Biosorption of nickel(II) from aqueous solution by brown algae: Equilibrium, dynamic and thermodynamic studies

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ABSTRACT

The biosorption characteristics of nickel(II) ions using the brown algae (*Cystoseria indica*, *Nizmuddinia zanardini*, *Sargassum glaucescens* and *Padina australis*) were investigated. Experimental parameters affecting the biosorption process such as pH level, contact time, initial metal concentration and temperature were studied. The equilibrium data fitted very well to the Langmuir adsorption model in the concentration range of nickel(II) ions and at all the temperatures studied. Evaluation of the experimental data in terms of biosorption dynamics showed that the biosorption of nickel(II) onto algal biomass followed the pseudo-second-order dynamics well. The calculated thermodynamic parameters (ΔG°, ΔH° and ΔS°) showed that the biosorption of nickel(II) ions were feasible, spontaneous and endothermic at the temperature ranges of 293–313 K.

1. Introduction

As today's technology progresses and increment in industrial activities, a high volume of wastewater containing heavy metal is released to the natural environment. Heavy metal pose a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature. According to the World Health Organization (WHO), the metals of most immediate concern are cadmium, chromium, cobalt, copper, lead, nickel, mercury and zinc. In this way, Mining and metallurgy of nickel, stainless steel, nickel electroplating, battery and accumulator manufacturing, pigments, ceramic and porcelain enameling industries wastewaters contain an undesirable amounts of nickel(II) ions. Nickel at trace amount may be beneficial as an activator of some enzyme systems but if the nickel(II) ion intake over the permissible levels results in different types of diseases such as pulmonary fibrosis, lung cancer, renal edema, skin dermatitis and gastrointestinal disorder such as nausea, vomiting, diarrhea. For this reason, the Water Sanitation and Hygiene (WSH) under the World Health Organization (WHO) established the toxic limits of permissible concentrations of nickel at a level of Ni and insoluble compounds of Ni 1 mg m^{-3}, soluble compounds of Ni 0.1 mg m^{-3}, nickel carbonyl of 0.05–0.12 mg m^{-3} and nickel sulphide of 1 mg m^{-3} [1–7]. Because of the destructive effects of heavy metals, their removal from wastewater is an extremely significant step in the protection of the environment and human health. Conventional methods for removing metals from aqueous solutions include chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, solvent extraction, reverse osmosis, membrane technologies and evaporation recovery. These processes may be ineffective or extremely expensive especially when the metals in solution are in the range of 1–100 mg l^{-1}. Another major disadvantage with conventional treatment methods is the production of a toxic chemical sludge and its disposal/treatment becomes a costly affair and is not eco-friendly. Therefore, removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes great importance [3,8,9]. Biosorption, a property of certain types of inactive, dead microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions, is one of the most promising methods used in the removal of toxic metals from industrial waste streams and natural waters. The major advantages of the biosorption technology are its effectiveness in quickly reducing the concentration of heavy metals ions to very low levels with high efficiency and the use of inexpensive biosorbent materials. These characteristics make biosorption an ideal alternative for treating high volumes of low concentration complex wastewaters. Biosorption 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 [2,8,10]. Among biosorbent materials, algae have proved to

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be both economic and eco-friendly, as they are abundantly available, have regeneration and metal recovery potentiality, lesser volume of chemical and/or biological sludge to be disposed off, high efficiency in dilute effluents and high surface area to volume ratio. It provides a cost effective solution for industrial wastewater management [11]. The cell walls of brown algae generally contain three components: cellulose, the structural support; alginic acid, a polymer of mannuronic and guluronic acids and the corresponding salts of sodium, potassium, magnesium and calcium; and sulphated polysaccharides. These compounds contain several functional groups (amino, carboxyl, sulphate and hydroxyl) which could play an important role in the biosorption process [12]. The mechanism of binding metal ions by inactivated algal biomass may depend on the species and ionic charges of the metal ions, the algal organisms, the chemical compositions of the metal ion solution and other external environmental factors such as pH and temperature [3]. *Cystoseria indica* (*Cys*), *Nizmuddinia zanardini* (*Niz*), *Sargassum glaucescens* (*Sarg*) and *Padina australis* (*Pad*) are very abundant in the gulf of Oman in the coast of Chabahar, Iran and information about biosorption with them, is still scanty. The aim of the present work was to evaluate the sorption capacity of these four different type of algae in respect of nickel. In addition, the equilibrium, dynamic and thermodynamic parameters were calculated.

2. Mathematical description

The metal concentration in the liquid phase was determined at the beginning C_i (mg l^{-1}) and at the end C_f (mg l^{-1}). The following equation was used to compute biosorbent uptake capacity q (mg g^{-1}) where V (ml) is the volume of the solution and W (g) is the mass of the biosorbent [13]:

$$q = (C_i - C_f) \times \frac{V}{1000W} \tag{1}$$

2.1. Equilibrium parameters of biosorption

The equilibrium data, commonly known as adsorption isotherms, are the basic requirements for the design of the adsorption systems. Several isotherm equations have been used for the equilibrium modeling of biosorption systems. Both of these have been applied to nickel biosorption by *Cys*, *Niz*, *Sarg* and *Pad* data, the Langmuir and the Freundlich models.

If the metal ions are taken up independently on a single type of binding site in such a way that the uptake of the first metal ion does not affect the sorption of the next and the monolayer sorption onto a surface with a finite number of identical sites occurs, then the sorption process would follow the Langmuir adsorption isotherm equation. Langmuir, theoretically examined the adsorption of gases on solid surfaces, and considered sorption as a chemical phenomenon. Basically, the Langmuir isotherm equation is in the form of a hyperbolic function as below:

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

where q_{eq} (mg g^{-1}) is the equilibrium metal uptake capacity, C_{eq} (mg l^{-1}) is the equilibrium metal ion concentration, q_{max} (mg g^{-1}) is the maximum amount of the metal ion per unit weight of alga to form a complete monolayer on the surface bound at high C_{eq} and b (l mg^{-1}) is a constant related to the affinity of the binding sites. q_{max} represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent does not reach its full saturation in experiments. b corresponds to the concentration at which a metal ion amount of $q_{max}/2$

is bound and a high b value indicates a high affinity. q_{max} and b can be determined from the linear plot of $1/q_{eq}$ versus $1/C_{eq}$ [2,4,14–16].

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface and is commonly presented as Eq. (3):

$$q_{eq} = K_F C_{eq}^{1/n} \tag{3}$$

where K_F (mg g^{-1}) and n are the Freundlich constants related to the adsorption capacity and intensity of the sorbent, respectively. Rearranging Eq. (3) gives:

$$\log q_{eq} = \log K_F + \frac{1}{n} \log C_{eq} \tag{4}$$

where K_F and n can be determined from the linear plot of $\log q_{eq}$ versus $\log C_{eq}$.

Some authors explain that Langmuir isotherm corresponds to a dominant ion exchange mechanism while the Freundlich isotherm shows adsorption–complexation reactions taking place in the adsorption process [17,18].

2.2. Dynamic parameters of biosorption

In order to investigate the controlling mechanism of biosorption process such as mass transfer and chemical reaction, dynamic models have been used to test experimental data. In this study the pseudo-first-order and pseudo-second-order dynamic models were used to test the experimental data of nickel biosorption by *Cys*, *Niz*, *Sarg* and *Pad*. Pseudo-first-order Lagergren model considers that the rate of occupation of biosorption sites is proportional to the number of unoccupied sites:

$$\frac{dq_t}{dt} = k_1(q_{eq} - q_t) \tag{5}$$

where t (min) indicates time, q_t (mg g^{-1}) shows uptake capacity at t and k_1 (min^{-1}) shows the equilibrium rate constant of pseudo-first-order adsorption. After being integrated and rearranged:

$$\log(q_{eq} - q_t) = \log q_{eq} = \frac{k_1 t}{2.303} \tag{6}$$

where k_1 and q_{eq} can be determined from the linear plot of $\log(q_{eq} - q_t)$ versus t.

The adsorption dynamics may also be described by pseudo-second-order model. Pseudo-second-order model considers that the rate of occupation of biosorption sites is proportional to the square of the number of unoccupied sites:

$$\frac{dq_t}{dt} = k_2(q_{eq} - q_t)^2 \tag{7}$$

where t (min) shows time, q_t (mg g^{-1}) shows uptake capacity at t and k_2 (g mg^{-1} min^{-1}) shows the equilibrium rate constant of pseudo-second-order adsorption. After being integrated and rearranged:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \tag{8}$$

where k_2 and q_{eq} can be determined from the linear plot of t/q_t versus t. This model is more likely to predict dynamic behavior of biosorption with chemical sorption being the rate-controlling step. Due to the presence of greater number of metal ions in industrial wastewater, the sorption equilibrium was reached much faster due to faster occupancy of sorption sites by metal ions [6,13,19].

2.3. Thermodynamic parameters of biosorption

Both energy and entropy factors must be considered in thermodynamics, in order to determine whether a process will occur

spontaneously or not. The process of nickel(II) ion biosorption can be assumed by the following reversible process, which represents a heterogeneous equilibrium:

$$\text{Ni}^{2+} \text{ ion in solution } \leftrightarrow \text{Ni}^{2+} - \text{algal biomass} \qquad (9)$$

For such equilibrium reactions, the Gibbs free energy (ΔG°) was determined by the following equation:

$$\Delta G^\circ = -RT \ln k_0^c \qquad (10)$$

where R is the universal gas constant, $8.314\,\text{J mol}^{-1}\,\text{K}^{-1}$, T is the absolute temperature in K and k_0^c is the equilibrium constant. The Gibbs free energy indicates the degree of spontaneity of the adsorption process, where more negative values reflect a more energetically favourable adsorption process. The relationship between the equilibrium constant, k_0^c and the temperature is given by the Van't Hoff equation:

$$\ln k_0^c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (11)$$

The entropy change of biosorption, ΔS°, and the enthalpy change of biosorption, ΔH° can be obtained from the slope and intercept of a Van't Hoff plot of $\ln k_0^c$ versus $1/T$. In this study, the thermodynamic parameters have been calculated using the Langmuir isotherm, i.e., by replacing the equilibrium constant, k_0^c from Eqs. (10) and (11) by the Langmuir isotherm constant, b (l mol^{-1}) [4].

3. Experimental

3.1. Preparation of algae and nickel solutions

Cys, *Niz*, *Sarg* and *Pad*, brown algae, obtained from gulf of Oman in the coast of Chabahar, Iran were sun-dried on the beach and then extensively washed with distilled water and dried in an oven at 60 °C overnight. The dried biomass was ground in a laboratory blender and sorted using the standard test sieves. The batch of biomass with particle size 1.0–1.25 mm was selected for the experiments.

Nickel solutions were prepared by diluting 1000 mg l^{-1} nickel stock solution which was obtained by dissolving a weighed quantity of nickel in chloride salt form, NiCl$_2$·6H$_2$O, analytical grade. Diluted solutions were prepared at room temperature in distilled and deionized water. The range of concentrations of prepared solutions changed between 6 and 201 mg l^{-1}. The pH level of each solution was adjusted to desired level with diluted or concentrated HCl and NaOH solutions before mixing the dried algae with the solution.

3.2. Analysis of nickel concentration

The concentration of residual nickel(II) in the biosorption medium was determined using an atomic absorption spectrophotometer (Varian – spectra – AA – 200) at the wavelength of 232 nm.

3.3. Batch biosorption studies

The experiments were conducted in 250 ml Erlenmeyer flasks containing 100 ml of nickel(II) synthetic solutions. The flasks were shaken on a shaker incubator at a constant rate of 120 rpm. The suspensions were brought to the desired pH by adding 0.1 N HCl or NaOH during the sorption process and the volume of HCl or NaOH added was recorded. Before analysis the samples were removed from the shaker after a specified time and the solutions were filtered through filter paper (Whatman No. 40, ashless) and the supernatant fraction was analyzed for the remaining nickel(II) ions.
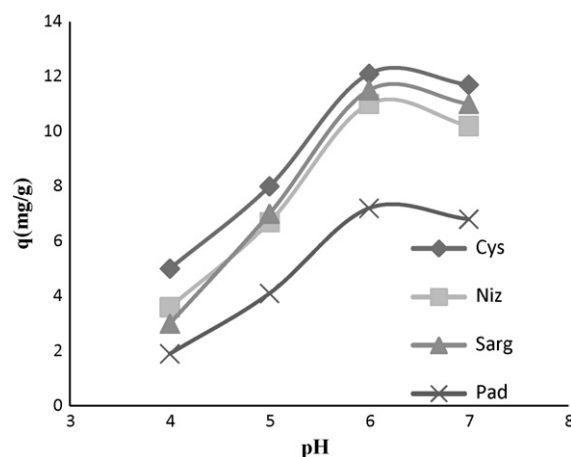

Fig. 1. Effect of pH on biosorption of nickel (biomass dose = 1 g l^{-1}; initial nickel(II) ion concentration = 30 mg l^{-1}; temperature = 30 °C; agitation speed = 120 rpm; contact time = 120 min).

Uptake values were determined as the difference between the initial concentration and the one in the supernatant. To Investigate the effect of pH, initial metal concentration, temperature and contact time, different pH (4–7), initial metal concentration (6–201 mg l^{-1}), temperature (20, 30, 40 °C) and contact time (10, 20, 30, 40, 50, 60, 90, 120, 150 min) were considered during the study. All experiments were carried out at least twice. Values used in calculations were the arithmetic averages of the experimental data.

4. Results and discussion

4.1. Influence of pH

PH level seems to be the most important parameter for controlling the biosorption process. The pH level affects the network of negative charges on the surface of the biosorbing cell walls and the chemistry of the walls, as well as physicochemistry and hydrolysis of the metal. It can be seen From Fig. 1 that the adsorption capacity of nickel increases as the pH increase, and reaches the maximum at pH 6, then decreases as the pH continue increasing. Because H$^+$ vies with metal ion in lower pH, the sorbent surface takes up more H$^+$, consequently reducing metal ions bind on the sorbent surface. At higher pH levels, the sorbent surface takes more negative charges, thus attracting greater metal ions. But with further increase in pH level, the formation of anionic hydroxide complexes decreases the concentration of free metal ion, thereby the adsorption capacity of metal ion was decreased. Hydroxide precipitation occurs at pH > 8.3 for Ni(OH)$_{2(s)}$. According to the results of this initial experiment, further biosorption investigations were performed at pH value of 6 as an optimal value [18,20,21].

4.2. Influence of contact time

The rate of adsorption is a very important factor in the reactor design and the optimization process in industry. The effect of contact time on the equilibrium uptake of nickel(II) ions on the *Cys*, *Niz*, *Sarg* and *Pad* for an initial nickel(II) ion concentration of 200 mg l^{-1} is shown in Fig. 2. According to this figure, biosorption capacity increased with increasing contact time and almost 60% of nickel was removed by dried algal biomass in the first 20 min of contact time. Equilibrium was reached in a contact time of 120 min. This figure also verifies that the sorption took place in two stages: a very rapid surface adsorption and a slow intracellular diffusion [1,2].
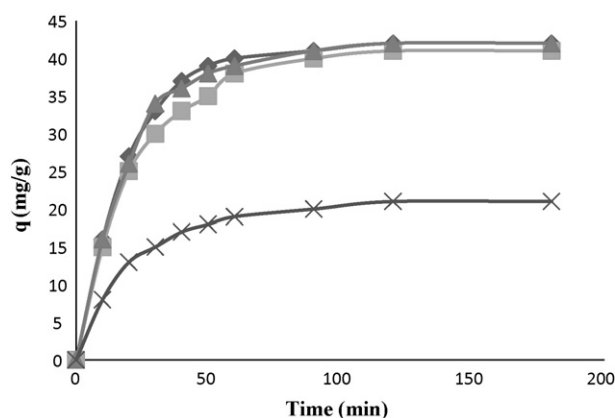
Fig. 2. Effect of sorption time on biosorption of nickel (initial pH = 6; biomass dose = 1 g l⁻¹; initial nickel(II) ion concentration = 200 mg l⁻¹; temperature = 40 °C; agitation speed = 120 rpm).

Table 2
Langmuir and Freundlich parameters for nickel sorption by algal biomass.

T (°C)	Langmuir			Freundlich		
	q_{max}	b	R^2	K_F	$1/n$	R^2
Cys						
20	47.619	0.031	0.999	2.748	0.564	0.957
30	47.619	0.035	0.997	3.126	0.522	0.957
40	50	0.038	0.999	3.273	0.546	0.967
Niz						
20	50	0.023	0.999	2.099	0.6	0.973
30	52.632	0.028	0.998	2.624	0.577	0.971
40	55.556	0.031	0.999	3.006	0.562	0.968
Sarg						
20	52.632	0.022	0.998	2.037	0.612	0.974
30	55.556	0.026	0.996	2.735	0.569	0.964
40	55.556	0.031	0.999	3.034	0.563	0.962
Pad						
20	23.8	0.022	0.999	1.076	0.581	0.969
30	26.316	0.025	0.999	1.432	0.548	0.96
40	27.027	0.026	0.999	1.503	0.547	0.958

4.3. Influence of temperature and initial metal concentration

The effect of temperature on nickel(II) ion uptake capacity of *Cys*, *Niz*, *Sarg* and *Pad* was studied at different initial metal ion concentration and Table 1 presents the biosorption of nickel(II) ion as a function of initial metal concentration and temperature after 120 min. It was shown that the removal of nickel(II) ion increased with increasing temperature up to 40 °C. This indicated that the adsorption of nickel(II) ion on *Cys*, *Niz*, *Sarg* and *Pad* was controlled by an endothermic process. The sorption of nickel(II) ions by dried algal biomass may involve not only a physical but also a chemical sorption. This effect may be due to the fact that at higher temperatures an increase in active sites occurs due to bond rupture.

As a rule, increasing the initial metal concentration results in an increase in the biosorption capacity because it provides a driving force to overcome mass transfer resistance between the biosorbent and biosorption medium. So higher sorption capacities were obtained at higher initial concentrations for nickel(II) at all temperatures studied (Table 1) [14].

4.4. Determination of equilibrium model constants

The analysis of equilibrium data is important for developing an equation that can be used for design purposes. For this study, in order to get the equilibrium data, initial nickel concentrations were

changed while the biomass weight in each sample was kept constant. Two hours of equilibrium periods for sorption experiments were used to ensure equilibrium conditions. This time was chosen considering the results of dynamics of nickel removal by *Cys*, *Niz*, *Sarg* and *Pad* which was presented prior to this one. The Langmuir and Freundlich adsorption constants evaluated from the isotherms at different temperatures and their correlation coefficients are presented in Table 2. As can be seen from Table 2, the correlation coefficient for the Freundlich adsorption isotherm was found to be lower than 0.974. Fig. 3 indicated the data linearized to fit the Langmuir equation. According to the results, the equilibrium adsorption data was better fitted to Langmuir adsorption isotherm model than Freundlich adsorption model and high regression correlation coefficients (>0.995) were found, suggesting that this model is very suitable for describing the biosorption equilibrium of nickel by the algal cells in the concentration and temperatures range studied. The applicability of the Langmuir isotherm model to the nickel-dried algae system implies that monolayer biosorption conditions exit under the experimental conditions used. The maximum capacity q_{max} determined from the Langmuir isotherm defines the total capacity of the biosorbent for nickel. The adsorption capacity of biosorbent, increases with increase in temperature. The value of q_{max} obtained at 40 °C appears to be higher in comparison with the uptake obtained at other temperatures. A higher value of b also

Table 1
Effect of initial Ni(II) concentration on the sorption capacity at equilibrium at different temperatures (pH 6; biomass dose = 1 g l⁻¹; agitation speed = 120 rpm).

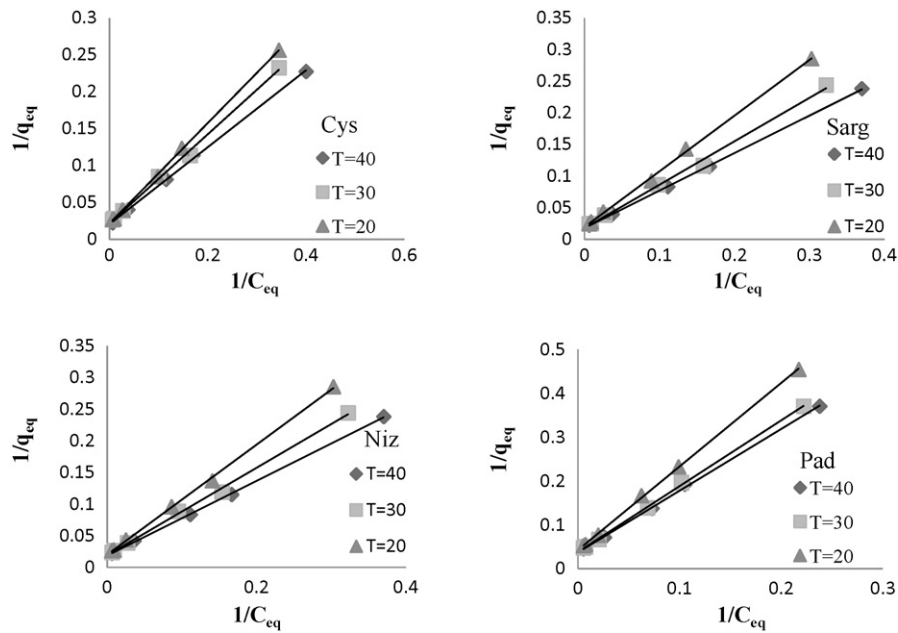| T (°C)	C_i (mg l⁻¹)	Cys, q (mg g⁻¹)	Niz, q (mg g⁻¹)	Sarg, q (mg g⁻¹)	Pad, q (mg g⁻¹)
20	6.8	3.9	3.5	3.5	2.2
	14.9	8.1	7.3	7	4.3
	22	11.8	10.4	10.8	6
	63	25	23	23	13
	151	36	36	36	18
	201	37	38	40	19
30	7.2	4.3	4.1	4.1	2.7
	14.9	8.8	8.4	8.6	5.1
	21.8	11.8	11.3	11.6	7.2
	63	26	26	26	15
	151	36	38	40	20
	201	38	43	41	21
40	6.9	4.4	4.2	4.2	2.7
	14.7	8.8	8.7	8.7	5.2
	21	12.3	12	12	7.3
	52	25	24	25	14
	151	41	41	41	21
	201	45	45	45	22

Fig. 3. The linearized Langmuir adsorption isotherms of nickel(II) by dried algal biomass.
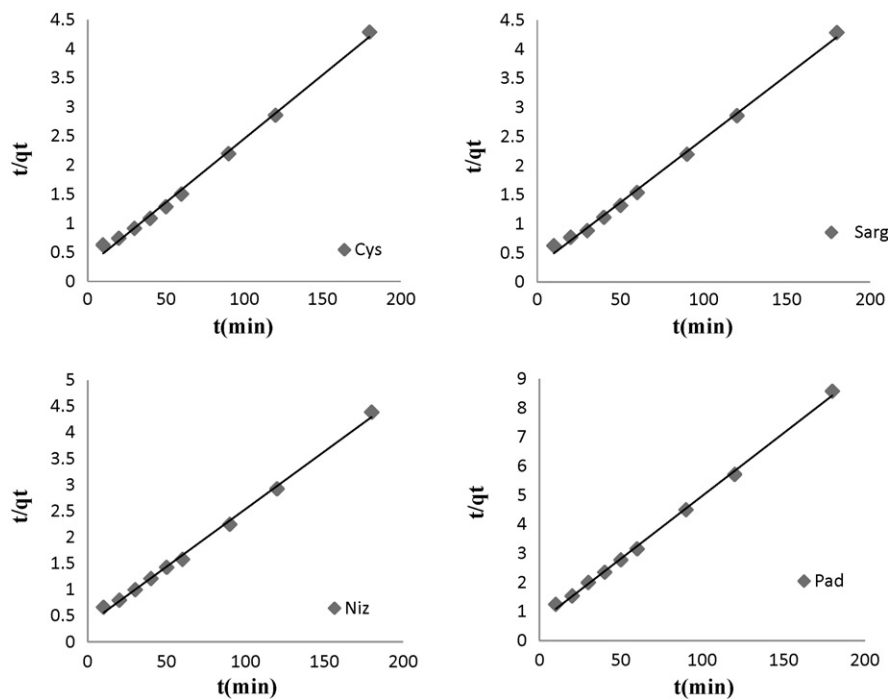

Fig. 4. The linearized pseudo-second-order biosorption dynamics of nickel.

implied strong bonding of nickel to the dried *Cys*, *Niz*, *Sarg* and *Pad* at this temperature.

4.5. Determination of dynamic constants

In this study, the pseudo-first-order and pseudo-second-order rate equations were applied to fit the experimental sorption data of nickel(II) ions on the dried *Cys*, *Niz*, *Sarg* and *Pad* biomass. The slope and intercept of plot of $\log(q_{eq} - q_t)$ versus t were used to obtain the first-order rate constant k_1 and equilibrium uptake q_{eq}. The pseudo-second-order biosorption rate constant (k_2) and q_{eq} values were determined from the slope and intercept of the plot of t/q_t against

Table 3
Comparison between adsorption parameters of Lagergren pseudo-first-order and pseudo-second-order dynamic models.

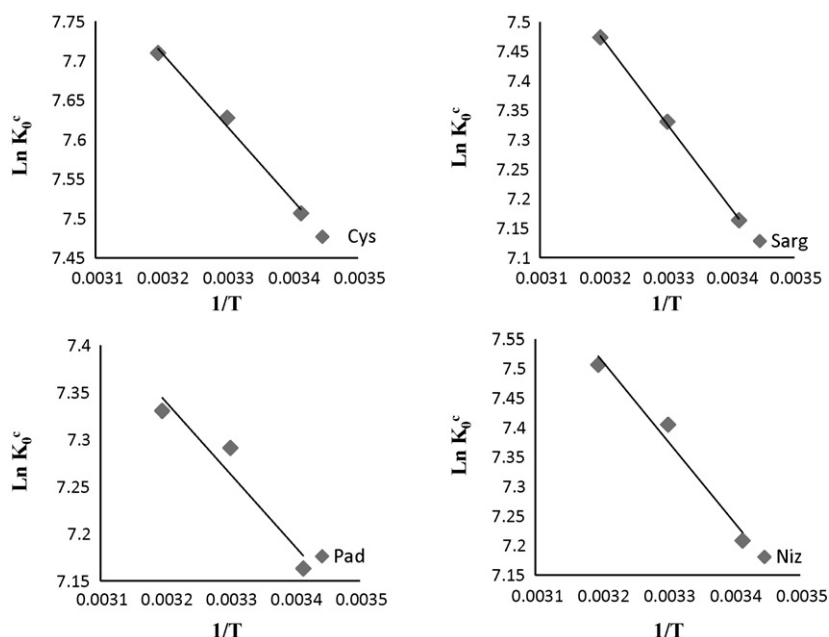|	$q_{eq,exp}$	Pseudo-second			Pseudo-first		
		$q_{eq,cal}$	k_2	R^2	$q_{eq,cal}$	k_1	R^2
Cys	42	47.619	0.002	0.996	34.914	0.044	0.968
Niz	41	45.455	0.001	0.997	39.264	0.039	0.994
Sarg	42	47.619	0.002	0.996	35.645	0.041	0.985
Pad	21	23.256	0.003	0.998	17.338	0.032	0.982

Fig. 5. The Van't Hoff equation plot.

time, t (Fig. 4). The values of the rate constants obtained for various temperatures are given in Table 3 along with the corresponding correlation coefficients. As can be seen from Table 3, the correlation coefficient for the pseudo-first-order dynamic model was found to be lower than 0.994. It was also noticed that the correlation coefficient, R^2, for the pseudo-second-order rate equation was greater than 0.996. Hence, it was concluded that this sorption system was better described by second-order rate equation than by first order.

4.6. Determination of thermodynamic constants of biosorption

The Gibbs free energy changes for the biosorption process are presented in Table 4. As it is seen from this table all the Gibbs free energy change values are negative. A negative value of ΔG° indicates the feasibility of the process and spontaneous nature of the biosorption. The standard enthalpy and entropy changes of biosorption determined from the $\ln k_0^c$ versus $1/T$ plot were 7.775 kJ mol^{-1} and 0.890 kJ mol^{-1} K^{-1} for the sorption of nickel on the dried Cys, 11.415 kJ mol^{-1} and 0.990 kJ mol^{-1} K^{-1} for the sorption of nickel on the dried Niz, 11.823 kJ mol^{-1} and

0.999 kJ mol^{-1} K^{-1} for the sorption of nickel on the dried $Sarg$ and 6.403 kJ mol^{-1} and 0.815 kJ mol^{-1} K^{-1} for the sorption of nickel on the dried Pad, respectively (Fig. 5). The positive value of ΔH° suggests the endothermic nature of biosorption and the positive value of ΔS° confirms the increased randomness at the solid–solution interface during biosorption [14].

5. Conclusion

The abilities of $C.$ $indica$, $N.$ $zanardini$, $S.$ $glaucescens$ and $P.$ $australis$ to adsorb nickel(II) were investigated in a batch system. It was seen that the pH level, time, temperature and initial metal ion concentration highly affect the biosorption capacity of the sorbent. The optimum pH level for biosorption of nickel(II) was found to be 6 for all the four algae under study. Biosorption capacity increased as metal ion concentration and temperature increased. The equilibrium behavior of biosorption of nickel(II) ion was tested using Langmuir and Freundlich models. The Langmuir equation was found to be the better model that represented the biosorption data. The suitability of the first- and second-order dynamic equations, model for the biosorption of Ni(II) onto dried algal biomass were also discussed. The pseudo-second-order dynamic model agreed very well for the biosorption of nickel(II) onto dried algal biomass. Thermodynamic constants for biosorption were also evaluated using equilibrium constants changing with temperature. The negative values of ΔG° indicated the spontaneity of the process. The positive value of ΔH° indicated that Ni(II) biosorption process was endothermic and the positive value of ΔS° showed the increase of randomness during Ni(II) biosorption process. Consequently, alga biosorption methods are still being developed and much more work is required. Some practical applications have been achieved, and the fundamentals look promising: algae have the potential to remove metal ions to very low concentrations and to accumulate large amounts of specific toxic elements.

Table 4
Thermodynamic parameters for the adsorption of nickel.

T (°C)	b (l mg^{-1})	ΔG (kJ mol^{-1})
Cys		
20	0.031	−18.285
30	0.035	−19.215
40	0.038	−20.063
Niz		
20	0.023	−17.558
30	0.028	−18.653
40	0.031	−19.533
$Sarg$		
20	0.022	−17.450
30	0.026	−18.466
40	0.03	−19.448
Pad		
20	0.022	−17.450
30	0.025	−18.367
40	0.026	−19.076

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