Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1094424

57 (2016) 18490–18499
August

Taylor & Francis
Taylor & Francis Group

Biosorption performance of the lichen biomass (*Diploicia canescens*) for the removal of nickel from aqueous solutions

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Received 4 April 2015; Accepted 1 September 2015

ABSTRACT

This study was focused on lichen biomass *Diploicia canescens* as an alternative biosorbent for the removal of nickel from aqueous solution. Experiments are carried out as a function of solution pH, biosorbent dosage, contact time, and temperature. The equilibrium data were applied to the Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models. The maximum Ni(II) sorption capacity of *D. canescens* was found to be 66.7 mg/g at pH 5, biomass concentration 4 g/L, contact time 60 min, and temperature 20˚C. From the D–R isotherm model, the mean free energy was calculated as 11.2 kJ/mol, indicating that the biosorption of Ni(II) ions was taken place by chemical ion exchange. The biosorption kinetics were best described by the pseudo-second-order model. The thermodynamic parameters showed that the biosorption process was feasible, spontaneous, and exothermic. FTIR and EDAX analysis revealed that the whole biosorption process is mainly dominated by ion exchange mechanism, accompanied by a certain amount of surface complexation.

Keywords: *Diploicia canescens*; Biosorption; Kinetic; Isotherm; FTIR and EDAX analysis; Thermodynamic; Nickel(II)

1. Introduction

Rapid industrialization has accentuated environmental pollution problems causing the deterioration of several ecosystems with the accumulation of many pollutants, such as toxic metals. Heavy metal pollution represents an important problem due to its toxic effect and accumulation throughout the food chain leading to serious ecological and health problems.

Nickel receives wide attention by environmentalists as one of the most toxic heavy metals.

The main anthropogenic pathway through which Ni(II) enters the water bodies is via wastes from industrial processes such as electroplating, plastics manufacturing, metal finishing, nickel–cadmium batteries, fertilizers, pigments, mining, and metallurgical operations [1]. Nickel toxicity may be observed by a variety of syndromes and effects including renal dysfunction, gastrointestinal distress, e.g., nausea, vomiting, diarrhea, pulmonary fibrosis, and skin dermatitis [2–4]. Because of the toxicity and bioaccumulation, Ni(II) is considered as a priority pollutant by the US Environmental Protection Agency. The maximum permissible concentration of nickel in drinking water is 0.02 mg/L according to a US-EPA report [5].

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In view of the toxicity and to meet regulatory safe discharge standards, it is essential to remove nickel from wastewaters/effluents before it is released into the environment.

Conventional wastewater treatments such as chemical precipitation, ion exchange, reverse osmosis, coagulation–precipitation, electrochemical operation, and filtration have several disadvantages including high-energy requirements, incomplete metal removal, and high capital investment and running costs [6,7]. Hence, there is a crucial need for the development of a method that is not only cost-effective, but can also be easily implemented.

In this endeavor, biosorption has emerged as an alternative and sustainable strategy for cleaning up water. Biosorption can be defined as a property of certain types of inactive, dead microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions. It can be considered a collective term for a number of passive, metabolism independent, accumulation processes and may include physical and/or chemical adsorption, ion exchange, coordination, complexation, chelation, and microprecipitation [8,9]. The main advantages of this technique are the reusability of biomaterial, low operating cost, high adsorption capacity, short operation time, and no production of secondary compounds which might be toxic [10].

Various types of biomass have been used as the biosorbent for the removal of toxic metals. Among these, lichens are chosen in this study because of their abundant availability, low cost, and high metal uptake capacity. Lichens are symbiotic organisms built from fungi and a photosynthetic partner, which is either alga or *Cyanobacterium* [11,12]. They usually grow on rocks, non-fertile ground, and as epiphytes on trees and leaves [13]. Lichens are considered as indicator of environmental quality due to their ability to accumulate and retain a variety of contaminants, particularly heavy metals. Besides, many kinds are used for human nutrition, animal nutrition, the production of colors, perfumes, alcohols, and in the medical industry [14]. *Diploicia canescens* is crustaceous lichen usually found in sheltered locations, but exposed to sunlight, such as under the overhang of a cliff. It grows on trees and stone, being found more frequently on trees. It was common on Elm trees and may become common again when these trees reestablish themselves [14]. There is currently no research regarding the biosorption potential of this biomass.

The goal of our study was to assess the nickel(II) biosorption potential of *D. canescens* biomass. For this purpose, biosorption process was characterized under different operating conditions such as initial pH, sorbent dosage, contact time, and temperature. Experimental data as functions of temperature and time were evaluated with the pseudo-first-order and the pseudo-second-order kinetic models. The Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models were applied to the equilibrium data. The desorption performance and regeneration ability of the biosorbent were studied. IR spectral analysis and energy dispersive spectroscopy (EDS) were also employed to understand the mode of metal–biomass interaction.

2. Materials and methods

2.1. Materials

The lichen biomass of *D. canescens* was harvested from Elm trees grown in the forest of Belgorod (southwest of Moscow) in June–July of 2013. The samples were washed with deionized water and dried for 48 h in an oven at 70˚C. The inactivated dried lichen biomass was chopped, sieved, and the particles with an average size of 0.6 mm were used for biosorption experiments.

2.2. Reagents and equipment

Stock metal solution at various concentrations was prepared by dissolving nickel nitrate (analytical reagent grade, Sigma-Aldrich (Ireland)). The pH of the solution was monitored in a 5500 EUTECH pH Meter using FET solid electrode calibrated with standard buffer solutions by addition of 0.1 mol/L HNO_3 and 0.1 mol/L NaOH solutions as per the required pH value. The metal concentration was measured using an atomic absorption spectrophotometer (SHIMADZU AA-680, Japan). FTIR spectroscopy was used to detect vibration frequency changes in the algal sorbent. The spectra were collected by an FTS-135 (Bio-Rad, Belgium) spectrometer within the range 400–4,000 cm^{-1} using a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample). Energy dispersive spectroscopy (EDS, OXFORD Inca 350, UK) was used to analyze the variation in chemical elemental composition of *D. canescens* surface before and after lead biosorption.

2.3. Batch biosorption experiments

The biosorption equilibrium experiments of Ni(II) were performed using a batch process to determine the amount of metal ion adsorbed by biomass samples under the effect of contact time, biosorbent dosage, pH, and temperature of adsorption medium. Necessary

amount of the dried biomass was equilibrated in a series of aqueous solutions (25 ml) placed in conical flasks containing different amounts of metal at a constant pH, which was adjusted with 0.1 M HNO_3 or 0.1 M NaOH solution at the beginning of each experiment. The flasks were shaken for the desired contact time in an electrically thermostatic reciprocating shaker (Selecta multimatic-55, Spain) at 100 rpm. The experiments were repeated at 293, 303, 313, and 323 K. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were centrifuged and the centrifugate was analyzed for metal concentration using flame AAS. The percent biosorption of metal ion was calculated as follows (Eq. (1)):

$$\text{Biosorption}\,(\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final (or equilibrium) metal concentrations, respectively.

To ensure the accuracy, reliability, and reproducibility of the collected data, the measurements were carried out in duplicated and the average values are presented. Biosorption experiments for the effect of pH were conducted using a solution having 10 mg/L of Ni(II) concentration with a biomass dosage of 4 g/L. Throughout the study, the contact time was varied from 5 to 90 min, the pH from 2 to 8, the initial metal concentration from 10 to 400 mg/L, and the biosorbent dosage from 0.1 to 20 g/L.

2.4. Desorption procedure

The desorption studies of Ni(II) from the lichen biomass of *D. canescens* were carried out using 0.5 M HNO_3 (10 mL) and 0.5 M HCl (10 mL). After the determination of metal content of the final solutions, the biomass was washed with excess of the acid solution and deionized water in order to reuse for next experiment. Consecutive sorption–desorption cycles were repeated ten times to establish the reusability of the biosorbent for Ni(II) removal from aqueous solution.

3. Results and discussion

3.1. Effect of pH solution

The pH of the adsorbate solutions is an important parameter governing adsorption on different adsorbents [15]. In principle, the dependence of metal uptake on pH can be associated with both the surface functional groups on the adsorbent as well as the metal chemistry of the solution. The effect of pH on the biosorption of Ni(II) by *D. canescens* biomass is presented in Fig. 1.

It is obvious from the figure that the biosorption yield of Ni(II) increased from 25 to 83% when the pH was raised from 2 to 4. The maximum biosorption was found to be 98% for Ni(II) ions at pH 5. At lower pH values (pH < 2), nickel removal was inhibited, possibly as a result of the competition between hydrogen and nickel 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. As the pH increased, the ligands such as carboxylate groups in *G. verrucosa* alga would be deprotonated, increasing the negative charge density on the biomass surface, raising the attraction of metallic ions with positive charge and allowing the sorption onto the cell surface [16,17]. Decrease in biosorption at higher pH (pH > 5) is not only related to the formation of soluble hydroxylated complexes of the metal ions, but also to the ionized nature of the cell wall surface of the biomass under the studied pH [18]. According to the results of this initial experiment, further biosorption investigations were performed at pH value of 5 as an optimal value.

3.2. Effect of biomass dosage

The biomass dosage is an important parameter because this factor determines the biosorption capacity of a biosorbent for a given initial concentration of the adsorbate. The effect of biomass dosage on the biosorption of Ni(II) ions was studied using different biomass dosage in the range 0.1–20 g/L (Fig. 2).

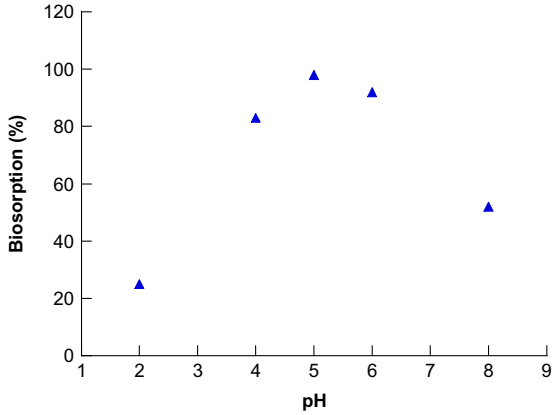

Fig. 1. Effect of pH on biosorption of Ni(II) onto *D. canescens* biomass (metal concentration: 10 mg/L, temperature: 20°C).

It is clear from the figure that the percentage of Ni^{2+} biosorption raises with increase in biomass dosage from 0.1 to 4 g/L. There is no significant increase in removal of Ni(II) when biosorbent dosage increases beyond 4 g/L. This suggests that after a certain biosorbent dosage, the maximum biosorption is attained and hence the amount of ions remains constant even with further increase in the surface area of the biosorbent, which in turn increases the number of binding sites. However, at high sorbent dosages, the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, resulting in low metal uptake [19,20]. Therefore, the optimal biomass dosage was selected as 4 g/L for the further experiments.

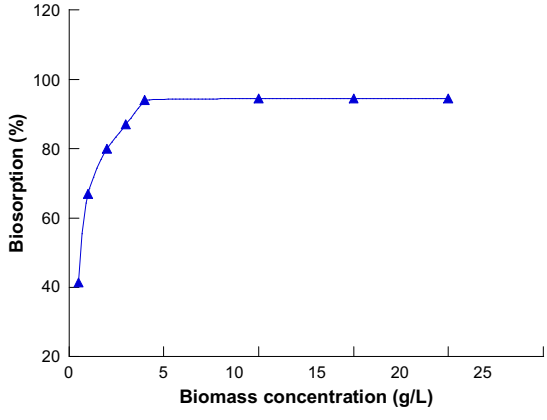

Fig. 2. Effect of biomass dosage on biosorption of Ni(II) by *D. canescens* biomass (metal concentration: 10 mg/L, pH 5, temperature: 20˚C).

3.3. Effects of contact time and temperature

Equilibrium time is another important parameter to heavy metals wastewater treatment process. The effect of contact time on the biosorption of Ni(II) from aqueous solution is shown in Fig. 3.

The result shows that the biosorption was rapid in the initial stages of the process and increased with an increase in contact time up to 60 min. After this period, the biosorption capacity of biomass did not significantly change up to 80 min. This is obvious from the fact that a large number of surface sites are available for biosorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to be occupied because of repulsion between the solute molecules of the solid and bulk phases [21,22]. Therefore, the optimum contact time was selected as 60 min for further experiments.

Fig. 3 also shows the effect of the temperature on the biosorption of Ni(II) by *D. canescens*. The biosorption yield decreased from 97 to 80% as temperature was raised from 20 to 50˚C. Therefore, the Ni^{2+} biosorption occurred exothermically. The decreasing in biosorption efficiency may be attributed to either the damage of active binding sites in the adsorbent or increasing tendency to desorb metal ions from the interface to the solution [23]. The optimum solution temperature was selected as 20˚C for further biosorption experiments.

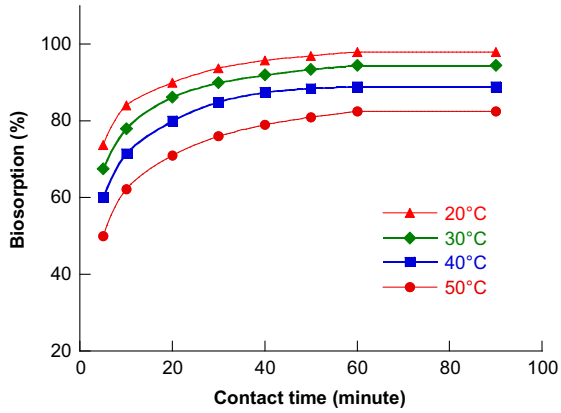

Fig. 3. Effect of contact time and temperature on biosorption of Ni(II) by *D. canescens* biomass (metal concentration: 10 mg/L, biomass dosage: 4 g/L, pH 5).

3.4. Biosorption isotherms

Analysis of equilibrium data is important for developing an equation that can be used to compare different biosorbents under different operational conditions and to design and optimize an operating procedure. To examine the relationship between sorption and aqueous concentration at equilibrium, various sorption isotherm models are widely employed for fitting the data. In this study, the equilibrium data were evaluated by three isotherms models, namely the Langmuir, Freundlich, and D–R isotherm models.

The Langmuir model is based on the assumption that the maximum sorption occurs when a saturated monolayer of solute molecules is present on the sorption surface, and the energy of sorption is constant, with no migration of sorbate molecule in the surface plane. The model can take the following linear form [24]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (2)$$

where q_e is the equilibrium metal ion concentration on the biosorbent (mg/g), C_e is the equilibrium metal ion

concentration in the solution (mg/L), q_{max} is the monolayer biosorption capacity of the biosorbent (mg/g), and K_L is the Langmuir biosorption constant (L/mg) relating the free energy of adsorption. The values of q_{max} and Langmuir constant K_L were calculated from the slope and intercept of the linear plot of C_e/q_e vs. C_e (Fig. 4).

According to this figure, the value of correlation coefficient ($R^2 = 0.999$) shows that the biosorption of nickel ions onto *D. canescens* biomass fitted well the Langmuir model indicates the formation of monolayer coverage of heavy metal ions on the outer surface of biosorbent. The maximum biosorption capacity (q_m) and Langmuir constant (K_L) were found to be 66.7 mg/g and 2.57×10^{-2}, respectively. A comparison of the sorptive capacity, $q_{max,}$ of *D. canescens* biomass with other biosorbents reported in the literature is given in Table 1. The biosorption capacity of *D. canescens* biomass obtained for nickel(II) ions in this study was found to be comparable and moderately higher than that of the majority of other biosorbents mentioned [3,25–28]. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups, and surface area. However, it can be noteworthy that the *D. canescens* biomass has important potential for the removal of Ni(II) ions from aqueous solution.

The Freundlich isotherm model assumes that the removal of metal ions occurs on a heterogeneous adsorbent surface, and the model can be applied for multilayer sorptions. This model can be written in linear form [29]:

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \quad (3)$$

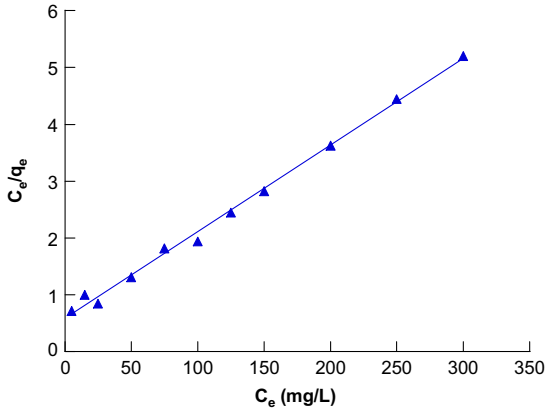

Fig. 4. Langmuir isotherm plots for biosorption of Ni(II) onto *D. canescens* biomass (biomass dosage: 4 g/L, contact time: 60 min, pH 5, temperature: 20°C).

where k_f*is* a constant related to the biosorption capacity and $1/n$ is an empirical parameter related to the biosorption intensity of the adsorbent. The Freundlich isotherm constants k_f and $1/n$ were calculated from the slopes and intercepts of the linear plot of log q_e vs. log C_e (Fig. 5).

From the plot, the values of k_f and $1/n$ were found to be 5 and 0.46, respectively. The $1/n$ values were between 0 and 1, indicating that the biosorption of Ni (II) onto *D. canescens* biomass was favorable at studied conditions. However, compared to the R^2 values, 0.96 with that obtained from the Langmuir model, it can be remarkably noted that the Langmuir isotherm model is better fitted the equilibrium data.

The empirical equation proposed by Dubinin and Radushkevich was widely used to describe the adsorption of gases and vapors on microporous solids [30]. In the case of liquid phase adsorption, several studies have shown that the adsorption energy could be estimated according to the D–R equation. This theory assumes that there is a variable adsorption potential where the free energy of adsorption is related to the degree of pore filling. The D–R isotherm equation [31] can be expressed linearly as:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (4)$$

where q_e is the amount of metal ions adsorbed on per unit weight of adsorbent (mol/L), q_m is the maximum adsorption capacity (mol/g), β is the activity coefficient related to adsorption mean free energy (mol^2/J^2), and is the Polanyi potential [$\varepsilon = RT \ln(1 + 1/C_e)$].

The equilibrium data, according to the R^2 value of 0.996, fitted well to the D–R isotherm model (Fig. 6). From the intercept of the plots, the q_m value was found to be 4.25×10^{-3} mol/g. The adsorption mean free energy (E, kJ/mol) is as follows:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (5)$$

The E (kJ/mol) value gives information about adsorption mechanism, physical, or chemical. If it lies between 8 and 16 kJ/mol, the adsorption process takes place chemically and while $E < 8$ kJ/mol, the adsorption process proceeds physically [32]. The mean adsorption energy was calculated as 11.2 kJ/mol for the biosorption of Ni(II)) ions. These results indicated that the biosorption processes of Ni(II) onto *D. canescens* biomass may be carried out via chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [33].

Table 1
Comparison of biosorption capacity of *D. canescens* biomass for Ni(II) with that of other adsorbent

Adsorbent	pH	Temperature (°C)	q_m (mg/g)	Refs.
Nettle ash	6	25	192.3	[25]
Spirulina platensis	5	20	69.04	[26]
Baker's yeast	6.75	27	8.2	[27]
Cassava peel	4.5	30	57	[28]
Clinoptilolite	5	20	39.7	[3]
Diploicia canescens	5	20	66.7	Present study

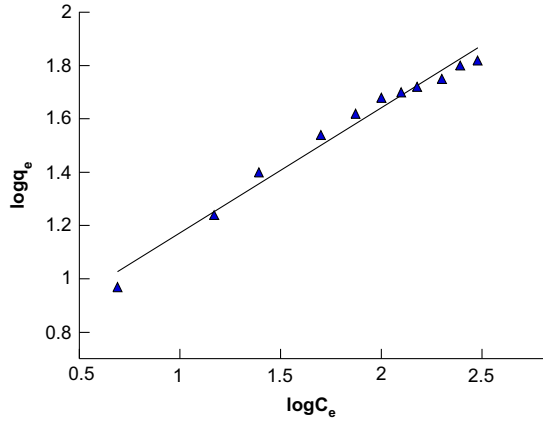

Fig. 5. Freundlich isotherm plots for biosorption of Ni(II) onto *D. canescens* biomass (biomass dosage: 4 g/L, contact time: 60 min, pH 5; temperature: 20°C).

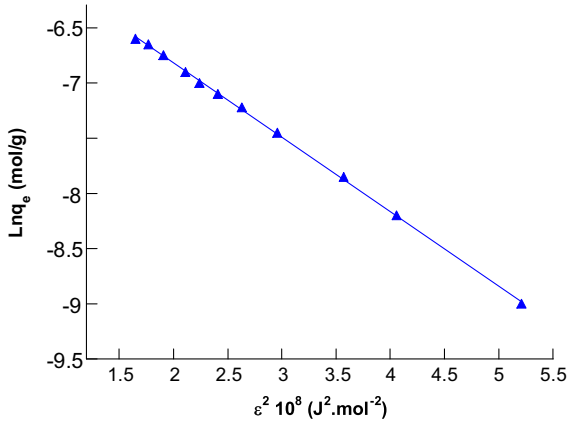

Fig. 6. D–R isotherm plots for adsorption of Ni(II) onto *D. canescens* biomass (biomass dosage 10 g/L, contact time: 60 min; pH 5; temperature: 20°C).

3.5. Biosorption kinetics study

Adsorption kinetics shows the dependence on the physical and/or chemical characteristics of the adsorbent material which also influence the adsorption mechanism. In order to investigate the mechanism of adsorption, several different models have been used at different experimental conditions for adsorption processes. In this study, the biosorption equilibrium data were analyzed using two simplest kinetic models, pseudo-first-order and pseudo-second-order model.

The pseudo-first-order kinetic model assumes that the uptake rate of heavy metal with time is directly proportional to the amount of available active site on the adsorbent surface. The linearized form of the pseudo-first-order rate equation by Lagergren [34] is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

where q_t and q_e (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively, and k_1 is the rate constant of the equation (min^{-1}). The values of the rate constant, k_1, equilibrium biosorption capacity, q_e, and the correlation coefficient, R^2, were calculated from the plots of log ($q_e - q_t$) vs. t (figure is not shown) (Table 2).

A pseudo-second-order equation based on adsorption equilibrium capacity assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. Pseudo-second-order kinetics equation as expressed by Ho and Mc Kay can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \tag{7}$$

where k_2 (g/mg/min) is the rate constant of biosorption, q_2 is maximum biosorption capacity (mg/g) [35]. The values of q_2 and k_2 can be experimentally derived from the slope and the intercept of the plot t/q_t against t at different temperatures. The linear plots of t/q_t vs. t for the pseudo-second-order model for the biosorption of Ni(II) onto *D. canescens* biomass at 20–50°C were shown in Fig. 7.

The comparison of experimental biosorption capacities and the theoretical values estimated from

Table 2
Pseudo-first-order and pseudo-second-order parameters for the biosorption of Ni(II) onto *D. canescens* biomass at different temperatures

Temperature (°C)	$q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg/min)	$q_{e,cal}$ (mg/g)	R^2
20	2.45	$4.7.10^{-2}$	1.05	0.96	0.22	2.5	0.999
30	2.36	$4.3.10^{-2}$	0.95	0.97	0.18	2.43	0.998
40	2.22	$4.1.10^{-2}$	0.93	0.96	0.15	2.32	0.997
50	2.06	$3.9.10^{-2}$	0.92	0.97	0.13	2.13	0.998

the pseudo-first and second-order rate equations are presented in Table 2. The theoretical q_e values estimated from the pseudo-first-order kinetic model gave significantly different values than that of the experimental values, and the correlation coefficients were also found to be lower. These results indicate that the pseudo-first-order kinetics model does not describe biosorption of Ni(II) onto *D. canescens* biomass. The correlation coefficients for the linear plots of t/q against t for the second-order equation are close to 1 or equal to 1. The theoretical q_e values were very close to the experimental q_e values in the case of second-order kinetic model, and the maximum deviation was 0.16% at different temperatures. In the view of these results, it can be concluded that the biosorption of Ni (II) onto *D. canescens* biomass is better described by the second-order equation suggesting that chemisorption was the rate determining step.

3.6. Thermodynamic parameters

The variation in the extent of biosorption with respect to temperature has been explained on the basis of thermodynamic parameters, viz. changes in Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). These parameters were calculated by the following equations:

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{(Van't Hoff equation)} \tag{8}$$

$$\Delta G^\circ = -RT \ln K_L \tag{9}$$

where K_L is the Langmuir constant (L/mol), T is absolute temperature (K), R is gas constant. When $\ln K_L$ vs. $1/T$ is plotted (Fig. 8), ΔH° and ΔS° values can be computed from slope and intercept of the Van't Hoff equation. The calculated parameters were given in Table 3.

The negative ΔG° values indicated thermodynamically feasible and spontaneous nature of the biosorption. It was also noted that the change of free energy decreases with increase of temperature. This could be possible because fewer active sites are available on the surface of adsorbents or because the mobility of metal ions in the solution increases with increase in temperature.

The negative value of ΔH° is indicator of exothermic nature of the biosorption and also its magnitude gives information on the type of biosorption, which can be either physical or chemical. Therefore, the ΔH° values showed that the biosorption process of Ni(II) onto *D. canescens* biomass was taken place via chemisorption [36]. The negative ΔS° value (−45.16 J/mol K) suggests a decrease in the randomness at the solid/solution interface during the biosorption process [37].

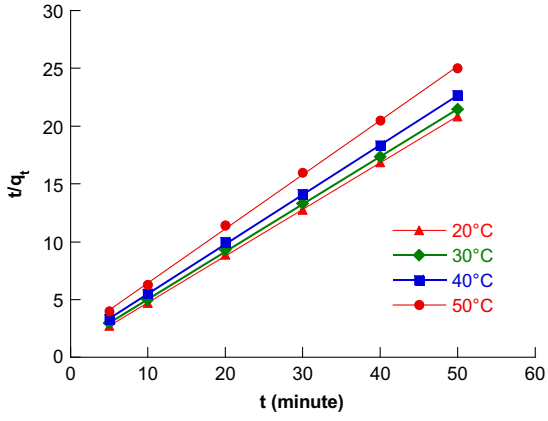

Fig. 7. Pseudo-second-order kinetic plots at different temperatures (pH 5, biosorbent dosage: 4 g/L, contact time: 60 min).

3.7. FTIR analysis

The FTIR spectrum is carried out as a qualitative analysis to determine the main functional groups that are involved in the biosorption process. The FTIR spectrum pattern of *D. canescens* biomass before and after biosorption process is shown in Fig. 9.

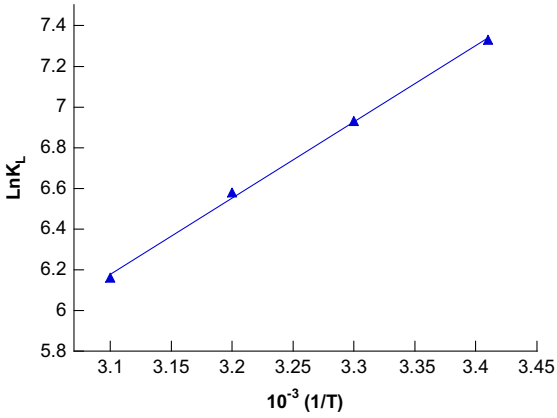

Fig. 8. Determination of thermodynamic parameters for biosorption of Ni(II) onto *D. canescens* biomass.

Table 3
Thermodynamic parameters for Ni(II) biosorption onto *D. canescens* biomass

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)
293	−17.85	−31.14	−45.16
303	−17.45		
313	−17.12		
323	−16.54		

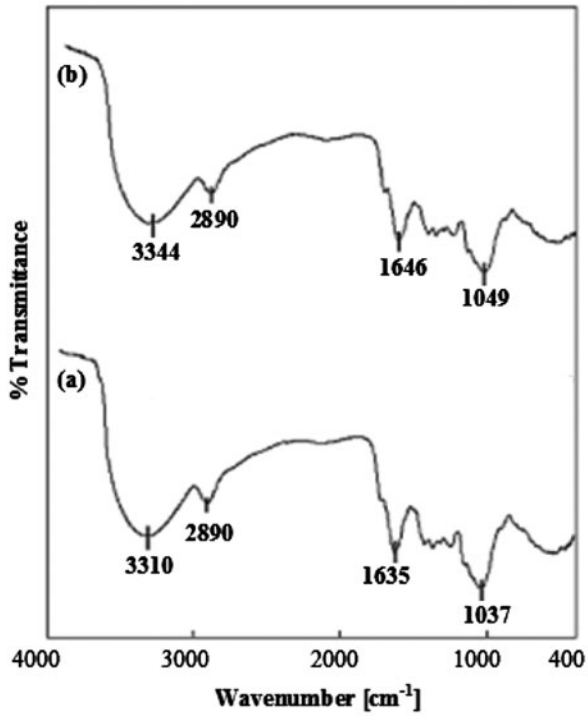

Fig. 9. IR spectra of the pristine (a) and Ni(II) loaded *D. canescens* biomass (b).

The broad and strong band at 3,310 cm^{-1} was due to bounded hydroxyl (–CHOH) or amine ($–NH_2$) groups. The peak at 1,635 cm^{-1} was attributed to stretching vibration of carboxyl group (–CO). The band observed at 1,037 cm^{-1} was assigned to C–O stretching of alcohols and carboxylic acids. The peak observed at 2,890 cm^{-1} may be attributed to the –CH group. After Ni(II) biosorption, the asymmetrical stretching vibration at 3,310 was shifted to 3,344 cm^{-1}. The carboxyl (C=O) peak was observed at 1,646 cm^{-1} for Ni(II)-loaded biomass samples. In addition, after loading metal ion, the peak of C–O groups shifted to 1,049 cm^{-1}. No obvious shift of –CH group after biosorption of metal ions was observed. These results indicated that carboxyl (–COOH), hydroxyl (–CHOH), and amine ($–NH_2$) groups were mainly involved in the biosorption of Ni(II) onto *D. canescens* biomass (Fig. 9).

3.8. EDAX analysis of biosorbent

EDAX analysis provides elemental information through analysis of X-ray emissions caused by a high-energy electron beam. EDAX technique can beneficially be employed to understand the elemental composition of the biosorbent. In this study, X-ray dispersion analysis of the pristine as well as nickel loaded *D. canescens* biomass was conducted (Fig. 10). The EDAX spectrum of raw biomass indicated the presence of Na, K, Ca, Mg, Mn, Cl, and S as natural species on the biosorbent. Whereas, after Ni(II) biosorption, elements such as calcium and magnesium signals almost undetected and nickel signals are now distinctive. This indicates the possibility of nickel replacing calcium and magnesium from the cellular material. Thus, the present results could be indicative of the presence of ion exchange mechanism between these elements and Ni(II) on the surface of the biomass.

3.9. Desorption efficiency

The regeneration of the biosorbent is one of the key factors in assessing their potential for commercial application. Desorption of Ni(II) from the *D. canescens* biomass was also studied using 0.5 MHCl and 0.5 $MHNO_3$. For the desorption studies, 10 mL of each eluent was used. The highest recovery was found to be 95 and 83% using HCI and HNO_3, respectively.

In addition, as it can be seen from Fig. 11, the high stability of *D. canescens* biomass permitted ten times of

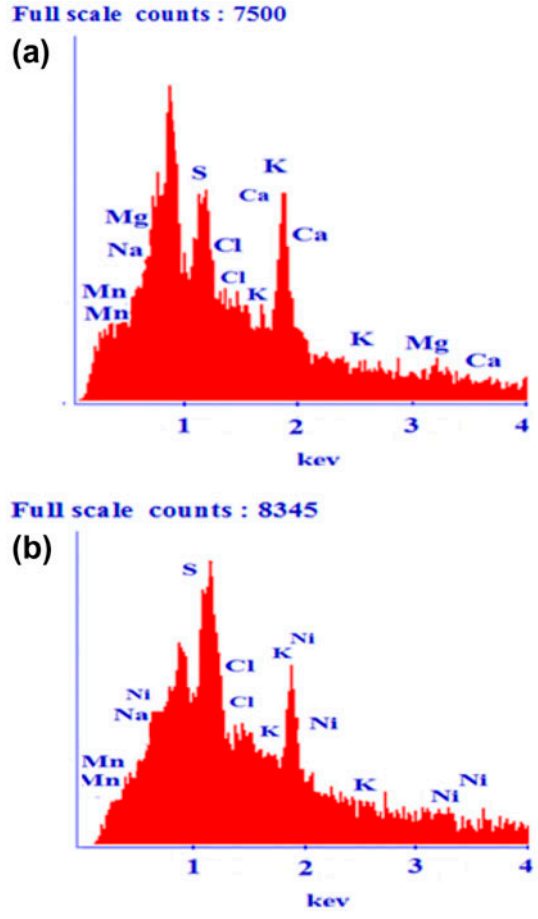

Fig. 10. EDAX spectra of *D. canescens* biomass before (a) and after (b) nickel biosorption.

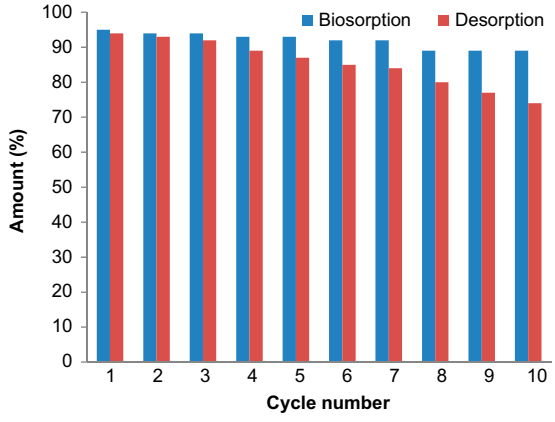

Fig. 11. Biosorption–desorption efficiency with cycle number (biomass concentration: 4 g/L, contact time: 60 min, temperature: 20°C).

biosorption–desorption process along the studies with a decrease about 20% in recovery of Ni(II). These results indicated that the heat inactivated *D. canescens* biomass offers potential to be used repeatedly in Ni(II) biosorption studies without any detectable loss in the total biosorption capacity.

4. Conclusion

This study was carried out to evaluate the potential use of the lichen biomass (*D. canescens*) to remove nickel(II) ions from aqueous solution. In batch mode studies, the biosorption was dependent on solution pH, biosorbent dose, contact time, and temperature. The Langmuir isotherm models defined the equilibrium data precisely compared to Freundlich model and the maximum biosorption capacity obtained was 66.7 mg/g. The calculated mean free energy (11.2 kJ/mol) from the D–R model indicated that the biosorption of Ni(II) using *D. canescens* took place by chemical ion exchange. The kinetic results revealed that the pseudo-second-order model was the best kinetic model for the description of the biosorption mechanism. The data obtained from thermodynamic studies indicated the feasibility, exothermic, and spontaneous nature of the biosorption process at 20–50°C. According to variations in EDAX and FTIR spectra before and after biosorption, it is considered that ion exchange was the major removal mechanism and a certain amount of surface complexation mechanism coexisted. The overall results indicated that the lichen biomass *D. canescens* can be used as promising biosorbent for the treatment of wastewaters containing heavy metal because of advantages of being natural, low-cost biomass, high uptake capacity, renewable, and rapid biosorption rate.

References

[1] I. Alomá, M.A. Martín-Lara, I.L. Rodríguez, G. Blázquez, M. Calero, Removal of nickel(II) ions from aqueous solutions by biosorption on sugarcane bagasse, J. Taiwan Inst. Chem. Eng. 43 (2012) 275– 281
[2] N. Akhtar, J. Iqbal, M. Iqbal, Removal and recovery of nickel(II) from aqueous solution by loofa sponge-immobilized biomass of *Chlorella sorokiniana*: Characterization studies, J. Hazard. Mater. 108(1–2) (2004) 85–94.
[3] Y. Hannachi, A. Ghorbel, T. Lasram, T. Boubaker, Removal of Ni(II) ions from aqueous solutions using clinoptilolite: Equilibrium, kinetic and thermodynamic studies, Chem. Ecol. 28 (2012) 481–495.
[4] Y. Hannachi, N.A. Shapovalov, A. Hannachi, Adsorption of nickel from aqueous solution by the use of low-cost adsorbents, Korean J. Chem. Eng. 27 (2010) 152–158.

[5] M.R. Samarghandi, S. Azizian, M. Shirzad Siboni, S.J. Jafari, S. Rahimi, Removal of divalent nickel from aqueous solutions by adsorption on to modified holly sawdust: Equilibrium and kinetics, Iran J. Environ. Health Sci. Eng. 8 (2011) 181–188.
[6] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407–418.
[7] S. Chakravarty, A. Mohanty, T.N. Sudha, A.K. Upadhyay, J. Konar J.K. Sircar, A. Madhukar, K.K.Gupta, Removal of Pb(II) ions from aqueous solution by adsorption using bael leaves (*Aegle marmelos*), J. Hazard. Mater. 173 (2010) 502–509.
[8] Z. Aksu, İ. Alper İşoğlu, Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, Process Biochem. 40 (2005) 3031–3044.
[9] M. Torab-Mostaedi, M. Asadollahzadeh, A. Hemmati, A. Khosravi, Equilibrium, kinetic and thermodynamic studies for biosorption of cadmium and nickel on grapefruit peel, J. Taiwan Inst. Chem. Eng. 44 (2013) 295–302.
[10] K. Vijayaraghavan, Y.S. Yun, Bacterial biosorbents and biosorption, Biotechnol. Adv. 26 (2008) 266–291.
[11] A. Sarı, M. Tuzen, Ö.D. Uluözlü, M. Soylak, Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass, Biochem. Eng. J. 37 (2007) 151–158.
[12] O.D. Uluozlu, A. Sari, M. Tuzen, M. Soylak, Biosorption of Pb(II) and Cr(III) from aqueous solution by lichen (*Parmelina tiliaceae*) biomass, Bioresour. Technol. 99 (2008) 2972–2980.
[13] X. Lin, Y.J. Cai, Z.X. Li, Q. Chen, Z.L. Liu, R. Wang, Structure determination, apoptosis induction, and telomerase inhibition of CFP-2, a novel lichenin from *Cladonia furcata*, Biochim. Biophys. Acta (BBA), Gen. Subj. 1622 (2003) 99–108.
[14] M. Millot, S. Tomasi, E. Studzinska, I. Rouaud, J. Boustie, Cytotoxic constituents of the lichen *Diploicia canescens*, J. Nat. Prod. 72 (2009) 2177–2180.
[15] A. Grimm, R. Zanzi, E. Björnbom, A.L. Cukierman, Comparison of different types of biomasses for copper biosorption, Bioresour. Technol. 99 (2008) 2559–2565.
[16] M. Safiur Rahman, M. Rafiqui Islam, Effects of pH on isotherms modeling for Cu(II) ions adsorption using maple wood sawdust, Chem. Eng. J. 149 (2009) 273–280.
[17] A.Y. Dursun, A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger*, Biochem. Eng. J. 28 (2006) 187–195.
[18] K. Chojnacka, Biosorption of Cr(III) ions by eggshells, J. Hazard. Mater. 121 (2005) 167–173.
[19] Y. Hannachi, A. Rezgui, T. Boubaker, Biosorption potential of the mediterranean plant (*Posidonia oceanica*) for the removal of Cu^{2+} ions from aqueous media: Equilibrium, kinetic, thermodynamic and mechanism analysis, Korean J. Chem. Eng. 31 (2014) 1211–1218.
[20] Y. Prasanna Kumar, P. King, V.S.R.K. Prasad, Adsorption of zinc from aqueous solution using marine green algae—*Ulva fasciata* sp., Chem. Eng. J. 129 (2007) 161–166
[21] K. Saltalı, A. Sarı, M. Aydın, Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality, J. Hazard. Mater. 141 (2007) 258–263.
[22] T. Akar, Z. Kaynak, S. Ulusoy, D. Yuvaci, G. Ozsari, S.T. Akar, Enhanced biosorption of nickel(II) ions by silica-gel-immobilized waste biomass: Biosorption characteristics in batch and dynamic flow mode, J. Hazard. Mater. 163 (2009) 1134–1141.
[23] A.B. Dekhil, Y. Hannachi, A. Ghorbel, T. Boubaker, Removal of lead and cadmium ions from aqueous solutions using the macroalga *Caulerpa racemosa*, Chem. Ecol. 27 (2011) 221–234.
[24] I. Langmuir, The adsorption of gases on plane surface of glass, mica and platinum, J. Am. Chem. Soc. 40 (1916) 1361–1368.
[25] H. Zavvar Mousavi, S.R. Seyedi, Nettle ash as a low cost adsorbent for the removal of nickel and cadmium from wastewater, Int. J. Environ. Sci. Technol. 8 (2011) 195–202.
[26] A. çelekli, H. Bozkurt, Biosorption of cadmium and nickel ions using *Spirulina platensis*: Kinetic and equilibrium studies Desalination 275 (2011) 141–147.
[27] V. Padmavathy, Biosorption of nickel(II) ions by baker's yeast: Kinetic, thermodynamic and desorption studies, Bioresour. Technol. 99 (2008) 3100–3109.
[28] A. Kurniawan, A.N. Kosasih, J. Febrianto, Y.H. Ju, J. Sunarso, N. Indraswati, S. Ismadji, Evaluation of cassava peel waste as lowcost biosorbent for Ni-sorption: Equilibrium, kinetics, thermodynamics and mechanism, Chem. Eng. J. 172 (2011) 158–166.
[29] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385–470.
[30] U.R. Malik, S.M. Hasany, M.S. Subhani, Sorptive potential of sunflower stem for Cr(III) ions from aqueous solutions and its kinetic and thermodynamic profile, Talanta 66 (2005) 166–173.
[31] M.M. Dubinin, E.D. Zaverina, L.V. Radushkevich, Sorption and structure of active carbons I. Adsorption of organic vapors, Z. Fiz. Khim. 21 (1947) 1351–1362
[32] F. Helfferich, Ion Exchange, McGraw Hill, New York, NY, 1962, p. 166.
[33] M.A. Abdullah, A.G. Devi Prasad, Biosorption of Nickel (II) from aqueous solutions and electroplating wastewater using Tamarind (*Tamarindus indica* L.) Bark, Aust. J. Basic Appl. Sci. 4 (2010) 3591–3601.
[34] S. Lagergren, Zur theorie der sogenannten, adsorption geloster stoffe (About the theory of so-called adsorption of soluble substances), Kunglia a sevenska venten skapasa kademiens, Hand lingar 24 (1898) 1–39.
[35] Y.S. Ho, G. McKay, D.J. Wase, C.F. Forster, Study of the sorption of divalent metal ions onto peet, Adsorpt. Sci. Technol. 18 (2000) 639–650.
[36] L. Deng, Y. Su, H. Su, X. Wang, X. Zhu, Sorption and desorption of lead(II) from wastewater by green algae *Cladophora fascicularis*, J. Hazard. Mater. 143 (2007) 220–225.
[37] R.A. Anayurt, A. Sari, M. Tuzen, Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass, Chem. Eng. J. 151 (2009) 255–261.