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Agro waste material as ecofriendly adsorbent for the removal of Zn(II): isotherm, kinetic, thermodynamic and optimization studies

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ABSTRACT

Contamination of environment by heavy metals posed significant threat to human, animals and plants health due their accumulation in the living tissues and their non-degradability. Excess of zinc in living system is detrimental to health adverse effects therefore; this work investigates the feasibility of removal of Zn^{2+} from aqueous solution using agricultural biowaste adsorbent prepared from groundnut shell. Effects of some important parameters such as pH, initial metal concentrations, temperature and adsorbent dosage on adsorption process were investigated. These factors were optimized by Box-Behnken experimental design using Design Expert 6.0. The prepared biosorbent was characterized using Scanning electron microscopy (SEM), Fourier Transform Infrared (FT-IR) and X-ray dispersion (XRD). Data from kinetic study was analyzed with pseudo-first-order and pseudo-second-order kinetic models while equilibrium data were evaluated using Langmuir and Freundlich isotherm models. The surface morphology of groundnut shell revealed porous pores indicatives of available sites for sorption of metal ion on the surface of the groundnut shell. The adsorption kinetics of the metals ions followed pseudo-first-order with average rate constants of 5.63×10^{-2}. Langmuir adsorption isotherm fitted the isotherm study with R^2 >0.9 while the maximum adsorption capacities of 23.46 mg g^{-1}. Negative values of $\Delta G°$ obtained from thermodynamic evaluations revealed that the adsorption process is spontaneous. The values $\Delta H°$ and $\Delta S°$ obtained respectively are 29.90 and 105 J mol^{-1} K^{-1}. Prediction of regression models was in good agreement with experimental result. This study showed that groundnut shell to be a good adsorbent for the removal of Zn(II) from aqueous solution.

Keywords: Agricultural biowaste; Groundnut shell; Heavy metals; Kinetics and isotherm

1. Introduction

Heavy metal pollutants in the environment pose significant threat not only to man but also to plants and animals [1–3]. Their toxicity even at low concentration coupled with their ability to bioaccumulate and non-degradable in nature is of great concern. Metals of immediate concern include; copper, chromium, arsenic, lead, nickel, iron, zinc etc., because living organism require them in varying amounts for proper functioning. Zinc is an essential element requires for some biological activities such as a cofactor for many enzymes, essential for DNA replication, development and growth of pregnancy and it active role in the mineralization of biological systems, insufficiency as well as excess of zinc in human system can cause diseases and results to health challenges [4–6].

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Zinc can enter into environment through some anthropogenic process which include vulcanization, paints, galvanization, pigments, fabrication of alloys, cosmetics and insecticides [7], its acute and adverse effects include; diarrhea, vomiting, nausea, abdominal cramps, loss of appetite, headache [5,6] while its chronic effects from the intake of 150–450 mg per day can altered iron function, reduce the levels of high-density lipoproteins, damage immune function, results in low copper status and neurological disorder [6,7]. Thus, the removal of zinc ions from contaminated water becomes imperative.

Heavy metals concentration are usually in low concentration in waste water discharged to environment, hence efficient methods are required for their removal [8]. Methods such as chemical precipitation, ion exchange, filtration, electrochemical treatment and reverse osmosis have been applied for their removal [9]. The main disadvantages of these methods include the relatively low efficiency of treatment in wastewater especially at lower metal ion concentrations, also they are energy-intensive and large quantities of secondary impurities are generated. Hence there is need to develop innovative and cost-effective materials for the treatment of heavy metal contaminated wastewater. Of all the physical processes used for the wastewater treatment, adsorption technique has gained favor due to their effective removal of pollutants that are too stable for conventional methods of wastewater treatment. Activated carbon is a prominent adsorbent used in industrial processes for variety of separation and purification process, due to their extended surface area, high adsorption capacity, micro porous structure and special surface reactivity. However, commercial activated carbon remains an expensive material. Thus, the use of non-conventional and cost-effective materials such as industrial by-products and agriculture wastes that are locally available can partially resolve the problem. These materials can be chemically modified and used as a low-cost bio-char adsorbent for wastewater treatment [10]. Many low-cost adsorbents have been reported in literature for the sorption of metal ion from aqueous solution, and these include activated carbon, starch, zeolite, sawdust and coconut dregs residue [11–15].

Biosorption is an innovative biotechnology that utilizes low-cost biosorbents for the removal of metal ion from aqueous solution with superior advantages such as; high efficiency and selectivity even at low metal ion concentrations, energy-saving, broad operational range of pH and temperature, easy reclamation of metals and easy recycling of the biosorbent [16]. Problems of generation of secondary impurity can also be overcome by the use of natural biosorbents that produce minute solid wastes that can be disposed in landfill or easily managed by incineration [17]. The conversion of agro-waste to useful biomaterial has added different dimension to the utilization of agricultural waste for value added products Many agricultural and biological based materials have been utilized as biosorbent for the removal of Zn^{2+} from aqueous media, these include; coconut husk [18]; orange residue [19]; sea weeds [20], maize leaf [21], coffee husk [22], coffee residue [23], wheat straw [24], corn silk [25], tea waste [26] and Plantain stalk [27] to mention but few. Nigeria is the third largest producer of groundnut with about 3.0 million metric tonne per annum [28]. It is a source of protein and oil, it is consumed locally in various forms and an industrial raw material for vegetable oil extraction. Its cake is used as feed supplements for livestock. It huge cultivation resulted in generation of large amount carbonaceous, fibrous solid waste which encounters disposal problem, it is generally burnt off or left littering the street in a non eco-friendly manner that can trigger green house effect. Therefore conversion of groundnut shell to adsorbent will eliminate improper disposal and added value to the waste.

This study investigates the uptake of Zn^{2+} using groundnut shells under different initial conditions (pH, temperature, biomass concentration and sorption time). Pseudo-first order and pseudo-second order kinetic models were used to correlate the experimental data and to determine the kinetic parameters. Langmuir and Freundlich adsorption isotherms were chosen to describe the biosorption equilibrium. Least square fit method of analysis was applied to the models to determine their appropriateness. Box-Behnken experimental design was used for the optimization study of effect of the pH, initial concentration and biomass dosage at equilibrium. The result of which was statistically studied using analysis of variance (ANOVA).

2. Materials and methods

2.1. Synthesis of biosorbent

Groundnut shell were collected at Osiele Market in Abeokuta, wash thoroughly under running tap to remove dirt, then with distilled water and dried at 105°C for 6 h. The dried shell was then pulverized and sieved to select sample <300 μm. The pulverized sample was soaked in dilute nitric acid for 10 min to remove any inherent metals, washed with distilled water to neutrality, then dried in oven at 105°C for 4 h and stored in the airtight container prior to usage. The surface morphology was studied with scanning electron microscope using a Hitachi (Japan) S-3000H electron microscope with an accelerating voltage of 15 kV equipped EDAX for elemental analysis. Fourier Transform Infrared (FT-IR) Spectroscopy, the various functional groups present was determined using Fourier Transform Infrared (FT-IR) spectroscopy TENSOR 27, series FT-IR spectrometer, Germany. X-Ray Diffraction (XRD) Analysis was by X-ray diffraction (XRD) using X-pert PRO, PANalytical, Netherland diffractometer.

2.2. Biosorption experiments

The biosorption experiments of Zn(II) were conducted in batch method, which permits complete evaluation of parameters that influence the adsorption process. The adsorption isotherm, kinetic and thermodynamics studies procedures follow the method earlier discussed [29–34].

2.3. Adsorption isotherms study

Data obtained from equilibrium studies of the biosorption process were analyzed with Langmuir and Freundlich isotherm models. The Langmuir isotherm assumes monolayer coverage of adsorbate over a homogenous adsorbent surface without any interactions between the adsorbed molecules. The isotherm can be expressed as [29]:

$$Q_{eq} = \frac{Q_{max} b C_e}{1 + b C_e} \quad (1)$$

where C_e is the equilibrium concentration of Zn(II) in (mg L^{-1}), q_e is the concentration of Zn(II) adsorbed in (mg g^{-1}), Q_{max} is the monolayer adsorption capacity in (mg g^{-1}) and b is the Langmuir constant which described the free energy of adsorption in (L g^{-1}).The degree of suitability of the Langmuir adsorption isotherm was estimated from the value of separation factor, (R_L) which can be expressed in the following equation [30]:

$$R_L = \frac{1}{(1 + b_c)} \quad (2)$$

The value of R_L indicated the type of Langmuir isotherm to be irreversible if $R_L = 0$, favorable when $0 < R_L < 1$, linear when $R_L = 1$ and unfavorable when $R_L > 1$ [31].

The Freundlich model is an empirical equation that predicts surface heterogeneity of monolayer active sites with interaction between the adsorbed molecules [32]. This isotherm can be expressed as Eq. (3) [29–34]:

$$Q_{eq} = K_F C_e^{\frac{1}{n}} \quad (3)$$

where K_F and n are Freundlich constants which described the extent of adsorption and the intensity of adsorption respectively.

2.4. Adsorption isotherms study

In order to investigate the mechanisms of the adsorption process, pseudo-first order (Eq. (4)) and pseudo-second-order kinetic models (Eq. (5)) were applied to describe the data obtain from the time dependent biosorption studies. The detail about these models had been explained elsewhere [29–34]. The least square fit was also used to obtain the parameters as described in the isotherm studies.

$$Q_t = Q_e (1 - e^{-k_1 t}) \quad (4)$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (5)$$

where k_1 and k_2 are pseudo-first and pseudo-second order the rates constant of adsorption, The values of Q_e is the theoretical equilibrium amount obtained from the least square fit of Q_t vs. t at different solutes concentrations.

2.5. Experimental design

Biosorption of metal ions depends largely on the pH, adsorbent dosage and initial metal concentration, these factor were used to design the experiment in order to optimize the biosorption process. Box–Behnken experimental design was used, in which the three variables: pH (1–8), biosorbent dosage (0.01–0.1 g) and concentration (50–250 mg L^{-1}) were evaluated at equilibrium at three levels each using Design Expert 6.0.

3. Results and discussions

The Scanning Electron Micrograph (SEM) of the groundnut shell is as presented in Fig. 1. The surface morphology revealed rough and porous surfaces indicating the presence of adsorption sites for the Zn(II).The EDAX analysis as presented in Fig. 1(b) showed that groundnut shell is rich in some mineral elements including Na, Mg and Ca.

Fig. 2 shows the XRD analysis of the groundnut shell, the curve revealed prominent peaks at 2θ = 15.3°, 22.7° and 35.2°. The broadness of the peak at 22.7° is an indication of the armophous nature of the groundnut shell powder.

The FT-IR spectra of the groundnut shell before and after adsorption is presented in Fig. 3. The spectra displayed broad band in the region of 3,400, 2,806 and 1,617 cm^{-1}. These bands correspond to the free O–H stretching vibration of –OH group in cellulose, C–H stretching vibration and O–H bending of absorbed water respectively [35]. The strong absorption frequency at 1,407 cm^{-1} belongs to C–O stretching vibration of phenyl group in lignin. After adsorption, shifting and reduction in wavenumber and intensity respectively are noted in the spectra, suggesting a chemical interaction between the Zn(II) and functional groups on the adsorbent.

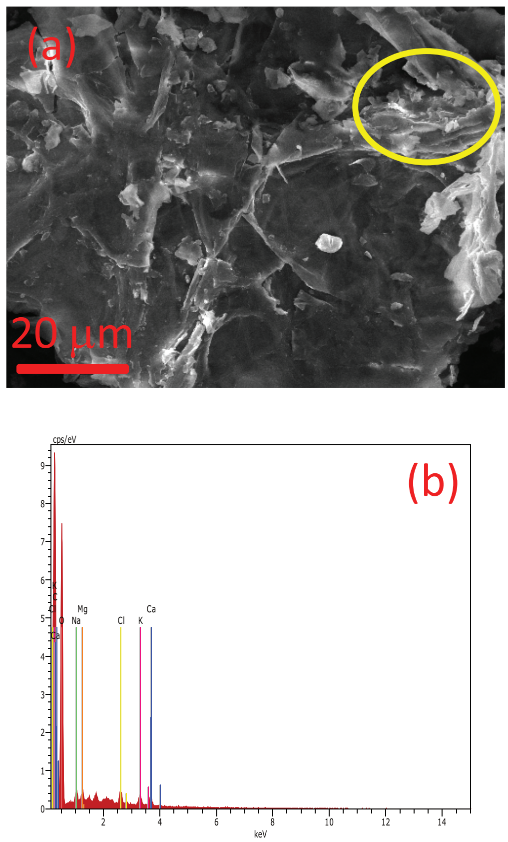


Fig. 1. (a) SEM image and (b) EDAX analysis of groundnut shell.

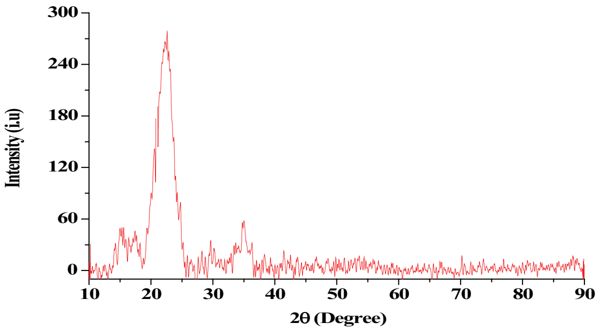


Fig. 2. X-ray diffraction (XRD) analysis of groundnut shell.

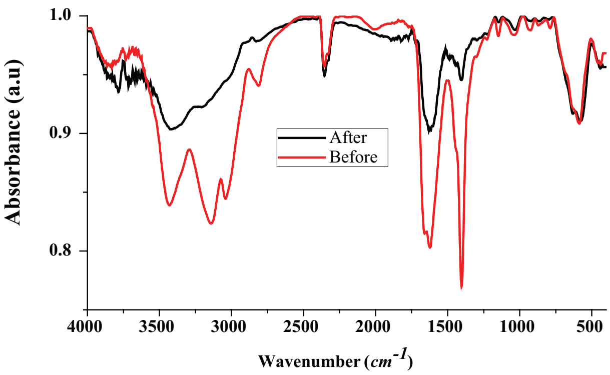


Fig. 3. X-ray diffraction (XRD) analysis of groundnut shell before and after adsorption.

3.1. Effect of biosorbent dosage

The effect of the biosorbent dosage on the efficiency of Zn(II) removal is presented in Fig. 4. The efficiency increases with increase in biomass dosage, which implies that more active sites were available for the biosorption of the metal ion. 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 [36].

3.2. Effect of Zn(II) concentrations

Fig. 5 shows the effect of initial metal concentration on the biosorption process, it is obvious that increase Zn(II) ion lead to increase removal. This observation may be attributed to increase in diffusion driving force as a result of concentration differences between adsorbates and adsorbents would at higher initial concentration. The faster diffusion rate of Zn(II) ion across the external boundary layer and within the pores, resulting in increased percentage removal. Similar trend was observed for quantity absorbed, which indicates that sorption capacity increased with increase in initial metal ion concentration on the biomass. This pattern implied that surface saturation is dependent on the initial metal ion concentrations. At low concentrations, adsorption sites took up the available metal more quickly, but at higher concentrations, the need to diffuse to the biomass surface and the influence of solvation on metal ion will slow the diffusion.

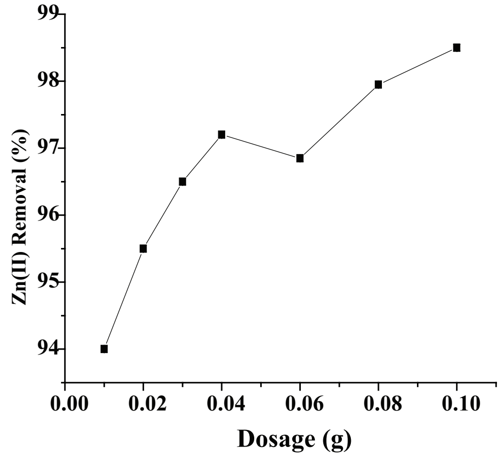


Fig. 4. Effect of adsorbent dosage on removal efficiency of Zn(II) ion.

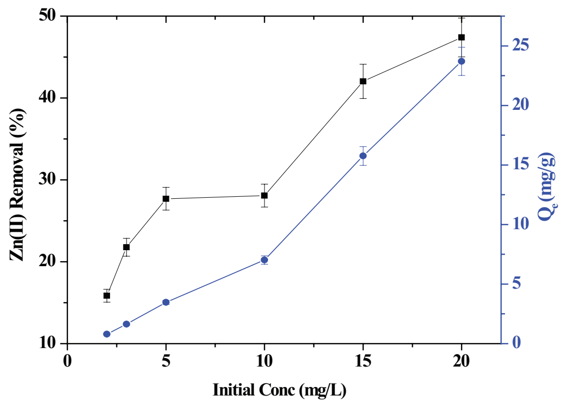


Fig. 5. Effect of initial metal concentration on the quantity removed and removal efficiency of Zn(II) ion.

3.3. Effect of hydrogen ion concentrations

Hydrogen ion concentration otherwise known as potential hydrogen (pH) affects the chemistry of the adsorbent and adsorbate as well as their interaction. Fig. 6 shows the effect of pH on the biosorption of Zn(II) on groundnut shell, the lower adsorption observed at low pH may be as a result of strong competition between metal ions and H^+ ions for the active sites on the surface, as the pH increases the corresponding increase in the percentage removal may be as a result of deprotonation of the active site, leading to more site being available for metal ion removal. At pH 7, the increase in removal can also be attributed to the precipitation of the Zn(II) out of the solution, similar observation was also been reported [37].

3.4. Adsorption isotherms

Fig. 7 shows the isotherm plot of the two models while their parameters are presented in Table 1. The values of the correlation coefficients, R^2 estimated from the least square fit statistic on Micro Math Scientist software were compared.

The maximum adsorption capacity (Q_{max}) was 23.46 mg g^{-1} by using the Langmuir monolayer equation.

The separation factor, RLo btained for this study was 0.91, while the Freundlich isotherm parameter, n was 3.96, these values respectively indicated favorable adsorption process. The results obtained from this study showed that groundnut shell is a good biosorbent for Zn^{2+} removal and it compete favorably with other biomass for the same purpose as shown in Table 2.

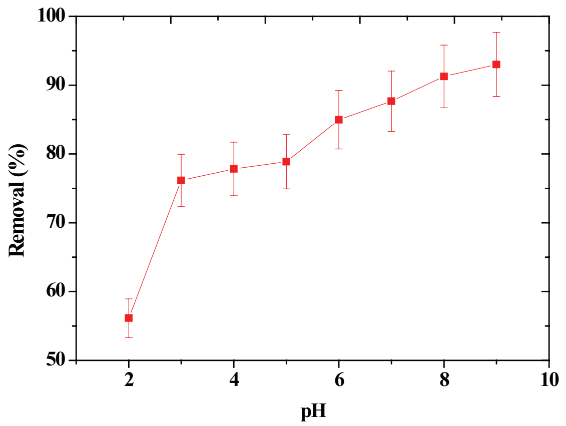


Fig. 6. Effect of pH on the removal efficiency of Zn(II) ion.

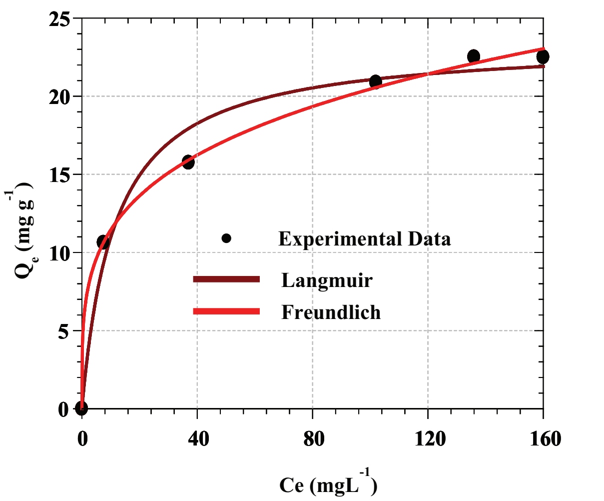


Fig. 7. Isotherm fits for the adsorption Zn(II) on groundnut shell.

Table 1
Isotherm parameters for the biosorption Zn(II) ion on groundnut shell

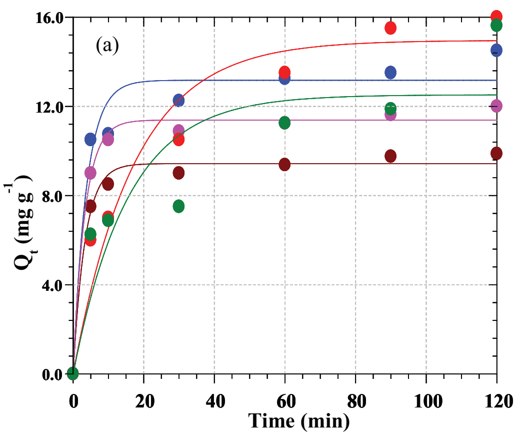
Isotherms	Parameter	
Langmuir	Q_{max} (mg g^{-1})	23.46
	b (L mg^{-1})	0.088
	R_L	0.091
	R^2	0.980
Freundlich	K_F ((mol g^{-1})(mol L^{-1})$^{-1/n}$)	6.40
	n	3.96
	R^2	0.998

3.5. Adsorption kinetics studies

The plots of pseudo-first-order and pseudo-second order models are as shown in Figs. 8(a) and (b) respectively, while their physical parameters are as summarized in Table 3. The correlation coefficient values for both models were close to unity but on comparing the experimental adsorption capacity

Table 2
Comparison of the Zn^{2+} biosorption capacities of different biosorbents

Biosorbent	Q_{max} (mg g^{-1})	Reference
Coconut husk	17.857	[18]
Orange waste	43.412	[19]
Seaweed	49.54	[20]
Maize leaf	23.64	[21]
Coffee husk	12.987	[22]
Coffee residue	4.44	[23]
Wheat straw	3.25	[24]
Corn silk	12.56	[25]
Tea waste	14.2	[26]
Plantain stalk	24.6	[27]
Groundnut shell	23.46	This study



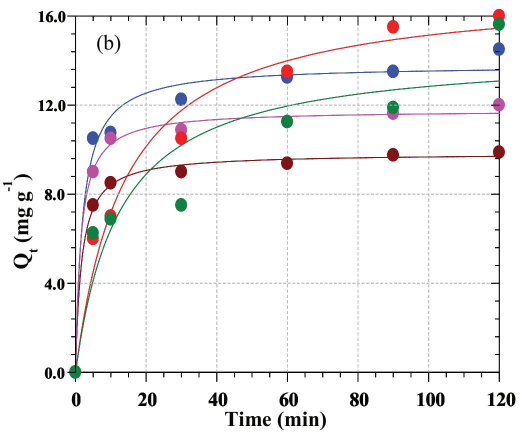


Fig. 8. (a) Pseudo-first order (b) pseudo-second order kinetic fits for the adsorption Zn(II) ionon groundnut shell.

Table 3
Kinetic parameters for the biosorption Zn(II) ion on groundnut shell

First order					Second order		
C_o(mg L^{-1})	$Q_{e,\exp}$(mg g^{-1})	$Q_{e,\mathrm{cal}}$(mg g^{-1})	k_1(min^{-1})	R^2	$Q_{e,\mathrm{cal}}$(mg g^{-1})	k_2(L mg^{-1} min^{-1})	R^2
50	9.875	9.434	0.297	0.990	9.84	0.060	0.997
100	14.500	13.173	0.267	0.961	13.80	0.036	0.984
150	12.000	11.389	0.300	0.992	11.78	0.057	0.996
200	16.000	14.962	0.058	0.946	17.27	0.004	0.977
250	15.625	12.521	0.064	0.800	14.44	0.006	0.870

Table 4
Thermodynamic parameters for adsorption of Zn(II) on groundnut shell

Temperature (K)	K_d	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	R^2
303	2.122	–1.915	29.9	104.6	0.9202
308	2.757	–2.440			
318	3.233	–3.490			
323	4.9	–4.015			

($q_{e,\exp}$) values with the calculated adsorption capacity ($Q_{e,\mathrm{cal}}$) values, showed closed agreement with second-order model. Thus, the adsorption of Zn(II) onto groundnut shell followed a pseudo-second-order kinetic model.

3.6. Thermodynamic study

The distribution of the solutes molecules or ions between the adsorbent and solution at equilibrium is written as:

$$\text{Solute}_{\text{solution}} \rightleftarrows \text{Solute}_{\text{adsorbed}} \quad (6)$$

The equilibrium constant, K_d can be expressed according to the concentrations in each of the medium as:

$$K_d = \frac{\text{Solute}_{\text{adsorbed}}}{\text{Solute}_{\text{solution}}},\ K_d = \frac{Q_e}{C_e} \quad (7)$$

The equilibrium constant K_d is the temperature dependent and it is used in determining the thermodynamics parameters, $\Delta G°$, $\Delta H°$ and $\Delta S°$ using the relation in Eq. (8) to obtain a van't Hoff isotherm [38] that relates the equilibrium constant with other thermodynamic parameters (Eq. (9))

$$\Delta G° = -RT \ln K_D \quad (8)$$

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (9)$$

The van't Hoff plot for the adsorption of Zn(II) ion is presented in Fig. 9 while the thermodynamics parameters are presented in Table 4.

The thermodynamic parameters revealed negative free energy, $\Delta G°$ which decreases with increase temperature, which implied that the adsorption process spontaneous

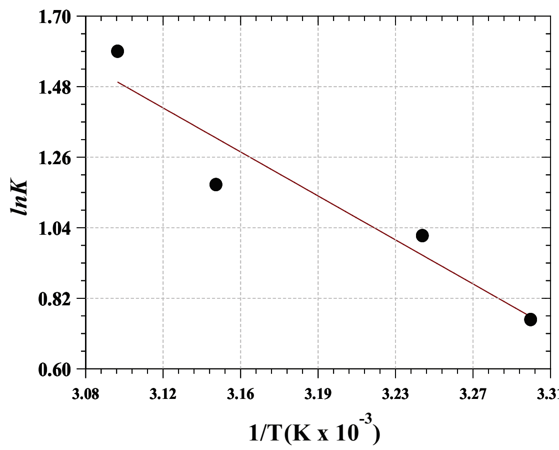


Fig. 9. Thermodynamics fit for biosorption of Zn(II) on groundnut shell.

especially at lower temperature. The process is endothermic as shown by $\Delta H°$ value while the positive $\Delta S°$ value suggests increased randomness at the solid/solution interface during the adsorption process.

3.7. Optimization study

The Box-Behnken experimental design matrix was calculated using the Design Expert 6.0, the different experiments suggested by the software with experimental outcome (percentage Zn(II) removal), the calculated values (predicted) and the difference (residue) are presented in Table 5. The 2FI, quadratic and cubic models were fit for the experimental data to find the regression equation, the evaluation of the models showed that the cubic model was aliased and therefore have misleading response contour, hence the quadratic model was selected for its higher F values than 2FI model. The second order polynomial equation was given by Eq. (10) in terms actual factors for the prediction of response.

Table 5
Box-Behnken design matrix for the optimization of variable and the response

Run	Concentration (mg L^{-1})	pH	Dosage (g)	Actual	Predicted	Residual
1	150	8	0.01	97.75	94.49	3.26
2	150	8	0.1	73.71	72.73	0.98
3	150	4.5	0.05	93.79	93.65	0.14
4	250	4.5	0.1	97.35	97.02	0.33
5	150	4.5	0.05	73.71	72.73	0.98
6	250	8	0.05	98.40	99.59	–1.19
7	50	4.5	0.1	87.72	88.38	–0.66
8	50	1	0.05	98.77	94.19	4.57
9	150	1	0.01	93.81	93.65	0.16
10	50	4.5	0.1	99.25	95.14	4.12
11	250	4.5	0.01	72.86	76.98	–4.12
12	50	4.5	0.1	91.72	90.53	1.19
13	250	1	0.05	69.66	68.93	0.73
14	50	8	0.05	93.34	93.65	–0.31
15	150	1	0.1	82.46	86.45	–3.98
16	150	4.5	0.05	73.71	72.73	0.98
17	150	1	0.01	87.72	88.38	–0.66

Table 6
ANOVA for response surface quadratic model

	Sum of squares	DF	Mean square	*F* value	Prob > *F*
Source model	1,757.12	9	195.24	15.43	0.0008
A	351.87	1	351.87	27.81	0.0012
B	72.07	1	72.07	5.70	0.0484
C	302.30	1	302.30	23.89	0.0018
A^2	13.44	1	13.44	1.069	0.3370
B^2	84.48	1	84.48	6.68	0.0363
C^2	34.83	1	34.83	2.76	0.1411
AB	81.11	1	81.11	6.41	0.0391
AC	59.29	1	59.29	4.69	0.0672
BC	156.55	1	156.55	12.37	0.0098
Residual	88.58	7	12.65		
Lack of fit	88.44	2	44.22	1,542.64	<0.0001
Pure error	0.14	5	0.029		
Correlation total	1,845.70	16			

$$\text{Removal} = 93.50 - 0.105\text{ A} + 3.048\text{ B} + 35.006\text{ C} + 0.000205\text{ A}^2 - 0.420\text{ B}^2 - 1633.177\text{ C}^2 + 0.0129\text{ AB} + 1.068\text{ AC} - 37.031\text{ BC} \quad (10)$$

The analysis of variance (ANOVA) for the surface response is presented in Table 6, higher values of *F* and smaller value of Prob > *F* indicate a more significant corresponding coefficient term [39]. The values of Prob > *F* less than 0.05 indicate that the process is significant, therefore the terms A, B, C, AB, BC, B^2 and were significant and A^2, AC and C^2 are insignificant model terms. The value of *F* for this model was 15.42. The degrees of freedom for lack of fit and pure error obtained for this study indicate that the model is sound. The goodness of fit depends on the statistical information of the response (Table 7). The R^2, and adjusted R^2 and predicted R^2 are relatively high, signifying that there was a good concurrence between the experiment and the predicted values. The R^2 indicates that 95.7% of variability falls within the explanation capacity of the model while only 5.3% could not be accounted for by the independent variable. The values of the coefficient of variance and standard deviation indicate a satisfactory degree of precision while adequacy precision value greater than 4 confirm that adequate signal of 11.75 obtained for the model can be used to navigate the design space.

The response surface curves for the effect of the interaction between the independent variables and removal efficiency of the Zn(II) by the groundnut shell are

Table 7
Statistical information of the response

R-squared	0.952
Adj *R*-squared	0.890
Coefficient of variation	4.07
Adequacy precision	11.75
Standard deviation	3.56

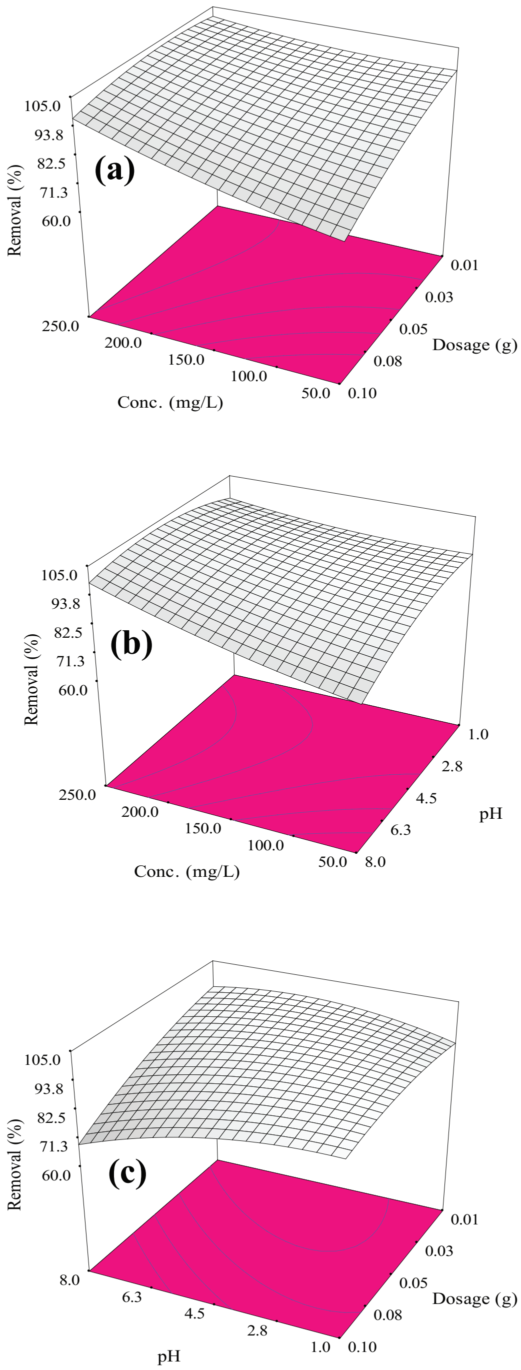


Fig. 10. Response surface plots for the optimization of Zn(II) biosorption by groundnut shell (a) concentration and dosage (b) concentration and pH (c) pH and dosage.

presented in Fig. 10. The influence of interaction of biosorbent dosage and initial Zn(II) concentration shows that as increase dosage led to increase in removal efficiency up to around 100% as the initial concentration also increases. pH interactions with both the initial Zn(II) and adsorbent revealed that as pH increases there is reduction in the efficiency of the removal of Zn(II) ions which may be attributed to the formation of hydroxide at higher pH and subsequent precipitation. The removal efficiency decreases from above 95% to nearly 72% as the pH increases, reverse were observed as Zn(II) concentration and adsorbent dosage increases. The numerical optimization of the studied parameters revealed that the optimized conditions for maximum removal efficiency of groundnut shell for Zn(II) is 99.72% obtainable at pH 4.32, adsorbent dosage of 0.04 mg and initial concentration of 220.88 mg L^{-1}.

4. Conclusions

This study successfully used groundnut shell as a biosorbent for the removal of Zn(II) from aqueous solution. The characterization of the biosorbent revealed the presence of functional groups relevant for physio-chemical interactions between the metal ion and the biosorbent, the amorphous nature of the biosorbents. The isotherm and kinetic study revealed that the Freundlich isotherm model best fitted the equilibrium adsorption data, however Langmuir isotherm showed that the biosorbent has maximum adsorption capacity of 26.46 mg g^{-1}. Kinetic models analysis showed a better fit with pseudo-second order model. The thermodynamic parameters showed that the process is highly favorable at lower temperature, and exothermic in nature. The optimization study revealed that the quadratic model of better represent the interaction of the factors affecting the biosorption with $R^2 > 0.9$. Therefore, groundnut shell is a viable biosorbent for effective removal of Zn ions from aqueous solutions and can be applied in the remediation of contaminated water.

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