Biosorption of Nickel Ion by Chitosan-immobilized Brown Algae *Laminaria japonica*

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Highly toxic nickel is released into the environment from a number of industrial processes, but current techniques for its removal are expensive and may cause secondary pollution. We developed a biosorbent of chitosan-immobilized brown algae (*Laminaria japonica*). The effects of different parameters on the adsorption capacity and biosorption-desorption of Ni^{2+} from aqueous solution were evaluated. Kinetic studies showed that the adsorption of Ni^{2+} by the immobilized algal beads followed second-order kinetics. When the adsorbent dose was increased, the biosorption capacity decreased and the removal efficiency increased. Ni^{2+} biosorption by the immobilized algae cell beads was a good fit for the Langmuir and Freundlich isotherm models. In addition, the regenerated biosorbent by 1 mol L^{-1} HCl or 1 mol L^{-1} HNO_3 could be reused, and maintained 90 % removal efficiency for at least three cycles.

Key words:
Biosorption, chitosan, immobilization, nickel, *Laminaria japonica*

Introduction

Nickel is released into the environment by a large number of processes, such as electroplating, leather tanning, wood preservation, pulp processing, and steel manufacturing. High concentrations of Ni^{2+} may be toxic and harmful to organisms in water, and also to consumers of aquatic organisms.[1] Many processes are used to remove heavy metals from industrial effluents, including chemical precipitation, coagulation, solvent extraction, membrane separation, ion exchange, and adsorption. However, compared with biosorption processes, these methods are expensive and may cause secondary pollution.[2–3]

Biosorption involves using biological material to remove metal or metalloid species, compounds, and particulates from solution.[4] Many biosorbents such as fungi, bacteria, and yeast have recently been evaluated for their ability to sequester heavy metals. Among these, brown algal biomass has proven highly effective, reliable and predictable in the removal of metal ions such as Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} from aqueous solutions.[5–9] The biosorption capability of brown algae has been attributed mainly to the cell wall, which has a fiber-like structure and an amorphous embedding matrix of various polysaccharides. One type of these polysaccharides, alginate, has been reported to have high affinity for divalent cations.[10]

Laminaria japonica is a species of brown algae abundant and ubiquitous in the littoral zones of the world. To date, some applications in environmental science have utilized this species. Due to the high uptake capacity (0.7–1.85 mmol g^{-1} for Pb^{2+}, Cd^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Cr^{6+}) of *L. japonica* and its low cost, it is a promising adsorbent.[9,11–14] However, algae as biosorbents are usually used in powder form. Due to the low density and strength of powdered algae, this introduces practical problems in continuous processes, such as softening upon contact with water, and difficult separation from the water. Therefore, cell immobilization or chemical modification is required for the practical application of algae.[1]

The objective of this work was to prepare a new biosorbent with the brown algae *L. japonica* as the biomaterial and chitosan as a carrier. The Ni^{2+} adsorption and desorption characteristics of the immobilized *L. japonica* sorbent were investigated. This included evaluating the effect of different parameters, such as contact time, initial pH, adsorbent dose, and initial Ni^{2+} concentration, on the sorption capacity. Equilibrium modeling was carried out using the Langmuir and Freundlich isotherm equations.

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Materials and methods

Preparation of the biosorbent

L. japonica was sourced in Qingdao (China). It washed several times with deionized water to eliminate impurities and freeze dried for 24 h. The dried biomass was crushed and ground to granules of 0.3–80 μm and stored in a desiccator.

Immobilized beads of powdered *L. japonica* in a chitosan matrix were prepared by ionic polymerization in sodium pyrophosphate and potassium oxalate solution. First, the powdered *L. japonica* cells were suspended in a chitosan solution (1 % in acetic acid) and agitated. The mixture was smashed in an ultrasonic cell pulverizer for a set time, and then dropped into a mixed solution of 2 % sodium pyrophosphate and 4 % potassium oxalate using a peristaltic pump. The drops of chitosan solution gelled into 2 ± 0.1 mm diameter beads upon contact with the mixed solution. The immobilized algal cell beads were stored in the mixed solution for at least 1 h to complete gelation. The beads were rinsed and then frozen dry for 12 h before use. Blank chitosan beads were also prepared in a chitosan solution by the above method without algae.

Biosorption experiments

All sorption experiments were performed by agitating 100 mL of the appropriate concentration metal solution and with a set amount of adsorbent in 300 mL bottles at 200 rpm. The nickel solutions, which were prepared using $NiSO_4 \cdot 6H_2O$, were placed in a water bath shaker at room temperature for a predetermined time. The initial pH was adjusted using dilute hydrochloric acid and sodium hydroxide solutions.

All experiments in this work were conducted in duplicate and the average results were presented.

Analysis

The concentration of metal ions was determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES IRIS AP; Thermo Jarrell Ash Co., USA).

Biosorption-desorption cycle experiments

For adsorption-desorption studies, 2 g L^{-1} immobilized algal beads were placed in a Ni^{2+} solution and agitated for 5 h. The Ni^{2+} loaded beads were collected and gently washed with deionized water to remove any unadsorbed Ni^{2+}. The beads were agitated with a set volume of various eluents, including 0.005 mol L^{-1} ethylenediamine tetraacetic acid (EDTA), 1 mol L^{-1} HCl, and 1 mol L^{-1} HNO_3, in a water bath shaker at room temperature (25 °C).[15] After desorption, the beads were immersed in 1 mol L^{-1} sodium hydroxide solution for 10 min to neutralize any surplus hydrogen ions on the beads. To test the reusability of the beads, the adsorption-desorption cycles were repeated five times with the same beads and new eluents.

Evaluation of adsorption

The biosorption properties of the immobilized algal beads and the desorption efficiency of the desorbents were evaluated. This involved calculating uptake capacity, removal efficiency and desorption efficiency using the following equations:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$\eta = \frac{C_0 - C_e}{C_0} \cdot 100\ \% \tag{2}$$

$$\gamma = \frac{C_i}{C_0 - C_e} \cdot 100\ \% \tag{3}$$

where q_e is the equilibrium uptake capacity (mg g^{-1}), C_0 is the initial Ni^{2+} concentration (mg L^{-1}), C_e is the equilibrium Ni^{2+} concentration (mg L^{-1}), V is the volume of the solution (L), m is the mass of the sorbent (g), η is the removal efficiency, C_i is the desorbed Ni^{2+} concentration (mg L^{-1}), and γ is the desorption efficiency.

Results and discussion

Optimization of the adsorbent beads preparation

The effect of the chitosan concentration used in preparation of immobilized algal beads on Ni^{2+} removal was investigated. Of the concentrations (1.5–2.5 %) tested, 2.5 % chitosan solution provided the highest removal efficiency of Ni^{2+} and the most simple and convenient preparation of the adsorbent beads. Consequently, this concentration of chitosan was used in subsequent preparation of the adsorbent beads. The biomass concentration in the chitosan solution was determined to be 13 g L^{-1} based on the removal of Ni^{2+}.

Biosorption kinetics

The biosorption kinetics of Ni^{2+} on the sorbents were studied. The amount of Ni^{2+} adsorbed by the immobilized algal beads increased until 300 min, after which it remained constant (Fig. 1). This is consistent with previous studies on the kinetics of metal ion removal by algae, which have shown that sorption is initially rapid and then slows down.[1,16]

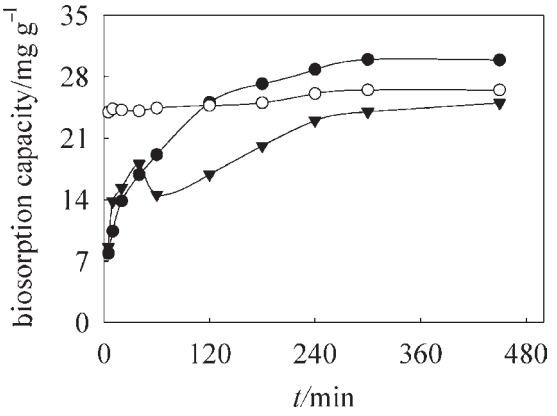


Fig. 1 – *Effect of contact time on adsorption of Ni^{2+}: ○ powdered L. japonica, ● immobilized algal beads, and ▼ blank beads. Experimental conditions: initial Ni^{2+} concentration, 80 mg L^{-1}; biosorbent dose, 2.0 g L^{-1}; pH, 5.5; temperature, 25 °C.*

In contrast, the sorption of Ni^{2+} on powdered *L. japonica* reached equilibrium in five minutes. The sorption processes of Ni^{2+} by the immobilized algal beads and the blank beads were similar in the first 60 minutes and then differed drastically after that point. It indicated that the powdered *L. japonica* in the immobilized sorbent played a dominant role in the adsorption of Ni^{2+} and immobilization of the algae affects the adsorption process of Ni^{2+} on the algae cells.

Pseudo-first order and pseudo-second order kinetics and intraparticle diffusion were utilized to model the experimental adsorption data.

The pseudo-first order kinetic model is given by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)(t = 0, q_t = 0) \qquad (4)$$

The linear form of eq. (4) is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t \qquad (5)$$

where k_1 is the equilibrium constant of the first-order model, q_t is the uptake capacity at time t, and q_e is the equilibrium uptake capacity.

The pseudo-second order kinetic model is given by:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2(t = 0, q_t = 0) \qquad (6)$$

The linear form of eq. (6) is:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k_2} = \frac{t}{q_e} + \frac{1}{h} \qquad (7)$$

where k_2 is the equilibrium constant of the second-order model, and $h = q_e^2 k_2$ represents the initial rate constant.

The intra-particle diffusion model is given as:

$$q_t = k_{id} t^{1/2} \qquad (8)$$

where q_t is the uptake capacity at time t, and k_{id} is the rate constant of intraparticle diffusion.[17]

Figs. 2(a), (b), and (c) illustrate the linear plots of log $(q_e - q_t)$ against t, t/q_t against t, and q_t against $t^{1/2}$, respectively.

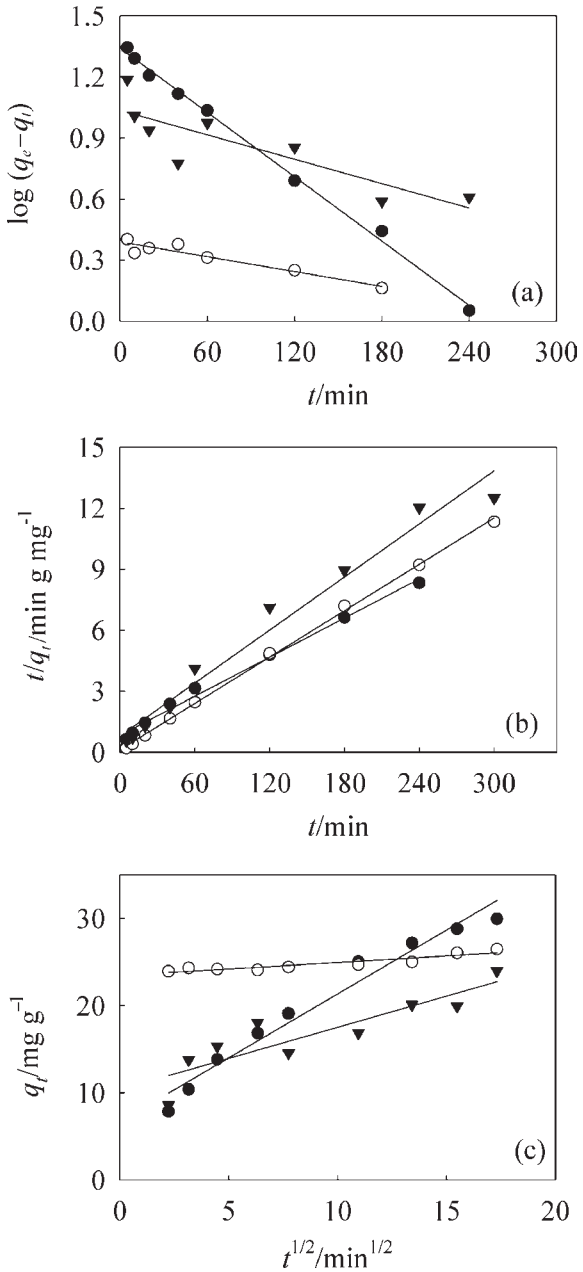


Fig. 2 – *Kinetics of Ni^{2+} adsorption for (a) pseudo first-order, (b) pseudo second-order, and (c) intraparticle diffusion models: ○ powdered L. japonica, ● immobilized algal beads, and ▼ blank beads. Experimental conditions: initial Ni^{2+} concentration, 80 mg L^{-1}; pH, 5.5; biosorbent dose, 2.0 g L^{-1}.*

The sorption kinetic parameters and correlation coefficients for the three kinetic models are presented in Table 1. Although the correlation coefficients of the three kinetic models for the immobilized algal beads were all high ($R^2 > 0.96$), the equilibrium biosorption capacity (32.25 mg g^{-1}) determined by the pseudo-second order model approached the experimental value (29.94 mg g^{-1}). The intraparticle diffusion model did not have an intercept equal to zero (Fig. 2(c)), which indicated that intraparticle diffusion is not the only rate-controlling step of the kinetic process. The pseudo-second order model can describe the sorption kinetics of the Ni^{2+} on the immobilized sorbent ($R^2 = 0.992$). According to the mechanism of the second-order model, the sorption of Ni^{2+} on the immobilized sorbent involved chemical sorption process. The chemical adsorption process is the main rate-limiting step, which may be connected with the covalent interaction of electron exchange and sharing between biosorbent and metal ions. The adsorption of Ni^{2+} on powdered *L. japonica* was also a good fit to the pseudo-second order model ($R^2 = 0.999$). This suggested that the powdered *L. japonica* in the immobilized sorbent plays a dominant role in the adsorption of Ni^{2+}.

Seen from Fig. 2(c), the boundary layer diffusion effect was greater on the adsorption of Ni^{2+} by powdered *L. japonica* than that of immobilized algal beads and blank beads according to the larger intercept.[17] In addition, the k_2 value of 0.017 g mg min^{-1} for adsorption of Ni^{2+} on powdered *L. japonica* was higher than that of immobilized algal beads (0.001 g mg min^{-1}). It could be inferred that immobilization could impact the adsorption process but not the biosorption capacity of powdered *L. japonica*.

Table 1 – *Kinetic model parameters for the adsorption of Ni^{2+} by algal beads*

		Immobilized algal cell beads	Powdery algae	Blank chitosan beads
Equilibrium biosorption capacity/mg g^{-1}		29.9	26.5	24.0
First-order kinetic model	q_e (mg g^{-1})	22.0	2.45	10.9
	k_1 (min^{-1})	0.012	0.003	0.005
	R^2	0.996	0.911	0.728
Second-order kinetic model	q_e (mg g^{-1})	32.25	26.0	23.0
	k_2 (g mg min^{-1})	0.001	0.017	0.002
	R^2	0.992	0.999	0.973
Intra-particle diffusion model	k_{id} (mg g^{-1} $min^{-1/2}$)	1.46	0.15	0.72
	R^2	0.966	0.856	0.789

Effect of the biosorbent dose on Ni^{2+} removal

The effect of adsorbent dose (0.5–7.5 g L^{-1}, the concentration of immobilized algal beads in solution) on the adsorption properties was studied at pH 5.5 at a fixed initial metal concentration of 80 mg L^{-1}. As the adsorbent dose increased, the Ni^{2+} removal efficiency increased and the biosorption capacity of the adsorbent beads decreased (Fig. 3). The increase in removal efficiency is due to an increase in the number of the binding sites as the adsorbent dose increases.[18,19] High concentrations of adsorbent can act like a screen to prevent the conjunction of metal ions and adsorption sites. The lower utilization of the adsorbents adsorptive capacity results in less commensurate increase in biosorption capacity.[15,20]

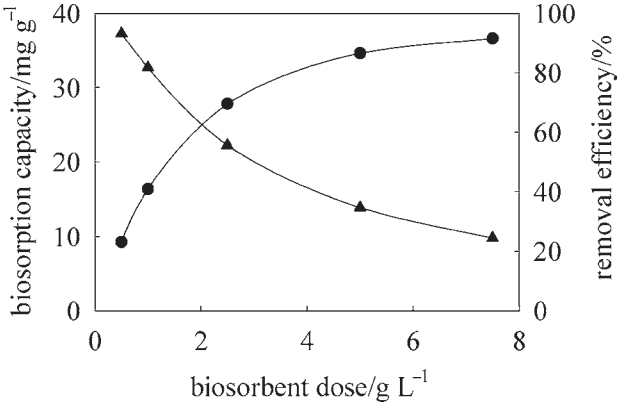


Fig. 3 – *Effect of the biosorbent dose on Ni^{2+} adsorption: ▲ biosorption capacity, and ● removal efficiency. Experimental conditions: initial Ni^{2+} concentration, 80 mg L^{-1}; pH, 5.5; temperature, 25 °C.*

Effect of initial Ni^{2+} concentration

Adsorption of Ni^{2+} by the beads was carried out at different initial metal ion concentrations (10–200 mg L^{-1}). The removal efficiency of Ni^{2+} decreased and the uptake capacity of the adsorbent increased with increasing initial Ni^{2+} concentrations (Fig. 4). Some studies have reported that the initial concentration provides an important driving force to overcome the mass transfer resistance of Ni^{2+} between the aqueous and solid phases.[21,22] Otherwise, increasing initial metal ion concentrations increase the chance of collisions between metal ions and

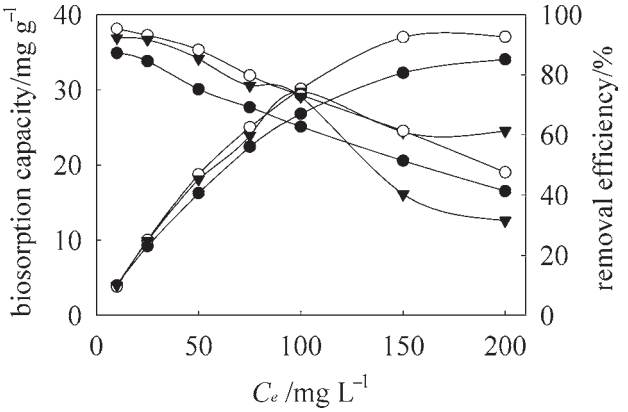


Fig. 4 – *Effect of the initial Ni^{2+} concentration on Ni^{2+} adsorption ○ powdery L. japonica, ● immobilized algal beads and ▼ blank beads. Experimental conditions: pH, 5.5; biosorbent dose, 2.0 g L^{-1}; temperature, 25 °C.*

sorbents. This enhances the adsorption process and increases the uptake capacity. However, as the initial concentration of Ni^{2+} increases, the adsorption sites reach saturation at the point of adsorption equilibrium. Consequently, the Ni^{2+} removal efficiency decreases with increasing Ni^{2+} concentration. In addition, the adsorption of Ni^{2+} by the immobilized algal beads, powdered *L. japonica*, and blank beads showed the same patterns, and were effective in the removal of low concentration nickel ions from aqueous solution. So the initial Ni^{2+} concentration 80 mg L^{-1} was chose in further studies.

Effect of pH

The effect of initial pH (2–8) on Ni^{2+} removal was studied at an initial Ni^{2+} concentration of 80 mg L^{-1}. The Ni^{2+} removal efficiency was very low at pH 2, and then increased until pH 3. From pH 3–8 the biosorption of Ni^{2+} was constant (Fig. 5).

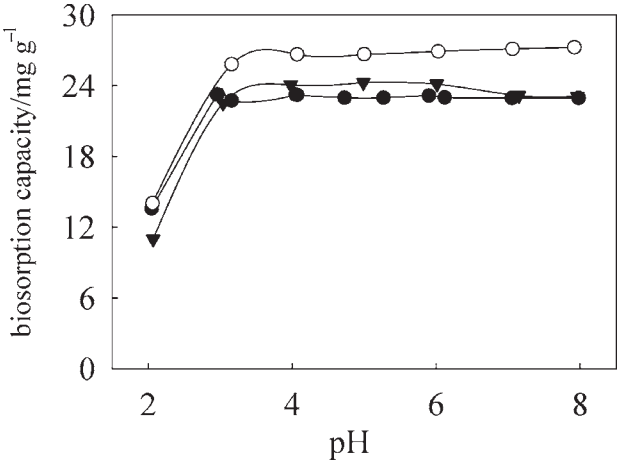


Fig. 5 – *Effect of pH on Ni^{2+} adsorption: ○ powdered L. japonica, ● immobilized algal beads, and ▼ blank beads. Experimental conditions: initial Ni^{2+} concentration, 80 mg L^{-1}; biosorbent dose, 2.0 g L^{-1}; temperature, 25 °C.*

Similar patterns were observed for the powdered algae, blank beads, and immobilized algal beads. The pH is expected to influence both metal binding sites on the cell surface and metal chemistry in water. At low pH, protons can compete effectively with Ni^{2+} for the binding sites, and the protonated binding sites are no longer able to bind Ni^{2+} from solution. As the initial pH increases, the ligands of the algae cell, such as carboxyl, phosphate, imidazole and amino groups, become negatively charged and attract the metal ions, which increases biosorption onto the cell surface.[23,24] Higher pH values were not examined, because at pH values >8.0 precipitation of the metal can occur due to metal hydroxide formation. The biosorption of Ni^{2+} by the immobilized algal beads could be adapted to solutions with wide range pH values (3–8).

Biosorption isotherms

Biosorption isotherm curves, derived from the equilibrium batch sorption experiments, were used to characterize the interaction of Ni^{2+} with the immobilized algal beads. The Langmuir model is based on the assumptions that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant, and there is no migration of absorbate molecules in the surface plane.[4] The Langmuir adsorption isotherm has traditionally been used to quantify and contrast the performance of different biosorbents.[25] Maximum biosorption capacity (Q_{max}) is determined by non-linear regression from isotherm studies. In comparison, the Freundlich isotherm is an empirical model that is based on sorption on a heterogeneous surface. It is assumed that the adsorption energy of a metal binding to a site on an adsorbent depends on whether the adjacent sites are already occupied.[26]

Analysis of the equilibrium data is important to develop an equation which accurately represents the results, and which could be used for design purposes. For each isotherm, the initial Ni^{2+} concentrations were varied while the adsorbent dose in each sample was kept constant (2 g L^{-1}). In this case, the Langmuir equation (eq. (9)) is traditionally applied:

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \tag{9}$$

The following form is the linearization of eq. (9):

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}} \tag{10}$$

where b is the sorption equilibrium constant.

The Freundlich isotherm is defined as follows:

$$q_e = KC_e^{1/n} \tag{11}$$

The linear form of eq. (11) is given by:

$$\ln q_e = \ln K + \left(\frac{1}{n}\right) \ln C_e \tag{12}$$

where K and n are empirically determined constants, with K being related to the maximum binding capacity, and n related to the affinity or binding strength.

The linearized Langmuir and Freundlich adsorption isotherms of Ni^{2+} obtained at 25 °C are given in Fig. 6. The adsorption parameters and their correlation coefficients are presented in Table 2. The correlation coefficients of the two models for the immobilized beads and powdered *L. japonica* were high ($R^2 > 0.94$), which indicates that the two models can be used to describe the adsorption of nickel on the immobilized beads and powdered *L. japonica*. The adsorption of Ni^{2+} on the sorbent is both a physical and chemical process, and is to heterogeneous surface or surfaces supporting sites of varied affinities.[27] The correlation coefficient for the Freundlich model of the blank beads is very low. According to the maximum uptake capacity and correlation coefficients, the immobilized algal beads and powdered *L. japonica* have the same adsorption properties for Ni^{2+}. This suggests *L. japonica* plays an important role in the adsorption of Ni^{2+} by the beads.

Using the Langmuir isotherm, the Q_{max} of Ni^{2+} by the immobilized algal beads, powdered *L. japonica* and blank beads was 38.3, 39.5 and 25 mg g^{-1} (Table 3), respectively. These values indicate that the immobilization does not impact the adsorption of Ni^{2+} on powdered *L. japonica*.

The Q_{max} values reported for Ni^{2+} adsorption on various cells can be compared: *Sargassum natans* (Q_{max} 22.3–44.02 mg g^{-1}),[7] *Chlorella vulgaris* (31.3 mg g^{-1}),[1] *Ascophyllum nodosum* (40.5 mg g^{-1}), *Scenedesmus* (26.7 mg g^{-1}),[28] *Scenedesmus quadricauda* immobilized by Ca-alginate (30.4 mg g^{-1}),[8] and *L. japonica* immobilized in Ca-alginate gel (39.43 mg g^{-1}).[22] These results illustrate that immobilization of powdered *L. japonica* in chitosan gel provides a very good biosorbent for Ni^{2+} removal. Direct comparison of the reported biosorbents is

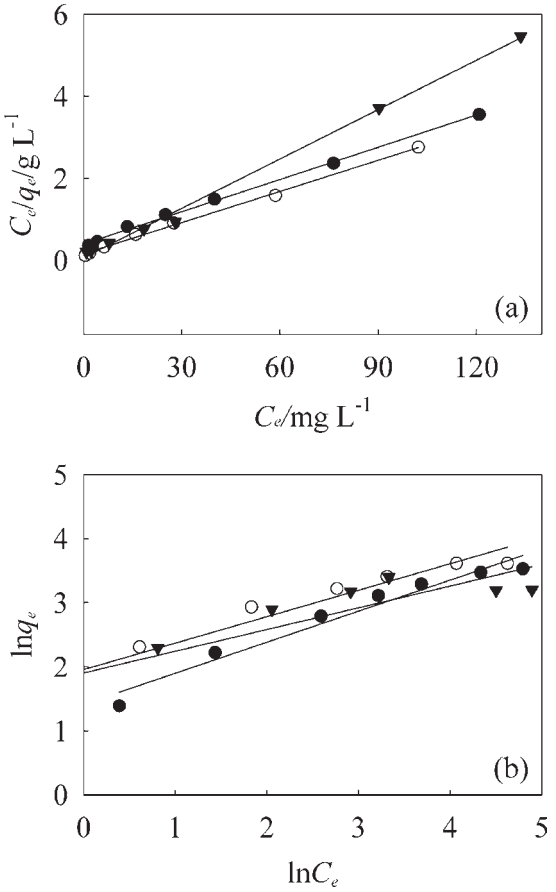


Fig. 6 – *The Langmuir (a) and Freundlich (b) isotherms for Ni^{2+} biosorption: ○ powdered L. japonica, ● immobilized algal beads, and ▼ blank beads. Experimental conditions: biosorbent dose, 2.0 g L^{-1}; pH, 5.5; temperature, 25 °C.*

Table 3 – *Percentage of Ni^{2+} desorbed from the algal beads with different solvents over five sequential cycles*

Cycle number		1	2	3	4	5
Removal efficiency (%)	HCl	71.73	90.39	95.48	51.51	36.3
	HNO_3	72.44	96.31	84.6	40.50	31.53

Table 2 – *Biosorption isotherms parameters for the adsorption of Ni^{2+} by algal beads*

	Langmuir model			Freundlich model		
	Q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	K ($mg^{(1-1/n)}$ $L^{1/n}$ g^{-1})	n	R^2
Immobilized algal cell beads	38.3	0.0648	0.997	4.11	2.07	0.960
Powdery algae	39.5	0.154	0.997	7.06	2.42	0.947
Blank chitosan beads	25	0.577	0.997	6.70	2.95	0.769

difficult due to variations in experimental conditions. However, it appears that the biosorption capacity of the biosorbent in the current study is high.

Biosorption-desorption cycles

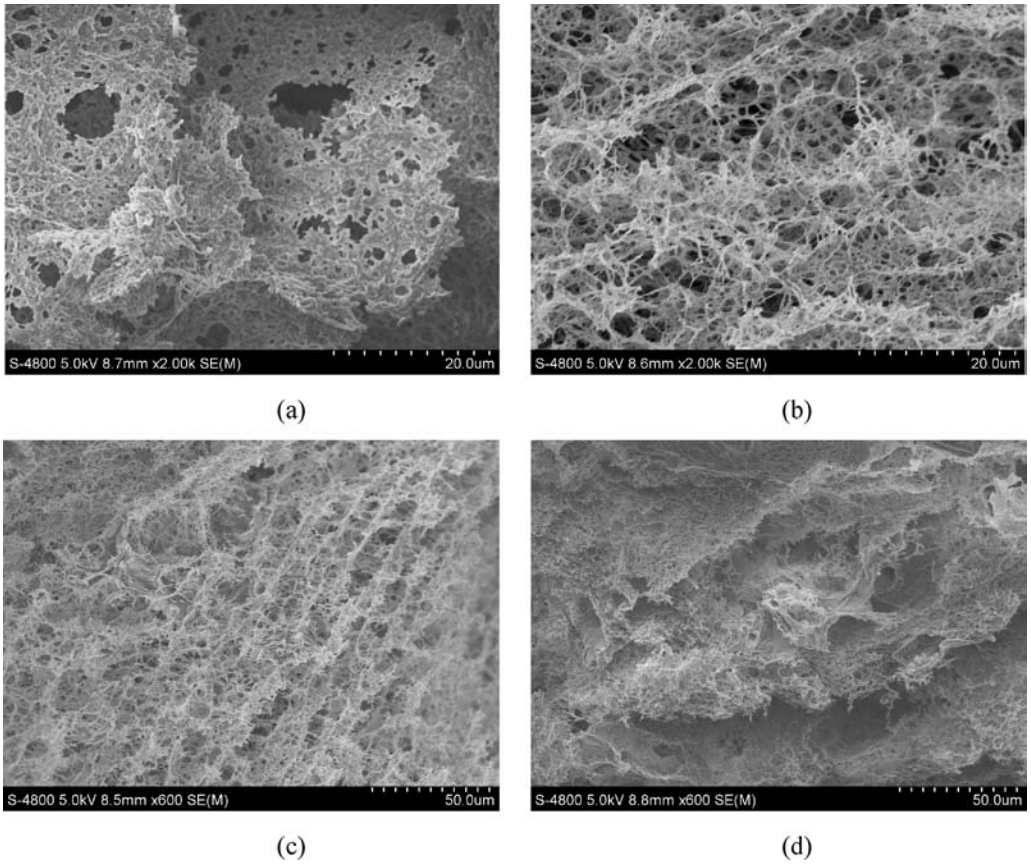
Desorption of metal ions from the loaded sorbent is required to recover the metal and reuse the sorbent. Elution is an effective method for this because it does not significantly reduce the binding capacity of the biomass and several cycles can be employed.

The Ni^{2+} desorption efficiency with 1 mol L^{-1} HCl or 1 mol L^{-1} HNO_3 approached >90 %, while with EDTA it was about 65 %. Consequently, 1 mol L^{-1} HCl or 1 mol L^{-1} HNO_3 could be used as an effective desorbent of Ni^{2+}.

To determine the reusability of the immobilized algal beads, adsorption-desorption cycles were repeated sequentially five times with the same beads. The removal efficiencies of the recycled beads were higher for the second and third cycles than the first (Table 3). This can be explained by the chemical modification of the sorbent beads by immersion in sodium hydroxide solutions, and an increase in new binding sites. The removal efficiencies decreased after three to five cycles. This was due to gradual destruction of the binding sites in the beads with each cycle. In addition the < 100 % desorption of adsorbed Ni^{2+} in each cycle, which resulted in carried over occupied adsorption sites from cycle to cycle. The relative efficiencies of adsorption and desorption indicate that recycling of the algal beads is feasible. The concentration ratio (the ratio of the concentration of the recovered metal to the concentration of metal in the original solution) value of Ni^{2+} was about 0.7 as *S*/*L* ratio (the ratio of adding amount of adsorbent to volume of desorbing agent) was 2 g L^{-1}. The metal ions in desorbent could be reused as metal chloride/nitrate.

Scanning electron microscopy

The blank and immobilized algal beads were characterized by scanning electron microscopy (Figs. 7(a) and (b), respectively). The internal structure of the immobilized algal beads is open, and different from that of the blank beads. The powdered *L. japonica* in the immobilized beads was embedded presenting fibrous structure after smashed in an ultrasonic cell pulverizer in the preparation of the immobilized beads, which is also beneficial for adsorption of Ni^{2+}. Figs. 7(c) and (d) are SEM images of the immobilized algal beads before and after ad-



F i g . 7 – *SEM images of blank beads (a) and immobilized algal beads (b) (×2000), and SEM images of the immobilized beads before (c) and after (d) adsorption (×600)*

sorption of Ni^{2+}. We can see that the open structure of the immobilized algal beads becomes closed after adsorption.

Conclusions

Immobilized *L. japonica* was prepared and used for the removal of Ni^{2+} from aqueous solution. The preparation of the sorbent beads was optimized based on the strength, adsorption properties, and modeling of the beads. Adsorption of Ni^{2+} onto the immobilized *L. japonica* followed pseudo-second order kinetics. The immobilization affected the adsorption process but not the adsorption capacity of powdered *L. japonica*. As the adsorbent dose increased, the Ni^{2+} uptake capacity decreased and the removal efficiency increased. The biosorption of Ni^{2+} by the sorbent occurred over a large pH range (3–8). The experimental results fit the Langmuir and Freundlich isotherm models. The powdered *L. japonica* in the immobilized beads played an important role in the adsorption of Ni^{2+}. The better desorbents were 1 mol L^{-1} HCl and 1 mol L^{-1} HNO_3. The immobilized *L. japonica* sorbent could be used at least three sorption/desorption cycles to remove Ni^{2+} from aqueous solutions.

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Symbols

q_e – equilibrium uptake capacity, mg g^{-1}
C_0 – initial Ni^{2+} concentration, mg L^{-1}
C_e – equilibrium Ni^{2+} concentration, mg L^{-1}
V – volume of the solution, L
m – mass of the sorbent, g
η – removal efficiency, –
C_i – desorbed Ni^{2+} concentration, mg L^{-1}
γ – desorption efficiency, –
k_1 – equilibrium constant of the first-order model, min^{-1}
q_t – uptake capacity at time t, mg g^{-1}
t – biosorption time, min
k_2 – equilibrium constant of the second-order model, g mg min^{-1}
h – initial rate constant of the second-order model, mg g^{-1} min^{-1}
k_{id} – rate constant of intraparticle diffusion model, mg g^{-1} $min^{-1/2}$
t/q_t – min g mg^{-1}
$t^{1/2}$ – $min^{1/2}$
Q_{max} – maximum biosorption capacity, mg g^{-1}
b – equilibrium constant of Langmuir model, L mg^{-1}
K – empirically determined constant of Freundlich model, $mg^{(1-1/n)}$ $L^{1/n}$ g^{-1}
n – empirically determined constant of Freundlich model, –
C_e/q_e – g L^{-1}

References

1. *Abu Al-Rub, F. A., El-Naas, M. H., Benyahia, F.,* Process Biochem. **39** (2004) 1767.
2. *Wang, J. L., Chen, C.,* Biotechnol. Adv. **24** (2006) 427.
3. *Rangsayatorn, N., Pokethitiyook, P., Upatham, E. S.,* Environ. Int. **30** (2004) 57.
4. *Wang, J. L., Chen, C.,* Biotechnol. Adv. **27** (2009) 195.
5. *Saygideger, S., Gulnaz, O., Istifli, E. S., Yucel, N.,* J. Hazard. Mater. **B126** (2005) 96.
6. *Roberto, H., Pablo, L., Carlos, R. C.,* Water Res. **39** (2005) 3199.
7. *Davis, T. A., Volesky, B., Alfonso, M.,* Water Res. **37** (2003) 4311.
8. *Bayramoğlu, G., Yakup Arıca, M.,* Bioresour. Technol. **100** (2009) 186.
9. *Liu, Y. H., Cao, Q. L., Luo, F., Chen, J.,* J. Hazard. Mater. **163** (2009) 931.
10. *Chojnacka, K., Chojnacki, A., Górecka, H.,* Chemosphere **59** (2005) 75.
11. *Ghimire, K. N., Inoue, K., Ohto, K., Hayashida, T.,* Bioresour. Technol. **99** (2008) 32.
12. *Luo, F., Liu, Y. H., Li, X. M., Xuan, Z. X., Ma, J. T.,* Chemosphere. **64** (2006) 1122.
13. *Wang, X. S., Li, Z. Z.,* Clean. **37** (2009) 663.
14. *Wang, X. S., Li, Z. Z., Sun, C.,* J Hazard. Mater. **153** (2008) 1176.
15. *Jeon, C., Park, K. H.,* Water Res. **39** (2005) 3938.
16. *Singh, R. S., Singh, V. K., Tiwari, P. N., Singh, J. K., Sharma, Y. C.,* Environ. Technol. **30** (2009) 355.
17. *Laohaprapanon, S., Marques, M., Hogland, W.,* Clean. **38** (2010) 1055.
18. *Tüzüna, İ., Bayramoğlub, G., Yalçin, E.*, J Environ. Manage. **77** (2005) 85.
19. *Gok, C., Aytas, S.,* J. Hazard. Mater. **168** (2009) 369.
20. *Lodeiro, P., Rey-Castro, C., Barriad, J. L.,* J Colloid and Interface Sci. **289** (2005) 352.
21. *Hashima, M. A., Chub, K. H.,* Chem. Eng. J. **97** (2004) 249.
22. *Xu, Z. Z., Fan, W. H., Feng, L. J.,* Prog. Environ. Sci. Technol. **1** (2007) 1122.
23. *Yang, L., Chen, J. P.,* Biores. Technol. **99** (2008) 297.
24. *Romera, E., González, F., Ballester, A.,* Bioresour. Technol. **98** (2007) 3344.
25. *Lin, C., Lai, Y.,* J. Hazard. Mater. **137** (2006) 99.
26. *Vijayaraghavan, K., Padmesh, T. V. N., Palanivelu, K., Velan, M.,* J. Hazard. Mater. **B133** (2006) 304.
27. *Tuzena, M., Sarl, A., Mendila, D.,* J. Hazard. Mater. **165** (2009) 566,
28. *Hu, Z. L., Wong, Y., Tam, F. Y.,* Acta Botanica Sinica. **44** (2002) 97.