc (II) ions biosorption by peanut hulls (*Arachis hypogaea* Linn.) (biosorbent dose concentration: 5 mg/ml, zinc (II) ion concentration: 10 mg/L, contact time: 60 minutes, temperature: 30⁰C)

Effect of biosorbent dose

Effect of biosorbent dose of biosorption of metal ions onto biosorbent which is an important parameter was studied while conducting batch studies. The biosorption capacity of zinc (II) ions on to peanut hulls (*Arachis hypogaea* Linn.) by varying biosorbent dose from 1.0mg/ml to 20 mg/ml is as shown in Fig. 4. From the results it was found that biosorption of zinc (II) ions increases with increase in biosorbent dose and is highly dependent on biosorbent concentration. Increase in percent biosorption by increase in

biosorbent dose is because of increase of ion exchange site ability, surface areas and the number of available biosorption sites. The point of saturation for peanut hulls (*Arachis hypogaea* Linn.) was found at 5 mg/ml of biosorbent dose with maximum removal efficiency. The decrease in efficiency at higher biosorbent concentration could be explained as a consequence of partial aggregation of biosorbent which results in a decrease in effective surface area for metal uptake. The biosorbent dose 5mg/ml was chosen for all further studies.

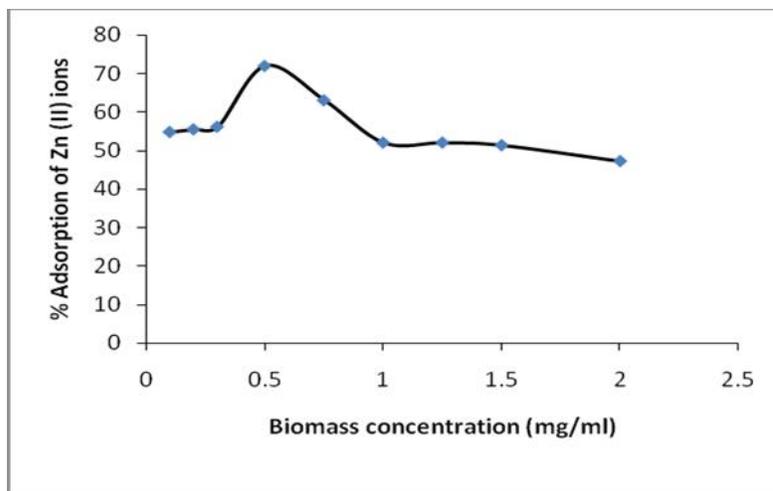


Fig.4. Effect of biosorbent dose concentration on zinc (II) ions biosorption by peanut hulls (*Arachis hypogaea* Linn.) (pH: 6, zinc (II) ions concentration: 10 mg/L, contact time: 60 minutes, temperature: 30⁰C)

Effect of contact time

Contact time plays an important role in affecting efficiency of biosorption. Contact time is the time needed for biosorption process to achieve equilibrium when no more changes in adsorptive concentration were observed after a certain period of time. The contact time which is required to achieve equilibrium depends on the differences in the characteristics properties of the biosorbents. In order to optimize the contact time for the maximum uptake of zinc (II) ions, contact time was varied between 5 minutes-180 minutes on the removal of zinc (II) ions from aqueous solutions in the concentration of zinc (II) ions 10 mg/L, adsorbent dose 5mg/ml, optimum pH 6.0 and

30°C temperature. The results obtained from the adsorption capacity of zinc (II) ions onto peanut hulls (*Arachis hypogaea* Linn.) showed that the biosorption increases with increase in contact time until it reached equilibrium. The optimum contact time for biosorption of zinc (II) ions onto peanut hulls (*Arachis hypogaea* Linn.) was 60 minutes with 68.49 % removal. The rapid uptake of zinc (II) ions is due to the availability of ample active sites for biosorption. A further increase in the contact time has a negligible effect on the biosorption capacity of zinc (II) ions biosorption. So a contact time of 60 minutes was fixed for further experiments.

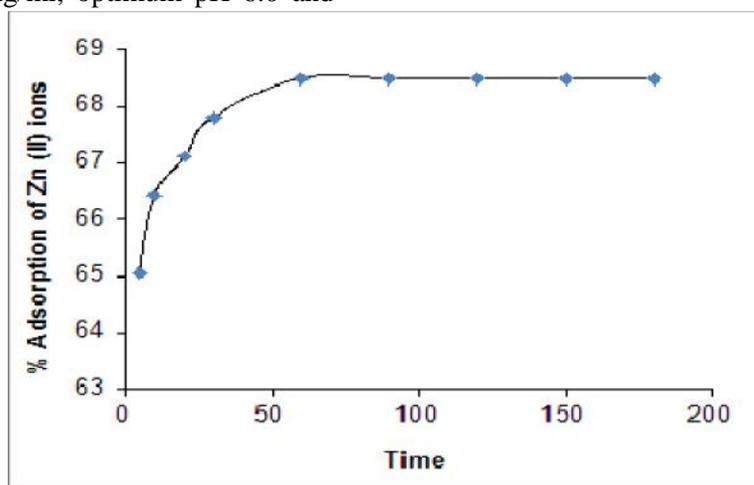


Fig.5. Effect of time on zinc (II) ions biosorption by peanut hulls (*Arachis hypogaea* Linn.) (pH: 6, biosorbent dose concentration: 5 mg/ml, zinc (II) ions concentration: 10 mg/L, temperature: 30°C)

Effect of initial zinc (II) ions concentration

The effect of initial zinc (II) ions concentration from 5mg/L-300 mg/L on the removal of zinc (II) ions from aqueous solutions at biosorbent dose 10 mg/ml and at optimum pH 6.0 at 30°C temperature was studied. On

increasing the initial zinc (II) ions concentration, the total zinc (II) ions uptake increased appreciably 42.50 % to 78.54 % at zinc (II) ions concentration ranges from 5 mg/L- 300 mg/L.

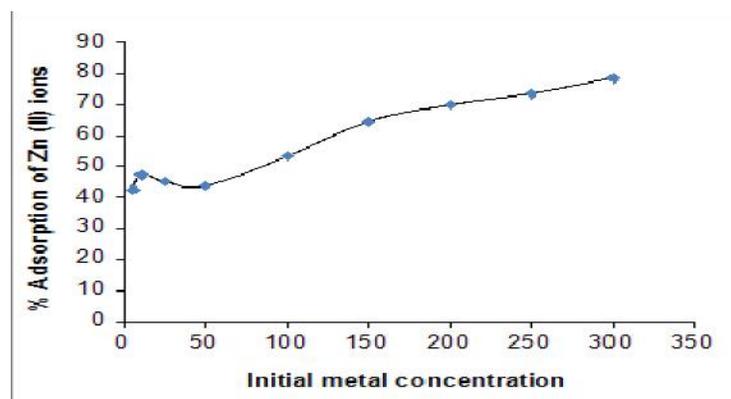


Fig.6. Effect of initial metal concentration on zinc (II) ions biosorption by peanut hulls (*Arachis hypogaea* Linn.) (pH: 6, biosorbent dose concentration: 5 mg/ml, contact time: 60 minutes, temperature: 30°C)

Adsorption isotherm models

The analysis of the adsorption isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. The experimental data were applied to the two-parameter isotherm models; Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin.

Langmuir adsorption isotherm (Langmuir, 1918)

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by,

$$q = \frac{q_m b C_e}{1 + b C_e} \tag{3}$$

where q_m is the maximum biosorption capacity of biosorbent (mg g^{-1}). b is the Langmuir biosorption constant (L mg^{-1}) related to the affinity between the biosorbent and biosorbate.

Linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constants and is represented as:

$$\frac{1}{q} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \tag{4}$$

The linear plots of $1/q_e$ vs $1/c_e$ is shown in Fig.7 (a). The two constants b and q_m are calculated from the slope ($1/q_m \cdot b$) and intercept ($1/q_m$) of the line. The values of q_m , b and regression coefficient (R^2) are listed in Table 1.

Maximum biosorption capacity of biosorbent (q_m) is found to be 14.492mg per g of biosorbent which is higher than the other biosorbents used by many authors.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the biosorbate and biosorbent using separation factor or dimensionless equilibrium parameters, R_L expressed as in the following equation;

$$R_L = \frac{1}{1 + b C_i} \tag{5}$$

Where b is the Langmuir constant and C_i is the maximum initial concentration of zinc (II) ions. The value of separation parameters R_L provides important information about the nature of biosorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The R_L was found to be 0.2444-0.9510 for concentration of 5 mg/L -300 mg/L of zinc (II) ions. They are in the range of 0-1 which indicates favorable biosorption (Malkoc and Nuhoglu, 2005).

Biosorption can also be interpreted in terms of surface area coverage against initial metal ion concentration and separation factor. Langmuir model for surface area of biosorbent surface has been represented in the following equation:

$$b C_i = \frac{\theta}{1 - \theta} \tag{6}$$

where θ is the surface area coverage. The θ was found to be 0.0489-0.7555 for concentration of 5 mg/L -300 mg/L of zinc (II) ions.

Freundlich adsorption isotherm (Freundlich, 1906)

Freundlich equation is represented by;

$$q = KC_e^{1/n} \tag{7}$$

where K and n are empirical constants incorporating all parameters affecting the biosorption process such as, biosorption capacity and biosorption intensity respectively.

Linearized Freundlich biosorption isotherm was used to evaluate the sorption data and is represented as;

$$\log q_e = \log K + \frac{1}{n} \log C_e \tag{8}$$

Equilibrium data for the biosorption is plotted as $\log q_e$ vs $\log C_e$, as shown in Fig. 7(b). The two constants n and K are calculated from the slope ($1/n$) and intercept ($\log K$) of the line, respectively. The values of K , $1/n$ and regression coefficient (R^2) are listed in Table 1.

The n value indicates the degree of non-linearity between solution concentration and biosorption as follows: if $n = 1$, then biosorption is linear; if $n < 1$, then biosorption is chemical process; if $n > 1$, then biosorption is a physical process. A relatively slight slope and a small value of $1/n$ indicate that, the biosorption is good over entire range of concentration. The n value in Freundlich equation was found to be 0.9451. Since $n < 1$, this indicates the chemical biosorption of zinc (II) ions onto peanut hulls (*Arachis hypogaea* Linn.). The higher value of K (21.72) indicates the higher biosorption capacity of the biosorbent.

Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm (Dubinin and Radushkevich, 1947)

Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as;

$$\ln q_e = \ln q_m - \beta C_e^2 \tag{9}$$

Where q_m is the maximum sorption capacity, β is the activity coefficient related to mean sorption energy and $\ln q_m$ is the polanyi potential, which is calculated from the following relation;

$$\ln q_m = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{10}$$

Equilibrium data for the biosorption is plotted as $\ln q_e$ vs C_e^2 , as shown in Fig 7(c). The two constants β and q_m are calculated from the slope ($-\beta$) and intercept ($\ln q_m$) of the line, respectively. The values of biosorption energy E was obtained by the following relationship.

$$E = \frac{1}{\sqrt{-2\beta}} \tag{11}$$

The values of q_m , E and regression coefficient (R^2) are listed in Table 1.

The mean free energy gives information about biosorption mechanism, whether it is physical or chemical biosorption. If E value lies between 8 KJ mol⁻¹ and 16 KJ mol⁻¹, the biosorption process take place chemically and $E < 8$ KJ mol⁻¹, the biosorption process of the physical in nature (Olivieri and Brittenham, 1997). In the present work, E value (0.267 KJ mol⁻¹) which is less than 8 KJ mol⁻¹, the biosorption of zinc (II) ions onto biosorbent is of physical in nature (Sawalha et al., 2006).

Temkin adsorption isotherm (Temkin and Pyzhev, 1940)

Linearized Temkin adsorption isotherm is given by the equation:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{12}$$

where b_T is the Temkin constant related to heat of sorption (J/mol) and A_T is the Temkin isotherm constant (L/g). Equilibrium data for the biosorption is plotted as q_e vs $\ln C_e$, as shown in Fig. 7 (d). The two constants b_T and A_T are calculated from the slope (RT/b_T) and intercept ($RT/b_T \ln A_T$) of the line, respectively. The values of A_T , b_T and regression coefficient (R^2) are listed in Table 1.

Table: 1. Adsorption isotherm constants for biosorption of zinc (II) ions by peanut hulls (*Arachis hypogaea* Linn.)

Langmuir constants			Freundlich constants			DKR constants				Temkin constants		
q_m	B	R^2	K	$1/n$	R^2	q_m		E	R^2	A_T	b_T	R^2
14.492	0.0103	0.992	21.72	1.058	0.957	10.601	-7E-6	0.267	0.627	5.3601	278.450	0.621

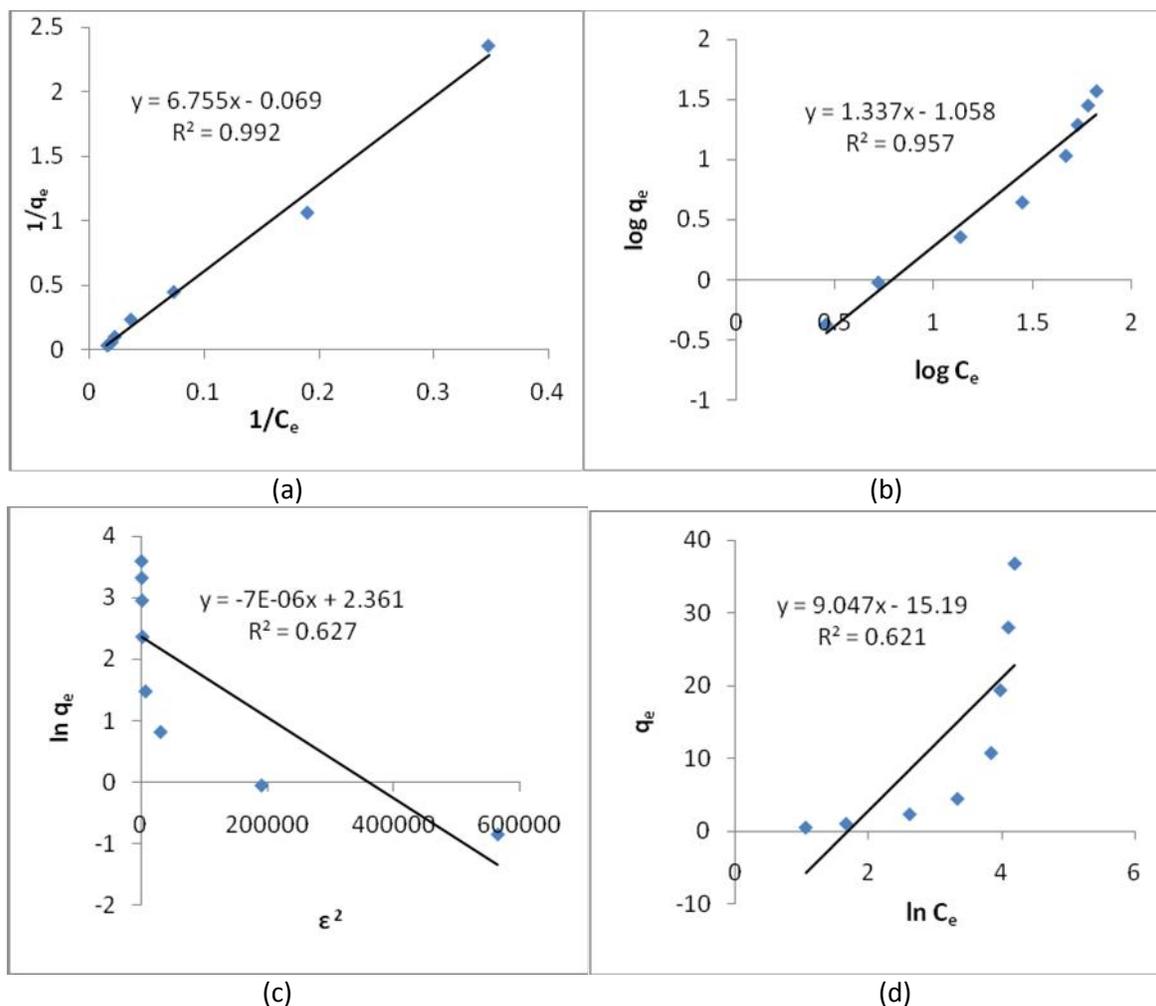


Fig.7.Adsorption isotherm models (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for biosorption of zinc (II) ions by peanut hulls (*Arachis hypogaea* Linn.)(pH: 6.0, biosorbent dose concentration: 5 mg/ml, contact time: 60 minutes, temperature: 30⁰C)

Adsorption Kinetics

As aforementioned, a lumped analysis of biosorption rate is sufficient to practical operation from a system design point of view. The commonly employed lumped kinetic models, namely (a) the pseudo-first-order equation (Lagergren, 1898) (b) the pseudo-second-order equation (Mckayet al., 1999) (c) Elovich equation (Chien and Clayton, 1980) (d) Weber and Morris intraparticle diffusion rate equation (Weber and Morris, 1963) are presented below;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{13}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{14}$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{15}$$

$$q_t = k_i t^{0.5} + c \tag{16}$$

where q_e (mg g^{-1}) is the solid phase concentration at equilibrium, q_t (mg g^{-1}) is the average solid phase concentration at time t (min), k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the pseudo-first-order and pseudo-second-order rate constants, respectively. The symbols of ($\text{mg g}^{-1} \text{min}^{-1}$) and (g mg^{-1}) are Elovich coefficients representing initial sorption rate and desorption constants, respectively. k_i ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intra particle diffusion rate constant, c is intercept.

If the biosorption follows the pseudo-first-order rate equation, a plot of $\ln(q_e - q_t)$ against time t should be a straight line. Similarly, t/q_t should change lineally with time t if the biosorption process obeys the pseudo-second order rate equation. If the biosorption process obeys Elovich rate equation, a plot of q_t against $\ln t$ should be a straight line. Also a plot of q_t against $t^{0.5}$ changes lineally the biosorption process obeys the Weber & Morris intra particle diffusion rate equation.

Biosorption of zinc (II) ions on to biosorbent was monitored at different specific time interval. The zinc (II) ions uptake was calculated from the data obtained. From the zinc (II) ions uptake was plotted against time to determine a suitable kinetic model, the biosorption data was fitted into pseudo-first-order rate equation, pseudo-second-order rate equation, Elovich equation and the Weber & Morris intra particle diffusion rate equation. The pseudo-first-order equation was plotted for $\ln(q_e - q_t)$ against t (Fig. 8 (a)). The values of q_e and k_1 values were calculated from the slope (k_1) and intercept ($\ln q_e$) of this plot and shown in Table 2. Pseudo-first-order kinetic model showered the correlation value ($R^2 = 0.979$) being lower than the correlation coefficient ($R^2 = 1.000$) for the pseudo-second-order equation. Kinetic biosorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the biosorbent and the ions adsorbed onto it (Septum et. al., 2007). The pseudo-second-order equation was plotted for t/q_t against t (Fig. 8 (b)). The values of q_e and k_2 are calculated from the slope ($1/q_e$) and intercept ($1/k_2 q_e^2$) of the plot and values are shown in Table 2. Pseudo-second-order kinetic model showered the strongest correlation ($R^2 = 1.000$). This suggests that zinc (II) ions biosorption occurs in a monolayer fashion and which relies on the assumption that chemisorption or chemical biosorption is the rate-limiting step. Zinc (II) ions react chemically with the specific binding sites on the surface of biosorbent. The Elovich equation was plotted for q_t against $\ln t$ (Fig. 8 (c)). The values of k_i and c are calculated from the slope (k_i) and the intercept ($\ln c$) of the plot and values are shown in Table 2.

The Elovich equation has been used to further explain the pseudo-second-order equation with the assumption that the actual biosorption surface is energetically heterogeneous. Elovich equation showed a correlation value ($R^2 = 0.892$) being lower than the correlation coefficient for the pseudo-first-order and pseudo-second-order equation. Therefore, this could be used to explain that the biosorption surface is energetically heterogeneous (Thomas and Thomas, 1997). The intraparticle diffusion rate equation was plotted for q_t against $t^{0.5}$ (Fig. 8 (d)). The value of k_i and c are calculated from the slope (k_i) and intercept (c) of the plot and values are shown in Table 2. The Weber and Morris intra particle diffusion rate equation showed a lowest correlation value ($R^2 = 0.720$) being lower than the correlation coefficient for the Elovich equation, pseudo-first-order and pseudo-second-order equation. The intercept of the plot does not pass through the origin, this is indicative of some degree of boundary layer control and intraparticle pore diffusion is not only rate-limiting step (Weber and Morris, 1963). The plot of intraparticle diffusion rate equation showed multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of biosorbate through the solution to the external surface of biosorbent or the boundary layer diffusion of solute molecules. The second portion describes ion stage, where intra particle diffusion is a rate limiting. The third portion is attributed to the final equilibrium stage. However the intercept of the line fails to pass through the origin which may attribute to the difference in the rate of mass transfer in the initial and final stages of biosorption (Panday et al., 1986).

Table: 2. Adsorption kinetic data for biosorption of zinc (II) ions by peanut hulls (*Arachis hypogaea* Linn.)

Pseudo-first-order model			Pseudo-second-order model			Elovich equation			Intra particle rate diffusion equation		
q_e	K_1	R^2	q_e	K_2	R^2			R^2	K_i	c	R^2
11.634	0.060	0.979	1.3736	2.3877	1.0	1.7054×10^{29}	55.55	0.892	0.005	1.313	0.720

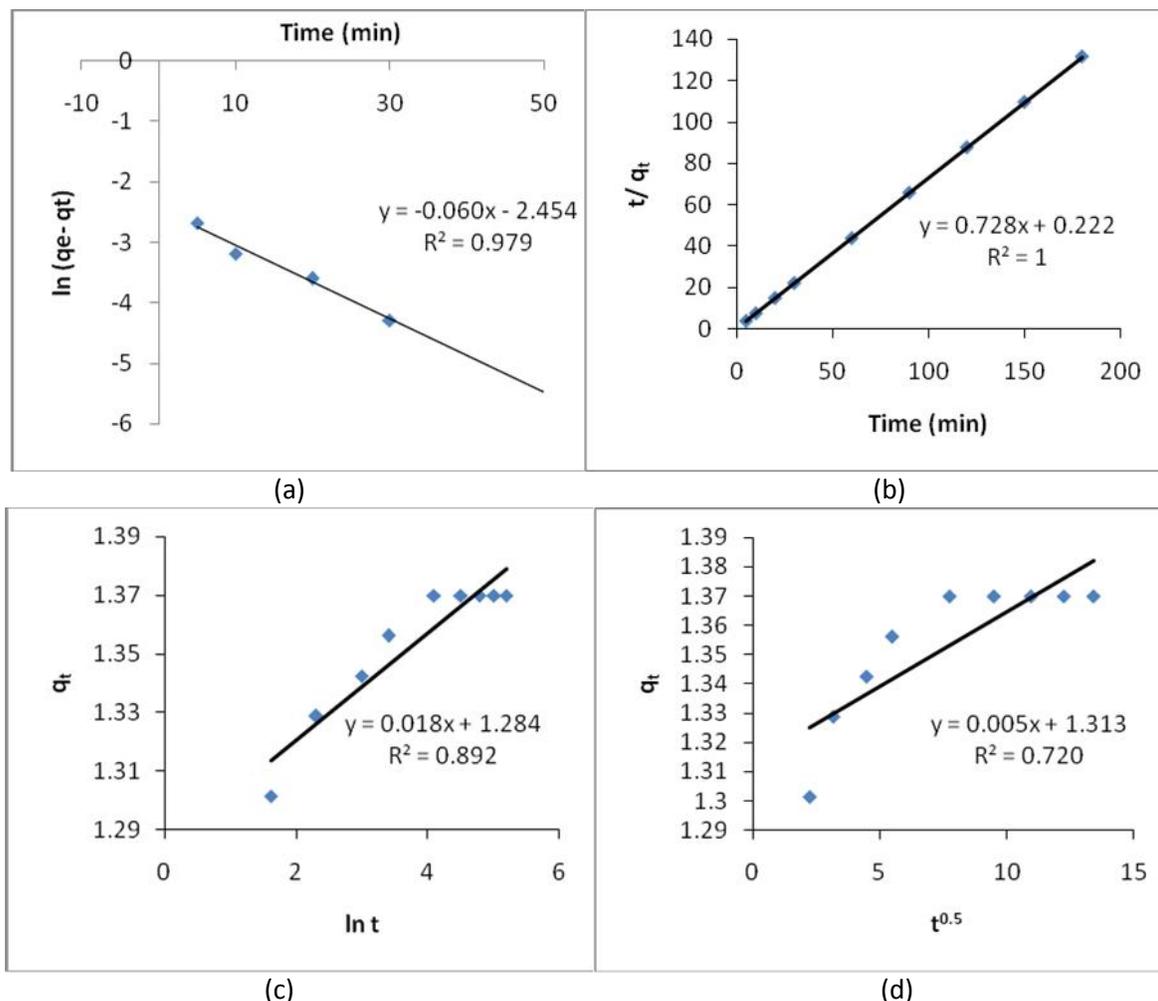


Fig.8. Adsorption kinetic models (a) pseudo-first-order equation, (b) pseudo-second-order equation, (c) Elovich equation and (d) Weber and Morris intra-particle diffusion rate equation, for biosorption of zinc (II) ions by peanut hulls (*Arachis hypogaea* Linn.) (pH: 6.0, biosorbent dose concentration: 5 mg/ml, zinc (II) ions concentration: 10 mg/L, temperature: 30°C)

Thermodynamic study

The effect of temperature on removal of zinc (II) ions from aqueous solutions in the zinc (II) ions concentration 10 mg/L and biosorbent dose 5mg/ml with optimum pH 6.0 was studied. Experiments were carried out at different temperatures from 30°C-70°C. The samples were allowed to attain equilibrium. Sorption slightly increases from 30°C-50°C. The equilibrium constant (Catena and Bright, 1989) at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \quad (17)$$

$$\Delta G^0 = -RT \ln K_c \quad (18)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (19)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (20)$$

where K_c is the equilibrium constant, C_e is the equilibrium concentration of zinc (II) ions in solution (mg/L) and C_{Ae} is the zinc (II) ions concentration adsorbed on the adsorbent per liter of solution at equilibrium (mg/L). G^0 , H^0 and S^0 are changes in standard, Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol K), respectively. R is the gas constant (8.314 J/mol K), T is the temperature (Kelvin). The values of H^0 and S^0 were determined from the slope (H^0/R) and the intercept (S^0/R) from the plot of $\ln K_c$ versus $1/T$ (Fig. 9.). The values of equilibrium constant (K_c), standard Gibbs free energy change (G^0), standard enthalpy change (H^0) and the

standard entropy change (S^0) calculated in this work were presented in Table 3. The equilibrium constant (K_c) increases with increase in temperature, which may be attributed to the increase in the pore size and enhanced rate of intra particle diffusion. The standard Gibbs free energy change (G^0) is small and negative and indicates the spontaneous nature of the

biosorption. The values of G^0 were found to decrease as the temperature increases, indicating more driving force and hence resulting in higher biosorption capacity. The value of H^0 was positive, indicating the endothermic nature of the biosorption of zinc (II) ions onto peanut hulls (*Arachis hypogaea* Linn.) The positive values of S^0 shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process.

Table: 3. Thermodynamic parameters of biosorption of zinc (II) ions by peanut hulls(*Arachishypogaea* Linn).

T (Kelvin)	K_c	$-G^0$ (kJ/mol)	H^0 (kJ/mol)	S^0 (J/mol K)
303	2.3182	2.1178	4.1400	20.6020
313	2.3953	2.2730		
323	2.5609	2.5251		

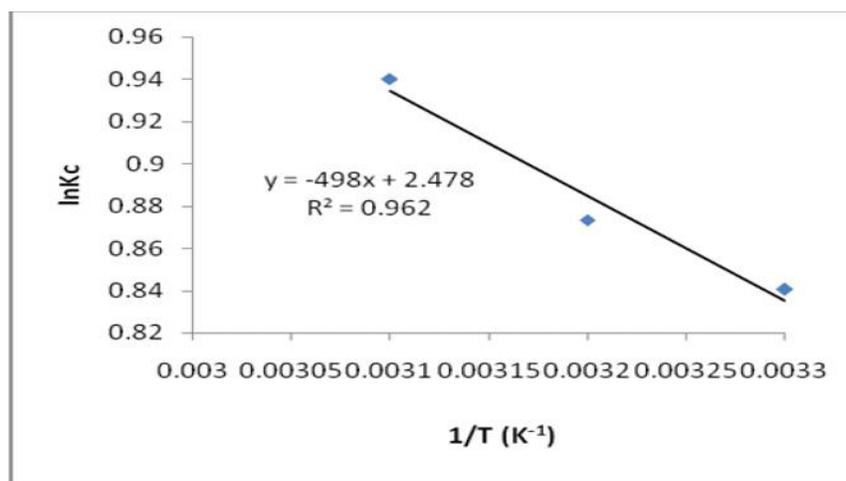


Fig.9. Determination of thermodynamic parameters for biosorption of zinc (II) ions by peanut hulls(*Arachis hypogaea* Linn.)(pH: 6.0, biosorbent dose concentration: 5 mg/ml, zinc (II) ions concentration: 10 mg/L, contacttime: 60 minutes)

Conclusion

The present investigation reveals that peanut hulls (*Arachis hypogaea* Linn.) can be an inexpensive, excellent biosorbent for the removal of zinc (II) ions from aqueous solutions. FTIR analysis of biosorbent confirmed that hydroxyl, carbonyl and carboxyl group, so that the cell wall surface of the biosorbent that may interact with the zinc (II) ions. The SEM represents a porous structure with large surface area. The optimal parameters such as solution pH, biosorbent dose, initial zinc (II) ions concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of zinc (II) ions onto peanut hulls(*Arachis hypogaea* Linn.). The

maximum zinc (II) ion loading capacity (q_e) of peanut hulls(*Arachis hypogaea* Linn.) was found to be 14.492 mg g⁻¹ with perfect fit to Langmuir isotherm model and follows pseudo-second order kinetics. The thermodynamic study confirmed that reaction of biosorption of zinc (II) ions onto peanut hulls (*Arachis hypogaea* Linn.) is spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that peanut hulls (*Arachis hypogaea* Linn.) has considerable biosorption capacity, available in abundant, non-hazardous agro material could be used as an effective indigenous material for treatment of wastewater stream containing zinc (II) ions.

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