Biosorption of zinc from aqueous solution using *Azadirachta indica* bark: Equilibrium and kinetic studies

P. King [a,*], K. Anuradha [a], S. Beena Lahari [a],
Y. Prasanna Kumar [b], V.S.R.K. Prasad [a]

[a] *Environmental Pollution Control Engineering Laboratory, Department of Chemical Engineering,*
A.U. College of Engineering, Andhra University, Visakhapatnam 530003, India
[b] *Department of Chemical Engineering, GMR Institute of Technology, GMR Nagar, Rajam 532127, India*

Abstract

The removal of zinc ions from aqueous solutions on the biomass of *Azadirachta indica* bark has been studied by using batch adsorption technique. The biosorption studies were determined as a function of contact time, pH, initial metal ion concentration, average biosorbent size and biosorbent dosage. The equilibrium metal uptake was increased and percentage biosorption was decreased with an increase in the initial concentration and particle size of biosorbent. The maximum zinc biosorption occurred at pH 6 and percentage biosorption increases with increase in the biosorbent dosage. Experimental data obtained were tested with the adsorption models like Langmuir, Freundlich and Redlich–Peterson isotherms. Biosorption isothermal data were well interpreted by Langmuir model with maximum biosorption capacity of 33.49 mg/g of zinc ions on *A. indica* bark biomass and kinetic data were properly fitted with the pseudo-second-order kinetic model.
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Keywords: *Azadirachta indica* bark; Biosorption; Isotherms; Kinetic studies

1. Introduction

Excess heavy metals are introduced into aquatic ecosystems as by-products of industrial processes and acid-mine drainage residues. They are highly toxic as ions or in compound forms: they are soluble in water and may be rapidly absorbed into living organisms [1]. Removal of heavy metals from wastewater is usually obtained by physical and chemical processes which include precipitation, coagulation, reduction, membrane processes, ion exchange and adsorption. However, the application of such processes is often restricted because of technical and/or economical constraints [2]. Biosorption may be a suitable wastewater technology to remove heavy metals as demonstrated by several researchers because it is possible to use cheap adsorption materials that can be competitive with the conventional technologies [3,4]. Zinc is one of the most important metal often found in effluents discharged from industries involved in acid-mine

drainage, galvanizing plants, natural ores and municipal wastewater treatment plants and not biodegradable and travels through the food chain via bioaccumulation. Moreover high intakes of these metals can cause liver, kidney and pancreas damage [5]. Several adsorbents were used for removal of heavy metals from wastewater [6]. Therefore there is significant interest regarding zinc removal from wastewater [7,8] and its toxicity for humans at levels of 100–500 mg/day [9]. WHO recommended [10] the maximum acceptable concentration of zinc in drinking water as 5.0 mg/L.

In this work, the biosorption of zinc ions by *Azadirachta indica* bark was studied with the effects of pH, initial concentration, biosorbent dosage, and biosorbent particle size.

2. Materials and methods

2.1. Preparation of biosorbent

The brown colored neem bark (*A. indica*) used in the present study was collected from the college of engineering, Andhra University, Visakhapatnam. The collected *A. indica* bark was

* Corresponding author. Tel.: +91 891 2844894.
 E-mail address: p_king@rediffmail.com (P. King).

Nomenclature

A, B	Redlich–Peterson isotherm constants (L/mg)
b	sorption equilibrium constant (L/mg)
C	concentration of solute in the solution (mg/L)
C_{eq}	equilibrium concentration of zinc (mg/L)
C_f	final concentration of zinc (mg/L)
C_i	initial concentration of zinc (mg/L)
D_p	biosorbent size (μm)
g	Redlich–Peterson isotherm exponent
k_f	Freundlich isotherm coefficient
k_1	pseudo-first-order constant (1/min)
k_2	pseudo-second-order constant (g/mg min)
m	intensity (g/L)
q	metal uptake (mg/g)
q_{eq}	amount biosorbed per unit weight of biosorbent at equilibrium (mg/g)
q_{max}	q_{eq} for a complete monolayer (mg/g)
r	correlation coefficient
t	time of contact (min)
W	weight of biosorbent (g)

washed with deionized water several times to remove dirt particles. The washing process was continued till the wash water contains no dirt. The washed *A. indica* bark was then completely dried in sunlight for 20 days. The resulting product was directly used as biosorbent. The dried bark was then cut into small pieces and powdered using domestic mixer. In the present study the powdered materials in the range of 75–283.5 μm average particle size were then directly used as biosorbent without any pretreatment.

2.2. Chemicals

Stock solutions of zinc concentration 1000 mg/L was prepared by dissolving 3.93 g of $ZnSO_4 \cdot 7H_2O$ in 1000 mL of distilled water. The solution was prepared using standard flasks. The range of concentration of the prepared metal solutions varied between 20 and 100 mg/L. The solutions were prepared by diluting the zinc stock solution, which were obtained by dissolving in deionized water. The pH of the solutions was adjusted with 0.1 N H_2SO_4 and NaOH. Blank experiments were conducted to ensure that no adsorption was taking place on the walls of the apparatus used.

2.3. Biosorption experiments

Batch biosorption equilibrium experiments were conducted in 250 mL stoppered conical flasks at a constant agitation speed. All the experiments were carried out at room temperature (30 ± 1 °C). The concentrations of the metal ions before and after sorption were determined using atomic absorption spectrophotometer by monitoring the absorbance for the metal ion used. The amount of metal adsorbed by *A. indica* bark was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$q = (C_i - C_f)\frac{V}{M} \tag{1}$$

where q is the metal uptake (mg/g), C_i and C_f are the initial and final metal concentrations in the solution (mg/L), respectively, V the solution volume (mL) and M is the mass of biosorbent (g).

The Langmuir sorption [11] isotherm has been successfully applied to many pollutant adsorption processes and has been the most widely used adsorption isotherm for the adsorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent.

The Langmuir equation used is

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{bq_{max}} + \frac{1}{q_{max}}C_{eq} \tag{2}$$

where C_{eq} is the equilibrium concentration (mg/L), q_{eq} the amount of metal ion sorbed (mg/g); q_{max} the q_{eq} for a complete monolayer (mg/g) and b is the sorption equilibrium constant (L/mg). A plot of C_{eq}/q_{eq} versus C_{eq} should indicate a straight-line of slope $1/q_{max}$ and an intercept of $1/bq_{max}$.

Freundlich [12] studied the sorption of a material onto animal charcoal and found that if the concentration of solute in the solution at equilibrium, C_{eq}, was raised to the power m, the amount of solute adsorbed being q_{eq}, then C_{eq}^m/q_{eq} was a constant at a given temperature. This fairly satisfactory empirical isotherm can be used for non-ideal sorption and the Freundlich model is represented by the equation:

$$q_{eq} = K_f C_{eq}^m \tag{3}$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as

$$\log q_{eq} = \log K_f + m \log C_{eq} \tag{4}$$

Jossens et al [13] modified the three-parameter isotherm proposed by Redlich and Peterson [14] to incorporate features of both the Langmuir and Freundlich equations. The Redlich–Peterson model is represented as follows:

$$q_{eq} = \frac{AC_{eq}}{1 + BC_{eq}^g} \tag{5}$$

Applying the natural logarithm of both sides:

$$\ln\left(A\frac{C_{eq}}{q_{eq}} - 1\right) = g\ln(C_{eq}) + \ln(B). \tag{6}$$

Although a linear analysis is not possible for a three parameter isotherm, three isotherm constants, A, B and g, can be evaluated from the pseudo-linear plot represented by Eq. (6) using a trail and error optimization method. A general trail and error procedure which is applicable to computer operations was developed to determine the coefficient of determination, r^2 for a series of values of A for the linear regression of $\ln(C_{eq})$ on $\ln[A(C_{eq}/q_{eq})-1]$ and to obtain the best value of A which yields a maximum "optimized" value for r^2.
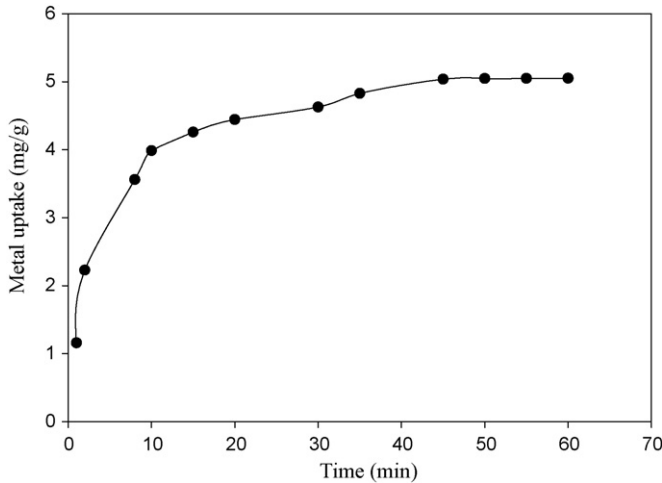
Fig. 1. Effect of contact time on biosorption of zinc by *Azadirachta indica* bark for 20 mg/L of metal and 0.1 g/30 mL of biomass concentration (pH 6).
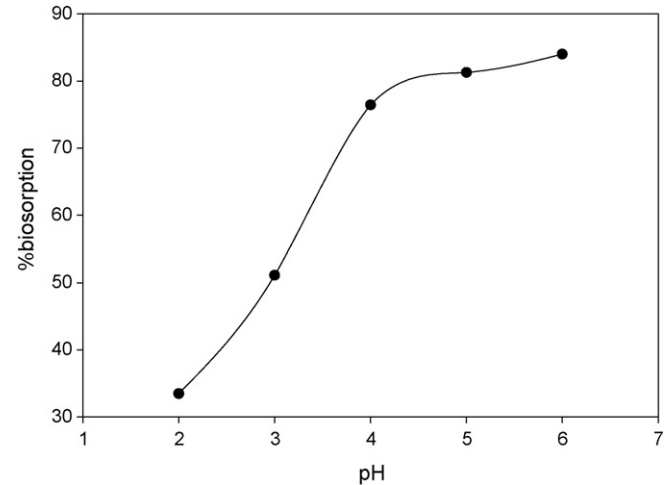
2.4. Biosorption kinetics

The kinetics studies were carried out by conducting batch biosorption experiments with different initial zinc concentrations. Samples were taken at different time periods and analyzed for their zinc concentration.

3. Results and discussion

3.1. Effect of contact time

Time course profile for the biosorption of zinc for a solution of 20 mg/L is shown in Fig. 1. The data showed that a contact time of 45 min was required to achieve an optimum biosorption and there was no significant change in concentration of the metal ion with further increase in contact time. Therefore, the uptake and unadsorbed zinc concentrations at the end of 45 min are given as the equilibrium values, q_{eq} (mg/g) and C_{eq} (mg/L). For further studies of biosorption with other variable parameters the optimum time of 45 min has been chosen for contact period.

Fig. 2. Effect of metal ion concentration on the biosorption of zinc by *A. indica* bark at 0.1 g/30 mL of biosorbent concentration (pH 6).

Fig. 3. Effect of pH on zinc biosorption for 20 mg/L of metal and 0.1 g/30 mL of biomass concentration.

3.2. Effect of initial metal ion concentration

Experiments were undertaken to study the effect of the initial metal ion concentration on zinc removal kinetics from the solution. The results obtained are shown in Fig. 2. The obtained curve showed that the metal uptake increases with increase in initial concentration of metal ion while the percentage biosorption of zinc decreases with an increase in initial metal ion concentration. The increase of metal uptake is a result of the increase in the driving force, i.e. concentration gradient, with an increase in the initial zinc ion concentrations (from 20 to 100 mg/L). However, the percentage biosorption of zinc ions on *A. indica* bark was decreased from 84 to 70%, respectively. Though an increase in metal uptake was observed, the decrease in percentage biosorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage biosorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of zinc displays an opposite trend. At lower concentrations, all zinc
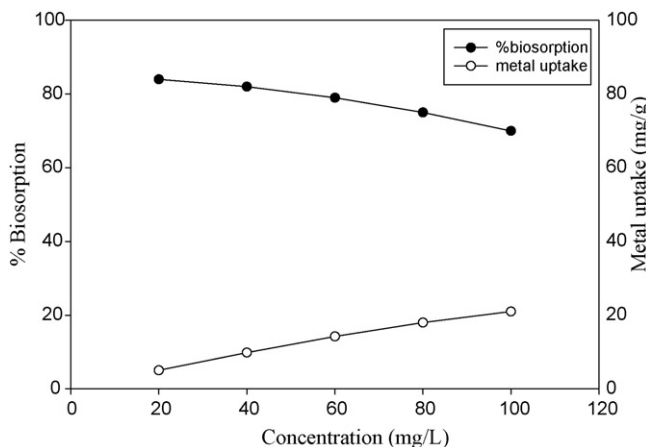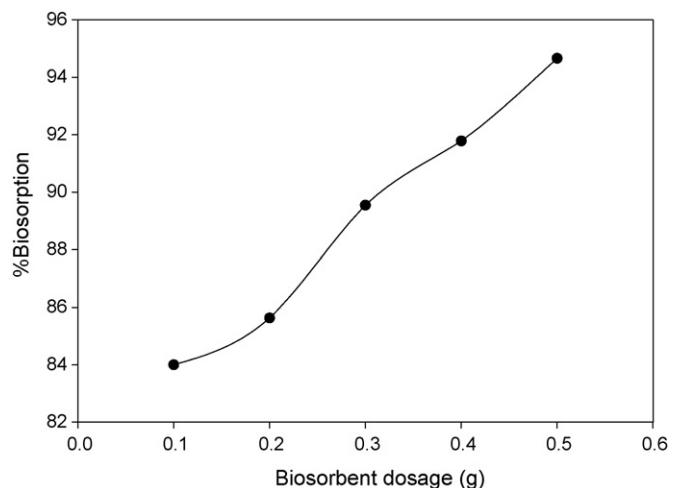

Fig. 4. Effect of biosorbent dosage on biosorption of zinc for 20 mg/L of metal concentration (pH 6).
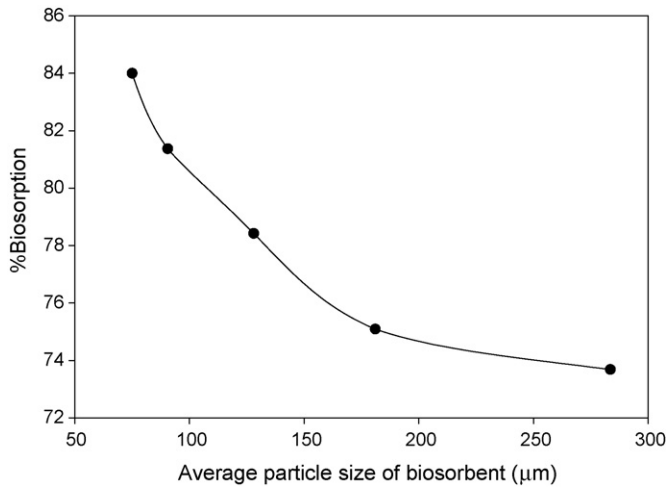
Fig. 5. Effect of average particle size of biosorbent on biosorption of zinc for 20 mg/L of metal and 0.1 g/30 mL of biosorbent concentration (pH 6).

Fig. 6. Equilibrium curves for zinc onto *A. indica* bark.

ions present in solution could interact with the binding sites and thus the percentage biosorption was higher than those at higher initial zinc ion concentrations. At higher concentrations, lower biosorption yield is due to the saturation of biosorption sites. As a result, diluting the wastewaters containing high metal ion concentrations can increase the purification yield.

$$biosorption\,(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (7)$$

The metal uptake was calculated by the simple concentration difference method. The initial concentration C_i (mg/L) and the final metal concentration C_f (mg/L) at any time were determined and the metal uptake q_{eq} (mg metal adsorbed/g adsorbent) was calculated from the mass balance as follows:

$$q_{eq} = \frac{V(C_i - C_{eq})}{1000\,W} \qquad (8)$$

3.3. Effect of pH

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions, on the functional groups of the biomass cell walls. Thus pH is an important parameter on biosorption of metal ions from aqueous solutions. *A. indica* bark presents a high content of ionizable groups (carboxyl groups) on the cell wall polysaccharides, which makes it very liable to the influence of the pH. As shown in Fig. 3, the uptake of free ionic zinc depends on pH. The biosorption of metallic ion was observed to increase with increase in pH up to a value of 6. At pH values lower than 4, zinc removal was inhibited, possibly as a result of the competition between hydrogen and metal ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cation as in consequence of the repulsive force. As the pH increased the legends such as carboxylate groups would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface [15].
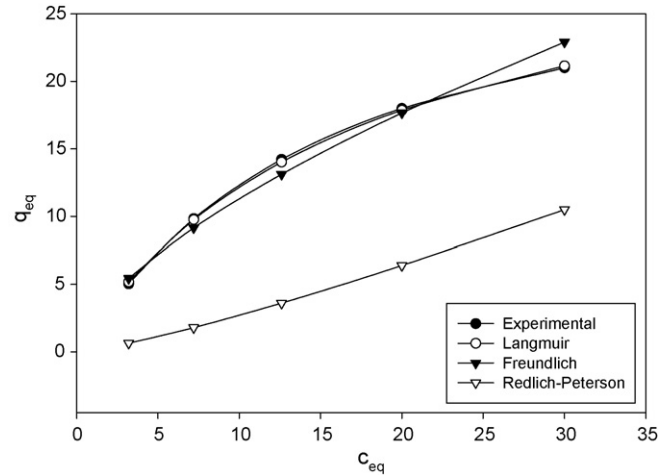
3.4. Effect of biosorbent dosage

For studying the effect of biosorbent dosage on removal of zinc ion, the biosorbent dosage is changed from 0.1 to 0.5 g, fixing other parameters like initial concentration at 20 mg/L, pH 6 and particle size 75 μm. The contact time was 45 min for zinc as stated in the earlier section. The biosorption plot of Fig. 4 shows an increase in % biosorption with an increase in biosorbent dosage. This is because of the availability of more binding sites for complexation of metal ions.

3.5. Effect of biosorbent particle size

Fixing the initial concentration of solution at 20 mg/L, pH 6, the fixed volume of 30 mL solution is allowed for 45 min for zinc biosorption with 0.1 g each of the varied size of particles of biosorbent ranging from 75 to 283.5 μm, the plot (Fig. 5) drawn for the variation of the percentage biosorption against particle size, shows that with increase in particle size the biosorption decreases. This is due to less surface area available with increased particle size, thus reducing the biosorption.

4. Biosorption equilibrium

The equilibrium biosorption of zinc on the *A. indica* bark as a function of the initial concentration of zinc is shown in Fig. 6. The Langmuir, Freundlich and Redlich–Peterson models were used to describe the equilibrium sorption isotherms and the calculated results of these models are given in Table 1.

Table 1
Langmuir, Freundlich and Redlich–Peterson isotherm constants and correlation coefficients

Langmuir model	Freundlich model	Redlich–Peterson model
q_{max} (mg/g) = 33.49	k_f = 2.578	A (L/g) = 0.932
b (l/mg) = 0.05717	m (g/L) = 0.6423	B (L/mg) = 5.424
r^2 = 0.9985	r^2 = 0.9807	r^2 = 0.2252

It is found that the biosorption of zinc on the *A. indica* bark was correlated well with the Langmuir equation as compared with other two equations under the concentration range studied (Fig. 6).

5. Biosorption kinetics

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Fig. 1 shows the plot between the metal uptake, q (mg/g) versus time, t (min) for initial solute concentration of 20 mg/L. From the figure it was observed that q-value increased with increase in contact time. The kinetics of the adsorption data was analyzed using two kinetic models, pseudo-first order and pseudo-second order. These models correlate solute uptake, which are important in predicting the reactor volume. These models are explained as follows.

5.1. Pseudo-first-order model

The possibility of adsorption data following Lagergren [16] pseudo-first-order kinetics is given by

$$\frac{dq}{dt} = k_1(q_{eq} - q) \tag{9}$$

Integrating Eq. (9) with respect to integration conditions $q = 0$ at $t = 0$ to $q = q$ at $t = t$, the kinetic rate expression becomes:

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_1}{2.303}t \tag{10}$$

In order to obtain the rate constant, the straight-line plot (not shown) of $\log (q_{eq} - q)$ versus time was made for *A. indica* bark for initial zinc concentration, 20 mg/L. The intercept of the plot should be equal to $\log q_{eq}$. However, if q_{eq} from intercept does not equal to the equilibrium metal uptake then the reaction is not likely to be first order even this plot has high correlation coef-
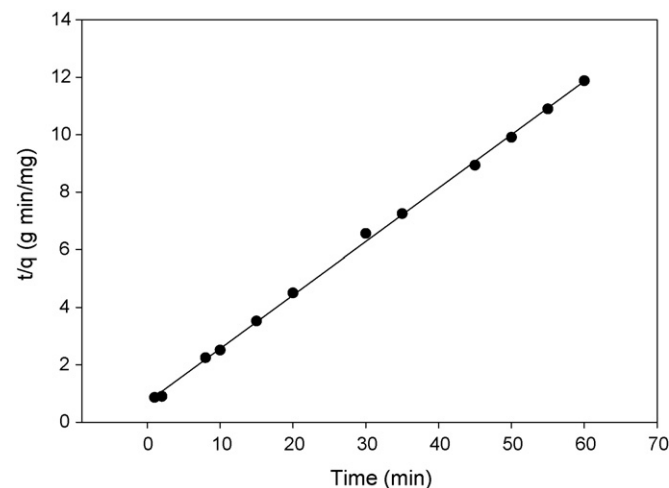

Fig. 7. Pseudo-second order adsorption of zinc by *A. indica* bark for 20 mg/L of metal and 0.1 g/30 mL of biomass concentration.

Table 2
Kinetic constants for zinc onto *Azadirachta indica* bark

	Pseudo-first order	Pseudo-second order
k	0.039	0.0494
q_{eq} (calculated)	2.0763	5.376
q_{eq} (experimental)	5.3148	5.1788
r^2	0.5339	0.9991

ficient with the experimental data. Correlation coefficient was found to be 0.5339, and the calculated q_e is not equal to experimental q_{eq}, suggesting the insufficiency of pseudo-first-order model to fit the kinetic data for the initial zinc concentration examined.

5.2. Pseudo-second-order model

A pseudo-second-order model proposed by Ho and McKay [17] was used to explain the sorption kinetics. This model is based on the assumption that the adsorption follows second order chemisorption. The pseudo-second-order model can be expressed as

$$\frac{dq}{dt} = k_2(q_{eq} - q)^2 \tag{11}$$

Separating the variables in Eq. (11) gives:

$$\frac{dq}{(q_{eq} - q)^2} = k_2 dt \tag{12}$$

Table 3
Comparison of maximum capacity of *A. indica* bark for zinc with other adsorbents

Adsorbent	q_{max} (mg/g)	pH	Reference
Activated carbon	31.11	4.5	[18]
Streptoverticillium cinnamoneum	21.3	5.5	[19]
Fontinalis antipyretica	12	5.0	[20]
Asperigillus niger 405	4.7	5.0	[21]
Mucor rouxii (live)	4.89	5.0	[22]
Mucor rouxii (NaOH pretreated)	5.63	5.0	[22]
Mucor rouxii (Na$_2$CO$_3$ pretreated)	3.26	5.0	[22]
Mucor rouxii (NaHCO$_3$ pretreated)	6.28	5.0	[22]
Phanerochaete chrysorporium	39	7.0	[23]
Sargassum sp.	24.35	4.5	[24]
Animal bones	11.55	5.0	[25]
Na-Mont morillonite	3.61	5.0	[26]
Crushed concrete fines	33	5.5	[27]
Coir	8.6	5.5	[28]
Barley straw	5.3	5.5	[28]
Peat	11.71	5.5	[28]
Coniferous bark	7.4	5.5	[28]
Papaya wood	0.64	5.0	[29]
Penicillium digitatum	9.7	5.5	[30]
Syzygium cumini L.	35.84	6.0	[31]
Tectona grandis L.f.	16.42	5.0	[32]
A. indica bark	33.49	6.0	Present study

Integrating Eq. (12) for the boundary conditions $q = 0$ at $t = 0$ to $q = q$ at $t = t$, Eq. (12) simplifies to:

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \tag{13}$$

where t is the contact time (min), q_{eq} (mg/g) and q (mg/g) are the amount of metal adsorbed at equilibrium and at any time, t. Correlation coefficient was found to be 0.9991 for initial concentration 20 mg/L. If second order kinetics is applicable, the plot (Fig. 7) of t/q versus time of Eq. (13) should give a linear relationship from which the constants q_{eq} and k_2 can be determined. The rate constants and the correlation coefficients for both the tested models have been calculated and summarized in Table 2.

A comparison of the maximum capacity q_{max} of *A. indica* bark with those of some other adsorbents reported in literature is given in Table 3. Difference of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

6. Conclusions

The present study shows that the *A. indica* bark was an effective biosorbent for the biosorption of zinc ions from aqueous solution. The biosorption performances are strongly affected by parameters such as initial concentration, pH, biosorbent dosage, biosorbent average particle size. The equilibrium metal uptake was increased and percentage biosorption was decreased with increasing the initial concentration of metal ion. The plot of pH versus percentage biosorption shows the significant biosorption takes place at 6. The percentage biosorption increases with increase in the biosorbent dosage and decreases with increase in the average particle size of the biosorbent. The adsorption isotherms could be well fitted by the Langmuir equation. The kinetics of the biosorption of zinc was better described with second-order kinetics. Intra-particle diffusion might also have a significant role in the biosorption process slowing down the approach towards equilibrium.

References

[1] D.N. Lapedes, Encyclopedia of Environmental Science, McGraw Hill Book Company, New York, 1974, p. 259.

[2] L. Norton, K. Baskaran, S.T. McKenzie, Biosorption of zinc from aqueous solutions using biosolids, Adv. Environ. Res. 8 (2004) 629–635.

[3] K.H. Chong, B. Volesky, Description of 2-metal biosorption equilibria by Langmuir-type models, Biotechnol. Bioeng. 47 (1995) 451–460.

[4] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste, Water Res. 36 (2002) 2304–2318.

[5] C.L. Brierley, Metal Immobilization Using Bacteria, Microbial Mineral Recovery, McGraw Hill, New York, 1990, pp. 303-324.

[6] R.A. Shawabkeh, D.A. Rockstraw, R.K. Bhada, Copper and strontium adsorption by a novel carbon material manufactured from pecan shells, Carbon 40 (5) (2002) 781–786.

[7] J. Moore, S. Rama Moorthy, Heavy metals in natural waters, Applied Monitoring and Impact Assessment, Springer, New York, BioScience, 35 (1) (1985) 54.

[8] A.K. Bhattacharya, S.N. Mandal, S.K. Das, Adsorption of Zn(II) from aqueous solution by using different adsorbents, Chem. Eng. J. 123 (2006) 43–51.

[9] Agency for toxic substances and disease registry (ATSDR). http://www.atsdr.cdc.gov..

[10] A. Margot, T. Liosa, D. Tanaka, V. Flores, T. Nagase, M.T. Suzuki, React. Funct. Polym. 53 (2002) 91.

[11] I. Langmuir, The adsorption gases on plane surface of glass, mica and platinum, J. Am. Chem. Soc. 40 (1916) 1316–1368.

[12] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385–470.

[13] L. Jossens, J.M. Prausnitz, W. Fritz, E.U. Schlunder, A.L. Myers, Thermodynamics of multi-solute adsorption from dilute aqueous solution, Chem. Eng. Sci. 33 (1978) 1097–1106.

[14] O. Redlich, D.L. Peterson, A useful adsorption isotherm, J. Phys. Chem. 63 (1959) 1024.

[15] F. Martin-Dupont, V. Gloaguen, M. Guilloton, R. Granet, P. Krausz, Study of the chemical interaction between barks and heavy metal cations in the sorption process, J. Environ. Sci. Health: A 41 (2006) 149–160.

[16] S. Lagergren, S. Kungliga, Svenska ventenskapsakademiens, Handling Band 24 (4) (1898) 1.

[17] Y.S. Ho, G. Mckay, The kinetics of sorption of basic dyes from aqueous solution by sphagnum mass peat, Can. J. Chem. Eng. 76 (1998) 822–827.

[18] D. Mohan, K.P. Singh, Single and Multi component adsorption of cadmium and zinc using activated carbon derived from bagasse an agricultural waste, Water Res. 36 (2002) 2304–2318.

[19] P.R. Puranik, K.M. Pakanikar, Biosorption of lead and zinc from solutions using *Streptoverticillium cinnamoneum* waste biomass, J. Biotechnol. 55 (1997) 113–124.

[20] R.J.E. Martins, R. Pardo, R.A.R. Boaventura, Cadmium(II) and zinc(II) adsorption by the aquatic moss *Fontinalis antipyretica*: effect of temperature, pH and water hardness, Water Res. 38 (2004) 693–699.

[21] Z. Fillipovic-Kovacevic, L. Sipos, F. Briski, Biosorption of Cr, Cu, Ni and Zn ions onto fungal pellets of *Asperigillus niger* 405 from aqueous solutions, Food Technol. Biotechnol. 38 (2000) 211–216.

[22] G. Yan, T. Viraraghavan, Effect of pretreatment on the bioadsorption of heavy metals on *Mucor rouxii*, Water SA 26 (2000) 119–123.

[23] M.Y. Arica, C. Arpa, A. Ergene, G. Bayaramoglu, O. Gene, Ca-alginate as a support for Pb(II) and Zn(II) biosorption with immobilized *Phanerochaete chrysoporium*, Carbohyd. Polym. 529 (2003) 167–174.

[24] A.J.P. Erteves, E. Valdman, S.G.F. Leite, Repeated removal of Cd and Zn from an industrial effluent by waste biomass *Sargassum* sp., Biotechnol. Lett. 22 (2000) 499–502.

[25] F. Banat, S. Al-Asheh, F. Mohai, Batch zinc removal from aqueous solution using dried animal bones, Sep. Purif. Technol. 21 (2000) 155–164.

[26] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, Adsorption of heave metals on Na-montmorillonite: effect of pH and organic substances, Water Res. 37 (2003) 1619–1627.

[27] N.J. Coleman, W.E. Lee, I.J. Slipper, Interactions of aqueous Cu^{2+}, Zn^{2+}, and Pb^{2+} ions with crushed concrete fines, J. Hazard. Mater. B121 (2005) 203–213.

[28] K. Conrad, H.C.B. Hansen, Sorption of zinc and lead on coir, Bioresource Technol., 2006.

[29] M. Asma Saeed, W Akthter, M Iqbal, Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent, Sep. Purif. Technol. 45 (2005) 25–31.

[30] M. Galun, E. Galun, B.Z. Siegel, P. Keller, H. Lehr, S.M. Siegel, Removal of metal ions from aqueous solutions by *penicillium biomass*: kinetics and uptake parameters, Water Air Soil Pollut. 33 (1987) 359–371.

[31] N. Rakesh, Removal of lead and zinc from aqueous solution using *Syzygium cumini* L. as biosorbent, M.Tech. Thesis, Dept. of Chemical Engineering, Andhra University, Vishakapatnam, 2006.

[32] Y. Prasanna Kumar, Biosorption of copper and zinc using *Ulva fasciata* sp. and *Tectona grandis* L.f, Ph.D. Thesis, Dept. of Chemical Engineering, Andhra University, Visakhapatnam, 2006.