ELSEVIER

Journal of Hazardous Materials B139 (2007) 345–355

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Ni(II) biosorption by *Cassia fistula* (Golden Shower) biomass

Muhammad Asif Hanif [a], Raziya Nadeem [a], Haq Nawaz Bhatti [a,*], Najum Rashid Ahmad [a], Tariq Mehmood Ansari [b]

[a] *Department of Chemistry, University of Agriculture, Faisalabad 38040, Pakistan*
[b] *Department of Chemistry, Baha-u-Din Zakariya University, Multan 60800, Pakistan*

Received 6 May 2006; received in revised form 10 June 2006; accepted 13 June 2006
Available online 16 June 2006

Abstract

Cassia fistula is a fast-growing, medium-sized, deciduous tree which is now widely cultivated worldwide as an ornamental tree for its beautiful showy yellow flowers. Methods are required to reuse fallen leaves, branches, stem bark and pods when they start getting all over lawn. This investigation studies the use of these non-useful parts of *C. fistula* as naturally occurring biosorbent for the batch removal of Ni(II) in a well stirred system under different experimental conditions. The data showed that the maximum pH (pH_{max}) for efficient sorption of Ni(II) was 6 at which evaluated biosorbent dosage, biosorbent particle size, initial concentrations of Ni(II) and sorption time were 0.1 g/100 mL, <0.255 mm, up to 200 mg/L and 720 min, respectively. The experimental results were analyzed in terms of Langmuir and Freundlich isotherms. The Langmuir isotherm model fitted well to data of Ni(II) biosorption by *C. fistula* biomass as compared to the model of Freundlich. The kinetic studies showed that the sorption rates could be described better by a second order expression than by a more commonly applied Lagergren equation. The magnitude of the Gibbs free energy values indicates spontaneous nature of the sorption process. The sorption ability of *C. fistula* biomass for Ni(II) removal tends to be in the order: leaves < stem bark < pods bark. One hundred percent Ni(II) removal was achieved when the initial Ni(II) concentration was 25 mg/L. Due to its outstanding Ni(II) uptake capacity, *C. fistula* biomass proved to be an excellent biomaterial for accumulating Ni(II) from aqueous solutions.

Keywords: Sorption; Ni(II); Equilibrium; Kinetics; *Cassia fistula*

1. Introduction

Ni(II) is known environmental pollutant so its removal is of major importance as compared to other heavy metals. Ni(II) is frequently encountered together in industrial wastewaters, such as mine drainage, metal plating, paint and ink formulation and porcelain enameling [1]. Conventional methods such precipitation, oxidation/reduction, ion-exchange, filtration, membranes and evaporation are extremely expensive or inefficient for metal removal from dilute solutions containing 1–100 mg/L of dissolved metal. In this context the biosorption process has been recently being evaluated. The major advantages of biosorption of over conventional treatment methods include, low cost; high efficiency; minimization of chemical or biological sludge; no additional nutrient requirement; possibility of regeneration of biosorbent and metal recovery [1,2]. The mechanism of biosorption is complex, mainly comprising of ion-exchange, chelations, adsorption by physical forces, entrapment in inter and intra-fibular capillaries and spaces of structural polysaccharides network. Abundant materials have been suggested as potential biosorbent for heavy metals [1–3]. Numerous chemical groups have been suggested to contribute to biosorptive metal uptake [2]. The suggested groups include carboxyl, hydroxyl, carbonyl, sulfhydryl, thioether, sulfonate, amine, imine, amide, imidagole, phosphonate, and phospho-diester groups. The efficiency of biomass depends on factors such as number of sites on the biosorbent material, their accessibility and chemical state (i.e. availability), and the affinity between site and metal (i.e., binding strength) [3–7].

This study was carried out to optimize the laboratory conditions for the maximum biosorption of Ni(II) from aqueous solutions by *Cassia fistula* biomass. *C. fistula* belongs to family: Fabaceae, genus: *Cassia*, species: *fistula*. Its common names are Amaltas, Canafistula, Golden Shower, and Indian Labur-

* Corresponding author.
E-mail address: hnbhatti2005@yahoo.com (H.N. Bhatti).

0304-3894/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2006.06.040

num. It is a medium sized deciduous tree, 6–9 m tall with a straight trunk and spreading branches. This plant was chosen as biosorbent material because of its relative abundance in tropical countries and lack of information about its sorption abilities towards biosorption of Ni(II). The influence of different experimental parameters such as pH, biosorbent dosage, biosorbent particle size, initial concentrations of Ni(II) and sorption time on Ni(II) uptake was evaluated.

2. Materials and methods

2.1. Reagents

All the chemical reagents used in these studies were of analytical grade, including $NiSO_4{\cdot}6H_2O$ (Merck), Conc. HNO_3 (Merck) and Ni(II) atomic absorption spectrometry standard solution (1000 mg/L) (Fluka Chemicals).

2.2. *C. fistula* biomass

In the present study six different parts of *C. fistula* biomass were selected include leaves, stem bark, pods bark, branches, pods internal mass and pods bark ash. *C. fistula* biomass used in this work was harvested from University of Agriculture, Faisalabad, Pakistan, sampled, extensively washed with distilled water to remove particulate material from their surface, and oven dried at 60 °C for 72 h. One kilogram of biomass was sub sampled for use in the experiments. In order to ensure that homogeneous samples were collected, standard sampling techniques were applied. Dried biomass was cut, ground using food processor (Moulinex, France) and then sieved through Octagon siever (OCT-DIGITAL 4527-01) to obtain adsorbent with homogenous known particle size. The fraction with <0.255–0.710 mm was selected for use in the sorption tests. The sieved six sorbents were stored in an air tight plastic container for further experiments.

2.3. Ni(II) solutions

Stock Ni(II) solution (1000 mg/L) was prepared by dissolving 4.48 g of $NiSO_4{\cdot}6H_2O$ in 100 mL of deionized distilled water (DDW) and diluting quantitatively to 1000 mL using DDW, Ni(II) solutions of different concentrations were prepared by adequate dilution of the stock solution with DDW. Glassware and polypropylene flasks used were overnight immersed in 10% (v/v) HNO_3 and rinsed several times with DDW.

2.4. Determination of the Ni(II) contents in the solutions

The concentration of Ni(II) in the solutions before and after the equilibrium was determined by flame atomic absorption spectrometry (FAAS), using a Perkin-Elmer AAnalyst 300 atomic absorption spectrometer equipped with an air–acetylene burner and controlled by Intel personal computer. The hollow cathode lamp was operated at 15 mA and the analytical wavelength was set at 232 nm.

2.5. Batch biosorption studies

In all sets of experiments fixed volume of Ni(II) solution (100 mL) was thoroughly mixed with desired biosorbent dose (0.05, 0.1, 0.2 and 0.3 g) and size (<0.255, 0.255–0.355, 0.355–0.500 and 0.500–0.710 mm) at 30 °C and 100 rpm up to 24 h. To check the influence of pH, initial metal concentration and contact time different conditions of pH (3, 4, 5, 6, 7 and 8), initial metal concentration (25, 50, 100, 200, 400 and 800 mg/L) and contact time (15, 30, 60, 120, 240, 480, 720 and 1440 min) were evaluated during study. For adjusting the pH of the medium 0.1N solutions of NaOH and HCl were used. The flasks were placed on a rotating shaker (PA 250/25. H) with constant shaking. At the end of the experiment, the flasks were removed from the shaker and the solutions were separated from the biomass by filtration through filter paper (Whatman No. 40, ashless). Preliminary tests were performed at 30 °C using an initial Ni(II) concentration of 100 mg/L (initial pH 6.0), and 100 rpm for screening studies. The sorption time was 24 h and the equilibrium on Ni(II) uptake was attained.

2.6. Metal uptake

The Ni(II) uptake was calculated by the simple concentration difference method [4]. The initial concentration C_i (mg/L) and metal concentrations at various time intervals, C_e (mg/L), were determined and the metal uptake q_e (mg metal adsorbed/g adsorbent) was calculated from the mass balance equation (Eq. (1)) as follows:

$$q_e = (C_i - C_e)V/1000w \quad (1)$$

where V is the volume of the solution in mL and w the mass of the sorbent in g.

2.7. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was used to detect vibration frequency changes in the *C. fistula* biomass. The spectra were collected by FTS-135 (Bio-Rad) spectrometer within the range 400–4000 cm^{-1} using a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra. Spectra were plotted using the same scale on the absorbance axis.

2.8. Statistical analysis

All data represent the mean of three independent experiments. All statistical analysis was done using Microsoft Excel 2004, Version office Xp.

3. Results and discussion

3.1. Influence of initial pH

It is well known that the pH of the medium affects the solubility of metal ions and concentration of the counter ions on the

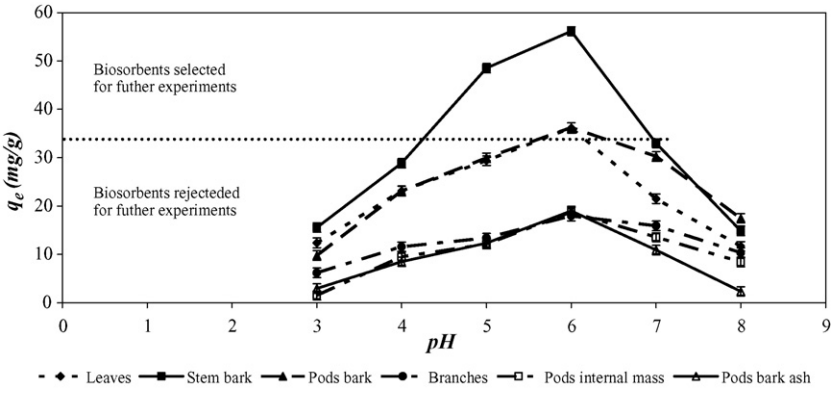

Fig. 1. Effect of pH on the biosorption of Ni(II) by *C. fistula* biomass.

functional groups of the biomass cell walls, so pH is an important parameter on biosorption of metal ions from aqueous solutions. *C. fistula* presents a high content of ionizable groups such as carboxyl, aldehydic, ketonic, alcoholic, and amino groups. Presence of these groups was confirmed by FTIR spectroscopic analysis (discussed in Section 3.11). As shown in Fig. 1 the uptake of free ionic Ni(II) depends on pH, increasing with the increase in pH from 3.0 to 6.0 and then decreasing in the range 7.0–8.0. Similar results have been reported in literature for different metal-biomass systems [5–8]. At pH values lower than 6.0, Ni(II) removal was partially inhibited, possibly as a result of the competition between hydrogen and Ni(II) ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. At pH value above isoelectric point, there is a net negative charge on the biomass cells and the ionic state of ligands is such to promote the uptake of metal ions. As the pH lowered, however, the over all surface charge on the biomass cells become positive, which will inhibit the approach of positively charge metal cations. It is likely that protons will then compete with metal ions for ligands and thereby decrease the interaction of metal ions with the cells [9]. The ionization constants of a number of carboxylic acids are above pH 5, so a biomass having carboxylic functional group has positive charge above this pH and negative charge below this pH. The intensity of induced charge on carboxylic group depends upon how lower or higher is the pH. At lower pH values carboxyl groups retained their protons reducing the possibility of binding to any positively charged ions. Whereas at higher pHs above 5, the carboxylate ($-COO^-$) ligands attract positively charged metal ions and binding occurs, indicating that the major process is an ion exchange mechanism that involve an electrostatic interaction between the positively charged groups in cell walls and metallic cations [9–11]. Therefore further experiments were carried out with initial pH value 6 since $NiSO_4$ hydrolyzes into insoluble $Ni(OH)_2$, which starts precipitating from solutions at higher pH values, making true sorption studies impossible, similar results have been reported for metal biosorption studies in literature [9–13]. One of the most important aspects that have to be evaluated in a biosorption study is the selection of suitable part of biomass able to sequester the largest amounts of metal of interest from its solution. One possible preliminary test that may be used to perform this selection is the effect of pH on metal uptake capacity of biomass (Fig. 1). This experimental procedure has been also used in other works [14–16] and it can give a rough characterization of the selected biomass mainly when ionic exchange is the prevalent mechanism in the removal of heavy metals from their solutions [17]. Keeping previous studies in mind leaves, stem bark and pods bark of *C. fistula* biomass having q_e more than 35 mg/g at pH 6 were selected for further biosorption studies.

3.2. Effect of biosorbent dose

Biosorbent dose is a significant factor to be considered for effective metal sorption. It determines the sorbent–sorbate equilibrium of the system [18]. The dependence of Ni(II) sorption on dose was studied by varying the amount of *C. fistula* biomass from 0.05 to 0.3 g/100 mL, while keeping other parameters (pH, sorbent particle size, initial metal concentration and contact time) constant. An increase in the amount of *C. fistula* biomass caused the sorptive capacity, q_e, to be reduced (Fig. 2). This effect was also reported in literature for biosorption phenomenon of heavy metals [12,19]. The effect was most marked with the sorption of Ni(II) by stem bark. In looking at this effect, it was pertinent to examine the data in relation to the theoretical maximum, assuming that all of the metal ions would be sorbed onto the *C. fistula* biomass. The results demonstrated that the biomass concentration strongly affected the amount of metal removed from aqueous solutions. Moreover, as the biomass concentration rises, the maximum biosorption capacity drops, indicating poorer biomass utilization (lower efficiency). The results can be explained as a consequence of a partial aggregation, which occurs at high biomass concentration giving rise a decrease of active sites [11,19–21].

3.3. Effect of particle size of biosorbent

The effect of altering the sorbents particle size on the q_e (mg/g) showed that, there was a more dominant removal of Ni(II) by the smaller particles (Fig. 3). This was most probably due to the increase in the total surface area, which provided more sorption sites for the metal ions. At smaller particles the removal efficiency for pods bark was maximum among three

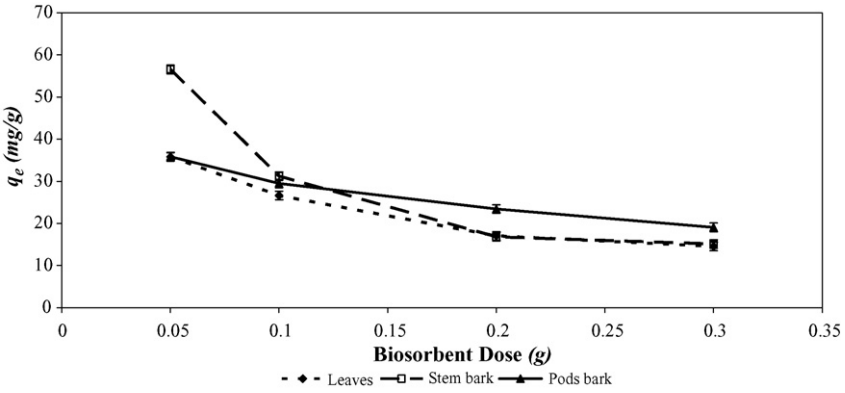

Fig. 2. Effect of sorbent dose on the biosorption of Ni(II) by *C. fistula* biomass.

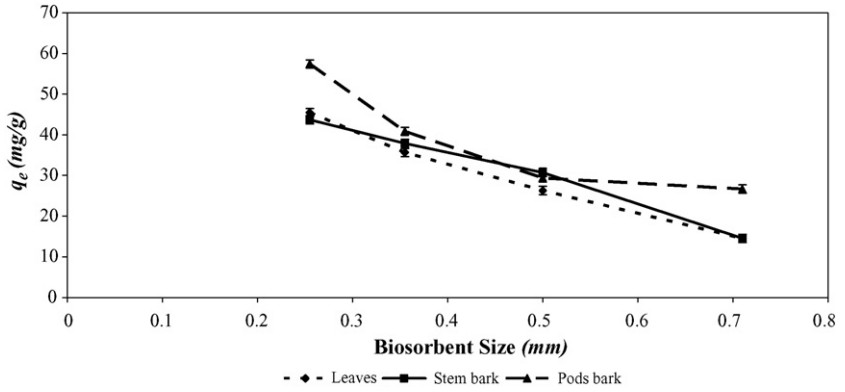

Fig. 3. Effect of different sorbent particle size on biosorption of Ni(II) by *C. fistula* biomass.

tested biosorbents while became almost the same for remaining two. This was not the case with the sorption of Ni(II) for the larger particle size. The enhanced removal of sorbate by smaller particles has been noted previously during a study for the color removal by silica [22].

3.4. Effect of initial metal concentration

The rate of adsorption is a function of the initial concentration of metal ions, which makes it an important factor to be considered for effective biosorption [18]. In general, the data revealed that sorption capacity increased with increase in initial metal ion concentration for Ni(II) on sorbents (Fig. 4). This sorption characteristic represented that surface saturation was dependent on the initial metal ion concentrations. At low concentrations, adsorption sites took up the available metal more quickly. However, at higher concentrations, metal ions need to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate [23].

3.5. Equilibrium modeling

Modeling the equilibrium data is fundamental for the industrial application of biosorption since it gives information for

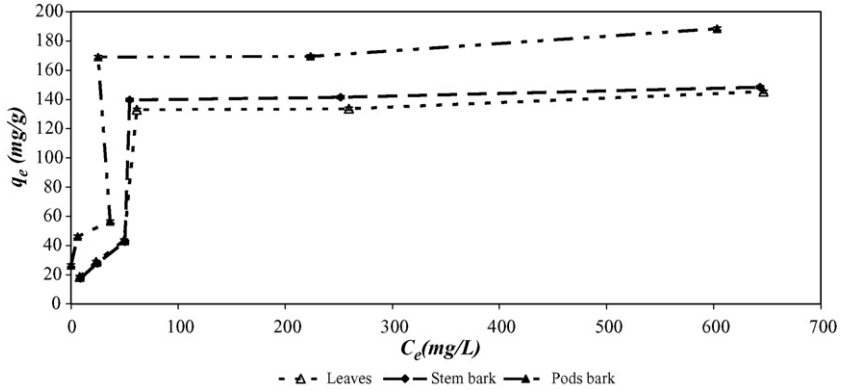

Fig. 4. Effect of different initial metal concentration on biosorption of Ni(II) by *C. fistula* biomass.

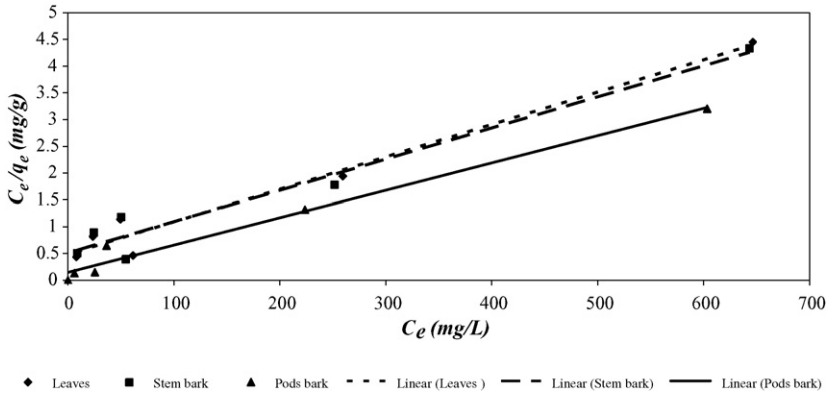

Fig. 5. Linearized Langmuir isotherm plot for biosorption of Ni(II) by *C. fistula* biomass.

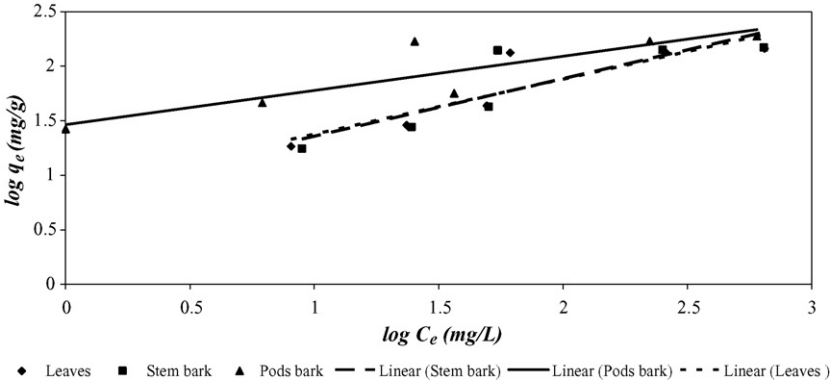

Fig. 6. Linearized Freundlich isotherm plot for biosorption of Ni(II) by *C. fistula* biomass.

comparison among different biomaterials under different operational conditions, designing and optimizing operating procedures [24]. To examine the relationship between sorbed (q_e) and aqueous concentrations (C_e) at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most widely used. The Langmuir and Freundlich adsorption constants evaluated from the isotherms with correlation coefficients are presented in Table 1. To get the equilibrium data, initial Ni(II) concentrations were varied while the biomass weight in each sample was kept constant. Twenty-four hours of equilibrium periods for sorption experiments were used to ensure equilibrium conditions. This time was chosen considering the results of kinetics of metal removal found in literature. The Langmuir (Fig. 5) model better represented the sorption process, in comparison to the model of Freundlich (Fig. 6) due to high value of correlation coefficient (Table 1). The Langmuir parameters can be determined from a linearized form of equation (Eq. (2)), represented by:

$$C_e/q_e = 1/X_m K_L + C_e/X_m \quad (2)$$

where q_e is the metal ion sorbed (mg/g), C_e the equilibrium concentration of metal ion solution, X_m and K_L are Langmuir constants. Sorption of Ni(II) by all biosorbents followed well Langmuir isotherm, which represents that monolayer of sorbate is formed on each biosorbent. Adsorption-partition constants were determined for Ni(II) using the following log form of the Freundlich isotherm (Eq. (3)):

$$\log q_e = (1/n)\log C_e + \log K \quad (3)$$

where q_e is the metal ion sorbed (mg/g), C_e the equilibrium concentration of metal ion solution, mg/L, K and n are Freundlich constants. The constants K and $1/n$ were determined by linear regression from the plot of $\log q_e$ against $\log C_e$. K is a

Table 1
Langmuir and Freundlich isotherm parameters for Ni(II) uptake by *C. fistula* biomass

Biosorbent	Langmuir isotherm parameters			Experimental value	Freundlich isotherm parameters			
	X_m (q_{max}) (mg/g)	K_L (L/mg)	R^2	q_{max} (mg/g)	q_{max} (mg/g)	K (mg/g)	R^2	$1/n$
Leaves	163.93	0.0126	0.9707	145.29	149.94	7.44	0.7890	0.5045
Stem bark	172.41	0.0020	0.9595	148.40	169.43	6.78	0.8317	0.5272
Pods bark	196.07	0.0345	0.9813	188.40	173.44	29.13	0.7651	0.3132

measure of the degree or strength of adsorption, while $1/n$ is used as an indication of whether adsorption remains constant (at $1/n$ 1= 1) or decreases with increasing adsorbate concentrations (with $1/n \neq 1$). The q_{max} value is the maximum value of q_e, which is important to identify which biosorbent has the highest metal uptake capacity and as such useful in scale-up considerations. The magnitude of the experimental q_{max} for *C. fistula* biomass were found to span to a range of values (145.29–188.40 mg/g), its comparison with theoretically calculated q_{max} values from Langmuir and Freundlich isotherm models is presented in Table 1. In present study maximum sorptive capacity was observed for *C. fistula* pods bark suggesting that it is a potential biosorbent for removal of Ni(II) from industrial wastewater as compared to other tested biosorbents.

3.6. Separation factor (R_L)

The shape of the Langmuir isotherm can be used to predict whether a sorption system is favorable or unfavorable in a batch adsorption process [13]. Accordingly, the essential features of the Langmuir isotherm was expressed in terms of a dimensionless constant called the equilibrium parameter, R_L, which is defined by the following relationship (Eq. (4)):

$$R_L = 1/(1 + K_L C_i) \quad (4)$$

where R_L is the a dimensionless equilibrium parameter or separation factor, K_L the constant from Langmuir equation and C_i the initial metal ion concentration of 100 mg/L. The parameter, R_L, indicates the shape of the isotherm and nature of the sorption process. R_L value between 0 and 1 represents favorable isotherm. The values of R_L for Ni(II) for *C. fistula* biomass was calculated from Eq. (4) and plotted against initial metal ion concentration. The data showed that, the sorption of Ni(II) on *C. fistula* biomass increased as the initial metal ion concentration increased from 25 to 800 mg/L, indicating that adsorption is even favorable for the higher initial metal ion concentrations (Fig. 7). The sorption process was favorable for Ni(II) removal at all concentrations investigated. According to this classification, removal ability tends to be in the order:

stem bark > leaves > pods bark

Above given order illustrates that initially equilibrium for Ni(II) uptake was more favorable for stem bark as compared to leaves and pods bark (Fig. 7), although its sorption capacity lies intermediate between leaves and pods bark (Table 1). The trend presented by R_L in Fig. 7 is also providing information that the *C. fistula* biomass is more effective and excellent adsorbent for Ni(II) at lower metal concentrations (up to 200 mg/L).

3.7. Surface coverage values (θ)

To account for the adsorption behavior of the Ni(II) on the *C. fistula* biomass, the Langmuir type equation related to surface coverage was used. The equation is expressed as follows (Eq. (5)):

$$KC_i = \theta/1 - \theta \quad (5)$$

where K is the adsorption coefficient, C_i the initial concentration and θ the surface coverage.

The fraction of biomass surface covered by metal ion was studied by plotting the surface coverage values (θ) against Ni(II) concentration. The data is presented in Fig. 8. The figure shows that, increase in initial metal ion concentration for *C. fistula* biomass increases the surface coverage on the biomass until the surface is nearly fully covered with a monomolecular layer. Further examination of Fig. 8 reveals that the surface coverage ceases to vary significantly with concentration of Ni(II) at higher levels and the reaction rate becomes independent of the Ni(II) concentration. Surface coverage value for different sorbents of *C. fistula* biomass was in following order:

pods bark > leaves > stem bark

Surface coverage value indicated that pods bark was more effective in uptake of Ni(II) from aqueous solutions at all initial concentrations as compared to other parts of *C. fistula* biomass, evaluated in study.

3.8. Distribution coefficient (D)

The relativeness of the biomass in removing the Ni(II) from aqueous solution was evaluated in terms of the distribution

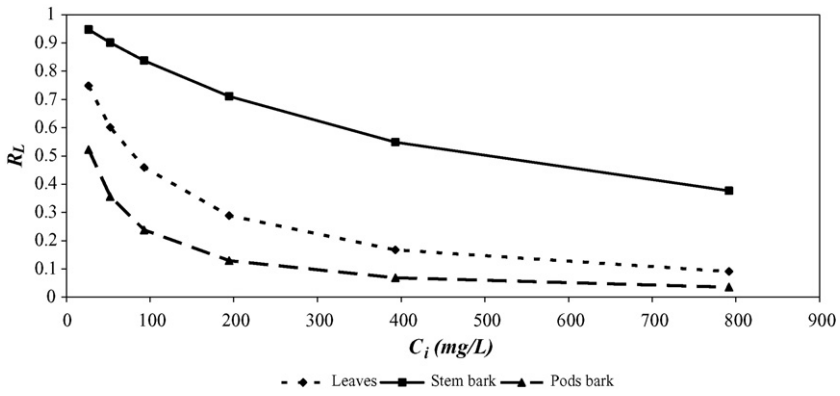

Fig. 7. Calculated separation factor (R_L) profile for biosorption of Ni(II) as function of initial metal concentration by *C. fistula* biomass.

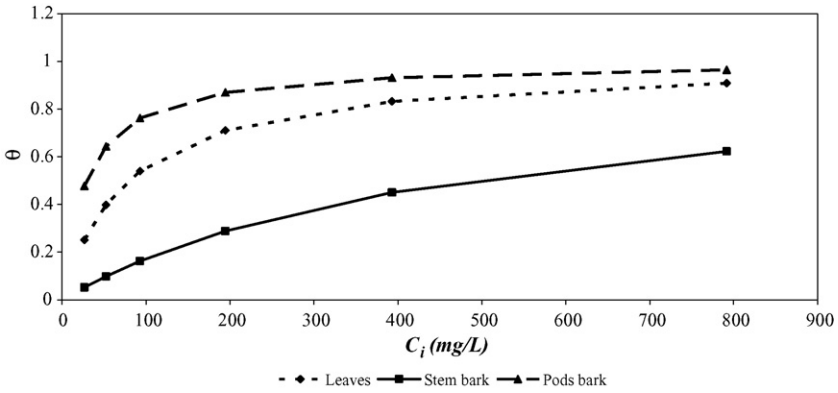

Fig. 8. A plot of surface coverage (θ) against concentration of Ni(II) (mg/L) for *C. fistula* biomass.

coefficient, D, which can be defined as "the ratio of the metal ion concentration in the adsorbent phase, to the concentration in the aqueous phase, M^{n+} sol". Table 2 shows the value of D for a range of Ni(II) concentrations. The results show that the concentration of Ni(II) at the sorbent–water interface is higher than the concentration in the continuous aqueous phase. This suggests that the biomass is effective in the removal of Ni(II) from aqueous systems. The nature of the sorbed species may be deduced from the fact that the metal ion is divalent. This indicates that two molecules of biomass were associated with Ni(II). Hence the composition of the sorbed complex and the probable mechanism may be given as follows (Eq. (6)):

$$M^{2+} + 2B - OH \leftrightarrow M(BO)_2 + 2H^+ \quad (6)$$

where M^{2+} is divalent metal ion, B is biomass molecule, OH is hydroxyl group and H^+ is proton.

3.9. Gibbs free energy (ΔG°_{ads})

The thermodynamics of the exchange process depends on the number of water molecules (n) replaced by the Ni(II). Since the most probable value of n is 2, the apparent Gibbs free energy of the adsorption processes (ΔG°_{ads}) corresponding to Ni(II) on the biomass are evaluated using the Bockris–Swinkel's adsorption isotherm equation as reported previously [25] with $n=2$ and θ-values. The equation is expressed as (Eq. (7)):

$$\Delta G^{\circ}_{ads} = -2.303RT \log \times \left[\{55.4\theta/C_i(1-\theta)\}\left\{\theta + \frac{n(1-\theta)^{n-1}}{n^n}\right\}\right] \quad (7)$$

where C_i is the initial concentration of Ni(II) ion in the solution. The values of ΔG°_{ads} were then evaluated with $n=2$ at various initial metal ion concentrations. The data is documented in Table 2. The negative values of ΔG° indicate the spontaneous adsorption nature of Ni(II) ion by the *C. fistula* adsorbents and suggest strong adsorption of Ni(II) ions on the biomass surface. In general, it is of note that up to −20 kJ/mol are consistent with electrostatic interaction between charged molecules and surface indicative of physisorption while more negative than −40 kJ/mol involve chemisorption, whether values between −20 to −40 kJ/mol indicate that both physisorption and chemisorption were responsible for adsorption. The order of magnitude of the values indicates a physical plus chemical mechanism for the adsorption of Ni(II) ions on to the *C. fistula* biomass except for *C. fistula* stem bark which followed physisorption at higher concentrations (400 and 800 mg/L).

Table 2
Distribution ratios, D, and apparent Gibbs free energy ΔG°_{ads} (kJ mol^{-1}) of Ni(II) between *C. fistula* biomass and aqueous phase

C_i (mg/L)	Leaves		Stem bark		Pods bark	
	D	ΔG°_{ads}	D	ΔG°_{ads}	D	ΔG°_{ads}
25	0.695	−24.686	0.663	−20.419	1.000	−26.865
50	0.550	−24.464	0.529	−20.359	0.881	−26.574
100	0.467	−24.230	0.458	−20.272	0.606	−26.343
200	0.683	−23.917	0.718	−20.093	0.869	−26.113
400	0.339	−23.667	0.359	−19.842	0.431	−25.973
800	0.183	−23.496	0.187	−19.545	0.237	−25.894

3.10. Biosorption kinetics of Ni(II)

In order to investigate the mechanism of biosorption and potential rate controlling step, such as mass transport and chemical reaction processes, kinetic models have been used to test the experimental data. Moreover, information on the kinetics of metal uptake is required for selecting of optimum conditions for full scale batch metal removal processes [26]. A kinetic study with different time intervals with fixed metal and biosorbent concentration was performed and the obtained results are presented Table 3. In first few minutes biosorption was sharp probably due to decrease in pH of solution because of proton released by the biosorbent. The rapid initial sorption was likely due to extra cellular binding and slow sorption phase likely resulted from intracellular binding. Maximum biosorption of Ni(II) occurred on pods bark.

Table 3
Sorption kinetics of Ni(II) onto *C. fistula* biomass

Biosorbent	t (min)	C_i (mg/L)	C_e (mg/L)	q (mg/g)	% removal
Leaves	15	197.44 ± 0.05	112.47 ± 0.01	84.97	43.03
	30		101.14 ± 0.05	96.30	48.77
	60		87.74 ± 0.04	109.70	55.56
	120		83.59 ± 0.06	113.85	57.66
	240		73.58 ± 0.04	123.86	62.73
	480		60.49 ± 0.07	136.95	69.36
	720		59.38 ± 0.08	138.06	69.92
	1440		63.58 ± 0.01	133.86	67.79
Stem bark	15	197.17 ± 0.09	126.76 ± 0.02	70.41	35.71
	30		115.28 ± 0.01	81.89	41.53
	60		97.89 ± 0.01	99.28	50.35
	120		96.47 ± 0.01	100.70	51.07
	240		87.6 ± 0.03	109.52	55.54
	480		73.49 ± 0.05	123.68	62.72
	720		72.95 ± 0.04	124.22	63.00
	1440		57.86 ± 0.01	139.31	70.65
Pods bark	15	197.56 ± 0.08	125.6 ± 0.02	71.96	36.42
	30		100.23 ± 0.04	97.33	49.26
	60		99.65 ± 0.05	97.91	49.55
	120		87.29 ± 0.01	110.27	55.81
	240		81.11 ± 0.02	116.45	58.94
	480		72.37 ± 0.07	125.19	63.36
	720		59.38 ± 0.08	138.18	69.94
	1440		28.36 ± 0.04	169.20	85.64

Kinetics of adsorption by any biological material has been widely tested by the first order expression given by Lagergren and pseudo second order approach (Figs. 9 and 10) [23,27,28]. The first order Lagergren equation (Eq. (8)) is [28]:

$$\log(q_e - q) = [\log q_e - \{(k_{1,ads}t)/2.303\}] \quad (8)$$

The pseudo second order equation (Eq. (9)) is [24];

$$t/q = 1/k_{2,ads}q_e^2 + t/q_t \quad (9)$$

where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t the mass of metal at time t (min), $K_{1,ads}$ the first order reaction rate constant of adsorption (per min), $K_{2,ads}$ the pseudo second order rate constant of adsorption (mg/g min). A comparison between Lagergren pseudo first order and to pseudo second order kinetic models is tabulated in Table 4. The Lagergren first order rate constant ($k_{1,ads}$) and q_e determined from the model indicate that this model failed to estimate q_e since the experimental values of q_e differed from those estimated. The coefficients of correlation for the second order kinetic model were approximately equal to one at given temperature (30 °C in present case) and the estimated values of q_e also agreed with the experimental ones. Both facts suggest that the sorption of Ni(II) ions followed the second order kinetic model which relies on the assumption that biosorption may be the rate-limiting step. The obtained kinetic information has a significant practical value for technological applications, since kinetic modeling successfully replaces time and material consuming experiments, necessary for process equipment design [26].

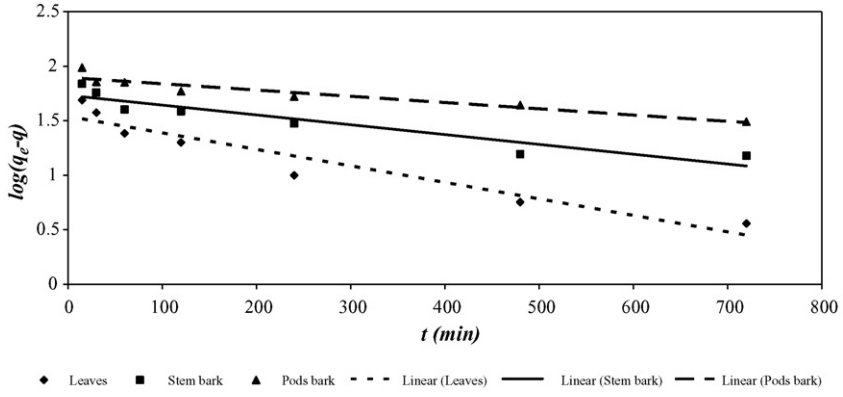

Fig. 9. Pseudo first order (Lagergren model) sorption kinetics plot of Ni(II) onto *C. fistula* biomass.

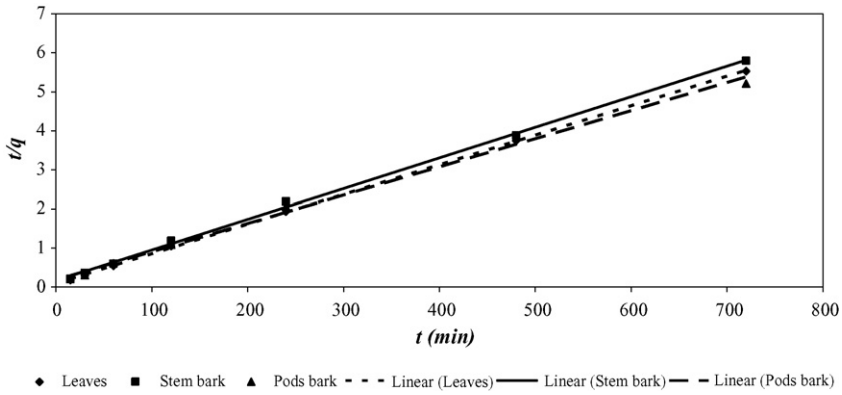

Fig. 10. Pseudo second order sorption kinetics plot of Ni(II) onto *C. fistula* biomass.

Table 4
Comparison between adsorption rate constants, q_e estimated and coefficient of correlation associated to the Lagergren pseudo first order and to pseudo second order kinetic models

Biosorbent	Pseudo first order kinetic model			Experimental	Pseudo second order kinetic model			
	q_e (mg/g)	$K_{1,ads}$ (min^{-1})	R^2	q (mg/g)	q_e (mg/g)	$K_{2,ads}$ (g/mg min)	h (mg/g min)	R^2
Leaves	34.64	6.51×10^{-4}	0.9162	145.29	135.13	4.29×10^{-4}	7.836	0.9998
Stem bark	54.1	3.90×10^{-4}	0.8826	148.40	140.84	1.67×10^{-4}	3.330	0.9963
Pods bark	78.90	2.60×10^{-4}	0.8995	188.40	169.49	8.14×10^{-5}	2.340	0.9828

3.11. Fourier transform infrared (FTIR) studies

The FTIR spectroscopic technique is an important tool to identify some characteristic functional groups, which are capable of adsorbing metal ions [29,30]. Pods bark is termed as more suitable biosorbent for Ni(II) uptake due to its high sorption capacity, in comparison to leaves and stem bark. The FTIR spectra of *C. fistula* (pods bark) biomass before and after Ni(II) sorption is shown in Fig. 11. The spectra indicate the presence of carboxyl groups. Carboxylic acids display a broad, intense –OH stretching absorption from 3300 to 2500 cm^{-1}, although the bands are dominated by the –OH stretch due to bonded water. Weaker –CH stretch bands are superimposed onto the side of the broad –OH band at 3000–2800 cm^{-1}. The bands observed at about 2851.45 cm^{-1} could be assigned to the –CH stretch. The peaks located at 1632–1623 cm^{-1} are characteristics of carbonyl group stretching from aldehydes and ketones. The spectral analysis before and after metal binding indicated that the –NH was

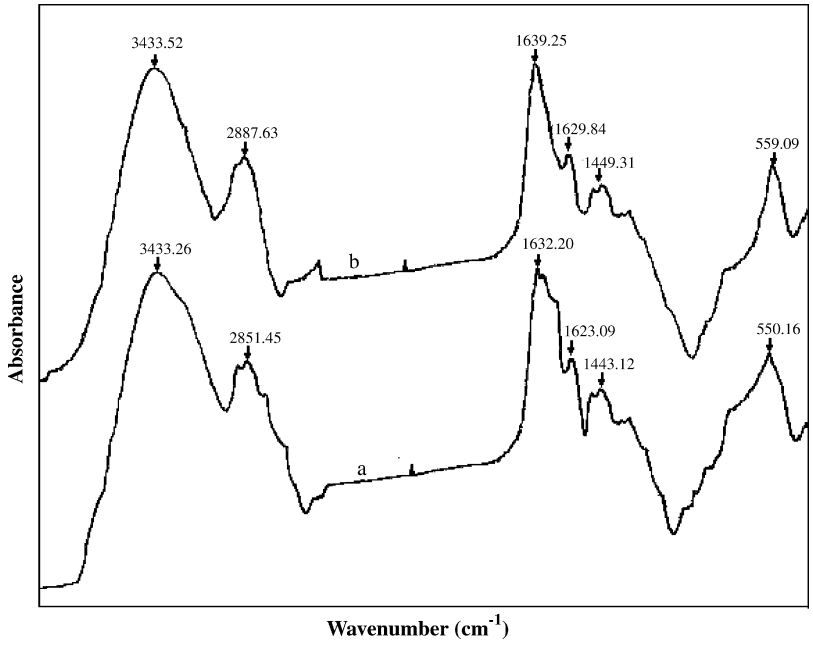

Fig. 11. FTIR spectra of *C. fistula* (pods bark) biomass: (a) before and (b) after Ni(II) sorption.

Table 5
Comparison of *C. fistula* with previously used biosorbents for the removal of Ni(II) from aqueous effluents

Biosorbent	q_{max} (mg/g)	Reference
Cassia fistula (Pods bark)	188.40	Present study
Saccharomyces cerevisiae	0.46	[31]
Phanerochaete chrysosporium	0.39	
Rice bran	100.00	[32]
Quercus ilex L. (Stem)	0.58	
Quercus ilex L. (Leaf)	0.62	[33]
Quercus ilex L. (Root)	0.67	
Cork biomass	10.10	[34]
Polyporous versicolor	57.00	[35]

also involved in metal biosorption. There was clear band shift and intensity decrease of the –NH band at 1443.12 cm^{-1}. The absorbance of the peaks in the metal loaded sample was substantially lower than those in the raw sample. This indicated that bond stretching occurred to a lesser degree due to the exchange of hydrogen ions with Ni(II), and subsequently peak absorbance was attenuated.

4. Conclusions

C. fistula biomass was selected for studying biosorption due to its originality as well as to access the possibility of utilizing a waste biomass to eradicate the metal pollution.

The following conclusions can be with drawn from present study:

- The harvesting of the *C. fistula* biomass is a relatively simple procedure, and can be obtained without excessive cost. Thus, non-living biomass of *C. fistula* (pods bark) presents sufficient biosorption capacity for Ni(II) ions, in comparison with other types (sources) of biosorbent materials found in literature (Table 5).
- The obtained results show that pH, biomass size, biomass dose, initial metal concentration and contact time highly affect the overall metal uptake capacity of biosorbent.
- The present results demonstrate that the Langmuir model fits better than the Freundlich model for the adsorption equilibrium data in the examined concentration range.
- The suitability of a pseudo second order chemical reaction for the sorption of Ni(II) ions onto this biomass was apparent, as this kinetic model describes adequately the largest part of the process.
- FTIR spectroscopic analysis described well metal uptake by functional groups in the cell wall of the *C. fistula* (pods bark) biomass. The functional groups involved in Ni(II) biosorption included carboxyl, carbonyl, alcoholic, and amino groups.

Acknowledgements

Authors are thankful to Prof. Dr. Munir Ahmad Sheikh (Chairman, Department of Chemistry, University of Agriculture, Faisalabad, Pakistan) for supporting this work.

References

[1] B. Volesky, Biosorption and Biosorbents. Biosorption of Heavy Metals, CRC Press, Boston, USA, 1990, pp. 3–5.
[2] R.H. Crist, K. Oberholser, N. Shank, M. Nguyen, Nature of bonding between metallic ions and algal cell walls, Environ. Sci. Technol. 15 (1981) 1212–1217.
[3] T.A. Davis, B. Volesky, R.H.S.F. Vieira, *Sargassum* seaweed as biosorbent for heavy metals, Water Res. 34 (2000) 4270–4278.
[4] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Prog. 11 (1995) 235–250.
[5] J.T. Matheickal, Q. Yu, Biosorption of lead (II) and copper (II) from aqueous solution by pre-treated biomass of Australian marine algae, Bioresour. Technol. 69 (1999) 223–229.
[6] Y. Sag, A. Kaya, T. Kutsa, The simultaneous biosorption of Cd (II) and Zn (II) on *Rhizopus arrhizus*: application of the adsorption models, Hydrometallurgy 50 (1998) 297–314.
[7] N.C.M. Gomes, V.R. Linardi, Removal of gold, silver and copper by living and nonliving fungi from leach liquor obtained from the gold mining industry, Revista de Microbiologia. 27 (1996) 218–222.
[8] J.L. Zhou, P.L. Huang, R.G. Lin, Sorption and desorption of Cu and Cd by macroalgae and microalgae, Environ. Pollut. 101 (1998) 67–75.
[9] Y. Sag, D. Ozer, T. Kutsal, A comparative study of the biosorption of lead (II) ions to *Z. ramigera* and *R. arrhizus*, Process Biochem. 30 (1995) 169–174.
[10] M.H. Jnr,.A.I. Spiff, Studies on the effect of pH on the sorption of Pb^{2+} and Cd^{2+} ions from aqueous solutions by *Calacdium biocolor* (Wild Cocoyam) biomass, Eur. J. Biotechnol. 7 (2004) 313–323.
[11] B. Cordero, P. Loderio, R. Herrero, M.E.S. de-Vicente, Biosorption of cadmium by *Fucus spiralis*, Environ. Chem. 1 (2004) 180–187.
[12] V. Padmavathy, P. Vasudevan, S.C. Dhingra, Biosorption of Ni(II) ions on Baker's yeast, Process Biochem. 38 (2003) 1389–1395.
[13] V.J.P. Poots, J. McKay, J. Healy, Removal of basic dye from effluent using wood as an adsorbent, J. Water Pollut. Control Fed. (1978) 926–934.
[14] F. Pagnanelli, M. Pietrangeli, L. Toro, M. Trifoni, F. Veglio, Biosorption of metal ions on *Arthrobacter* sp.: biomass characterization and biosorption modeling, Environ. Sci. Technol. 34 (2000) 2773–2778.
[15] S. Schiewer, B. Volesky, Modeling of the proton-metal ion exchange in biosorption, Environ. Sci. Technol. 12 (1995) 3049–3058.
[16] F. Veglio, A. Espositob, A.P. Reverberi, Standardisation of heavy metal biosorption tests: equilibrium and modeling study, Process Biochem. 38 (2003) 953–961.
[17] F. Veglio, F. Beolchini, A. Gasbarro, Biosorption of toxic metals: an equilibrium study using free cells, Process Biochem. 32 (1997) 99–105.
[18] N. Ahalya, R.D. Kanamadi, T.V. Ramachandra, Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal gram (*Cicer arientinum*), Eur. J. Biotechnol. 8 (2005) 258–264.
[19] S.Y. Quek, D.A.J. Wase1, C.F. Forster, The use of sago waste for the sorption of lead and copper, Water S. A. 24 (1998) 251–256.
[20] S.Y. Quek, B. Al-Duri, D.A.J. Wase, C.F. Forster, Coir as a biosorbent of copper and lead, Process Safety Environ. Protect. 76 (1998) 50–54.
[21] P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue, E.S. Upatham, Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*), Environ. Pollut. 125 (2003) 385–392.
[22] G. McKay, M.S. Otterburn, A.G. Sweeney, The removal of color from effluent using various adsorbents—III. Silica: rate processes, Water Res. 14 (1980) 15–20.
[23] M.H. Jnr, A.I. Spiff, Effect of metal ion concentration on the biosorption of Pb^{2+} and Cd^{2+} by *Caladium bicolor* (wild cocoyam), Afr. J. Biotechnol. 4 (2004) 191–196.
[24] B. Benguella, H. Benaissa, Cadmium removal from aqueous solution by chitin: kinetic and equilibrium studies, Water Res. 36 (2002) 2463–2474.
[25] H.B. Rudresh, S.M. Mayanna, Adsorption of *n*-decylamine on zinc from acidic solution, J. Environ. Sci. Technol. 122 (1977) 251–256.
[26] M.X. Loukidou, A.I. Zouboulis, T.D. Karapantsios, K.A. Matis, Equilibrium and kinetic modeling of chromium (VI) biosorption by *Aeromonas caviae*, Colloid Surf. A: Physicochem. Eng. Aspects 242 (2004) 93–104.

[27] C.W. Cheung, C.F. Porter, G. McKay, Sorption kinetics for the removal of copper and zinc from effluents using bone char, Purif. Technol. 19 (1997) 55–64.
[28] Y.S. Ho, D.A.J. Wase, C.F. Forster, Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat, Environ. Technol. 17 (1996) 71–77.
[29] P.X. Sheng, Y.P. Ting, J.P. Chen, L. Hong, Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, J. Colloid Interface Sci. 275 (2004) 131–141.
[30] C.R.T. Tarley, M.A.Z. Arruda, Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous effluents, Chemosphere 54 (2004) 987–995.
[31] St. Mihova, T. Godjevargova, Biosorption of heavy metals from aqueous solutions. http://www.ejournalistnet.com Issue 1; 2001.
[32] M.A. Farajzadeh, M.R. Vardast, Rice bran as an excellent sorbent for heavy metals from aqueous media, optimization of conditions, J. Chin. Chem. Soc. 50 (2003) 245–250.
[33] M.N.V. Prasad, H. Freitas, Removal of toxic metals from solution by leaf, stem and root phytomass of *Quercus ilex* L. (Holly oak), Environ. Pollut. 110 (2000) 277–283.
[34] N. Chubar, J.R. Carvaalho, M.J.N. Correia, Cork biomass as biosorbent for Cu (II), Zn (II) and Ni (II), Colloid Surf. 230 (2004) 57–65.
[35] F.B.D. Dilek, A. Erbay, U. Yetis, Ni (II) biosorption by *Polyporous versicolor*, Process Biochem. 37 (2002) 723–726.