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Biosorption of Nickel Ions by Immobilized Brown Algae *Laminaria japonica*

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Brown alga *Laminaria japonica* was immobilized using sodium alginate and glutin and used as biosorbent for removal of Ni^{2+} from aqueous solutions. The preparation conditions of the adsorbent beads were optimized by determining the optimal concentrations of the sodium alginate and glutin solution and the dose of *L. japonica*. The biosorption equilibrium of Ni^{2+} by the immobilized *L. japonica* beads is reached at 180 min. The initial pH of 4-7 has no appreciable influence on nickel biosorption. When the biosorbent dose is increased, nickel biosorption capacity decreases, whereas removal efficiency increases. An EDTA solution of 0.001 mol/L is the better desorbent. The regenerated biosorbent can be reused, with biosorption capacity decreasing by only 18 % after 5 cycles.

Key Words: Nickel ion biosorption, *Laminaria japonica*, Desorption, SEM.

INTRODUCTION

Biosorption can be defined as the removal of metal or metalloid species, compounds and particulates from solutions by biological materials, such as fungi, yeast and algae[1]. Compared with conventional methods such as chemical precipitation, coagulation, solvent extraction, membrane separation and ion exchange, the biosorption process offers several advantages, including low operating cost, minimization of the volume of chemical and biological sludge to be disposed of, no secondary pollution, high efficiency in detoxifying highly dilute effluents and no nutrient requirements[2]. The biomaterial acting as a biosorbent, however, usually introduces practical problems when used in continuous processes. These problems are low density and strength, softening and separation difficulty after contact with water. Thus, cell immobilization or chemical modification is required for the practical application of biomaterials[3].

Cell immobilization is an effective technique for fixing and retaining biomass on suitable natural or synthetic material support for a range of physical and biochemical unit operations[4]. The key to biosorption by immobilized biosorbents is the selection of biomaterials and carrier materials. Of the many types of biomaterials (*e.g.*, fungi, bacteria and yeasts) recently investigated for their ability to sequester heavy metals, brown algal biomass has been found to be an effective biosorbent in removing heavy metals from wastewater[5,6]. In view of their high biosorption capacity as well as low cost, *Laminaria japonica* (a kind of brown algae) was used in this study as the biomaterial for creating immobilized algae biosorbents. As a natural polymer, sodium alginate forming calcium alginate gel in a calcium chloride solution is a reliable carrier material because it incurs low cost, is non-toxic, produces no secondary pollution and has good biocompatibility and mass transfer performance. Soluble in hot conditions and forming reversible gels, glutin can play an important role in supporting the skeleton by remaining in stable form, bearing greater load and reducing the brittleness of the biosorbents. Therefore, sodium alginate and glutin were used as carrier materials in this research.

This study aims to prepare a biosorbent with brown alga *L. japonica* as the biomaterial and sodium alginate and glutin as carrier materials, as well as investigate the nickel biosorption and desorption performance of the immobilized *L. japonica* biosorbent. The preparation conditions were optimized by determining the optimal concentrations of the sodium alginate and glutin solution and the *L. japonica* dose. The effect of contact time, initial pH, adsorbent dose and initial nickel ion concentration on the sorption capacity was examined. Biosorbent characterization was performed by SEM analysis.

EXPERIMENTAL

Biosorbent preparation: *L. japonica* was washed and dried in a freezing drier for 24 h. The dried biomass was crushed, ground to powder and stored in a desiccator.

Mechanical and airflow grinding processes were applied to crush the dry algae. After mechanical grinding, part of the algae powder was divided into different particle sizes: 1-61, 61-150 and 150-180 μm. The remaining part was further ground into a particle size of 0.3-80 μm by airflow grinding. The nickel biosorption by the powdered algae of different particle sizes was compared.

Immobilized algae beads were prepared by entrapping the powdered *L. japonica* in an alginate matrix produced by ionic polymerization in a calcium chloride solution, according to the following steps: The powdered *L. japonica* was suspended in the sodium alginate and glutin solution, made by dissolving sodium alginate and glutin in deionized water that was kept at a temperature of 60 ºC with continuous agitation. The mixture was then dropped into a 4 % calcium chloride solution using a peristaltic pump. The drops of Na-alginate solution gelled into 2 ± 0.1 mm diameter beads that are in contact with the calcium chloride solution. The immobilized algal beads were stored in the calcium chloride solution for at least 4 h to complete gelation. The beads were rinsed and then dried in a freezing drier for 12 h prior to use.

The preparation conditions were optimized by changing the concentration of the sodium alginate and glutin solution, as well as the dose of *L. japonica*. The operational processes of the biosorbent preparation, molding of the biosorbent beads and biosorption capacity of the different beads by biosorption experiments were then compared. The blank alginate beads were prepared using the sodium alginate and glutin solution under the above mentioned conditions without algae.

Biosorption experiments: All biosorption experiments were conducted by adding the desired dose of biosorbent into 100 mL of the metal solution of desired concentration in 300 mL bottles with shaking for 300 min at room temperature. The initial solution pH was adjusted using dilute hydrochloric acid and sodium hydroxide solutions. The concentration of nickel ions was determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Perkin-Elmer 3300DV).

Biosorption-desorption cycle experiments: For the desorption studies, 2.5 g/L immobilized algae cell beads were placed in a nickel solution and agitated for 300 min. The beads loaded with Ni^{2+} were then collected and gently washed with deionized water to remove any unadsorbed Ni^{2+}. The beads were agitated with 100 mL of various desorbents including ethylenediaminetetraacetic acid (EDTA), HCl and HNO_3 in a water bath shaker at room temperature (25 ºC)[7]. To test the reusability of the beads, adsorption-desorption cycles were repeated 5 times using the same affinity adsorbent.

Evaluation method for biosorption: The biosorption properties of the immobilized algae beads and the desorption efficiency of the desorbents were evaluated in terms of uptake capacity, removal efficiency and desorption efficiency according to the following equations:

$$\eta = \frac{C_o - C_e}{C_o} \times 100\ \% \quad (1)$$

$$q_e = \frac{(C_o - C_e)V}{w} \quad (2)$$

$$\gamma = \frac{C_t}{C_o - C_e} \times 100\ \% \quad (3)$$

where q_e is the equilibrium biosorption capacity (mg/g), C_o denotes the initial Ni^{2+} concentration (mg/L), C_e is the equilibrium Ni^{2+} concentration (mg/L), V represents the volume of the solution (L) , w is the mass of the sorbent (g), η denotes the removal efficiency, C_i is the desorpted Ni^{2+} concentration (mg/L) and γ is the desorption efficiency.

RESULTS AND DISCUSSION

Biosorbent preparation

Effect of algae particle size on nickel ion removal: The result of nickel ion removal by the algae of different particle sizes (0.3-80, 1-61, 61-150 and 150-180 μm) is shown in Table-1. With decreasing algae particle size, the biosorption capacity of Ni^{2+} by the powdered algae increases to a certain extent. The removal efficiency of the powdered algae with the 0.3-80 μm particle size can reach 87.3 %. As the particle size of the powdered algae decreases, not only do the specific surface area of the powdered algae and the contact area of the algae cells with Ni^{2+} increase, but the functional groups of the cell wall for metal ion binding are also exposed. These changes are beneficial to Ni^{2+} removal. Thus, the immobilized biosorbent beads were prepared using the powdered algae with the particle size of 0.3-80 μm.

TABLE-1
EFFECT OF ALGAE PARTICLE SIZE ON BIOSORPTION OF NICKEL IONS

Algae particle size (μm)	Biosorption capacity (mg/g)	Removal efficiency (%)
150-180	26.68	83.79
61-150	26.36	82.79
1-61	27.16	85.3
0.3-80	29.96	87.3

Optimization of biosorbent bead preparation: Figs. 1(a) and 1(b) show the effect of the concentrations of the sodium alginate and glutin solution, respectively, in the preparation of the immobilized algae beads on nickel ion removal as the powdered *L. japonica* dose is kept constant. As shown in Fig. 1(a), without glutin in the carrier solution, the biosorption capacity of Ni^{2+} by the immobilized biosorbent beads is very low. When glutin is added, the biosorption capacity considerably increases; however, there is no clearly observable change in the biosorption capacity when the concentration of glutin is increased.

As seen in Fig. 1(b), the concentration of sodium alginate has little influence on nickel biosorption. When the concentration of sodium alginate is 2 %, the biosorption capacity of nickel ions is high and the biosorbent preparation and molding of the biosorbent beads are easily and conveniently carried out. A 2.5 % concentration of sodium alginate is excessively high for the favourable preparation of adsorbent beads. Therefore, the best concentrations of glutin and sodium alginate in the preparation of biosorbent beads are 0.5 and 2.0 %, respectively.

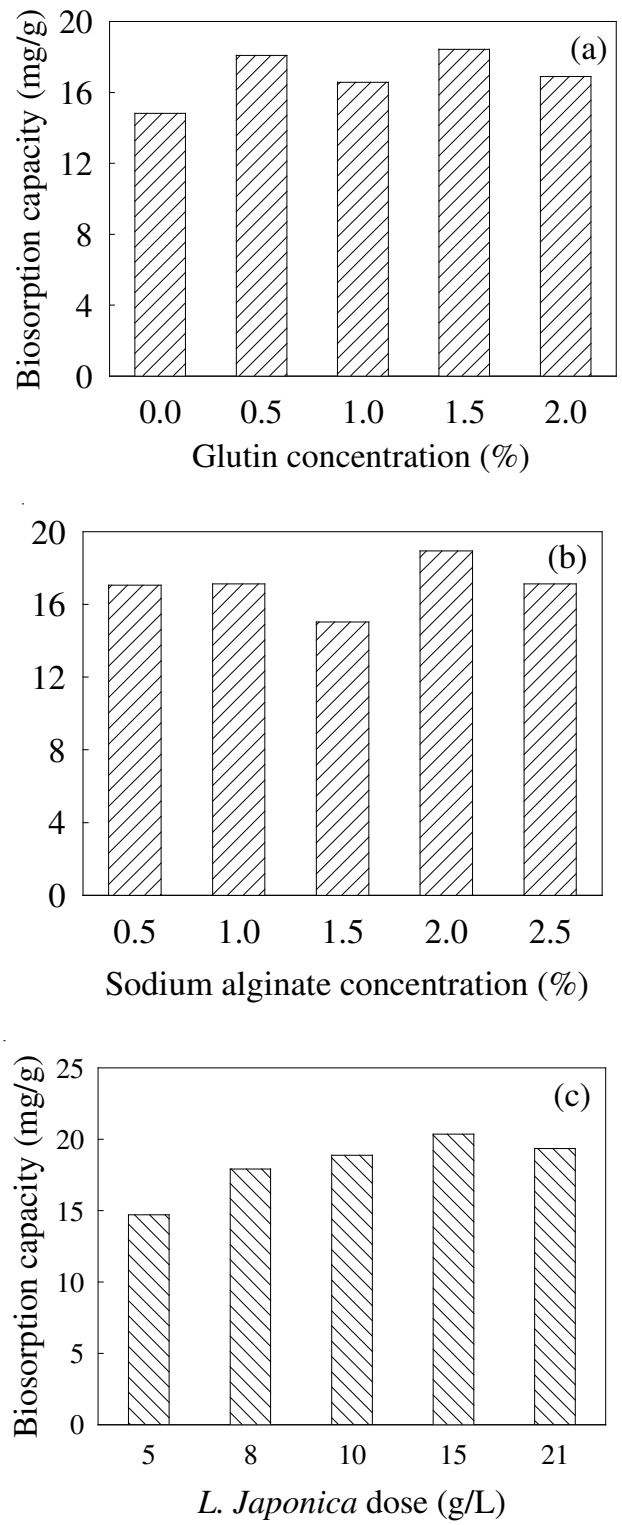

Fig. 1. Effect of the concentration of (a) glutin, (b) sodium alginate and (c) *L. japonica* dose on nickel ion removal

Fig. 1(c) shows the effect of the powdered *L. japonica* dose on nickel ion removal when the concentrations of glutin and sodium alginate are kept constant in the preparation of the biosorbent beads. The biosorption capacity increases with increasing *L. japonica* dose. A biomass concentration of 21 g/L, however, leads to an excessively high *L. japonica* dose. The optimum *L. japonica* dose, therefore, is 15 g/L.

The biosorbent beads prepared in these conditions have high strength and biosorption capacity, as well as regular shapes. The biosorption experiments were carried out using biosorbent beads that were prepared under the best conditions.

Effect of contact time on nickel ion removal: Contact time is a key parameter for designing sorption systems and is required in the selection of optimum operating conditions for the nickel ion removal process. Fig. 2 shows that biosorption equilibrium can be reached in 180 min with biosorbent beads. After this equilibrium period, the biosorption capacity of nickel ions by the powdered *L. japonica* does not appreciably change with time. The biosorption capacity of nickel by biosorbent beads is very rapid at the beginning, but gradually plateaus over time. This differs from the biosorption capacity of nickel by powdered *L. japonica*, in which equilibrium can be reached in 5 min. We can conclude that immobilization can affect nickel biosorption by algae cells. Compared with the biosorption capacity of nickel ions by three sorbents, powder algae cells > biosorbent beads > blank beads. It is also inferred that the powdered algae can play an important role in the biosorption of nickel ions in immobilized algae beads and immobilization can affect the biosorption capacity of algae to a certain extent.

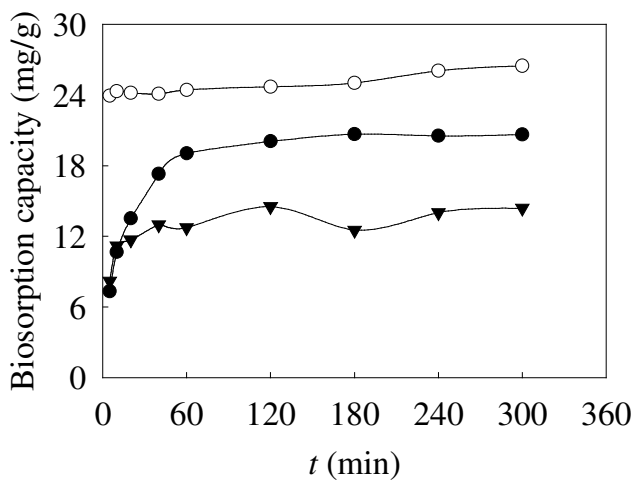

Fig. 2. Effect of contact time on nickel ion removal (○ powdery *L. japonica*, ● immobilized algae cell beads and ▼ blank beads)

Effect of biosorbent dose on nickel ion removal: The effect of a biosorbent dose of 1-10 g/L on biosorption at a fixed initial nickel concentration of 80 mg/L with pH 5.5 was studied. Fig. 3(a) illustrates that the removal efficiency of nickel ions increases, whereas the biosorption capacity of the biosorbent beads decreases when the biosorbent dose is increased from a given initial solute concentration. With increasing biosorbent dose, the number of binding sites increases, thereby increasing removal efficiency[8]. By producing a screen effect, high biosorbent concentration can prevent the conjunction of the metal ions and biosorption sites. There is less commensurate increase in biosorption capacity because of the lower adsorptive capacity utilization of the adsorbent[9,10]. When the biosorbent dose is 2.5 g/L, the removal efficiency is higher, enabling the effective use of the biosorbent. The subsequent studies were carried out at this dose.

Effect of initial nickel ion concentration: The effect of initial nickel ion concentration on biosorption was studied at different initial metal ion concentrations (10-200 mg/L). The results are shown in Fig. 3(b). The initial concentration provides an important driving force in overcoming mass transfer resistance of the nickel between the aqueous and solid phases[11,12]. With increasing initial nickel ion concentrations, which results in increased chances of collision between metal ions and sorbents, the biosorption capacity of the biosorbent increases. However, with increasing initial concentration, the removal efficiency of the nickel decreases because the adsorption sites saturate when the adsorption reaches equilibrium[13]. As seen in Fig. 3(b), the biosorption of nickel by the biosorbent beads, powdered *L. japonica* and blank beads show the same regularity and effectivity in the removal of low concentration nickel ions from aqueous solutions. The removal efficiency remains above 60 % when the concentration of nickel is lower than 50 mg/L, indicating that the biosorbent beads are suitable for treating wastewater with low nickel concentration.

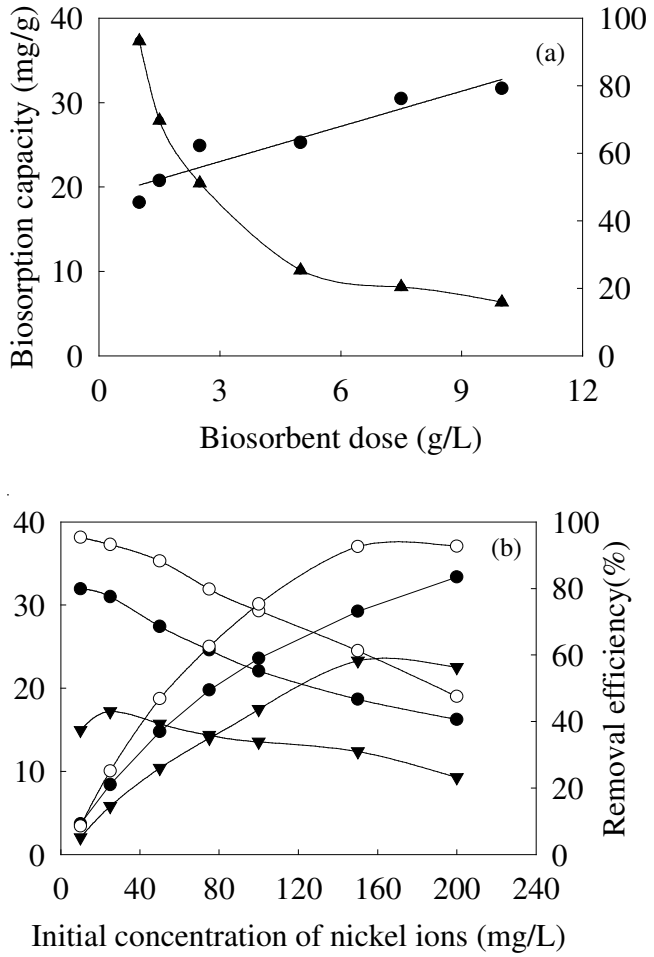

Fig. 3. Effect of the (a) biosorbent dose (▲ biosorption capacity and ● removal efficiency) and (b) initial nickel ion concentration on nickel ion removal (○ powdery *L. japonica*, ● immobilized algae cell beads and ▼ blank beads)

Effect of pH: Heavy metal sorption is highly pH dependent. The effect of initial pH on nickel ion removal was studied at 80 mg/L initial nickel concentration by changing the pH value from 2-7. The obtained results are plotted in Fig. 4, showing that the biosorption of Ni^{2+} by the biosorption beads is highly pH dependent. The sorption of Ni^{2+} by the powdered algae and blank beads shows the same phenomenon as that exhibited by biosorption beads. The removal efficiency of Ni^{2+} is extremely low at pH 2 and increases at pH 3; it remains constant at pH 4-7. The pH value is expected to influence both the metal binding sites on the algae cell surface and metal chemistry in water. The pH dependence of nickel biosorption can be explained by considering the nature of the biosorbent. The cell wall of algae contains a large number of surface-functional groups acting as binding sites. At low pH levels, protons can compete effectively with nickel ions for the binding sites of the biomass. The protonated binding sites are thus no longer available to bind nickel ions from the solution. As the pH increases, more ligands of the algae cell, such as carboxyl, phosphate, imidazole and amino groups, carry negative charges with a subsequent attraction of metal ions and biosorption onto cell surface increases[14-18]. We can conclude that biosorption of nickel ions by the immobilized algae beads adapts to the solution with the wide pH value range (4-7).

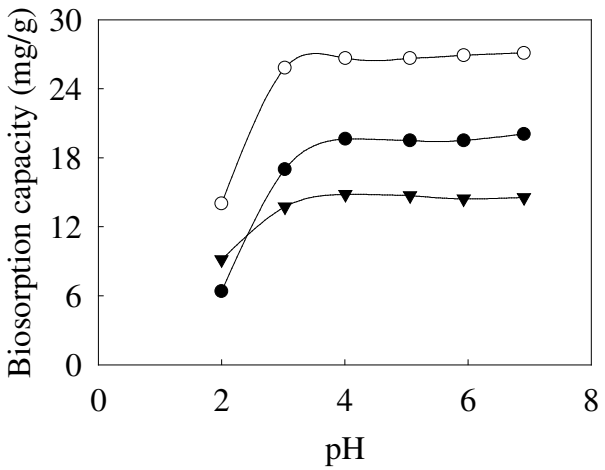

Fig. 4. Effect of pH on nickel ion removal (○ powdery *L. japonica*, ● immobilized algae cell beads and ▼ blank beads)

Biosorption-desorption cycles: The desorption process of heavy metal ions from loaded sorbents is very important if the biosorbent is to be applied to actual wastewater, the metal recovered and the sorbent reused. Figs. 5(a) and 5(b) show the desorption efficiency of nickel ions for various desorbents (HCl, HNO_3 and EDTA) of different concentrations and the second biosorption capacity of nickel ions by the corresponding biosorbents. The desorption efficiency levels of nickel ions using HCl, HNO_3 and EDTA all approach about 90 %, but the second biosorption capacity of nickel ions by the biosorbent after desorption by 0.001 mol/L EDTA is higher. Acids of high concentrations can destroy the structure of the algae cell wall and influence the biosorption capacity of nickel ions. Because EDTA is known as a highly strong chelating agent for many heavy metals, it was considered as a replacement for the groups on the bead complex with nickel ions and used to make complexes with nickel ions. Consequently, 0.001 mol/L EDTA was chosen as the desorbent.

The reusability of biosorbents can reduce costs and increase efficiency in environmental remediation. To achieve the reusability

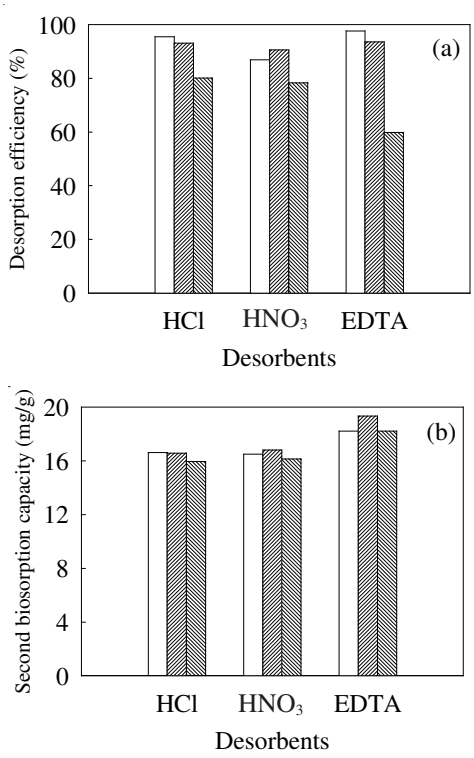

Fig. 5. Desorption efficiency of various desorbents of different concentrations (a) and the second removal efficiency of recycled beads (b) ▭ 1 mol/L HCl, HNO_3 and saturated EDTA; ▨ 0.1 mol/L HCl, HNO_3 and 0.001 mol/L EDTA; ▩ 0.01 mol/L HCl, HNO_3 and 0.005 mol/L EDTA

of the immobilized algae cell beads, sequential biosorption-desorption cycles were repeated five times using the same beads. The removal efficiencies of the recycled beads are shown in Table-2. The biosorption capacity decreases by 18 % after five consecutive adsorption-desorption cycles. This can be explained by the binding sites in the beads being destroyed gradually in each cycle and some of the adsorbed Ni^{2+} being undesorbed in the previous cycle; thus, the undesorbed Ni^{2+} still occupies the adsorption sites. Therefore, optimizing the biosorption-desorption conditions, improving biosorption ability and prolonging the operating life of the immobilized algae beads are needed. After examining the relative efficiencies of biosorption and desorption, we find that the reusability of sorbent beads is feasible. Consequently, immobilized *L. japonica* beads can be used as an economical alternative in actual processes.

TABLE-2
REGENERATION ON Ni^{2+} FOR IMMOBILIZED ALGAE BEADS

Cycle number	1	2	3	4	5
Biosorption capacity (mg/g)	20.7	17.4	16.3	16.0	16.4

Scanning electron microscopy: The blank and immobilized algae beads were characterized using a scanning electron microscope (SEM). Fig. 6 shows the SEM images of the surface and section of the blank and immobilized algae beads. The surfaces of the blank and immobilized algae beads are covered with wrinkles; however, the surface of the immobilized algae beads has more wrinkles than that of the blank beads. The internal structures of the blank and immobilized algae beads resemble a honeycomb. The powdered *L. japonica* in the

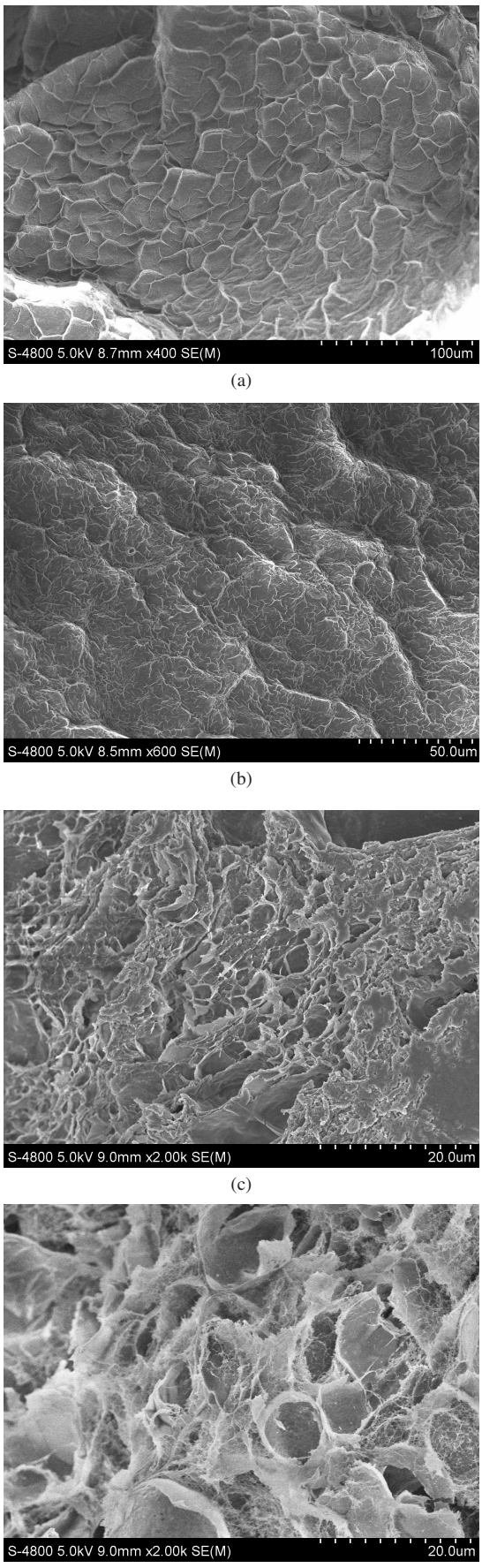

Fig. 6. SEM photographs of the surface of (a) blank beads (× 400) and (b) immobilized algae cell beads (× 600) and the section of (c) blank beads (× 2,000) and (d) immobilized algae cell beads (× 2,000)

immobilized beads is embedded in the internal structure, showing a flaky structure that is beneficial to the biosorption of nickel ions.

Conclusion

The preparation of an immobilized biosorbent with brown alga *L. japonica* as biomaterial, as well as sodium alginate and glutin as carrier materials, was investigated. The feasibility of this biosorbent for the removal of nickel ions from aqueous solutions was proved. The preparation of the biosorbent beads was optimized using biosorption capacity and modeling of the beads as bases. As biosorbent dose increases, nickel uptake capacity decreases, whereas removal efficiency increases. The biosorption of nickel ions by the biosorbent adapts to the solution with a wide pH range (4-7). The 0.001 mol/L EDTA solution is the best desorbent. Sequential biosorption-desorption cycles were repeated five times using the same beads, with biosorption capacity decreasing by 18 %. The immobilized *L. japonica* biosorbent can be used in successive sorption/desorption cycles to remove nickel ions from aqueous solutions. Thus, the immobilization of *L. japonica* by sodium alginate and glutin can provide an efficient and promising biosorbent for the removal of heavy metal ions from aqueous solutions.

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