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Kinetics, Equilibrium and Thermodynamic Studies of the Adsorption of Zinc(II) ions on *Carica papaya* root powder

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Abstract

The adsorption of Zn (II) ions on Carica papaya was studied. The effect of pH, biomass dosage, temperature, adsorption equilibrium and kinetics, were investigated. The optimum pH for the removal of Zn(II) was found to be 6.0. The Freundlich, Langmuir and Dubinin–Radushkevich (D–R) models were used for the mathematical description of the adsorption equilibrium of which the Freundlich and D-R fitted very well to the experimental data. The adsorption kinetics was well described by the pseudo-second order equation. The thermodynamic studies and sorption energy calculation using D-R isotherm model indicated that the adsorption processes were exothermic and physical in nature.

Keywords: *Carica papaya*, adsorption, isotherm, zinc, kinetics, equilibrium.

Introduction

Rapid industrialization has resulted in severe environmental and health problems to man. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products[1]. The presence of heavy metal ions is a major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, chlor alkali, radiator manufacturing, smelting, alloy industries and storage batteries industries, etc.[2].

Conventional metal removal techniques such as ion exchange, precipitation, membrane separation, electrochemical precipitation–filtration and reduction followed by chemical precipitation are often expensive or not sufficiently effective in the low concentration range[3-5]. Adsorption is one of the important procedures for the removal of trace heavy metals from aqueous solution. The main properties of the adsorbents for metal removal are strong affinity and high loading capacity. Hence, low cost adsorbents with high metal binding affinity need to be studied. In general, an adsorbent can be termed as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Of course improved sorption capacity may compensate the cost of additional processing. Therefore there is an urgent need that all possible sources of agro-based inexpensive adsorbents are explored and their feasibility for the removal of heavy metals be studied in detail. The literature review suggested that the numerous agricultural waste and/or natural adsorbents, microorganisms and algae, etc. have been used for the removal of Zn(II) from aqueous solution[6-10].

The aim of the present study was to investigate and explore the feasibility of natural adsorbents namely *Carica papaya* for the adsorption of zinc. The effect of pH, biomass concentration, initial metal concentration and contact time were determined. Kinetic models such as pseudo-first order, pseudo-second order, intraparticulate diffusion were used to describe the biosorption process. Moreover, the batch equilibrium process was explained using Langmuir, Freundlich and *D–R* models. The thermodynamic parameters such as entropy, enthalpy and the Gibbs free energy for the adsorption of zinc on *Carica papaya* were also obtained.

Material and Methods

Biomass preparation: The *Carica papaya* (pawpaw) root sample was collected from Ijebu-Ode area of Ogun state. Samples were washed several times using deionised water to remove extraneous and dust. It was then dried in an oven at 120ºC. The dried biomass was milled and filtered. The granules were sieved with a 150 µm sieve. The adsorbent was kept dry in a closed container until the time of use.

Solution preparation: A stock solution of 1000 mg/L $ZnSO_4$ (analytical reagent grade) in distilled water was prepared. From the stock solutions 10 mg/L, 20 mg/L and 30 mg/L were prepared in 250 mL standard flasks. The initial pH was adjusted with 0.1 M HCl and 0.1 M NaOH solutions using a pH meter (A TOAV pH meter (HM30P) calibrated with standard buffer solutions.

Biosorption experiments: Batch biosorption experiments were conducted to investigate the parametric effect of pH, initial zinc concentration, adsorbent dosage, contact time and temperature on zinc removal capacity of the *Carica papaya* root powder. The pH experiment was carried out by agitating 0.6 g of *Carica* *papaya* root powder with 25 mL of zinc solution of initial concentration 10 mg L^{-1} at different solution pH ranging from 2.0 to 7.0. The initial metal concentrations (10-30 mg/L) and the biomass dose (0.1-0.6 mg) experiments were carried out using conical flasks tightly covered with clean aluminium foil on an orbital shaker for 5 h at a speed of 120 rpm and a temperature of 30 ± 1°C. The sample was filtered using Whatmann No. 1 filter paper. The concentrations of zinc in the solutions before and after adsorption were determined using Perkin-Elmer atomic absorption spectrophotometer (AAS). Kinetic experiments were also carried out with 0.2 g of the adsorbent in which 10 mL of the solution was withdrawn at different intervals. Temperature effect was also determined by shaking the solution on a magnetic stirrer at 30, 40 and 50°C. The amounts of Ni (II) ions biosorption at equilibrium, q_e (mg/g), were calculated according to the following mass balance equation for the metal ion concentration

$$q_e = \frac{C_o - C_e}{m} V \quad (1)$$

Where q_e was the adsorption capacity at equilibrium, C_o and C_e are respectively initial and equilibrium concentrations of zinc (II), m is the mass of the *Carica papaya* and V is the volume of the zinc (II) solution. The percent sorption capacity was calculated from the equation

$$\%\ \text{sorption capacity} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

The experiments were carried out in triplicate.

Results and Discussion

Effect of pH: pH is a very vital parameter in adsorption because it governs the speciation of metals and also the dissociation of active functional sites on the adsorbents[11]. From figure-1 it is shown that the pH increased from 2 to 6 and then decreased. At lower pH adsorption was decreased due to the competition of the Zn (II)ions with the protons on the surface of the adsorbent. The increase in adsorption as the pH increased up to pH 6 was due to the decrease in protonation of the adsorbent surface in neutral or less acidic medium[12,13]. In addition, the surface charge of biomass (*Carica papaya*) is a function of the pH of the solution. The pH value, at which the surface charge is zero, is called the point of zero charge (PZC). The PZC of the adsorbent was 9.0 (figure-2) which were determined by the method described by Gupta and Nayak[14]. This implied that even though the optimum pH of adsorption was 6, the adsorption will not be as high as expected due to the electrostatic interaction of hydrogen ions with metal.

Effect of mass of biomass: The effect of the mass of adsorbent on adsorption of zinc was studied by changing the mass of the biosorbent dosage from 0.1 to 0.6 g. The percentage adsorption capacity increased with increase in adsorbent dosage. Figure-3 shows a gradual increase from 0.1 to 0.4 g. From 0.4 to 0.5 g the adsorption increased sharply with percentage adsorption capacity as high as 99.8%.

Effect of Initial concentration: The initial metal concentration has effect on the adsorption of metals by adsorbents. In figure-4, the percentage adsorption capacity increased with increase in the initial metal concentration. There is a sharp increase in adsorption when the initial zinc metal concentration increased from 10 to 20 mg/L. There is a gradual increase in adsorption capacity as the initial metal concentration increased from 20-50 mg/L.

Effect of contact time: Contact time profiles for the biosorption of 10-30 mg/L zinc (II) solutions are presented in figure-5. Adsorption rapidly increased in the first 10 minute. Data obtained from the biosorption of zinc ions on the *Carica papaya* showed that contact times of 50, 40 and 20 minutes were needed to achieve equilibria for metal concentrations of 10, 20 and 30 mg/L respectively. The rate of biosorption decreased with further increase in contact time. Similar result obtained by Atar *et al.*[15] showed that adsorption of Cd^{2+} and Zn^{2+} on boron enrichment process rapidly increased in the first 40 minutes of the reaction.

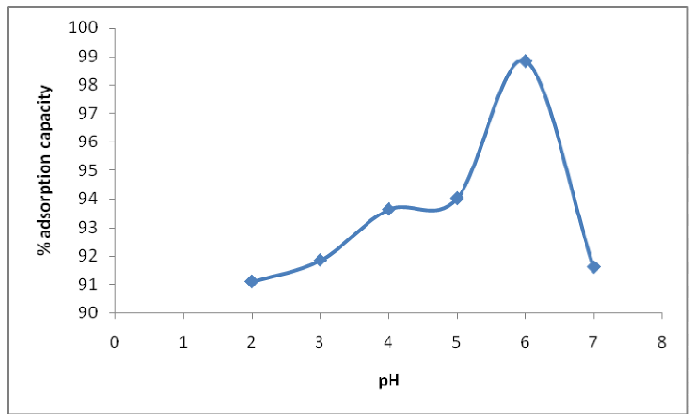

Figure-1
The effect of pH on the adsorption of Zinc on *Carica papaya*
Conditions: Temp= 30 ± 1°C, C_o= 25mg/L, agitation speed = 120 rpm

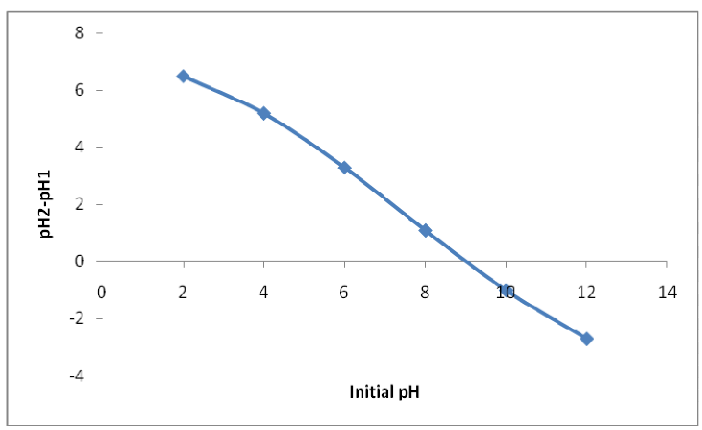

Figure-2
The effect of point of zero charge on the adsorption of zinc on *Carica papaya* at 30±1°C

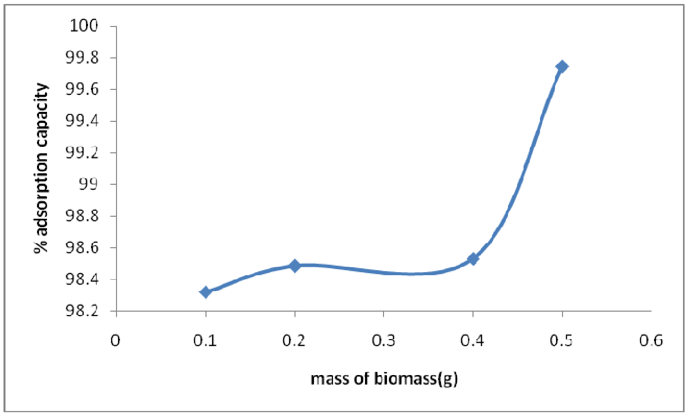

Figure-3
The effect of mass of biomass on the adsorption of zinc on *Carica papaya* Conditions: Temp= 30 ± 1°C, C_o= 25mg/L, agitation speed = 120 rpm

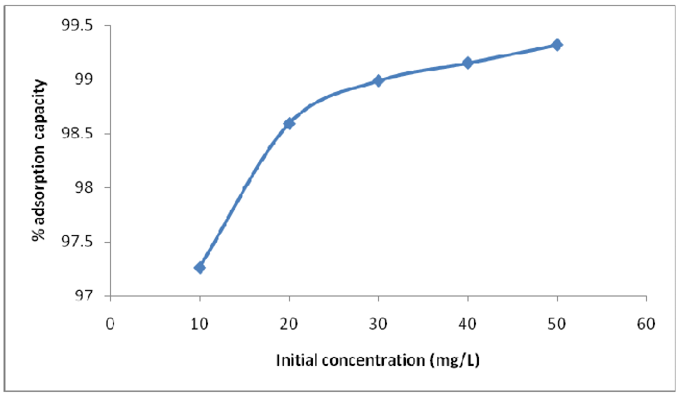

Figure-4
The effect of initial metal concentration on the adsorption of zinc on *Carica papaya* Conditions: Temp= 30 ± 1°C, w= 0.6 g, agitation speed = 120 rpm

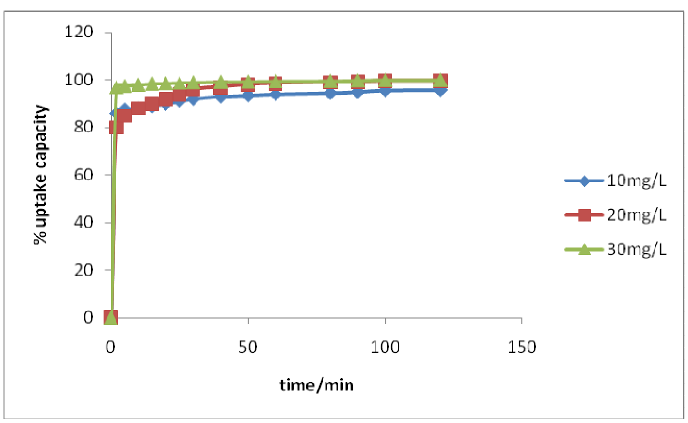

Figure-5
Effect of contact time on the adsorption of zinc on *Carica papaya* Conditions: Temp= 30 ± 1°C, agitation speed = 120 rpm, w = 0.2 g, contact time= 2h

Sorption isotherm: In this study, the adsorption equilibrium of zinc on *Carica papaya* was modeled using Langmuir, Freundlich and D-R isotherms. The Langmuir model is based on the assumption of a structurally homogeneous adsorbent where all adsorption sites are identical and energetically equivalent, and only monolayer adsorption occurs in the process[16]. The linear form of Langmuir equation is given by

$$\frac{C_e}{q_e} = \frac{1}{Q_o a} + \frac{C_e}{Q_o} \quad (3)$$

Where q_e is the monolayer biosorption capacity of the biosorbent (mg/g); 'and ais the Langmuir constant (L/g)', and is related to the free energy of biosorption. A plot of C_e/q_e versus C_e for the biosorption of Zn (II) ions onto *Carica papaya* (figure-6) gives a straight line of slope, $1/Q_o$, and intercept, $1/Q_o a$. The R^2 value in Table 1 suggests that the Langmuir isotherm is suitable for describing the adsorption of Zn (II) ions on *Carica papaya* at a temperature of 30 ± 1 °C. The maximum monolayer biosorption capacity was found to be 0.4 mg/g for Zn (II) ions at a temperature of 30 ± 1 °C and pH 6.0.

A dimensionless equilibrium parameter, E_L, proposed by Weber and Chakkravorti[17] described the favourability of adsorption. It is expressed as

$$E_L = \frac{1}{\left(1+aC_o\right)} \quad (4)$$

A favourable adsorption has its E_L value between 0 and 1, for unfavorable and linear adsorption E_L>1 and E_L = 1 respectively, while the adsorption operation is irreversible if E_L = 0. Value of E_L was calculated to give 0.02 for Zn(II) ions. This confirmed that *Carica papaya* is favourable for the biosorption of Zn (II) ions under conditions used in this study.

The Freundlich model is employed to describe heterogeneous system characterized by a heterogeneity factor of n[16]. This model describes reversible adsorption and is not restricted to the formation of the monolayer. Linear form of the Freundlich isotherm equation can be written as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

Where q_e is the equilibrium metal concentration on the biomass (mg/g); C_e is the equilibrium metal concentration in the solution (mg/L); K_F (L/g) and n (dimensionless) are Freundlich isotherm constants and are related to the sorption capacity and intensity, respectively. Freundlich constants K_F and n can be calculated from the slope and intercept of the linear plot (figure-7).

The Dubinin–Radushkevich (D–R) isotherm is more general than the Langmuir isotherm, because it does not assume a homogenous surface or constant sorption potential[18]. It is used to determine adsorption type: whether it is physical or chemical. The D–R equation is given by

$$q_e = \ln q_X - \beta \left[RT\ln\left(1 + \frac{1}{C_e}\right)\right]^2 \quad (6)$$

Where q_e is the amount of zinc (II) ions adsorbed at equilibrium, β is a constant related to the adsorption energy, q_x is the maximum adsorption capacity; ε is the Polanyi potential that is equal to

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \quad (7)$$

The linear form of equation (6) is, $\ln q_e = \ln q_x - \beta\varepsilon^2$ (8)

The D–R isotherm model fitted the equilibrium data as shown in Fig.8. Table 1 gives the R^2 value for the plot of q_e against ε^2. The q_x and β values were calculated from the slope and intercept of the plots and presented in Table 1. The mean free energy of biosorption, E, was obtained from the equation

$$E = 1/\sqrt{2\beta} \quad (9)$$

The magnitude of *E* value gives information about the biosorption mechanism as chemical ion-exchange or physical sorption. If *E* value is between 8 and 16 kJ/mol, the biosorption process is by chemical ion-exchange and if *E* < 8 kJ/mol, the biosorption process is of a physical nature. The mean biosorption energy was calculated and given in table-1. These results suggest that the biosorption processes of zinc (II) ions onto the studied *Carica papaya* was likely to take place by physical mechanism because the sorption energy is below the 8 kJ/mol. The D-R also fitted well (R^2 is 0.94) and can be used to suitably describe the adsorption of Zn (II) ions on *Carica papaya*.

Adsorption kinetics: To determine the adsorption kinetic of *Carica papaya* at different adsorbent dosage, two kinetics models, pseudo-first-order and pseudo second-order models were applied. The linearized form of Lagergren pseudo-first-order model is given by

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \quad (10)$$

Where q_e (mg/g) and q (mg/g) are the biosorption capacities of the biosorbent at equilibrium and at any time t, respectively; k_1 is the langergren rate constant of the pseudo- first order biosorption. The plots of $\log(q_e\text{-}q)$ versus t (min) for different concentrations of zinc gave straight lines (Figure not shown). From the plots, k_1 and q_e are determined from the slope and intercept respectively as shown in table-2.

The pseudo second order model: The linearized form of the pseudo-second order model of metal ions in solution is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t}t \quad (11)$$

Table-1
Langmuir, Freundlich and Dubinin–Radushkevich isotherms for zinc (II) ion biosorption on *Carica papaya* root powder

Langmuir				Freundlich		Dubinin–Radushkevich	
R^2	Q_o (mg/g)	K_L (L/mg)	E_L	R^2	K_F (mg/g)	R^2	E (J mol^{-1})
0.90	0.40	2.42	0.02	0.94	170.6	0.94	0.5

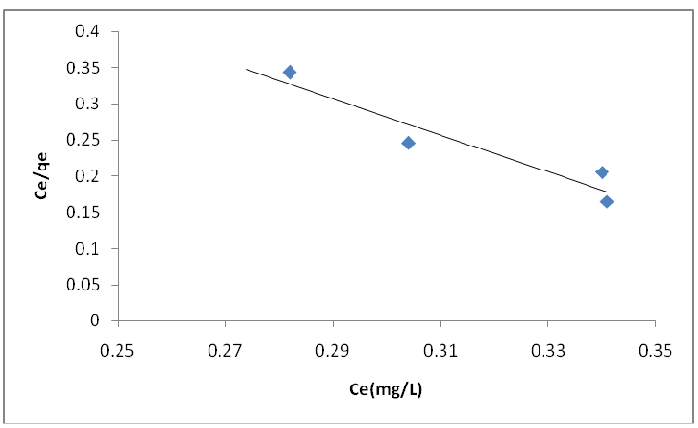

Figure-6
Langmuir isotherm for the adsorption of zinc on *Carica papaya* root powder, Conditions: Temp= 30 ± 1°C, C_o= 25mg/L, agitation speed = 120 rpm, w = 0.6 g

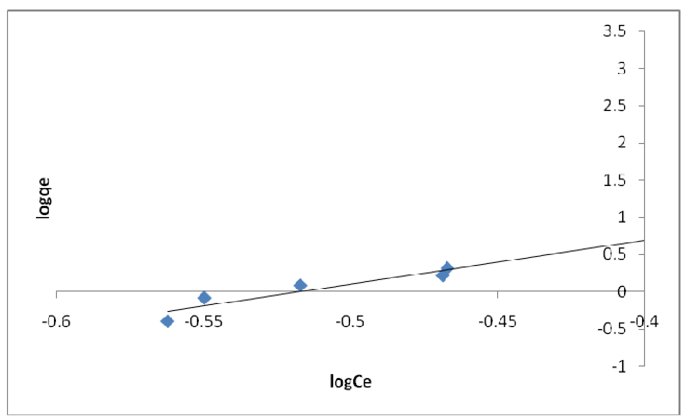

Figure-7
Freundlich isotherm for the adsorption of zinc on *Carica papaya* root powder Conditions: Temp= 30 ± 1°C, C_o= 25mg/L, agitation speed = 120 rpm, w = 0.6 g

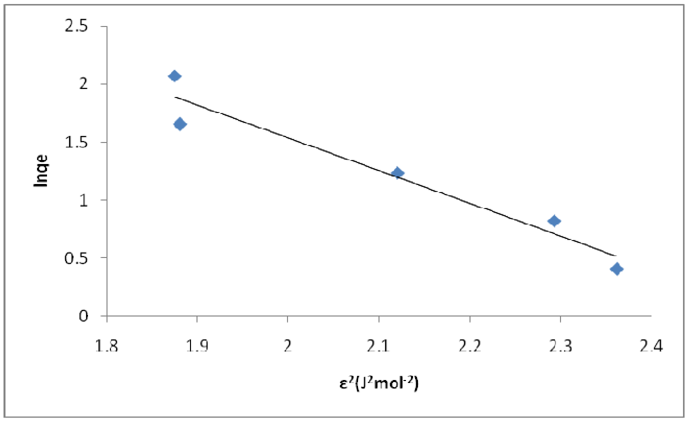

Figure-8
Dubinin–Radushkevich (D–R) plots for the adsorption of zinc (II) onto *Carica papaya* root. Conditions: Temp= 30 ± 1°C, C_o= 25mg/L, agitation speed = 120 rpm, w = 0.6 g

The kinetic data fitted very well to the pseudo-second-order model (figure-9) and the corresponding parameters obtained from fitting results are summarized in table-2. The pseudo-second order kinetic data in table-2 also shows that the uptake capacity obtained from kinetic result was consistent with the experimental data. Moreover, as the initial concentration increased the pseudo-second order rate constant also increased. These findings indicated that the pseudo-second-order kinetic model is more suitable to describe the Zn (II) biosorption onto *Carica papaya* root. In addition, the correlation coefficients showed very good fits for Zn (II) at all concentration ranges.

In order to examine the contribution of surface and pore diffusion to the overall process the Weber and Morris equation of the following form (equation. 12) was evaluated.

$$q_t = K_p t^{0.5} + c \tag{12}$$

Where K_P is the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$). The intra-particle diffusion rate constant was determined by plotting q_t against $t^{0.5}$. The plot shows two separate regions (figure not shown). The initial linear portion indicates the boundary layer effect while the second linear portion denotes intra-particle diffusion[19-21]. The larger the intercept the greater is the boundary layer effect. The intra-particle diffusion constant K_P (table-2) was obtained from the slope of the linear portion near equilibrium. Furthermore, the activation energy of the adsorption process can be calculated according to the Arrhenius equation[21]:

$$\ln K = \ln A - \frac{E_a}{RT} \tag{13}$$

Where A is the Arrhenius constant; E_a(J mol^{-1}) is the activation energy; R (J mol^{-1} K^{-1}) is the gas constant; T (K) is the absolute temperature. Information on the mechanism of the ion exchange process can be obtained by judging the value of E_a. In general, the sorption process is classified to be film-diffusion controlled when E_a is below 16 kJ mol^{-1}, particle-diffusion controlled when E_a is 16–40 kJ mol^{-1}, and chemical-reaction controlled when E_a is greater than 40 kJ mol^{-1}[22]. The activation energy of Zn (II) adsorption was 12.0 kJ mol^{-1}as reflected in table-3, and it suggested that this adsorption was film-diffusion-controlled. This also meant the involvement of weaker forces of attraction indicating physisorption

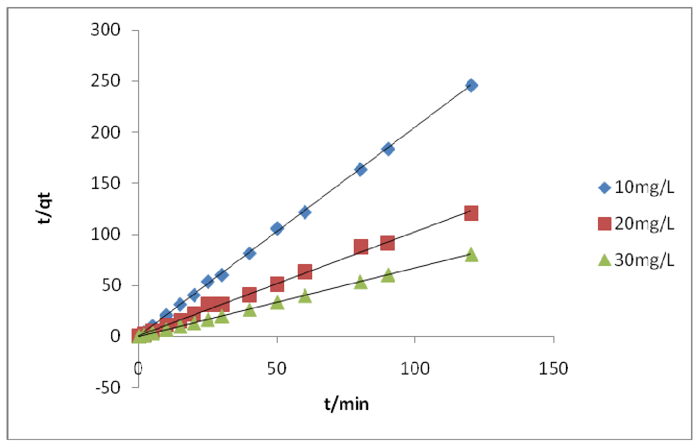

Figure-9
Pseudo second order kinetics for the adsorption of zinc on *Carica papaya* root powder Experimental condition: biosorbent dosage = 0.2 g, initial metal concentration = 20 mg/L, contact time = 2 h, shaking speed =120 rpm, temperature = 30 ± 1°C

Table-2
Comparison of pseudo–first order, pseudo-second order and intra-particle diffusion (Weber-Morris) kinetic models for the sorption of copper (II) ions on *Carica papaya* root powder

	Pseudo-First order			Pseudo-second order kinetic model			Weber-Morris model
Initial conc. (mg/L)	$q_{e(exp)}$ (mg/g)	k_1 (h)	$q_{e(calc)}$ (mg/g)	R^2	k_2	$q_{e(calc)}$ (mg/g)	k_p(g $(mgmin)^{-1}$)
10	0.084	0.011	0.118	1.000	279	0.090	49.0
20	0.993	0.009	0.275	0.999	0.99	0.985	133.3
30	1.499	3.599	0.027	0.999	0.57	1.486	16.7

Thermodynamic study: To study the thermodynamics of adsorption of zinc on *Carica papaya* root powder, the thermodynamic parameters; free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (S°) were calculated by using the following equations:

$$K_d = \frac{q_e}{Ce} \tag{14}$$

$$\Delta G = -RT\ln K_d \tag{15}$$

$$\ln K_d = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{16}$$

Where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature in Kelvin and K_d is the equilibrium constant.

The plot of $\ln K_d$ vs. 1/T was linear and the values of ΔH° and ΔS° were determined from the slope and intercept. The values of these parameters are presented in table-3. The value of enthalpy change ΔH° (0.186 $KJmol^{-1}$) is negative indicating adsorption is exothermic. Negative ΔG° values obtained was a reflection of the thermodynamically favorability and spontaneity of the reaction. The positive value of ΔS° reflected the good affinity of adsorbent for adsorbate and increased randomness during the sorption process. The values of ΔG^{o} at all temperatures studied as reflected in table-3 were indications that the sorption process was physisorption since the values are between-20to 0 kJ mol^{-1}.

Table-3
Thermodynamic parameters for the adsorption of zinc on *Carica papaya*

Metal conc. mg/L	$-\Delta H$ $kJmol^{-1}$	ΔS $Jmol^{-1}K^{-1}$	$-\Delta G$ ($kJmol^{-1}$)			E_a $KJmol^{-1}$
			303K	313K	323K	
20	0.186	23.4	8.95	8.84	8.73	12.0

Table-4 presents the adsorption capacities of selected adsorbents. The table shows that *Carica papaya* adsorption capacity is low compared to that of other adsorbents reflected on the table. This may be due to the fact that the pH of adsorption (6.0)is lower than the PZC(9.0) which consequently reduces the amount of zinc adsorption since the surface of the adsorbent was positively charged. This implied that even though the optimum pH of adsorption was 6, the adsorption will not be as high as expected due to the electrostatic interaction of hydrogen ions with metal.

Conclusion

Carica papaya root powder was used as adsorbent for the removal of zinc from aqueous solution. The pH, PZC, adsorbent dosage, initial concentration, contact time and temperature on the adsorption played significant roles in the zinc adsorption capacity of *Carica papaya* root powder. The maximum adsorption capability of *Carica papaya* reached was 0.4 mg g^{-1}. The pseudo-second-order model fitted the experimental data well. Isotherm modeling revealed that the Freundlich and D-R equations better described the adsorption of Zn on the *Carica papaya* as compared to Langmuir model. Negative values of free energy change, ΔG°, indicated that adsorption of Zn by *Carica papaya* was spontaneous and feasible. Change in enthalpy ΔH° also indicated negative value, and therefore, the adsorption mechanism was exothermic. The adsorption of Zn (II) ions was jointly controlled by film diffusion and intraparticle diffusion for the adsorbent used in this study. Further studies could be done on the modification of *Carica papaya* root powder which could yield higher result in the removal of zinc.

Table-4
Comparison of adsorption capacities of different adsorbents

Adsorbent	Adsorption Capacity (mg/g)	Reference
Coconut tree sawdust	3.60	19
Unmodified core fibre	1.83	23
Waste red mud	4.05	24
Barley straw	35.8	25
Almond shells	10.6	26
Jackfruit plant	6.13	27
Waste orange peel	22.4	28
Rice straw	3.15	29
Carica papaya	0.40	This study

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