

Full Length Research Paper

Biosorption of Zn(II) from an aqueous solution by *Erythrina variegata orientalis* leaf powder

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Accepted September 9, 2008

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, *Erythrina variegata orientalis* (Indian coral tree) leaf powder, as an adsorbent for removal of Zn(II) from aqueous solution. The influence of various process parameters like agitation time, adsorbent size and dosage, pH 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 3 and attains maximum when pH is 7. The agitation time is to be 60 min. The Langmuir isotherm is more suited for biosorption followed by Freundlich isotherm. The biosorption of Zn(II) follows pseudo-second-order kinetics and is exothermic, irreversible and spontaneous.

Key words: Biosorption, zinc, leaf powder, 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 problem 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

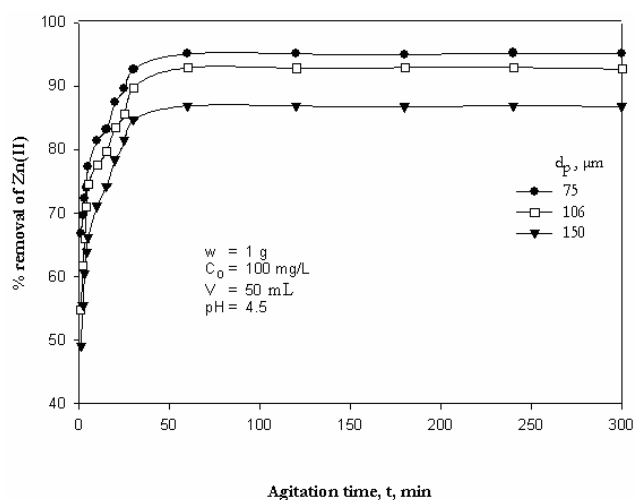
disposal of industrial effluents include chemical precipitation, ion exchange, liquid- liquid extraction, electrodialysis, adsorption and reverse osmosis. A major drawback with these conventional methods is the high operational cost. This demands more research for the development of a cost effective 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 et al., 1999), fly ash (Belgin, 2002) and others (Karthikeyan et al., 2004; Wang et al., 2003; Saha et al., 2002; Rao 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. Values of parameters investigated.

Parameter	Values investigated
Agitation time, t, min	1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 60, 120, 180, 240 & 300
Adsorbent size, d_p , μm	75, 106 & 150
Adsorbent dosage, w, g	0.5, 1, 1.5 & 2
Initial concentration of zinc in aqueous solution, C_o , mg/L	25, 50, 75, 100, 125, 150, 175 & 250
Volume of aqueous solution, V, mL	25, 50, 75, 100, 125 & 150
pH of the aqueous solution	2, 3, 4, 5, 6, 7, 8 & 9
Temperature, K	283, 293, 303, 313, 323 & 333

**Figure 1.** Effect of agitation time on % removal of Zn(II).

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 investigation is to explore the feasibility of biosorption for the removal of zinc from aqueous solution using plant based material, *Erythrina variegata orientalis* (Indian coral tree) leaf powder.

MATERIALS AND METHODS

Preparation of adsorbent

Mature *Erythrina variegata orientalis* leaves were collected from tall coral trees and were washed with water repeatedly to remove dust and soluble impurities. These leaves were dried at room temperature in shade. The leaves were sun-dried till they became crisp. The dried leaves were finely powdered and sized by passing it through a set of sieves ranging from 44 to 200 mesh size. The

powders of 75, 106 and 150 μm fractions were separated. These fractions were washed with distilled water till the washings were free of color and turbidity. After drying for several hours at room temperature, the powders used as an adsorbent. The leaf powder contains scoulerine, saponin, hydrocyanic acid, erythrine, hypaphorine ($\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2$), (+) coreximine, l-reticuline and erybidine (Compendium of Indian medical plants, 2: 303).

Preparation of zinc stock solution

All the chemicals used in this investigation were of analytical grade and all the solutions were made with distilled water. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (minimum assay 99%) was used as the source of Zn(II). 4.439 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 1L of distilled water to prepare 1000 mg/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 a specific amount of *erythrina variegata orientalis* leaf powder with 50 mL of aqueous solution of $C_o = 100$ mg/L at constant temperature (30°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, adsorbent size, dosage, initial concentration of zinc and volume of the aqueous solution, pH 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, 3, 4, 5, 10, 15, 20, 25, 30, 60, 120, 180, 240 and 300 min for various adsorbent dosages of 0.5, 1, 1.5 and 2 g of 75 μm size. The thermodynamic parameters are determined by adopting the same procedure at different temperatures for different volumes of the solutions. The extent of biosorption is found from the relation (or % removal) = $[(C_o - C_t) \times 100 / C_o]$. The amount of Zn(II) adsorbed per unit mass of the adsorbent, q in mg/gm = $(C_o - C_t) / m$. The values of parameters investigated are shown in Table 1.

RESULTS AND DISCUSSION

Equilibrium studies on biosorption of zinc

Effect of agitation time: The percentage removal of zinc is plotted against agitation time in Figure 1 for $w = 1$ g

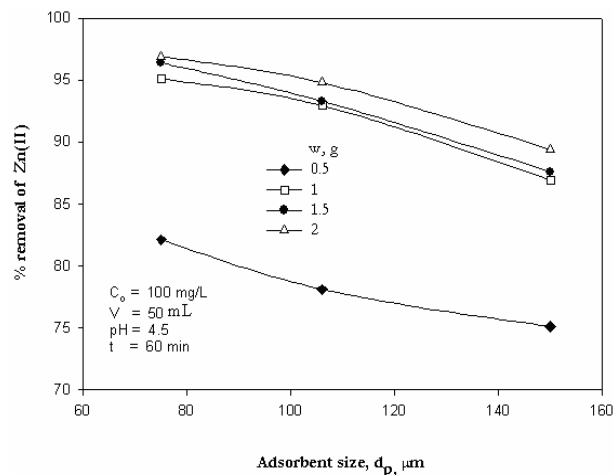


Figure 2. Variation of % removal of Zn(II) with adsorbent size.

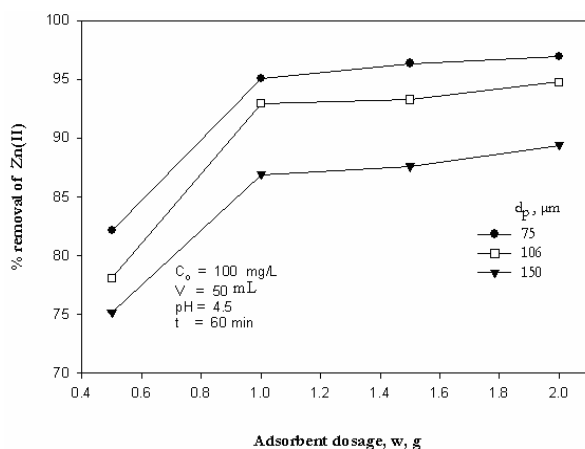


Figure 3. Influence of adsorbent dosage on % removal of Zn(II).

for various adsorbent sizes. For a typical experiment with 50 mL of aqueous solution ($C_o = 100$ mg/L) and a dosage of 1 g of 75 μm size, the % removal is aggressive in the first minute itself reaching 66.8%. The percentage removal is increased gradually to 95.1% in 60 min. The change in percentage removal of zinc becomes insignificant after 60 min. Hence, the equilibrium agitation time is 60 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. An equilibrium agitation time of 120 min was reported for the adsorbents, fly ash

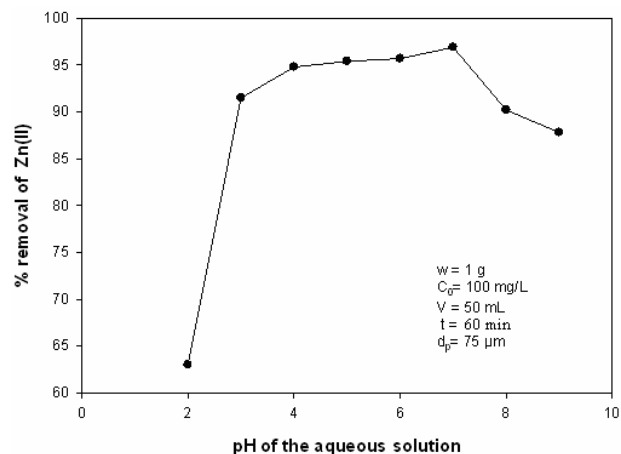


Figure 4. Effect of pH of aqueous solution on % removal of Zn(II)

(Belgin, 2002) and *Rhizopus arrhizus* (Preetha and Viruthagiri, 2005).

Effects of adsorbent size and dosage: The results obtained for biosorptive removal of Zn(II) with respect to adsorbent sizes are shown in Figure 2. The percentage removal of Zn(II) is increased with decreasing in size of the adsorbent. For an adsorbent dosage of 1g in 50 mL of aqueous solution ($C_o = 100$ mg/L), the biosorption is varied from 86.9 to 95.1% (4.425 to 4.785 mg/g) as the size decreases from 150 to 75 μm . Similar trends are observed with varying dosages of adsorbent ranging from 0.5 to 2 g. This phenomenon is expected as the size of the adsorbent decreases the surface area increases. The removal of zinc is decreased from 55 to 42.5%, as the adsorbent size is increased from 0.21 to 0.5 mm (Karthikeyan et al., 2004). With the decrease in adsorbent size from 212 to 75 μm (Kumar et al., 2006), the zinc uptake capacity onto *Tectona grandis* L. f. was increased from 3.25 to 4.38 mg/g. Figure 3 represents the variation in the percentage removal of Zn(II) with adsorbent dosage at equilibrium agitation time. The biosorption is increased from 82.1 to 96.9% (4.25 – 4.865 mg/g) for $d_p = 75$ μm as dosage is increased from 0.5 to 2 g. 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. Increase in the adsorbent dosage from 0.5 g (10 g/L) to 1 g (20 g/L) results in increase of % removal from 82.1% (4.245 mg/g) to 95.1% (4.785 mg/g). The increase in percentage removal is marginal from 95.1% for $w = 1$ g to 96.9% for $w = 2$ g. Hence, the effects of other parameters are obtained at $w = 1$ g. (Asma et al., 2005) varied the dosage of papaya wood from 0.5 to 20 g/L and reported decrease in uptake capacity from 8.56 to 0.64 mg/g for $C_o = 10$ mg/L.

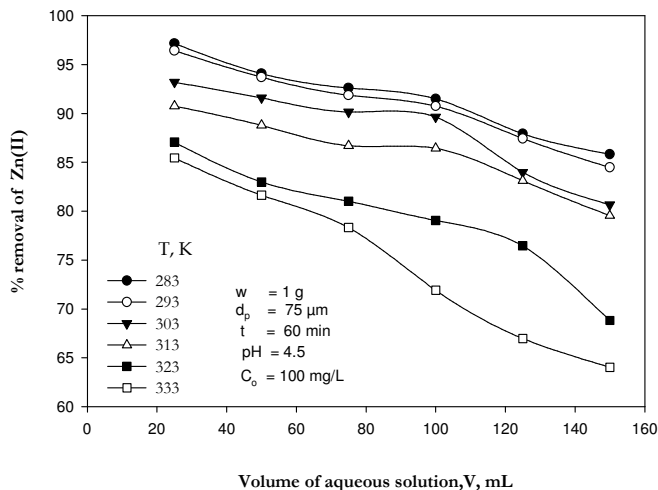


Figure 5. % removal of Zn(II) as a function of volume of aqueous solutions w.r.t temperature.

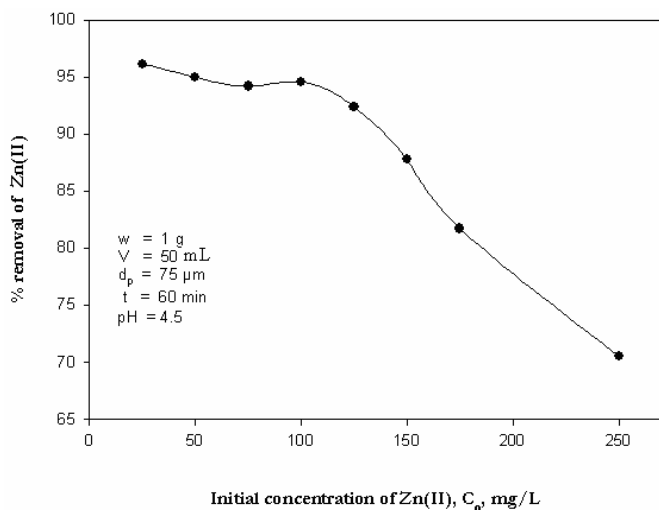


Figure 6. Impact of initial concentration of Zn(II) in aqueous solution on % removal of Zn(II)

Effect of pH of the aqueous solution

Figure 4 is a graph drawn between % removal of Zn(II) and pH of the aqueous solution with the biosorption data obtained by adding 1 g of 75 μm size adsorbent to 50 mL of aqueous solution. The extent biosorption is increased from 63 to 96.9% in the pH range from 2 to 7. A significant increase in percentage removal from 63 to 91.5% (3.5 – 4.66 mg/g) is obtained as pH increases from 2 to 3. The increase in percentage removal is marginal from 91.5 to 96.9% (4.66 - 4.875 mg/g) as pH increases from 3 to 7. An optimum pH of 7 was reported with banana and orange peel wastes (Annadurai et al., 2003) and fly ash (Belgin, 2002). The adsorption was also reported to be maximum with coir pith activated carbon when pH was above 6 (Santhy and Selvapathy, 2004). Optimum pH

value of 6 was reported by Yan (Guangyu and Thiruvengkatachari, 2003) with *Fungus mucor rouxii*. 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 volume of the aqueous solution and initial Zn(II) concentration in aqueous solution

The variation in % removal with the volume of the aqueous solution is shown in Figure 5. For an adsorbent dosage of 1g of 75 μm size, and $C_o = 100$ mg/L, the removal of Zn(II) from the aqueous solution steeply decreased from 93.2 to 80.7% (2.36 – 12.7 mg/g) as the volume of the Zn(II) solution increased from 25 to 150 ml. Such a behavior may be due to the exposure of higher amount of Zn(II) to the unaltered surface area of the adsorbent. The plots indicate that the extent of zinc removal decreased with an increase in temperature from 283 to 333 K. The effect of initial concentration of Zn(II) in the aqueous solution on percentage removal is shown in Figure 6. The percentage removal is decreased from 96.1% (1.1 mg/g) to 70.5% (11.3 mg/g) by varying Zn(II) concentrations in the aqueous solution from 25 to 250 mg/L. At lower C_o values, *erythrina variegata orientalis* leaf powder adsorbs more percentage of Zn(II). Lesser percentage of Zn(II) is removed at higher concentration in the aqueous solution. Such behavior can be attributed to the increase in the amount of adsorbate to the unchanging number of available active sites on the adsorbent. Senthilkumar studied the effect of C_o on uptake capacities using the adsorbent *ulva reticulata*, a green alga (Senthilkumar et al., 2006). They reported increased metal uptake capacities from 50 to 120 mg/g as C_o was increased from 250 to 1500 mg/L. With *T. grandis L.f.* leaves biomass (Kumar et al., 2006), the percentage adsorption was decreased from 73.1% (4.39 mg/g) to 43.2% (12.97 mg/g) as C_o was increased from 20 to 100 mg/L.

The principle driving force for metal ion biosorption is the net negative surface charge of the *erythrina variegata orientalis* leaf powder. It follows that higher the biomass electro-negativity, the greater is the attraction and adsorption of heavy metal ions. The presence of -COOH, -OH indicates the presence of polar groups on the surface of the adsorbent and is likely to give considerable cation exchange capacity to *erythrina variegata orientalis* leaf powder. 96.9% maximum biosorption of zinc is observed for 2 g of 75 μm adsorbent added to 50 ml of aqueous solution ($C_o = 100$ mg/L). Maximum uptake capacity of 13.3 mg/g is recorded with 1 g of 75 μm adsorbent added to 150 ml of aqueous solution containing 100 mg/L of zinc at 283 K.

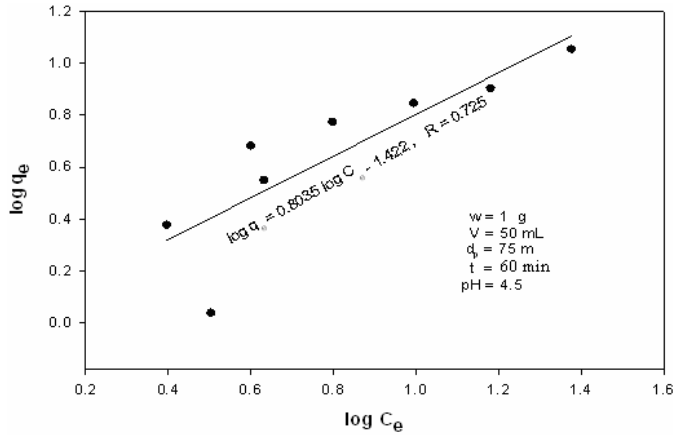


Figure 7. Freundlich isotherm for biosorption of Zn(II) w.r.t. initial concentration.

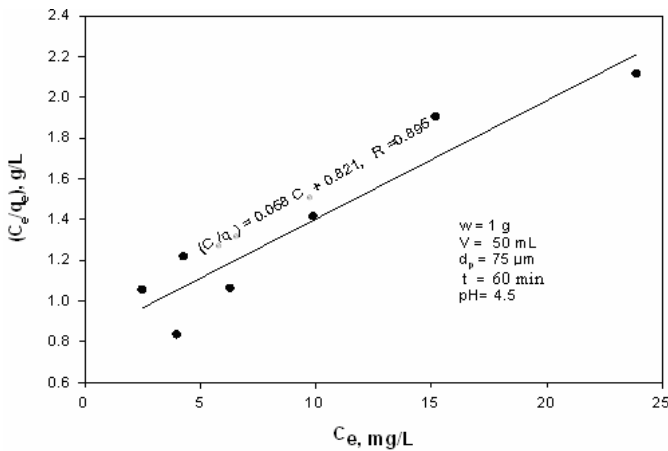


Figure 8. Langmuir isotherm for biosorption of Zn(II) w.r.t. initial concentration

Isotherms

An isotherm is the equilibrium relationship between the the concentration in the fluid phase and the concentration in the adsorbent at a given temperature. Freundlich isotherm (Freundlich, 1907) is $q_e = K_f C_e^n$ or $\log q_e = \log K_f + n \log C_e$. Freundlich isotherm is drawn between $\log C_e$ and $\log q_e$ shown in Figure 7. The following equation is obtained at $d_p = 75 \mu\text{m}$ varying the initial concentration of Zn(II):

$$\log q_e = 0.8035 \log C_e - 1.422 \quad R=0.725$$

The slopes (n) of the above equation is 0.8035 satisfying the condition of $0 < n < 1$ for favourable biosorption. Freundlich isotherm describes the biosorption with coir (Kathrine and Hans, 2007) and fungus mucor rouxii (Guangyu and Thiruvengkatachari, 2003). Langmuir isotherm (Langmuir, 1918) is the most widely used two-

parameter equation. The relationship is of a hyperbolic type form: $(C_e/q_e) = 1/bq_m + C_e/q_m$. Figure 8 is drawn between (C_e/q_e) and C_e for $d_p = 75 \mu\text{m}$ varying the initial concentration of Zn(II). The slope ($1/q_m$) and the intercept (b/q_m) are calculated from the plot drawn in fig.8. The equation obtained from the graph is:

$$(C_e/q_e) = 0.058 C_e + 0.821 \quad R = 0.895$$

The slope ($1/q_m$) is 0.058 and the intercept (b/q_m) is 0.821. The separation factor (R_L) value of $0.896 < 1$ indicates favourable biosorption. The correlation coefficient obtained for Langmuir isotherm is higher than that obtained for Freundlich isotherm. Yarn (Guangyu and Thiruvengkatachari, 2003) suggested Langmuir isotherm for biosorption with fungus mucor rouxii ($q_m = 16.62 \text{ mg/g}$ and $b = 0.8$). Biosorption with papaya wood (Asma et al., 2005) and *T. grandis L.f.* leaves biomass (Kumar et al., 2006) were explained by Langmuir isotherm. The values of various constants obtained for Zn(II)-Erythrina varie-gata orientalis leaf powder interactions at 303 K ($t = 60 \text{ min}$, $C_0 = 100 \text{ mg/L}$, $d_p = 75 \mu\text{m}$ and $w = 1 \text{ g}$) are shown in Table-2. Metal uptake capacities of Zn(II) by various adsorbents are shown in Table-3.

Kinetics of biosorption

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 (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: $(dq_t/dt) = K_{ad} (q_e - q_t)$. Plot of $\log (q_e - q_t)$ versus 't' gives a straight line for first order kinetics. In case of pseudo second order kinetics, $(dq_t/dt) = K (q_e - q_t)^2$ is applicable. This equation can be written as $(t/q_t) = (1/Kq_e^2) + (t/q_e)$. 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 of $\log (q_e - q_t)$ versus agitation time (t) for the present investigation is drawn in Figure 9 and the resulting equations are:

$$\begin{aligned} \log (q_e - q_t) &= -0.032 t + 0.113, \quad R=0.965 \text{ for } d_p=75 \mu\text{m} \\ \log (q_e - q_t) &= -0.054 t + 0.188, \quad R=0.829 \text{ for } d_p=106 \mu\text{m} \\ \log (q_e - q_t) &= -0.036 t + 0.207, \quad R=0.957 \text{ for } d_p=150 \mu\text{m} \end{aligned}$$

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 10 for $d_p = 75 \mu\text{m}$. The plots for $d_p = 106$ and $150 \mu\text{m}$ are not shown. The second order rate equations obtained are compiled in Table 4.

The results show that the correlation coefficients for second order rate equations (0.999) are higher than

Table 2. Various coefficients obtained in the present investigation

Freundlich isotherm			Langmuir isotherm			
K_f, Lg^{-1}	N	R	$q_m, mg/g$	b, Lmg^{-1}	R_L	R
1.422	0.8035	0.725	17.24	0.07	0.78	0.896

Table 3. Metal uptake capacities by various adsorbents.

Adsorbent	Metal uptake capacity, mg/g
Cork biomass [Natalia et al., 2004]	0.34
Palm tree leaves [Fahmi and Abu, 2006]	14.7
Tectona grandis L.f. biomass [Prasanna Kumar et al., 2006]	16.42
Marine micro algae [Senthilkumar et al., 2006]	36.1
Fungus mucor rouxii [Guangyu and Thiruvenkatachari, 2003]	7.75
PAN immobilized fungal biomass [Anastasios et al., 2003]	16.0
Present investigation	12.7

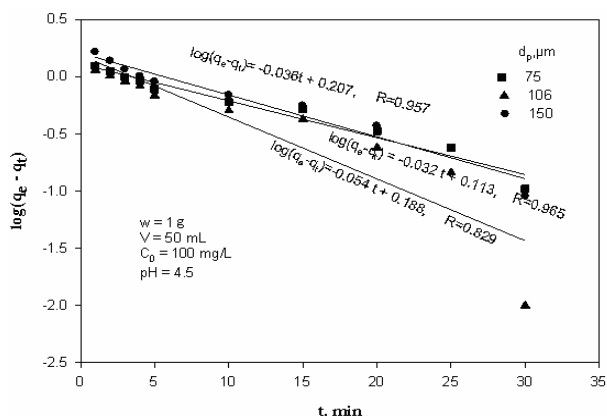


Figure 9. First order kinetics for biosorption of Zn(II).

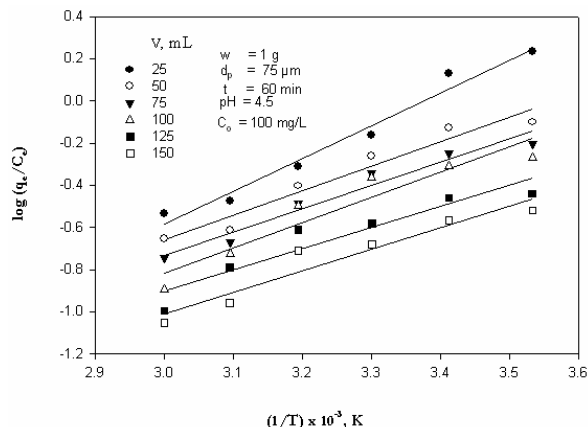


Figure 11. Effect of temperature on biosorption of Zn(II) for different volumes of aqueous solution.

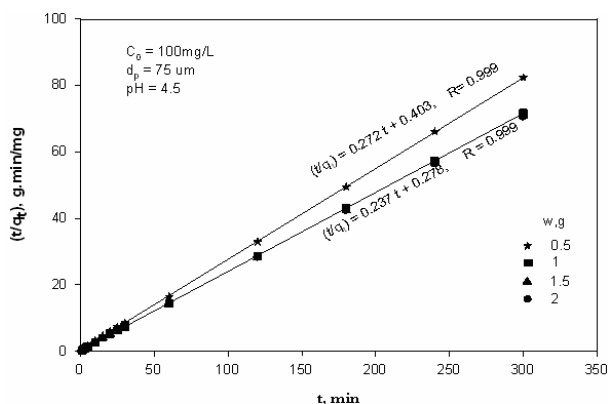


Figure 10. Second order kinetics for biosorption of Zn(II).

those for the first order rate equations. Hence, the pseudo second order rate equation is more suitable to explain the biosorption. The second order rate constant (K) values are varied from 0.159 to 0.285 g/(mg·min). Kinetic orders obtained for zinc with various adsorbents

are shown in Table 5.

Thermodynamics of Zn(II) biosorption

Biosorption is usually exothermic and the amount adsorbed at a given concentration decreases as the temperature increases, in accordance with Le-Chateliers principle. The thermodynamic criteria for biosorption is well explained by evaluation of the three important thermodynamic parameters. They are change in enthalpy (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS). Net enthalpy change (ΔH) is related to ΔG and ΔS as $\Delta G = \Delta H - T(\Delta S)$. The Van't Hoff's equation is

$$\log(q_e/C_e) = -(\Delta H/2.303R)(1/T) + (\Delta S/2.303R)$$

Where (q_e/C_e) is called the biosorption affinity. ΔH and ΔS values are calculated from

$$\text{slope} = -\Delta H/(2.303R) \text{ and intercept} = \Delta S/(2.303R)$$

Table 4. The equations, rate constants and correlation coefficients obtained

$d_p, \mu\text{m}$	w, g	Equation	R	K, g/(mg-min)
75	0.5	$(t/q_t) = 0.272 t + 0.403$	0.999	0.183
	1.0	$(t/q_t) = 0.237 t + 0.278$	0.999	0.202
	1.5	$(t/q_t) = 0.234 t + 0.273$	0.999	0.201
	2.0	$(t/q_t) = 0.233 t + 0.219$	0.999	0.248
106	0.5	$(t/q_t) = 0.286 t + 0.294$	0.999	0.279
	1.0	$(t/q_t) = 0.243 t + 0.347$	0.999	0.171
	1.5	$(t/q_t) = 0.241 t + 0.349$	0.999	0.166
	2.0	$(t/q_t) = 0.238 t + 0.273$	0.999	0.208
150	0.5	$(t/q_t) = 0.297 t + 0.308$	0.999	0.285
	1.0	$(t/q_t) = 0.259 t + 0.383$	0.999	0.175
	1.5	$(t/q_t) = 0.257 t + 0.415$	0.999	0.159
	2.0	$(t/q_t) = 0.253 t + 0.297$	0.999	0.216

Table 5. Order of the interactions for Zn(II) with various adsorbents

Adsorbent	Order
Papaya wood [Asma et al., 2005]	Second
Palm tree leaves [Fahmi and Abu, 2006]	Second
Rhizopus arrhizus [Preethi and Viruthagiri, 2005]	Second
Tectona grandis L.f. leaves [Prasanna Kumar et al., 2006]	Second
Marine micro algae [Santhikumar et al., 2006]	Second
Fngus mucor rouxii [Guangyu and Thiruvenkatachari, 2003]	Second
Present investigation	Second

Table 6. Thermodynamic parameters obtained in the present investigation

V, mL	- ΔH , J/mol	ΔS , J/(mol K)	- ΔG , kJ/mol at various temperatures					
			283 K	293 K	303 K	313 K	323 K	333 K
25	29.83	100.69	28.53	29.53	30.54	31.55	32.55	33.56
50	22.80	83.99	23.79	24.63	25.47	26.31	27.15	27.99
75	22.30	79.49	22.52	23.31	24.11	24.90	25.70	26.49
100	21.00	76.99	21.81	22.58	23.35	24.12	24.89	25.66
125	19.66	78.36	22.20	22.98	23.76	24.55	25.33	26.11
150	19.22	74.97	21.24	21.99	22.74	23.48	24.23	24.98

Experiments are conducted to understand the biosorption behavior of zinc with respect to temperature for $w = 1 \text{ g}$ and $d_p = 75 \mu\text{m}$ and the data are shown in Figure 11 with $\log(q_e/C_e)$ as a function of $(1/T)$. The equations obtained are:

$$\begin{aligned} \log(q_e/C_e) &= -1.558 (1/T) + 5.259 && \text{for } V = 25\text{mL} \\ \log(q_e/C_e) &= -1.191 (1/T) + 4.387 && \text{for } V = 50\text{mL} \\ \log(q_e/C_e) &= -1.165 (1/T) + 4.152 && \text{for } V = 75\text{mL} \\ \log(q_e/C_e) &= -1.0977 (1/T) + 4.021 && \text{for } V = 100\text{mL} \\ \log(q_e/C_e) &= -1.027 (1/T) + 4.093 && \text{for } V = 125\text{mL} \\ \log(q_e/C_e) &= -1.004 (1/T) + 3.916 && \text{for } V = 150\text{mL} \end{aligned}$$

Thermodynamic parameters calculated for biosorption of Zn(II) on to *Erythrina variegata orientalis* powder are

shown in Table 6.

In the present study, the negative value of ΔH indicates the biosorption to be exothermic. The positive value of ΔS indicates the spontaneous nature of biosorption. The negative value of ΔG indicates the feasibility and spontaneity of biosorption. Similar observations were reported with *Tectona grandis L.f.* leaves (Kumar et al., 2006). The endothermic and spontaneous nature of zinc biosorption was reported with palm tree leaves (Fahmi and Abu, 2006) and marine micro algae (Senthilkumar et al., 2006).

Conclusions

1. The equilibrium agitation time for the biosorption of

zinc (II) is 60 min for the adsorbent used.

- The percentage removal of zinc (II) increases with an increase in adsorbent dosage.
- As the initial zinc concentration in the aqueous solution increases, the percentage removal decreases.
- Percentage removal of zinc (II) from the aqueous solution is increased significantly with decrease in acidity and attains maximum at a pH of 7.
- Percentage biosorption of zinc (II) is increased from 49.1 to 96.9% in the range of variables studied
- The experimental data are well represented by Langmuir isotherm.
- The biosorption is exothermic, irreversible & spontaneous and follows pseudo second order kinetics.

NOMENCLATURE

b, Langmuir equilibrium constant, L/mg; **C_o**, Initial concentration of Zn(II) in aqueous solution, mg/L; **C_t**, Concentration of Zn(II) in aqueous solution after 't' min, mg/L; **C_e**, Equilibrium biosorption concentration of Zn(II), mg/L; **d_p**, Adsorbent size, μm ; ΔG , Change in Gibbs free energy, KJ/mol; ΔH , Change in enthalpy, J/mol; **K**, Second order rate constant, g/(mg min); **K_f**, Freundlich coefficient for Zn(II) in aqueous solution, L/g; **K_{ad}**, First order rate constant, min^{-1} ; **m**, Amount of adsorbent taken per 1L of aqueous solution, g/L; **n**, Freundlich constant for Zn(II) in aqueous solution; **q_e**, Mass of solute adsorbed per mass of adsorbent at equilibrium, = $(C_o - C_e)/m$, mg/g; **q_t**, Mass of solute adsorbed per mass of adsorbent at 't' min, = $(C_o - C_t)/m$, mg/g; **q_m**, Langmuir monolayer capacity, mg/g; **R_L**, Separation factor for Zn(II) in aqueous solution, $1/(1 + bC_e)$; **R**, Correlation coefficient; ΔS , Change in entropy, J/(mol K); **t**, Agitation time, min; **T**, Absolute temperature, K; **V**, Volume of aqueous solution, mL; **w**, Adsorbent dosage, g or g/L

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