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Full Length Research Paper

Equilibrium, kinetic, thermodynamic studies on biosorption of zinc (II) by *Ficus Hispida* leaf powder

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In the present investigation, the biosorption is carried out in a batch process to test the suitability of abundantly and freely available plant based material, Ficus *Hispida* leaf powder, as an biosorbent for removal of Zn (II) from aqueous solution. The influence of various process parameters like agitation time, pH, adsorbent dosage, size, temperature of the aqueous solution and initial zinc concentration is studied. It is observed that there is a significant increase in percentage removal of Zn (II) as pH increases from 2 to 4 and attains maximum when pH is 4. The agitation time is to be 25 min. The Freundlich isotherm is more suited for biosorption followed by langmuir isotherm. The biosorption of Zn (II) follows pseudo-second-order kinetics and is endothermic, irreversible and spontaneous.

Keywords: Biosorption, zinc, leaf powder, isotherms, kinetics.

INTRODUCTION

Pollution is 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. When zinc is present in the wastewater beyond the permissible limits of concentration, it becomes harmful to the living organisms.

The threshold limiting value of zinc in drinking water is 5 mg L^{-1} and in public sewage, inland surface water and marine water it is 15 mg/L (Drinking water specifications, IS-10500, 1991). Ingestion of >2 g/L causes toxic symptoms like fever, diarrhea, gastrointestinal tract irritation etc in humans. Hence, it is of prime importance to prevent the accumulation of zinc from exceeding its threshold concentration. The traditional techniques used for disposal of industrial effluents include chemical precipitation, ion exchange, liquid- liquid extraction, electrodialysis, adsorption and reverse osmosis. A major drawback with these conventional methods is the high operational cost. This demands more research for the development of a cost effective processes specially suited for small and medium industries. Among the methods for disposal of effluents, adsorption is a preferred potential alternative because of its high efficiency, easy handling and availability of adsorbents. A review of literature indicates extensive application of adsorption technique for the removal of toxic heavy metals from industrial effluents using various adsorbents like charcoal/coal (Mohan and Singh, 2002; Mishra and Chaudhury, 2004; Yuda et al., 2000; John and Gordon, 1999), fly ash (Belgin, 2002) and others (Karthikeya et al., 2004; Wang et al., 2003; Saha et al., 2002; Irena, 1999).

Successful metal biosorption has been reported by a variety of biological materials including papaya wood (Asma et al., 2005), cork biomass (Natalia et al., 2004) and coir (Kathrine and Hans, 2007). Another category of bio-mass that acts as adsorbent is plant leaves. The few cases investigated include palm tree leaves (Fahmi and Abu, 2006) and waste tea leaves (Ahluwalia and Goya, 2005). Sorption studies were carried out with coir pith

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Table 1. Range of variables investigated for zinc

Variables	Values investigated
Agitation time, t, min	1,2,4,6,8,10,15,20,25,30,35,40,45,50 and 60
Biosorbent size, d_p, μm	75,105,132,154 and 212
Biosorbent dosage, w, g/L	0.1,0.2,0.3,0.4 and 0.5
pH of the aqueous solution	2,3,4,5,6,7,8,9 and 10
Initial concentration of zinc in aqueous solution, C_0, mg/L	20,40,60,80 and 100
Temperature, T, K	303,308,313 and 318

activated carbon for the removal of Zn (II) (Santhy and Selvapathy, 2004). In the case of fungal biomass, removal of metal ions from aqueous solutions has been studied with strains of Aspergillus niger 405 (Eljka et al., 2000). A variety of low cost adsorbents like banana and orange peel waste (Annadurai et al., 2003), coniferous barks (Martin et al., 2002), solid waste from olive mills (Pagnanelli et al., 2002), saw dust (Sarvanane et al., 2002) etc. have been used for the removal of zinc from industrial effluents. The objective of the present nvestigation is to explore the feasibility of biosorption for the removal of zinc from aqueous solution using plant based material, *Ficus Hispida* leaf powder.

MATERIALS AND METHODS

Preparation of biosorbent

The *Ficus Hispida* leaves were collected from the surroundings of K.L University campus, Guntur, Andhra Pradesh, India. Leaves were washed with deionized water several times to remove dirt particles. Then the dried leaves were powdered using domestic grinder and the powder size of 75-212 μm, which were used as biosorbent without any pretreatment for lead biosorption.

Chemical

All the chemicals used in this investigation were of analytical grade and all the solutions were made with distilled water. $ZnSO_4$ $7H_2O$ (minimum assay 99%) was used as the source of Zn (II). 4.439 g of $ZnSO_4$ $7H_2O$ was dissolved in 1L of distilled water to prepare 1000mg/L of zinc stock solution. Synthetic samples of different concentrations of zinc were prepared from this stock solution by appropriate dilutions. The pH of the aqueous solution was adjusted to the desired value by addition of 0.1 M HNO_3 or 0.1M NaOH solution.

Procedure

The biosorption is carried out in a batch system by adding 0.1g of *Ficus Hispida* leaf powder with 30 mL of aqueous solution of C_0 =20 mg/L at constant temperature(30^{0}C). The mixture is agitated for a predetermined time interval in an orbital shaker at 160 rpm. The mixture is filtered and the filtrate is analyzed in an atomic absorption spectrophotometer (AAS, Perkin Elmer–3100 model, wave length is 213.9 nm) to obtain the residual zinc present in it. Similarly more samples are prepared in conical flasks and the above procedure is followed varying the agitation time, pH, adsorbent dosage, size, initial concentration of zinc and temperature of the aqueous solution. In order to determine the order of biosorption reaction, the above procedure is repeated for varying agitation times of 1, 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 40, 45, 50 and 60 min for various concentrations to fix the optimum agitation time. The optimum pH's of the aqueous solutions of various concentrations were also varied from pH vale 2 to 10. The adsorbent dosages of 0.1, 0.2, 0.3, 0.4, 0.5g were used with different concentrated solutions to find out the trend. The size of the biosorbent is also varied from 75μm to 212 μm for various concentrated solutions of zinc. The thermodynamic parameters are determined by adopting the same procedure at different temperatures for different concentrated solutions. The extent of biosorption is found from the relation (or % removal) = $[(C_0–C_f) \times 100/C_0]$. The amount of Zn (II) adsorbed per unit mass of the adsorbent, q in mg/gm = $(C_0–C_f)/m$. The values of parameters investigated are shown in Table 1.

RESULTS AND DISCUSSION

The effect of agitation time

The percentage removal of zinc is plotted against agitation time in Figure.1 for w = 0.1 g for various initial concentrations of zinc ion. For a typical experiment with 30 mL of aqueous solution (C_0 = 20 mg/L), a dosage of 0.1 g of 75 μm size and at a temperature of 30^{0}C the % removal is aggressive in the first minute itself reaching 54.32%. The percentage removal is increased gradually to 77.05% in 25 min. The change in percentage removal of zinc becomes insignificant after 25 min. Similarly the experiment is conducted for various initial ion

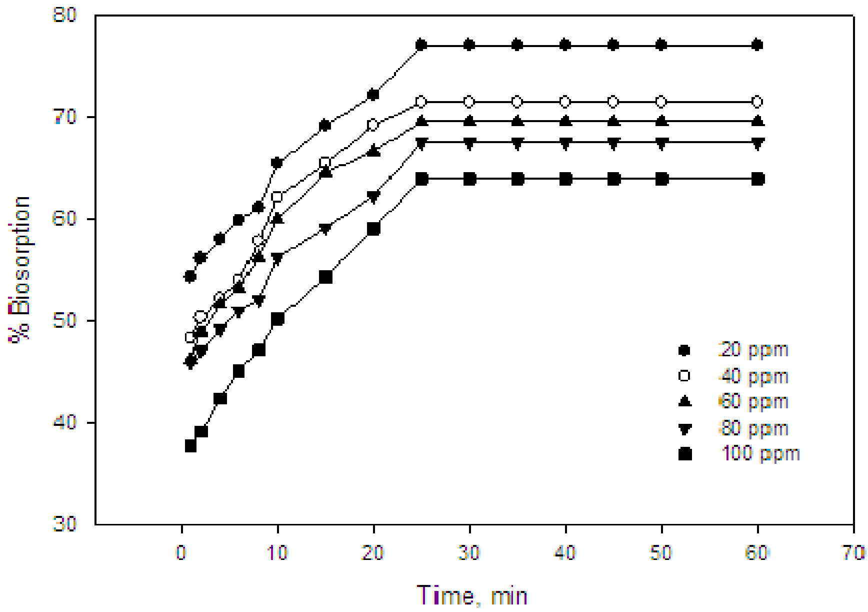

Figure 1. Effect of contact time on biosorption of zinc by *Ficus Hispida* L. for various concentrations of metal and 0.1g/30ml of biosorbent concentration.

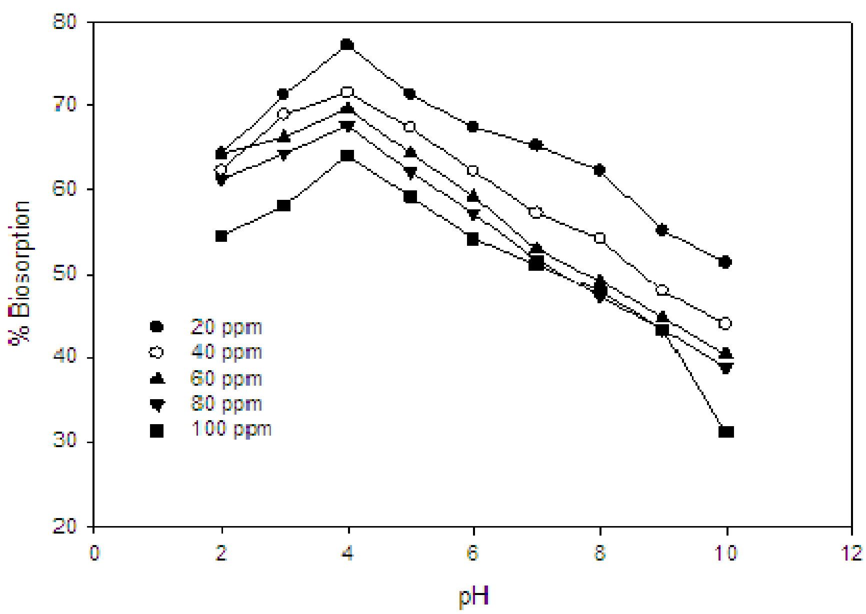

Figure 2. Effect of pH on zinc biosorption by *Ficus Hispida* L. for various concentrations of metal and 0.1g/30ml of biosorbent concentration.

concentrations (40, 60, 80, 100 mg/L) at the same conditions, which gives the same 25 min contact time. Hence, the equilibrium agitation time is 25 min as reported earlier with papaya wood (Asma et al., 2005). The percentage removal is higher in the initial stages because adequate surface area of the adsorbent is available for the biosorption of zinc. As the time increases, more amount of zinc is adsorbed on to the surface of the adsorbent resulting in reduced surface area available. Normally, the adsorbate forms one molecule thick layer over the surface. As this monomolecular layer covers the surface, the capacity of the adsorbent is exhausted attaining equilibrium.

Effect of pH

Figure.2 is a graph drawn between % removal of Zn (II)

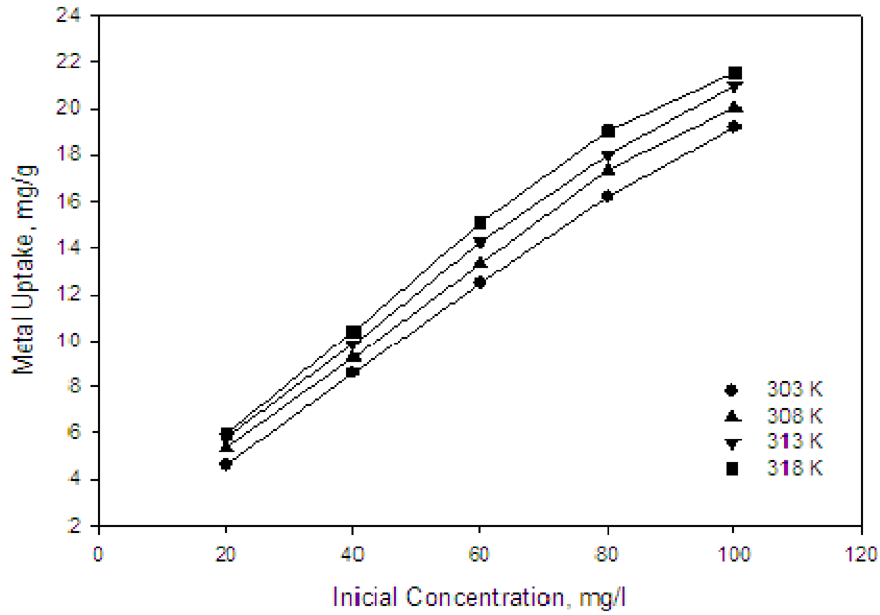

Figure 3. Effect of metal concentration on zinc metal uptake by *Ficus Hispida* L. at different temperature and 0.1g/30ml of biosorbent concentration.

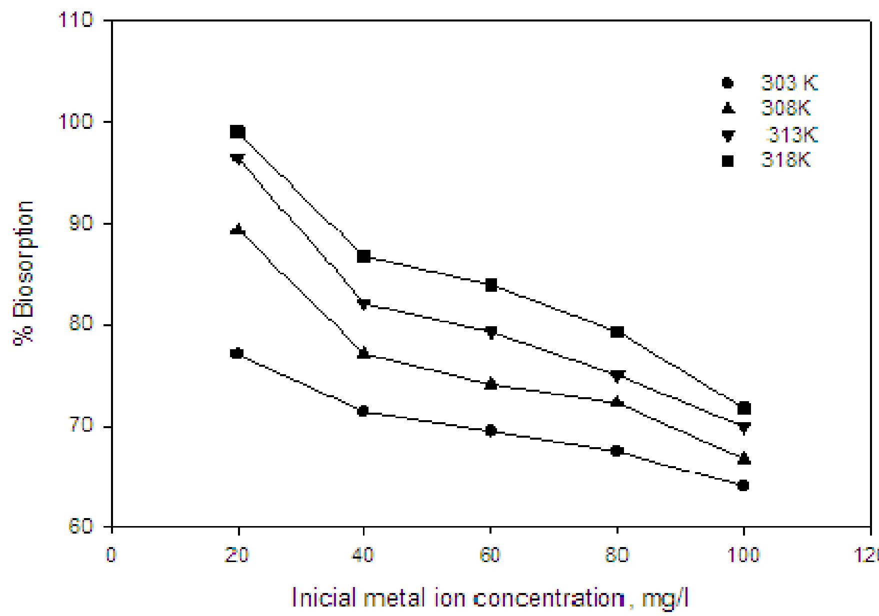

Figure 4. Effect of metal concentration on the biosorption of zinc by *Ficus Hispida* L. at different temperature and 0.1g/30ml of biosorbent concentration.

and pH of the various aqueous solutions with the biosorption data obtained by adding 0.1 g of 75 µm size biosorbent to 30 mL of aqueous solution. The extent biosorption is increased from 64 to 77% in the pH range from 2 to 4. A decrease in percentage removal from 71 to 51% from 5 to 10. Low pH depresses adsorption of Zn (II), which is due to competition of Zn (II) with H^+ ions for appropriate sites on the adsorbent surfaces. However, with increasing pH, this competition weakens and Zn (II) ions replace H^+ bound to the adsorbent for forming part of the surface functional groups such as -OH, -COOH etc.

Effect of Zn (II) metal ion concentration

Figure 3, 4 shows the effect of metal ion concentration on the adsorption of zinc by *Ficus hispida* L. The data shows that the metal uptake increases and the percentage

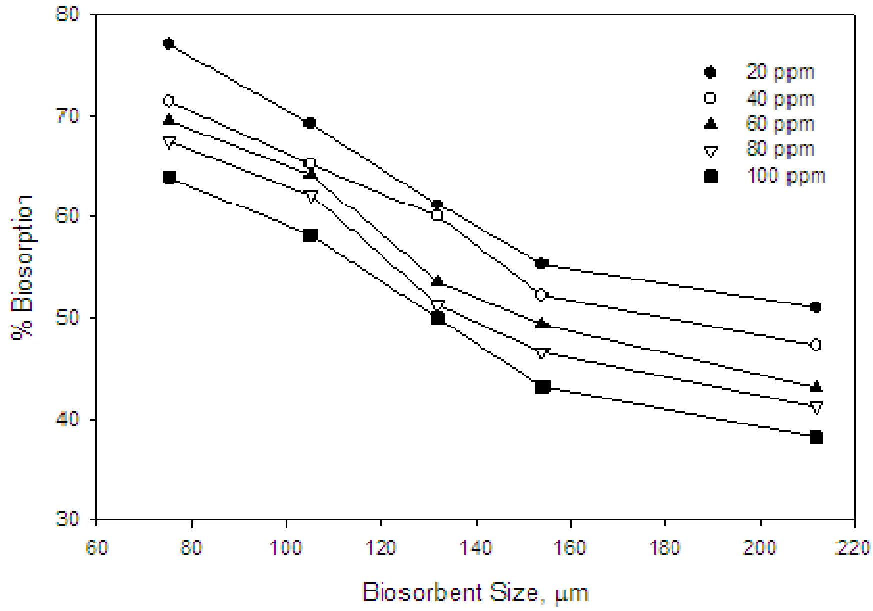

Figure 5. Effect of *Ficus Hispida* L. size on biosorption of zinc for various concentration of metal and 0.1g/30ml of biosorbent concentration.

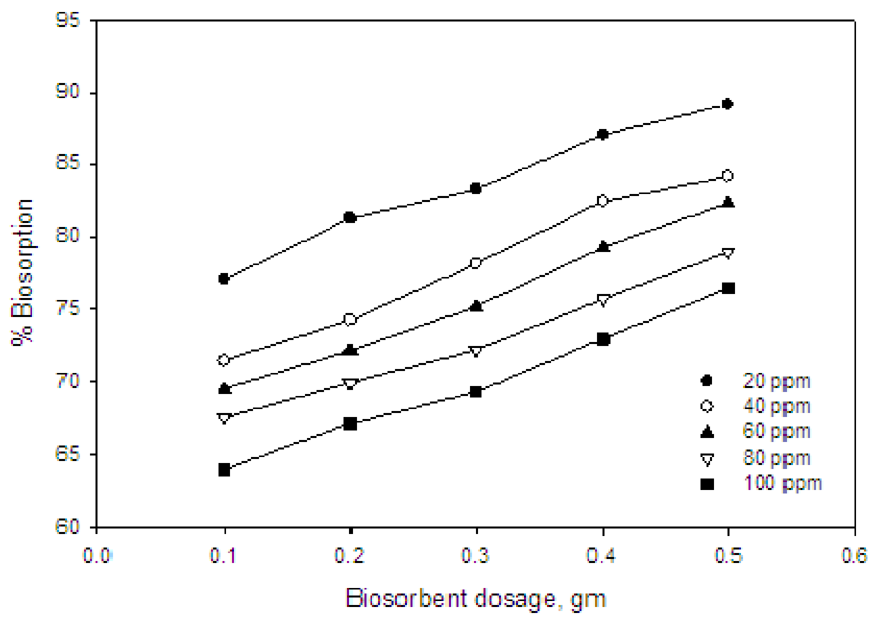

Figure 6. Effect of *Ficus Hispida* L. dosage on biosorption of zinc for various concentrations of zinc metal

adsorption of zinc decreases with increase in metal ion concentration. This increase is a result of increase in the driving force, i.e. concentration gradient. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of zinc displays an opposite trend. At lower concentrations, all zinc ions present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher zinc ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result, the purification yield can be increased by diluting the wastewaters conta-

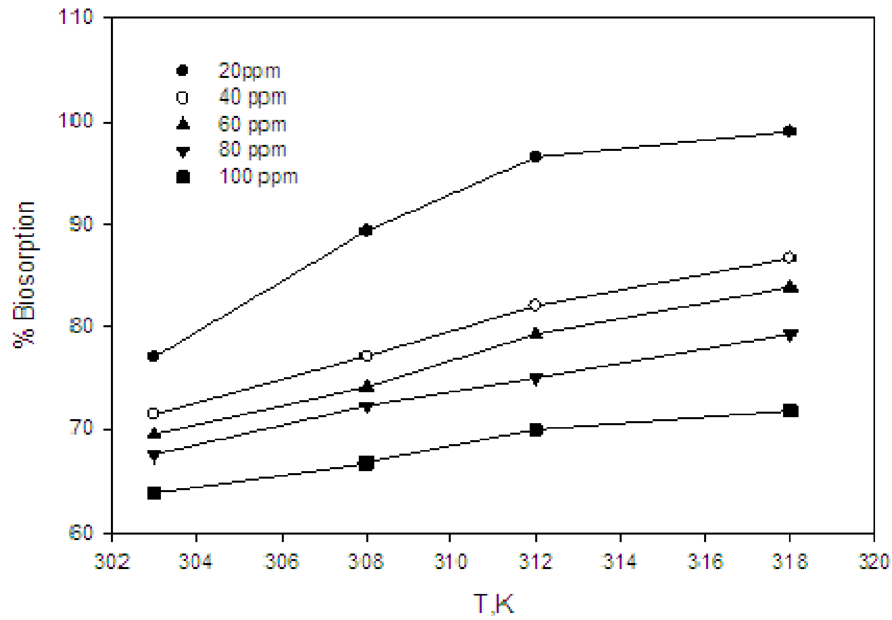

Figure 7. Effect of temperature on biosorption of zinc by *Ficus Hispida* L. for different concentrations of metal and 0.1g/30ml of biosorbent concentration

ining high metal ion concentrations.

Effect of biosorbent size and dosage

The results obtained for biosorptive removal of Zn (II) with respect to adsorbent sizes are shown in Figure 5. The percentage removal of Zn (II) is increased with decreasing in size of the adsorbent. For an adsorbent dosage of 0.1g in 30 mL of aqueous solution (C_0 = 20 mg/L), the biosorption is varied from 50.3 to 77.4% as the size decreases from 212 to 75 µm. Similar trends are observed with varying initial concentrations of metal ions of 40, 60, 80, 100 mg/L. This phenomenon is expected as the size of the adsorbent decreases the surface area increases. Figure.6 represents the variation dosage at equilibrium agitation time. The biosorption is increased from 77.5 to 89.3% for particle size of 75 µm as dosage is increased from 0.1 to 0.5g. The fraction of the metal removed from the aqueous phase increases with an increase in the dosage because the number of active sites available for metal biosorption would be more as the dosage increases.

Effect of temperature

The effect of temperature on biosorption of zinc was studied between 303 K to 318 K and results were depicted in Figure 7. The results show that biosorption increased with the rise in temperature.

Biosorption isotherms

Biosorption experiments were performed at room temperature (30 ± 1^0C) in a rotary shaker at 180 rpm using 250 mL Erlenmeyer flasks containing 30 mL of different zinc concentrations. After 1 hr of contact (according to the preliminary sorption dynamics tests), with 0.1 g *Ficus hispida* leaves biomass, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The metal content in the supernatant was determined using Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) after filtering the adsorbent with 0.45 µm filter paper. The amount of metal adsorbed by *Ficus hispida* leaves was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$q = \left(C_0 - C_f\right)\frac{V}{M} \qquad (1)$$

Where q is the metal uptake (mg/g); C_0 and C_f the initial and final metal concentrations in the solution (mg/L), respectively; V the solution volume (mL); M is the mass of biosorbent (g).The pH of the solution was adjusted by using 0.1N HCl and 0.1N NaOH.
The Langmuir (Langmuir, 1916) sorption model was chosen for the estimation of maximum zinc sorption by the biosorbent. The Langmuir isotherm can be expressed as

$$q = \frac{Q_{\max} bC_{eq}}{1 + bC_{eq}} \qquad (2)$$

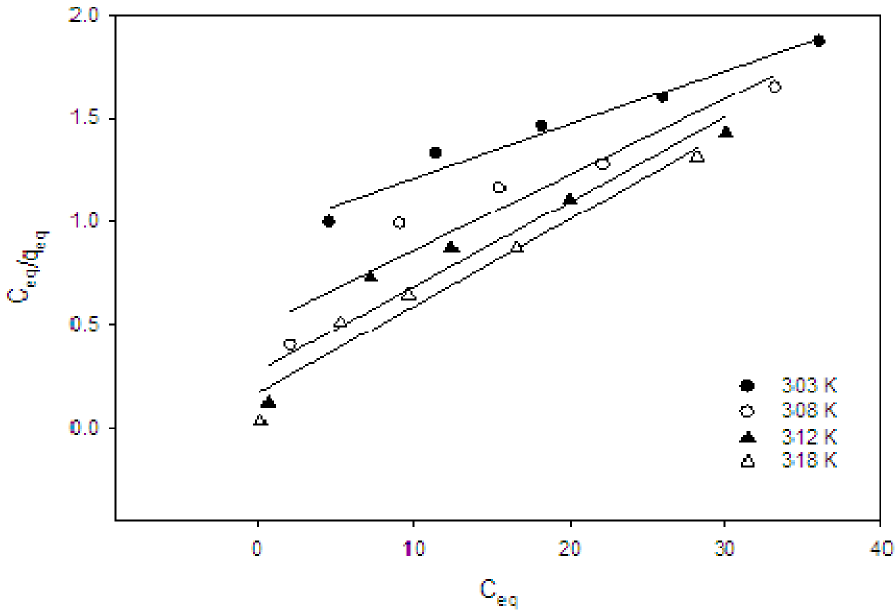

Figure 8. Langmuir biosorption isotherm for zinc by *Ficus Hispida* L. at different temperatures and 0.1g/30ml of biosorbent concentration

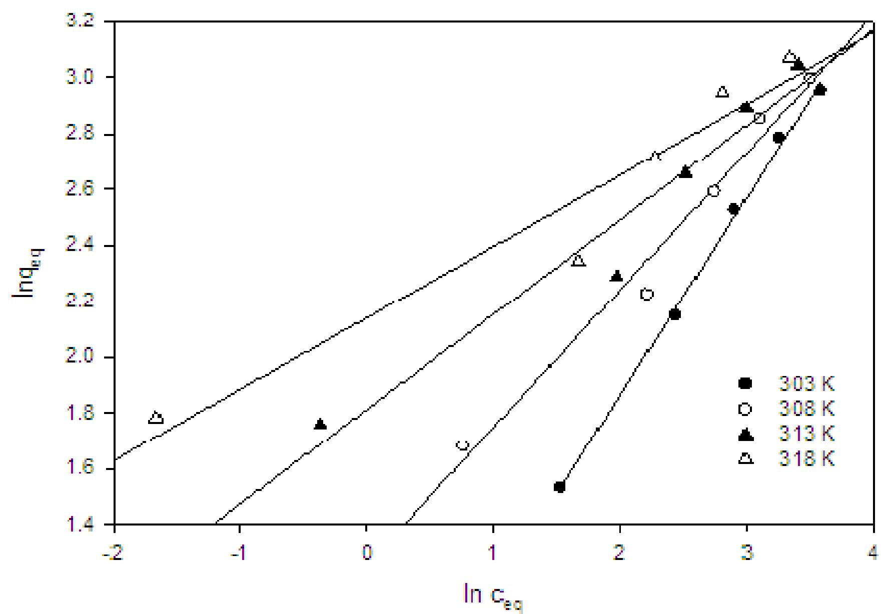

Figure 9. Freundlich biosorption isotherm for zinc by *Ficus Hispida* L. at different temperature and 0.1g/30ml of biosorbent concentration

Where Q_{max} indicates the monolayer adsorption capacity of adsorbent (mg/g) and the Langmuir constant *b* (L/mg) is related to the energy of adsorption. For fitting the experimental data, the Langmuir model was linearized as

$$\frac{1}{q} = \frac{1}{Q_{\max}} + \frac{1}{bQ_{\max}C_{eq}} \qquad (3)$$

The freundlich (Freundlich, 1906) model is represented by the equation:

$$q = KC_{eq}^{\frac{1}{n}} \qquad (4)$$

Where *K* (mg/g) is the Freundlich constant related to adsorption capacity of adsorbent and *1/n* is the Freundlich exponent related to adsorption intensity (dimensionless). For fitting the experimental data, the Freundlich model was linearized as follows:

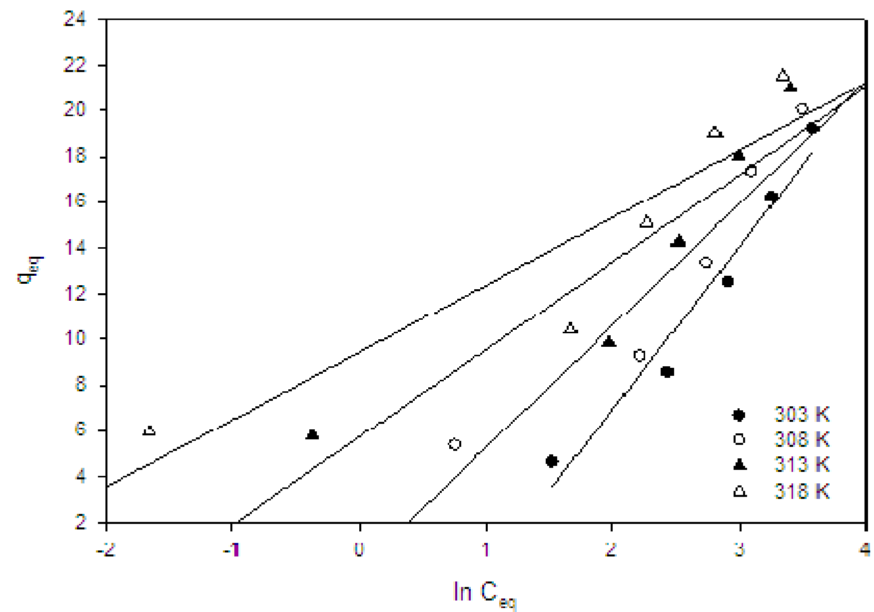

Figure 10. Temkin biosorption isotherm for zinc by *Ficus hispida* L. at different temperature and 0.1g/30ml of biosorbent concentration

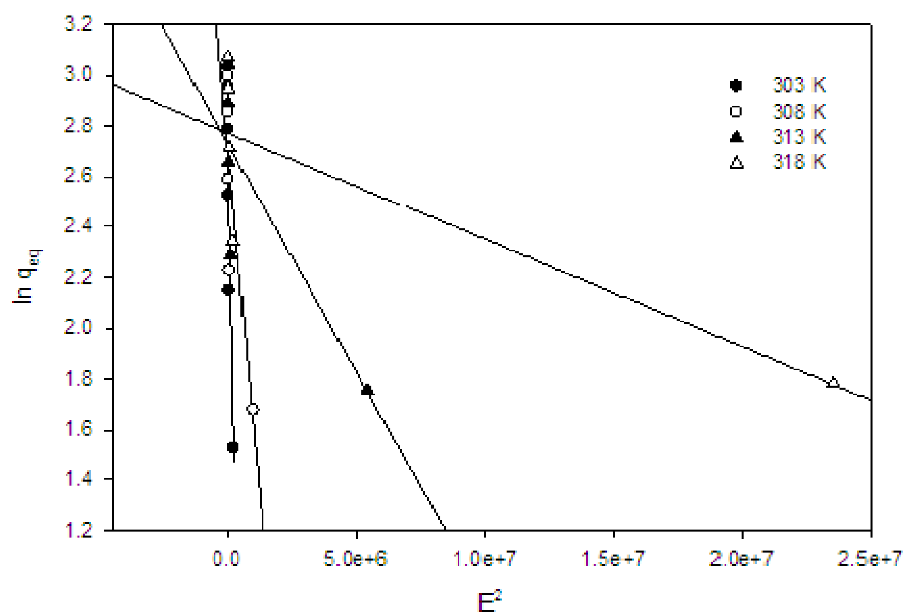

Figure 11. Dubinin-Radushkevich biosorption isotherm for zinc by *Ficus Hispida* at different temperature and 0.1g/30ml of biosorbent concentration.

$$\ln q = \ln K + \frac{1}{n} \ln C_{eq} \qquad (5)$$

The Temkin (Aharoni and Ungarish, 1977) isotherm has generally been applied in the following form:

$$q = \frac{RT}{b_T} \ln\left(A_T C_{eq}\right) \qquad (6)$$

Where A_T (L/mg) and b_T are Temkin isotherm constants.

The Dubinin–Radushkevich **(**D–R) (Santhi et al., 2010) model was also applied to estimate the porosity apparent free energy and the characteristics of adsorption. The D–R isotherm dose not assumes a homogeneous surface or constant adsorption potential. The D–R model has commonly been applied in the following Eq. (7) and its linear form can be shown in Eq. (8):

$$q_e = Q_m \exp(-K\varepsilon^2) \qquad (7)$$

Table 2. The values of parameters and correlation coefficients for each isothermal model for zinc biosorption with *Ficus Hispida* L.

Temp(K)	Langmuir			Freundlich		
	q_m,mg/g	b,L/mg	R^2	n	K_f, mg/g	R^2
303	38.22662	0.027566	0.96505464	1.415386	1.572601	0.9976635
308	27.06725	0.07547	0.91787270	2.028296	3.508567	0.9796230
313	24.2735	0.151156	0.92348859	2.942918	6.126652	0.9507550
318	23.72174	0.252042	0.95298566	3.90974	8.499153	0.9365863

Temp(K)	Tempkin			Dubinin Radushkevich			
	b	A_T,L/g	R^2	K,mol^2/KJ^2	Q_D,mg/g	R^2	E,KJ/mol
303	354.04	0.35943	0.9622463	0.012508698	15.11195	0.83556	6.3223
308	481.08	0.99293	0.9116530	0.002687611	14.95249	0.74523	13.639
313	680.68	4.48894	0.8602904	0.001648151	15.33723	0.71091	17.417
318	897.17	24.5937	0.8407047	0.001416815	15.99622	0.72351	18.785

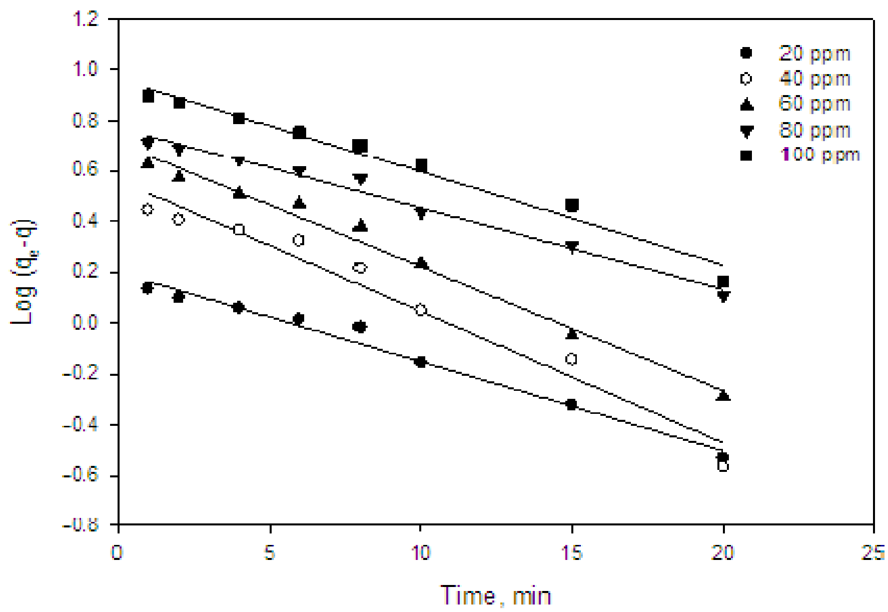

Figure 12. Pseudo-first order biosorption of zinc by *Ficus Hispida* L. for different concentrations of metal and 0.1g/30ml of biosorbent concentration

$\ln q_e = \ln Q_m - K\varepsilon^2$ (8)
where K is a constant related to the adsorption energy, Qm the theoretical saturation capacity, ε the Polanyi potential, calculated from Eq. (9).
$\varepsilon = RT(1+1/C_e)$ (9)

The slope of the plot of ln q_e versus ε^2 gives K (mol^2 $(kJ^2)^{-1}$) and the intercept yields the adsorption capacity, Q_m (mg g–1). The mean free energy of adsorption (E), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the K value using the following relation 10:
$E = 1/\sqrt{2K}$ (10)

The calculated value of D–R parameters is given in Table 2. The values of E calculated using Eq. (10) is below 1 KJ mol–1, which indicating that the physico-sorption process plays the significant role in the biosorption of zinc metal.

The equilibrium biosorption of zinc on the *Ficus hispida* L. as a function of the initial concentration of zinc is shown in Figure 8-11. There was a gradual increase of adsorption for zinc ions until equilibrium was attained. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models are often used to describe equilibrium sorption isotherms. The calculated results of the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm constants are given in Table 2.

It is found that the adsorption of zinc on the *Ficus hispida* L. was correlated well with the Freundlich and Langmuir as compared to Temkin and Dubinin–

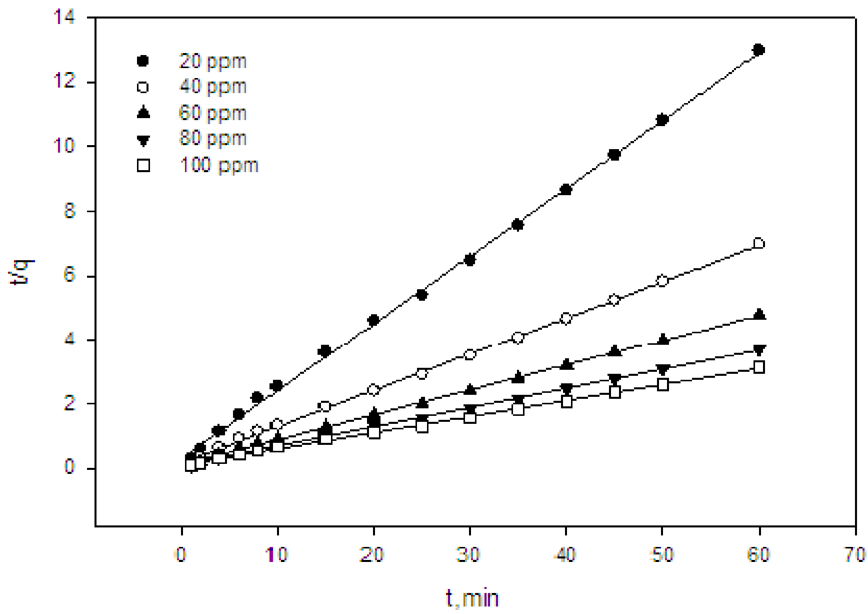

Figure 13. Pseudo-second order biosorption of zinc by *Ficus Hispida* L. for different concentrations of metal and 0.1g/30ml of biosorbent concentration.

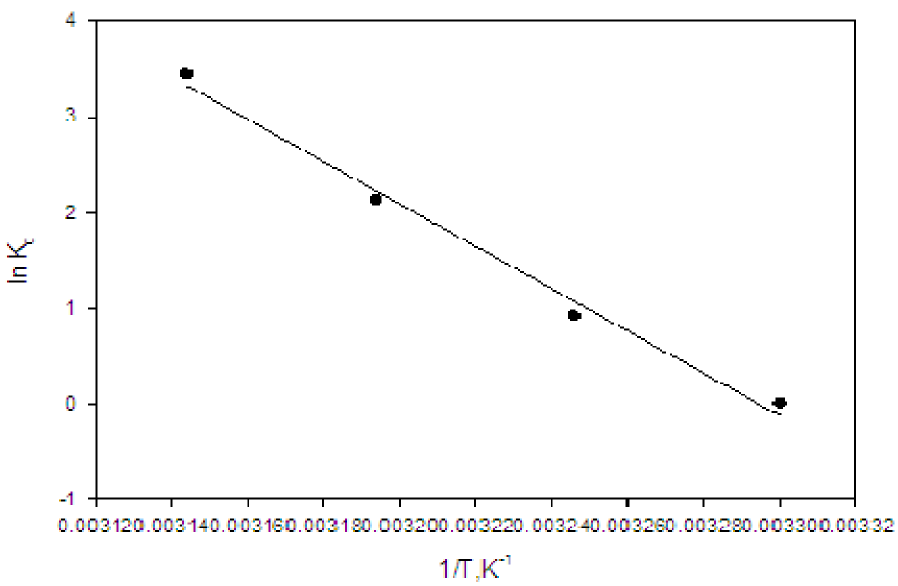

Figure 14. A plot of LnK_0 vs. 1/T for estimation of thermodynamic parameters for zinc biosorption with *Ficus Hispida* L.

Radushkevich isotherm equations under the concentration range studied. Examination of the Temkin, Dubinin–Radushkevich isotherm data shows that these isotherms were not modeled as well across the concentration range studied.

Biosorption kinetics

The data regarding biosorption kinetics is necessary for the design of industrial columns. The order of adsorbate – adsorbent interactions has been described traditionally by the pseudo first order model of (Lagergren et al., 1898) or by pseudo second order kinetics in certain cases. In the case of adsorption preceded by diffusion through a boundary, the kinetics in most cases follows pseudo first order rate of equation of Lagergren: $(d_{qt}/dt) = K_{ad}\ (q_e–q_t)$. Plot of log $(q_e–q_t)$ versus't' gives a straight line for first order kinetics. In case of pseudo second order kinetics, $(d_{qt}/dt) = K\ (qe–qt)^2$ is applicable. This equation

Table 3. Kinetic constants for zinc onto *Ficus Hispida* L.

Inicial Conc,mg/l	Pseudo first order			Pseudo second order			
	q_e, mg/g	K_1	R_1^2	q_e, mg/g	K_2	R_2^2	h, mg/g.min
20	1.577768	0.080665	0.98096	4.768339	0.139687	0.99902	3.176073
40	3.644838	0.118999	0.96398	8.840268	0.079459	0.99928	6.209736
60	5.09618	0.112183	0.98568	12.89681	0.055239	0.99934	9.187709
80	5.910625	0.073763	0.98338	16.80055	0.034074	0.99862	9.617598
100	9.211322	0.085073	0.97722	20.11774	0.021867	0.99801	8.850124

Table 4. Elvoich constants for zinc onto *Ficus Hispida* L.

Inicial Conc,mg/l	Elvoich model		
	α	β	R_3^2
20	3.039514	0.417322	0.92901
40	5.459722	0.839317	0.93396
60	7.95516	1.232022	0.94737
80	10.09907	1.603084	0.92554
100	10.11637	2.40164	0.93961

Table 5. Thermodynamic Parameters for zinc onto *Ficus Hispida* L.

Temperature (K)	Thermodynamic Parameters		
	ΔG^0, KJ/mol	ΔH^0, KJ/mol	ΔS^0, KJ/mol
303	-0.01805	183.7597	0.605402
308	-2.36361		
313	-5.5369		
318	-9.10263		

can be written as $(t/q_t) = (1/K_{qe}^2) + (t/q_e)$. If the pseudo-second order kinetics is applicable, the plot of (t/q_t) versus t gives a linear relationship that allows computation of q_e and K. Lagergren plot (Ho and McKay, 1998) of log $(q_e–q_t)$ versus agitation time (t) for the present investigation is drawn in Figure 12.

The pseudo-second-order model is applied to assess the suitability of the rate equation for the present data. The plots (t/q_t) versus (t) for the present data are shown in Figure.13 for dp= 75 µm.

The simple Elovich model may be expressed in the form of $q_t = \alpha + \beta \ln t$

A plot (Yadava et al., 1991) of q_t versus In *t* should give a linear relationship (Figure 14) for the applicability of the simple Elovich kinetic.

During the present study, the three different kinetic models were applied and the estimated model and the related statistic parameters are reported in Table 3 and 4. Based on linear regression (R^2 > 0.99) values, the kinetics of lead biosorbent can be described well by pseudo second-order equation.

Thermodynamic parameters

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Gibb's free energy change, $\Delta G°$, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if $\Delta G°$ is a negative value. The thermodynamic parameters of $\Delta G°$, enthalpy change, $\Delta H°$, and entropy change, $\Delta S°$, for the biosorption processes are calculated using the following equations (Bereket et al., 1997):

$$\Delta G° = - RT 1n K_a \quad (11)$$

and

$$\Delta G° = \Delta H° - T\Delta S° \quad (12)$$

Where R is universal gas constant (8.314 J/mol K) and T is the absolute temperature in K.

A plot of $\Delta G°$ obtained using *K*a of Langmuir versus temperature, *T*, was found to be linear (Figure14). The values of $\Delta H°$ and $\Delta S°$ were respectively determined from the slope and intercept of the plots. $\Delta H°$ and $\Delta S°$ for the sorption process were calculated to be 183.7597 kJ/mol and 0.605402 J/mol K, respectively. The negitive values of Δ*G*° confirm (Table 5) the feasibility of the process and the spontaneous nature of sorption with a high preference for zinc (II) to sorb onto *Ficus Hispida L.* The value of Δ*H*° and Δ*S*° were positive, indicating that the sorption reaction is endothermic and spontaneous at high temperatures.

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