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Enhanced biosorption of nickel(II) ions by silica-gel-immobilized waste biomass: Biosorption characteristics in batch and dynamic flow mode

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ABSTRACT

Batch and dynamic flow biosorption studies were carried out using the waste biomass entrapped in silica-gel matrix for the removal of nickel(II) ions from synthetic solutions and real wastewater. Batch biosorption conditions were examined with respect to initial pH, S/L ratio, contact time, and initial nickel ion concentration. Zeta potential measurements showed that immobilized biosorbent was negatively charged in the pH range of 3.0–8.0. The immobilized biomass was found to possess relatively high biosorption capacity (98.01 mg g^{-1}), and biosorption equilibrium was established in a short time of operation (5 min). The equilibrium data were followed by Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models. Scanning electron microscope analysis was used to screen the changes on the surface structure of the waste biomass after immobilization and nickel(II) biosorption. Sorbent–sorbate interactions were confirmed by Fourier transform infrared spectroscopy. The applicability of sorbent system was investigated in a continuous mode, and column studies were performed under different flow rate, column size, and biosorbent dosage. Also, the proposed sorbent system was successfully used to remove the nickel ions from industrial wastewater in dynamic flow treatment mode. The results showed that silica-immobilized waste biomass was a low-cost promising sorbent for sequester of nickel(II) ions from synthetic and real wastewater.

1. Introduction

Heavy metals are a group of pollutants that disperse both naturally and by human activities into the environment. Effluents from several industrial operations like electroplating, mining, and metal processing are one of the major contributors to unnatural metal contamination in water sources. Uncontrolled release of heavy metals into the environment can create toxic or inhibitory effect on living systems. Treatment of heavy metals from contaminated effluents using the currently practiced technologies appears to be inadequate and their use is often restricted because of secondary problems with metal-bearing sludge which are extremely difficult to be disposed [1,2].

Therefore environmentally friendly and cost effective new technologies are required for the removal of heavy metals from these waste streams by appropriate treatment before releasing into receiving water bodies. One of the promising alternatives that are receiving more attention is application of biosorption process based on metal–biomass interactions. Microbial and plant origin biomasses were successfully used as biosorbent material in many biosorption studies [3–6].

Biosorption process can use free and immobilized forms of biomasses. Especially, in column applications the use of immobilized form of biomasses provides some advantages, such as improved biosorption capacity and ability to regenerate and separate the biomass from bulk liquid. In addition, easy operation of repeated biosorption–desorption cycles with immobilized biomasses makes the biosorption process potentially more economic and competitive [7–10].

Therefore, some efforts have been made to develop new immobilized biosorbent systems for detoxifying the heavy metals from contaminated waters. Some natural or synthetic polymeric materials including alginates, carrageenan, agar, polyacrylates, silica gel, etc. [11,12] are commonly used as immobilization matrix. Silica gel is a nontoxic, inert, and efficient support and is generated by decreasing the pH value of alkali silicate solution to less than 10. Reactive sites of silica gel exist in large number, and therefore, the number of immobilized organic molecules is high, which results in good sorption capacity for metal ions [11,13–15].

In a recent study, we reported that the waste biomass of *Phaseolus vulgaris* L. can remove a textile dye AR57 [16] from aqueous media as the most potent biosorbent with the high biosorp-

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tion capacity (215.13 mg g^{-1}). However, no studies have thus far reported about the biosorption potential of this waste biomass for heavy metal removal from contaminated solutions. In this present study, we show that the waste biomass of *P. vulgaris* L. derived from canned food plant is capable of nickel(II) biosorption, and its nickel removal capacity was enhanced by immobilization with silica-gel matrix. Biosorption conditions of immobilized biomass were screened by varying the pH, sorbent dosage, contact time and initial metal ion concentration. The mechanism of the biosorption and the surface structure of the biomass were examined by FTIR and scanning electron microscope (SEM) analysis, respectively. Biosorption performance of the immobilized biomass was investigated in continuous mode in addition to determination of various isotherm parameters. Finally, its application for nickel biosorption in real wastewater conditions was also tested in a column.

2. Materials and methods

2.1. Preparation of the biosorbent

The biosorbent used in this study, *Phaseolus vulgaris* L., was provided as a waste biomass, from a canned food factory in Bartın, Turkey. It had been washed with deionized water three times, and dried at 80 °C, to obtain a constant weight. Next, it was grounded and sieved, using an ASTM Standard sieve, to select the particle sizes of 100 mesh and used for immobilization. An immobilization procedure previously described by Lopez et al. [17] was used with some modifications. About 10 g of silica gel was dissolved in 100 mL of 7% (w/v) aqueous solution of potassium hydroxide by heating. After cooling to 20 °C, 100 mL of suspension containing 5 g of biomass in deionized water was added and mixed. A measured amount of phosphoric acid solution (20%) was added, enough to provide the gel formation. The resulting gel was dried at 333 K for 12 h in an oven and subsequently used as a sorbent material in powdered form. Blank silica gel was prepared similarly without having waste biomass and tested for its nickel sorption capacity.

2.2. Biosorption in batch scale

The batch biosorption experiments were performed by mixing 0.1 g of immobilized biomass in 50 mL of synthetic solutions at 100 mg Ni(II) L^{-1} for the determination of optimum pH value. The pH of the solutions was adjusted to different values with 0.1N nitric acid (HNO_3) and 0.1N sodium hydroxide (NaOH). The mixtures were mixed on a magnetic stirrer at a rate of 200 rpm. The best amount of biomass was determined by changing the biomass dosage between 0.02 and 0.2 g in 50 mL of solution. The equilibrium time was studied within the time interval of 5–120 min, and the temperature of the solution was controlled at 25 ± 2 °C. Suspended solids were separated from the biosorption medium by centrifugation at 4500 rpm for 3 min and nickel(II) ion concentrations were then measured using Flame atomic absorption spectrophotometer. The equilibrium data were analyzed by some isotherm models by changing the initial nickel(II) ion concentration from 75 to 500 mg L^{-1} for immobilized biosorbent.

2.3. 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. The isotherm models are widely used parameters to examine the relationship between biosorption capacity and sorbate concentration at equilibrium. Among the various sorption isotherm models, Langmuir, Freundlich, and Dubinin–Radushkevich models are widely used for fitting the data.

2.3.1. Langmuir isotherm

The Langmuir isotherm model has been successfully applied to many biosorption processes and the basic Langmuir theory is that biosorption takes place at specific homogeneous sites within the biosorbent [18]. The Langmuir equation [19] is

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

where q_e and q_{max} are the equilibrium and monolayer biosorption capacities of the biosorbent (mol g^{-1}), respectively, C_e is the equilibrium Ni(II) concentration in the solution (mol L^{-1}) and K_L is the Langmuir constant (L mol^{-1}) related to the free energy of biosorption.

The Langmuir constant, K_L, can be used to determine the suitability of the biosorbent to sorbate by using Hall separation factor (R_L, dimensionless) and R_L can be calculated as follows [20]:

$$R_L = \frac{1}{1 + K_L C_o} \quad (2)$$

where C_o is the highest initial sorbate concentration (mol L^{-1}).

2.3.2. Freundlich isothrem

The Freundlich equation is an empirical expression based on biosorption on a heterogeneous surface. The Freundlich [21] model is represented by the equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where K_F (L g^{-1}) is Freundlich constant related to biosorption capacity of biosorbent and n (dimensionless) is Freundlich exponent indicating the biosorption intensity [21,22].

2.3.3. Dubinin–Radushkevich isotherm

Since the Freundlich and Langmuir isotherm models do not give any idea about the mechanism of biosorption, the equilibrium data are tested with the D–R isotherm model. Dubinin and Radushkevich [23] have reported that the characteristic biosorption curve is related to the porous structure of the sorbent. The Dubinin–Radushkevich (D-R) equation is generally expressed as follows:

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

where $\varepsilon = RT\ln(1 + 1/C_e)$ (Polanyi potential), q_m is the biosorption capacity (mol g^{-1}), β is the constant related to the biosorption energy, R is the gas constant (8.314 kJ mol^{-1}) and T is the absolute temperature (K).

Polanyi sorption theory assumed [24] fixed volume of sorption space close to the sorbent surface and existence of sorption potential over these spaces. The mean free energy of biosorption (E) can be calculated from the Eq. (5).

$$E = \frac{1}{(2\beta)^{1/2}} \quad (5)$$

2.4. Fixed-bed column studies

These experiments were performed in small-scale cylindrical fixed-bed columns. A known quantity of immobilized biomass was packed between two layers of glass wool into the column. Ni(II) ion solution was pumped from bottom to top through the column at a desired flow rate by a peristaltic pump (Ismatec ecoline). All the column studies were performed at room temperature of

25 ± 2 °C. Synthetic nickel(II) ion solution at an initial concentration of 100 mg L^{-1} and pH of 6.5 was fed into the column at different flow rates changing from 0.5 to 5.0 mL min^{-1}. The effluent was then collected to determine the nickel(II) ion content with FAAS and optimum flow rate was fixed for further column studies. In order to study the effect of internal diameter of column, experiments were performed in the column with a fixed biomass dosage of 0.08 g and the feeding flow rate of 1 mL min^{-1} and different i.d. (9–19 mm). The biomass dosage was also optimized in the continuous mode.

2.5. Application

The wastewater sample was collected from the main drain of the casting unit of a local metal processing industry from Eskişehir, Turkey, for the investigation of the matrix effect on the biosorption capacity of immobilized-waste biomass. The collected wastewater sample was placed in a sterile container, transferred to the laboratory, and stored at 5 °C. The experiments were carried out with and without spiked wastewater samples including the different metal ions. The spiked samples were prepared by including Ni(II) at concentrations of 50 and 100 mg L^{-1}. The application of the proposed biosorption method was investigated under the predetermined optimum column conditions.

2.6. Instrumentation

The concentration of residual nickel(II) after biosorption was determined by using a flame atomic absorption spectrophotometer (HITACHI 180-70 FAAS) at a wavelength of 232.0 nm. The pH of the solutions was measured with a digital pHmeter (WTW INOLAB 720). FTIR spectra of free unloaded immobilized and nickel(II) loaded immobilized biosorbent were recorded in a PerkinElmer Spectrum 100IR infrared spectrometer in the region of 400–4000 cm^{-1} with the samples prepared as KBr pellets under high pressure. The surface structure of the biosorbent material before and after immobilization and nickel(II) biosorption was characterized using scanning electron microscope (JEOL 560 LV SEM), with 20 kV and at 5000 times of magnification. Prior to analyze, samples were sputter coated with a thin layer of gold under argon atmosphere to improve the electron conductivity and the image quality. The surface charge of the immobilized biomass was measured using a Zeta potential analyzer (Malvern Zetasizer nano ZS).

3. Results and discussion

3.1. Effect of immobilization on the biosorption capacity of biomass

In order to investigate the effect of immobilization on the nickel(II) biosorption capacity of biomass, the silica gel and free biomass of *P. vulgaris* were assessed for their sorption ability at pH 6.5 and 100 mg L^{-1} of nickel ion concentration. The biosorption capacities were found to be 33.83 and 7.50 mg g^{-1} for silica gel and *P. vulgaris*, respectively, whereas the immobilized biosorbent has a biosorption capacity of 45.48 mg g^{-1} at the same conditions. Since the maximum biosorption was obtained with the immobilized form of biomass, further biosorption studies were carried out using silica-gel-immobilized waste biomass.

3.2. Effect of initial pH and surface charge of biomass

Previous studies on metal biosorption by free or immobilized biomass have indicated that pH has a significant effect on metal-binding capacity of biomass. The pH of the biosorption medium affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate, and amino groups on the biomass surface. The behavior of biosorbent is mainly related to the cell wall, which is considered as the primary sites of biosorption. The carboxylate and phosphate groups carry negative charges that allow the cell wall components to be able removers of metal ions [25]. Nickel(II) uptakes were determined at various pH values ranging from 1.0 to 8.0 for silica-gel-immobilized biomass. For each pH value, the Ni(II) concentration (100 mg L^{-1}), biosorbent dosage (2.0 g L^{-1}), temperature (25 °C), and agitation speed (200 rpm) were kept constant. The Ni(II) biosorption capacity of immobilized biomass enhanced notably with raising the pH up to 4.0 (Fig. 1). It is evidenced by the fact that the negative charge of biosorbent surface measured as zeta potential (ζ) becomes less as pH decreases (Fig. 2). ζ potential value at pH 1.0 was measured as +3.06 mV, whereas the value decreased to −24.40 mV at pH 4.0. Since the biosorption capacity and ζ potential of biomass remained nearly constant between pH 4.0 and 8.0, the further biosorption studies were carried out at pH 6.5 (original pH value of Ni(II) solution).

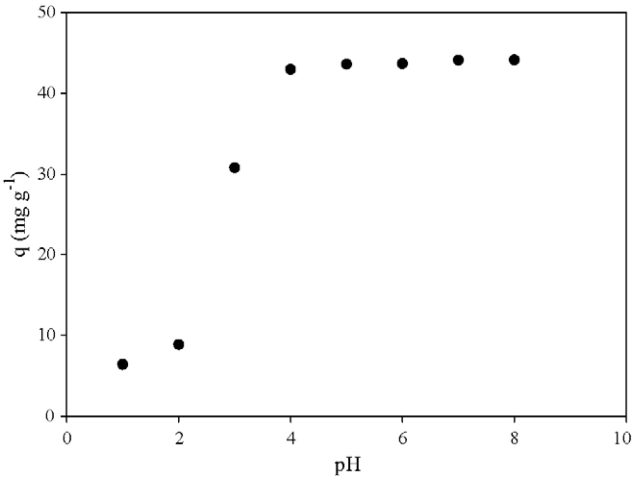

Fig. 1. Biosorption capacities for immobilized biomass at different pH values.

It was reported that the only Ni^{2+} species are found in the aqueous solutions at a pH range of 1–6.8 with a 0.1 M concentration of Ni^{2+}. In the case of 10^{-5} M Ni^{2+} only Ni^{2+} species are found in the aqueous solutions upto pH 8.3. In dilute solutions (10^{-5} M), Ni^{2+}

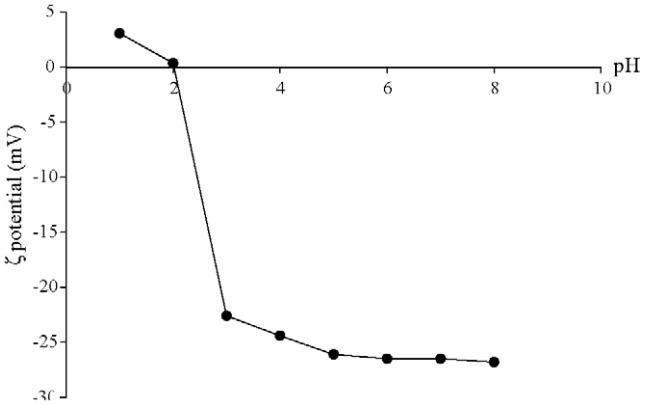

Fig. 2. ζ potentials of immobilized biomass as a function of pH.

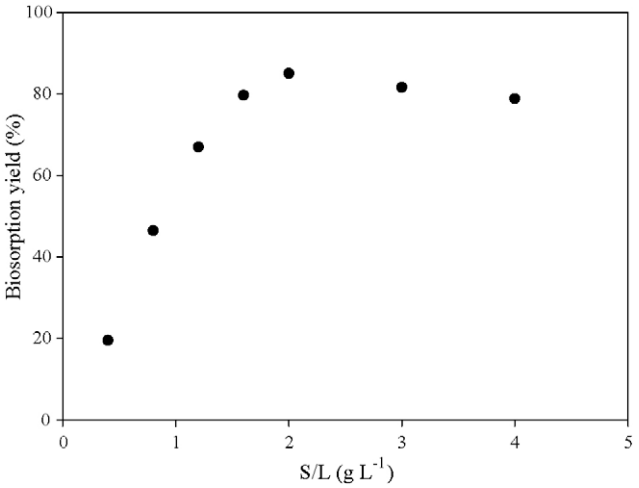

Fig. 3. Effect of solid to liquid ratio on the biosorption of nickel(II) by immobilized biomass.

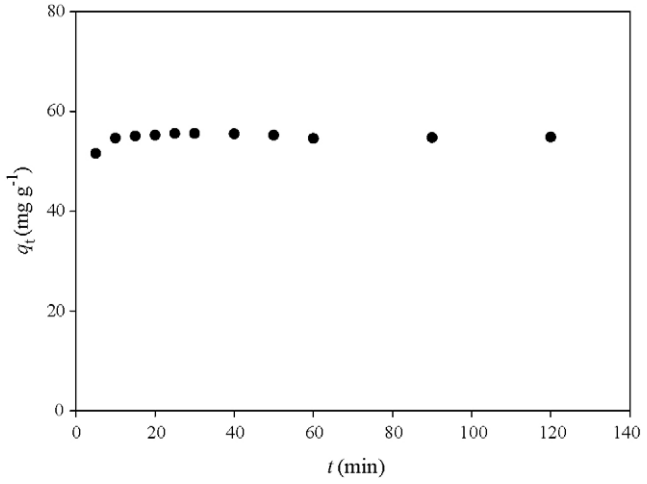

Fig. 4. Equilibrium time profile for the biosorption of nickel(II) onto immobilized biomass.

ions become precipitate in the form of $Ni(OH)_2$ at higher pH values greater than 8.3. About 10% of nickel is also found as $NiOH^+$ form at the same concentration and between pH 8 and 11 [26].

Since the all biosorption studies were carried out at pH value of 6.5, the only Ni^{2+} species were biosorbed by the immobilized biosorbent.

3.3. Effect of solid/liquid (S/L) ratio

The biosorption of nickel(II) ions onto immobilized biomass was examined by changing the S/L ratio in the range of 0.4–4.0 g L^{-1} while maintaining the other environmental parameters, such as volume of the solution, initial nickel(II) concentration, agitation speed, contact time, and pH constant. The results represented in Fig. 3 indicated that the yield of nickel(II) removal increased with the S/L ratio at the beginning, and the maximum biosorption yield was obtained at 1.6 g L^{-1}. Further increase in S/L ratio did not cause much increase in biosorption yield for nickel(II). Increase in biosorption yield with S/L ratio can be attributed to an increase in the biosorbent surface area and availability of more biosorption sites [27]. Therefore, 1.6 g L^{-1} would be the optimum S/L that would be required for cost-effective treatment of nickel(II) ions.

3.4. Equilibrium time for the biosorption of nickel(II)

Fig. 4 shows the plot of Ni(II) biosorption capacity of immobilized biomass against contact time. It can be seen that the biosorption was rapid in the initial stages and increased with rise in contact time up to 20 min at room temperature. After this time there was no considerable change in the biosorption capacity of biomass. This could be attributed to a large number of vacant binding sites, which are available for biosorption during the initial stage, and after an increase in contact time, the occupation of the remaining vacant sites will be difficult due to the repulsive forces between the Ni(II) ions on the solid and the liquid phases [28]. For instance, during 20 min, when the biosorption capacity for Ni(II) was 55.22 mg g^{-1}, it was observed as 54.83 mg g^{-1} in 120 min. Therefore, the optimum contact time was selected as 20 min for further experiments. This short contact time may also provide an advantage for the application of proposed biosorption method to real wastewater treatment systems.

3.5. Effect of initial Ni(II) concentration

The initial concentration of metal ion provides an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and the bulk phases [29]. Therefore, the biosorption of Ni(II) onto immobilized biomass was studied at different initial Ni(II) ion concentrations ranging from 75 to 500 mg L^{-1} at pH 6.5 and room temperature. The results are presented in Fig. 5 and obtained curve showed that the Ni(II) uptake increased with an increase in the initial concentration of metal ion. The increase in the biosorption capacity is due to the increase in the driving forces with an increase in the initial concentration of Ni(II) from 75 to 300 mg L^{-1}. At lower concentrations, all Ni(II) ions in the solutions could interact with the binding sites on the biosorbent and thus the biosorption capacity was sharply increased with increasing initial metal concentration. At higher concentrations, biosorption capacity was nearly constant due to the saturation of the biosorption sites [18]. The maximum equilibrium biosorption capacity of immobilized biomass for Ni(II) ions was found to be 1.541×10^{-3} mol g^{-1} (90.44 mg g^{-1}) at an initial concentration of 500 mg L^{-1}.

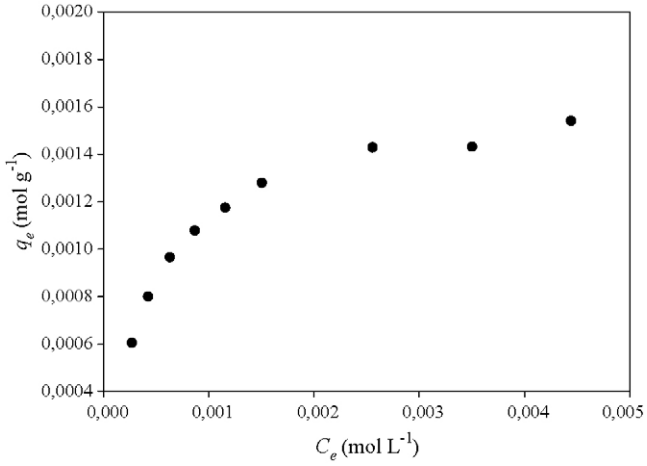

Fig. 5. Effect of initial Ni(II) ion concentration on the biosorption of Ni(II) onto immobilized biomass.

Table 1
Isotherm model parameters for the biosorption of Ni(II) ions onto immobilized biomass

Langmuir isotherm	q_{max} (mol g^{-1})	K_L (L mol^{-1})	r_L^2	R_L
	1.67×10^{-3}	2.12×10^{3}	0.999	5.24×10^{-2}
Freundlich isotherm	n	K_F (L g^{-1})		r_F^2
	3.23	8.91×10^{-3}		0.932
D–R isotherm	q_{max} (mol g^{-1})	β (mol^2 kJ^{-2})	r_{D-R}^2	E (kJ mol^{-1})
	2.48×10^{-3}	1.98×10^{-3}	0.958	11.31

3.6. Biosorption isotherms

The Langmuir, Freundlich, and D–R isotherm models were used to describe the equilibrium data in this study. The obtained isotherm model constants and r^2 values are included in Table 1. All equations fit the data reasonably well, but the best fit was obtained with the Langmuir isotherm model.

The fact that the fit obtained with Langmuir model showed the best results suggests that the binding of nickel(II) does occur as a monolayer on the surface of the biomass. The maximum monolayer biosorption capacity was found as 1.67×10^{-3} mol g^{-1} (98.01 mg g^{-1}) at room temperature and was consistent with the experimental data. Biosorption results and optimum pH values of Ni(II) reported by other researchers in the literature by various biosorbent materials are summarized in Table 2. Wase et al. [30] reported that the many biosorbents have lower sorption capacity for nickel than the other metals such as copper, cadmium, cobalt, chromium and lead. They also stated that this observation about nickel seems typical for many biosorbents. But in this study the maximum biosorption capacity of immobilized biosorbent for Ni(II) was found to be comparable and higher than that of many corresponding sorbents reported in the literature.

Greater values of K_L indicate the affinity of biosorbent to investigated metals and imply strong bonding of metal ions. R_L values obtained from Langmuir model can also be used for interpretation of the sorption type as follows [31]:

$R_L > 1$,	unfavorable
$R_L < 0$,	unfavorable
$R_L = 1$,	favorable (linear)
$0 < R_L < 1$,	favorable
$R_L = 0$,	irreversible

In this study R_L value found as 5.24×10^{-2} and also the shape of the curve (figure not shown) confirm favorable biosorption of Ni(II) onto immobilized biomass [22].

Freundlich constants K_F and n were found as 8.91×10^{-3} L g^{-1} and 3.23, respectively (Table 1). The magnitudes of K_F and n show easy biosorption of metal ions from aqueous medium and indicate favorable biosorption. These values were found high enough for the biosorbent material to be used for the removal of Ni(II) ions from aqueous solutions.

The D–R isotherm model constants were included in Table 1. The magnitude of E is useful for estimating the mechanism of biosorption process and it was found to be 11.31 kJ mol^{-1}. This value is within the energy range of biosorption reactions 8–16 kJ mol^{-1}. If the interval of (8–16 kJ mol^{-1}) is taken into consideration [32], the type of biosorption of Ni(II) onto immobilized biomass is chemical ion-exchange.

Table 2
Sorption results of nickel ions by different sorbents from the literature

Sorbent material	Nickel sorption capacity (mg g^{-1})	pH	References
Enteromorpha prolifera	65.36	4.3	[41]
Pseudomonas aeruginosa ASU 6a	113.6	7.0	[42]
Protonated rice ban	106.8	6.0	[43]
Bacillus thuringensis (vegetative cells)	21.5	6.0	[44]
Bacillus thuringensis (spore crystal mixture)	34.3	6.0	[44]
Ulva reticulata	62.3	4.5	[45]
Wine processing waste sludge	3.9	5.5	[46]
Baker's yeast	11.4	6.75	[47]
Streptomyces coelicolor	11.1	8.0	[48]
Thuja orientalis cones	12.42	4.0	[49]
Anaerobic granular biomass	26	5.5	[50]
Silica-gel-immobilized *P. vulgaris*	98.01	6.5	This study

3.7. Column studies

Although batch biosorption results give the fundamental information related to the biosorbent behavior and metal biosorption performance [33] a continuous mode of operation was preferred in large scale water treatment applications with the some advantages such as simple operation, high yield, easily scaled up from a laboratory-scaled procedure and easy regeneration of packed bed [34]. Therefore, the investigated immobilized biomass was also studied in continuous mode for the biosorption of Ni(II).

In order to investigate the effect of column size (bed height) on the biosorption performance, column i.d. was changed from 9 to 19 mm and the results were included in Table 3. The Ni(II) biosorption capacity of immobilized biomass increased from 40.26 to 50.03 mg g^{-1} when the column identical diameter was increased from 9 to 19 mm. The higher the column size the higher the surface area of biosorbent because the amount of loading biomass into column was kept constant. Therefore, the maximum biosorption capacity was obtained in column with highest i.d. of 19 mm.

In order to investigate the influence of flow rate through the column on the biosorption performance of immobilized biomass, flow rates ranging of 0.5–5.0 mL min^{-1} were used and the results are shown in Table 3. This table shows that lower flow rates resulted in higher removal capacity, and therefore, biomass was treated with Ni(II) solution at a flow rate of 1.0 mL min^{-1}. However, above this value of flow rate, the nickel(II) removal capacity starts to decrease. The higher the flow rate the lesser the nickel(II) residence time along the column. Vieira et al. [35] stated that there are two competing effects. If high flow rates favor the mass transfer between the metal and the biomass, then high flow rates reduce the contact time between them by reducing the solute residence time. Therefore, the choice of the best flow rate should be a compromise between these two opposing factors.

The biosorption efficiencies at different amount of biomass loaded into the column (bed depths) were also shown in Table 3. It was seen that as the biomass amount increased, Ni(II) ions had more time to contact with the biosorbent which resulted in higher biosorption efficiency of immobilized biomass. Because of an increase in the surface area of the biosorbent, which provided more binding sites for the biosorption, higher removal performance

Table 3
Effect of column internal diameter (i.d.), flow rate and S/L ratio on the biosorption performance of immobilized biomass in continuous mode

Column i.d. (mm)	9		11		13		19
q (mg g^{-1})	40.26		43.36		44.22		50.03
Flow rate (mL min^{-1})	0.5	1.0	2.0	3.0	4.0	5.0	
q (mg g^{-1})	47.90	46.50	32.69	21.00	19.06	20.41	
S/L ratio (g L^{-1})	0.4	0.8	1.2	1.6	2.0	3.0	4.0
Biosorption yield (%)	21.18	48.81	65.10	76.80	79.84	79.67	76.80

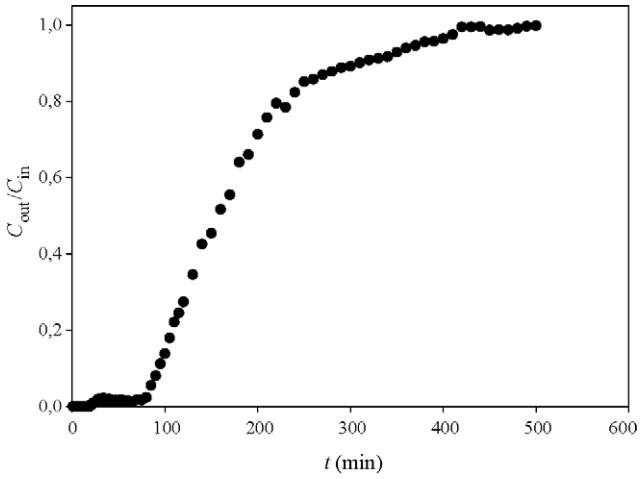

Fig. 6. Column breakthrough behavior of the immobilized biomass for Ni(II) ions.

was observed in the higher loaded column [36]. The biosorption efficiency did not significantly change above definite biomass amount due to the saturation of binding sites on the biosorbent. Hence, optimum amount of biosorbent for column biosorption of Ni(II) was selected as 0.08 g. This result was also consistent with the data obtained from batch procedure.

In order to investigate the breakthrough behavior of column, 100 mg L^{-1} Ni(II) solution was fed at 1.0 mL min^{-1} into a glass column with an internal diameter of 19 mm. The results are presented in Fig. 6. The typical S-shaped curve that is favorable for a continuous system was observed for the biosorption of Ni(II) by immobilized biomass. Before the breakthrough point, the concentration of nickel ion in effluent was too low and the breakthrough point emerged around 90 min. Biosorption column was saturated rapidly after breakthrough point. A sharply increase in breakthrough curve suggests the good biosorption performance of biomass [33] for nickel ions. Consequently, nickel ions were effectively removed in column operations by immobilized biosorbent developed in this study.

3.8. Biomass characterization and mechanism of biosorption

In order to analyze the morphology of the biosorbent surface before and after immobilization and Ni(II) biosorption, SEM micrographs were used. As seen in Fig. 7(a), before immobilization process, biosorbent was characterized as spherical shape, smooth surface and inner fullness, whereas after immobilization with silica gel (Fig. 7(b)), cavity and granular substances attached to rough biomass surface were observed. With the aid of SEM micrograph of Ni(II)-loaded biomass (Fig. 7(c)), some traps were observed in the pores, resulting in the irregular textures. The surface of Ni(II)-loaded immobilized biomass appeared to be vague and some particles were found on the surface of the biosorbent.

In order to ascertain *P. vulgaris* has been successfully immobilized with silica gel, FTIR analysis was used for free and silica-gel-immobilized biomass. In Fig. 8(a), the broad peak at 3420 cm^{-1} can be attributed to the —OH stretching vibrations for *P. vulgaris*. The peaks at 2955 and 2929 cm^{-1} are due to C—H stretching vibrations of —CH, $—CH_2$, and $—CH_3$ groups. The peaks at 1646 and 1448 cm^{-1} can be assigned to stretching vibrations of carboxylic and carboxylate groups, respectively. In the FTIR spectra of immobilized biomass (Fig. 8(b)), the absorption bands around 1100 (stretching frequency of Si—O—Si), 3401, and 1652 cm^{-1} (νOH vibrations) indicate that *P. vulgaris* has been successfully immobilized with silica gel. These absorption bands were not included in

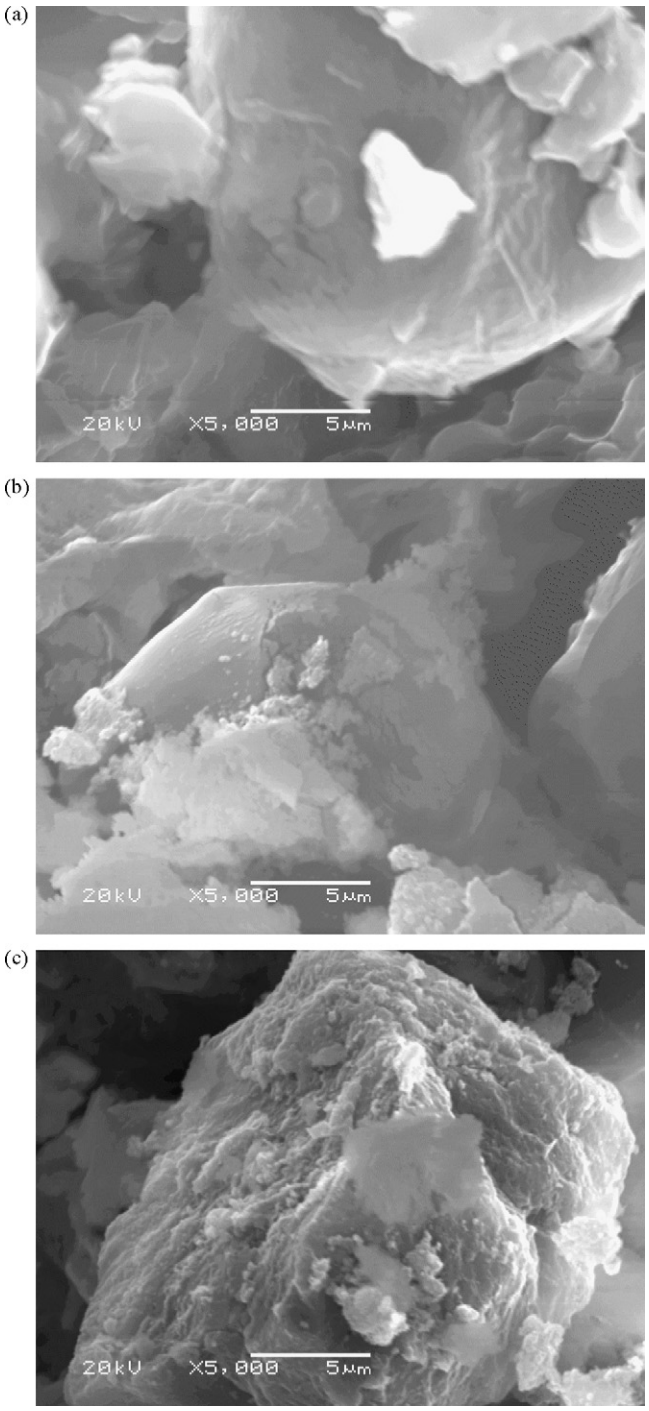

Fig. 7. SEM images for (a) *P. vulgaris*, (b) silica-gel-immobilized *P. vulgaris* and (c) Ni(II) loaded silica-gel-immobilized *P. vulgaris* at a magnificaiton of 5000×.

the FTIR spectra of free biomass. The stretching vibrations of P═O and P—OH groups were observed at 1159 and 1080 cm^{-1}, respectively, for only FTIR spectrum of *P. vulgaris* [37]. The band between 611 and 520 cm^{-1} for the free biomass represents C—N—C scissoring found only in protein structures, [38] which disappeared after immobilization of biosorbent. Fig. 8(c) shows the FTIR spectra of nickel(II)-loaded immobilized biomass. Since the intensity is a function of the electric dipole moment change and also the total number of functional groups on the biosorbent surface [39], the significant intensity decrease was observed for the peaks at 3401 and 1652 cm^{-1} after nickel(II) biosorption. Also for unloaded immobi-

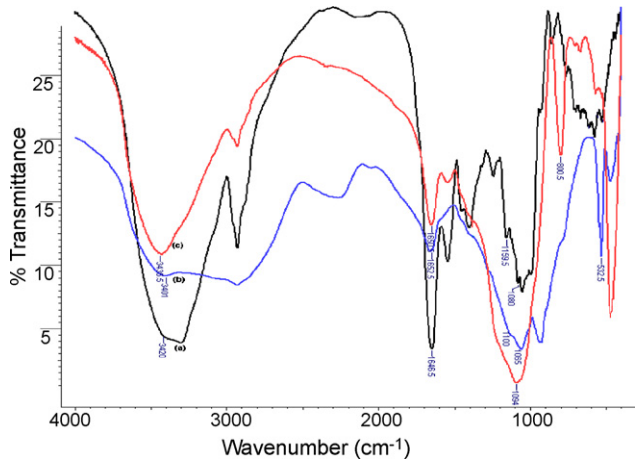

Fig. 8. FTIR spectra for (a) *P. vulgaris*, (b) silica-gel immobilized *P. vulgaris* and (c) Ni(II) loaded silica-gel immobilized *P. vulgaris*.

lized biomass the peak observed at 1065 cm^{-1} which assigned to —C—O stretching of alcoholic groups shifted to higher wavenumbers after the biosorption of nickel(II) ions. The most important evidence for the interaction of nickel(II) ion with the functional groups on the biosorbent was the new peak, which appeared at 800 cm^{-1} after Ni(II) biosorption. This peak is due to the complexation of Ni(II) with —C—S groups [40]. The formation of new peaks at 570 and 458 cm^{-1} in the FTIR spectra of nickel(II)-loaded biomass also indicates the metal–sulphur interaction.

From these observations, it may be concluded that many functional groups on the biosorbent surface act as binding sites for nickel(II) ion biosorption.

3.9. Real waste water application

In order to evaluate the potential performance of the immobilized-waste biomass for the removal of nickel(II) from a wastewater, an optimized biosorption procedure was tested with model wastewater samples, with and without spikes, at described optimum experimental conditions (pH: 7.0, biosorbent amount: 0.08 g, volume of wastewater: 50 mL). Some characteristics of wastewater and biosorption results for synthetic Ni(II) solutions and wastewater are presented in Tables 4 and 5, respectively. As seen in Table 4, when the pH of the wastewater is adjusted to 7.0, the concentration of some metal ions decreased due to the precipitation of metal ions in the form of metal hydroxide, except for sodium. Biosorption performance of immobilized biomass in wastewater varied from 3.13 to 21.0 mg g^{-1} (Table 5). The biosorption capacity of sorbent decreased in industrial wastewater spiked with Ni(II) at high concentrations, due to the presence of other metal ions in the wastewater along with the Ni(II), which interfere for the nickel sorption. However, in the light of these results it is concluded that the prepared immobilized sorbent was found to be very efficient for the removal of nickel(II) ions from real wastewaters.

Table 4
Some chemical characteristics of wastewater sample at various pH values

Parameters (mg L^{-1})	Effluent quality (pH 2.24)	Effluent quality (pH 7.0)
Copper	46.86	28.13
Lead	12.35	1.29
Nickel	12.05	9.43
Cadmium	14.83	10.41
Iron	214.00	110.00
Zinc	393.00	188.50
Sodium[a]	57.50	746.50
Potassium	230.50	78.50
Calcium	112.00	111.50
Magnesium	182.00	149.00

[a] Since the pH of the sample was adjusted to 7.0 with 0.1 N NaOH, the concentration of sodium increased.

Table 5
The application of the proposed method for removal of nickel(II)

Solution of nickel used	Ni(II) (mg L^{-1})	q_e (mg g^{-1})
Distilled water	10	2.46
Distilled water	50	19.72
Distilled water	100	46.97
Wastewater (without spiked)	9.43	3.13
Wastewater (with spiked)	50	10.88
Wastewater (with spiked)	100	21.00

4. Conclusion

The nickel biosorption potential of *P. vulgaris* waste biomass immobilized on silica-gel matrix was examined. The best nickel biosorption conditions were determined using batch and column mode studies for screening the factors, such as pH, biosorbent dosage, contact time, flow rate and column size. Isotherm analysis of equilibrium data showed that the biosorption pattern of immobilized biomass fitted with the Langmuir model. The maximum monolayer biosorption capacity of the proposed sorbent system was found to be 98.01 mg g^{-1}. The results indicated that the adjustment of operating conditions in batch and dynamic flow mode is important for the effective sequester of nickel ions from contaminated solutions. The SEM and FTIR analysis confirmed the interactions between Ni(II) ion and sorbent surface. Likewise, the proposed sorbent system can be effectively used to remove the nickel ions from industrial wastewater. Overall, it can be concluded that the proposed biosorbent system is practical and efficient for the removal of nickel contamination from synthetic and industrial effluents with the advantages of low preparation cost and large availability of the used waste biomass.

References

[1] B. Volesky, Detoxification of metal-bearing effluents: biosorption for the next century, Hydrometallurgy 59 (2001) 203–216.
[2] C.F. Forster, D.A.J. Wase, Biosorption of heavy metals: an introduction, in: D.A.J. Wase, C.F. Forster (Eds.), Biosorbents for Metal Ions, Taylor & Francis, London, UK, 1997, pp. 1–10.
[3] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol. 98 (2007) 2243–2257.
[4] C.E. Borba, R. Guirardello, E.A. Silva, M.T. Veit, C.R.G. Tavares, Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: experimental and theoretical breakthrough curves, Biochem. Eng. J. 30 (2006) 184–191.
[5] T. Akar, A. Cabuk, S. Tunali, M. Yamac, Biosorption potential of macrofungus *Ganoderma carnosum* for removal of lead(II) ions from aqueous solutions, J. Environ. Sci. Heal. A 41 (2006) 2587–2606.
[6] A. Cabuk, T. Akar, S. Tunali, S. Gedikli, Biosorption of Pb(II) by industrial strain of *Saccharomyces cerevisiae* immobilized on the biomatrix of cone biomass of *Pinus nigra*: equilibrium and mechanism analysis, Chem. Eng. J. 131 (2007) 293–300.
[7] R.S. Prakasham, J. Sheno Merrie, R. Sheela, N. Saswathi, S.V. Ramakrishna, Biosorption of chromium VI by free and immobilized *Rhizopus arrhizus*, Environ. Pollut. 104 (1999) 421–427.
[8] Paula Marques, Helena Maria Pinheiro, Maria Fernanda Rosa, Cd(II) removal from aqueous solution by immobilised waste brewery yeast in fixed-bed and airlift reactors, Desalination 214 (2007) 343–351.
[9] T. Akar, S. Tunali, A. Cabuk, Study on the characterization of lead (II) biosorption by fungus *Aspergillus parasiticus*, Appl. Biochem. Biotechnol. 136 (2007) 389–406.
[10] M.Z.-C. Hu, M. Reeves, Biosorption of uranium by *Pseudomonas aeruginosa* strain CSU immobilized in a novel matrix, Biotech. Prog. 13 (1997) 60–70.
[11] N. Rangsayatorn, P. Pokethitiyook, E.S. Upatham, G.R. Lanza, Cadmium biosorption by cells of *Spirulina platensis* TISTR 8217 immobilized in alginate and silica gel, Environ. Int. 30 (2004) 57–63.

[12] A. Çabuk, T. Akar, S. Tunali, Ö. Tabak, Biosorption characteristics of *Bacillus* sp. ATS-2 immobilized in silica gel for removal of Pb(II), J. Hazard. Mater. 136 (2006) 317–323.
[13] S. Marseaut, A. Debourg, P. Dostálek, J. Votruba, G. Kuncová, John M. Tobin, A silica matrix biosorbent of cadmium, Int. Biodeter. Biodegr. 54 (2004) 209–214.
[14] W. Ngeontae, W. Aeungmaitrepirom, T. Tuntulani, Chemically modified silica gel with aminothioamidoanthraquinone for solid phase extraction and preconcentration of Pb(II), Cu(II), Ni(II), Co(II) and Cd(II), Talanta 71 (2007) 1075–1082.
[15] D. Chaiko, J.P. Kopasz, A.J.G. Ellison, Use of sol–gel systems for solid liquid separation, Ind. Eng. Chem. Res. 37 (1998) 1071–1078.
[16] S. Tunali, A. Ozcan, Z. Kaynak, A.S. Ozcan, T. Akar, Utilization of the *Phaseolus vulgaris* L. waste biomass for decolorization of the textile dye Acid Red 57: determination of equilibrium, kinetic and thermodynamic parameters, J. Environ. Sci. Heal. A 42 (2007) 591–600.
[17] A. Lopez, N. Lazaro, A.M. Marques, The interphase technique: a simple method of cell immobilization in gel-beads, J. Microbiol. Methods 30 (1997) 231–234.
[18] P. King, K. Anuradha, S. Beena Lahari, Y. Prasanna Kumar, V.S.R.K. Prasad, Biosorption of zinc from aqueous solution using *Azadirachta indica* bark: Equilibrium and kinetic studies, J. Hazard. Mater. 152 (2008) 324–329.
[19] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
[20] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, Ind. Eng. Chem. Fundam. 5 (1966) 212–223.
[21] H.M.F. Freundlich, Über die adsorption in lösungen, Z. Phys. Chem. 57 (1906) 385–470.
[22] B. Kiran, A. Kaushik, Chromium binding capacity of Lyngbya putealis exopolysaccharides, Biochem. Eng. J. 38 (2008) 47–54.
[23] M.M. Dubinin, L.V. Radushkevich, Proc. Acad. Sci. U.S.S.R. Phys. Chem. Sect. 55 (1947) 331.
[24] J. Li, C.J. Werth, Modeling sorption isotherms of volatile organic chemical mixtures in model and natural solids, Environ. Toxicol. Chem. 21 (2002) 1377–1383.
[25] M. Dundar, C. Nuhoglu, Y. Nuhoglu, Biosorption of Cu(II) ions onto the litter of natural trembling poplar forest, J. Hazard. Mater. 151 (2008) 86–95.
[26] C.F. Baes Jr., R.E. Mesmer, The Hydrolysis of Cations, Robert E. Krieger Publishing Company, Florida, USA, 1986, pp. 241–246.
[27] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies, Sep. Purif. Technol. 53 (2007) 97–110.
[28] K. Vijayaraghavan, J. Mao, Y.S. Yun, Biosorption of methylene blue from aqueous solution using free and polysulfone-immobilized *Corynebacterium glutamicum*: Batch and column studies, Bioresour. Technol. 99 (2008) 2864–2871.
[29] S. Basha, Z.V.P. Murthy, B. Jha, Biosorption of hexavalent chromium by chemically modified seaweed, *Cystoseira indica*, Chem. Eng. J. 137 (2008) 480–488.
[30] D.A.J. Wase, C.F. Forster, Y.S. Ho, Low-cost biosorbents: batch processes, in: D.A.J. Wase, C.F. Forster (Eds.), Biosorbents for Metal Ions, Taylor & Francis, London, UK, 1997, pp. 141–163.
[31] S. Dahiya, R.M. Tripathi, A.G. Hegde, Biosorption of heavy metals and radionuclide from aqueous solutions by pre-treated arca shell biomass, J. Hazard. Mater. 150 (2008) 376–386.
[32] E. Oguz, Equilibrium isotherms and kinetics studies for the sorption of fluoride on light weight concrete materials, Colloid Surf. A 295 (2007) 258–263.
[33] K. Vijayaraghavan, Y.S. Yun, Biosorption of C.I. recative Black 5 from aqueous solution using acid-treated biomass of brown seaweed *Laminaria sp*, Dyes Pigments 76 (2008) 726–732.
[34] Z. Aksu, Ş. Şen Çağatay, F. Gonen, Continuous fixed bed biosorption of reactive dyes by dried *Rhizopus arrhizus*: determination of column capacity, J. Hazard. Mater. 143 (2007) 362–371.
[35] M.G.A. Vieira, R.M. Oisiovici, M.L. Gimenes, M.G.C. Silva, Biosorption of chromium(VI) using a *Sargassum* sp. packed-bed column, Bioresour. Technol. 99 (2008) 3094–3099.
[36] R. Han, D. Ding, Y. Xu, W. Zou, Y. Wang, Y. Li, L. Zou, Use of rice husk for the adsorption of congo red from aqueous solution in column mode, Bioresour. Technol. 99 (2008) 2938–2946.
[37] M.H. Han, Y.S. Yun, Mechanistic understanding and performance enhancement of biosorption of reactive dyestuffs by the waste biomass generated from amino acid fermentation process, Biochem. Eng. J. 36 (2007) 2–7.
[38] G. Bayramoğlu, G. Çelik, M.Y. Arica, Biosorption of Reactive blue 4 dye by native and treated fungus *Phanerocheate chrysosporium*: batch and continuous flow system studies, J. Hazard. Mater. 137 (2006) 1689–1697.
[39] K.K. Krishnani, X. Meng, C. Christodoulatos, V.M. Boddu, Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk, J. Hazard. Mater. 153 (2008) 1222–1234.
[40] S. Bayarı, A. Topaçli, B. Salih, Structural information on transition metal(II) complexes of 4,4′-bipyridyl and 4-phenylpyridine from their infrared spectra, J. Mol. Struct. 482–483 (1999) 165–169.
[41] A. Özer, G. Gürbüz, A. Çalimli, B.K. Körbahti, Investigation of nickel(II) biosorption on *Enteromorpha prolifera*: optimization using response surface analysis, J. Hazard. Mater. 152 (2008) 778–788.
[42] R.M. Gabr, S.H.A. Hassan, A.A.M. Shoreit, Biosorption of lead and nickel by living and non-living cells of *Pseudomonas aeruginosa* ASU 6a, Int. Biodeter. Biodegr. 62 (2008) 195–203.
[43] M.N. Zafar, R. Nadeem, M.A. Hanif, Biosorption of nickel from protonated rice bran, J. Hazard. Mater. 143 (2007) 478–485.
[44] A. Öztürk, Removal of nickel from aqueous solution by the bacterium *Bacillus thuringiensis*, J. Hazard. Mater. 147 (2007) 518–523.
[45] K. Vijayaraghavan, Biosorption of Nickel from synthetic and electroplating industrial solutions using a green marine algae *Ulva reticulata*, Clean 36 (2008) 299–305.
[46] C.C. Liu, M.K. Wang, Y.S. Li, Removal of nickel from aqueous solution using wine processing waste sludge, Ind. Eng. Chem. Res. 44 (2005) 1438–1445.
[47] V. Padmavathy, P. Vasudevan, S.C. Dhingra, Biosorption of nickel(II) ions on baker's yeast, Process Biochem. 38 (2003) 1389–1395.
[48] A. Öztürk, T. Artan, A. Ayar, Biosorption of nickel(II) and copper (II) ions from aqueous solution by *Streptomyces coelicolor* A3(2), Colloids Surf. B 34 (2004) 105–111.
[49] E. Malkoç, Nickel, (II) removal from aqueous solutions using cone biomass of *Thuja orientalis*, J. Hazard. Mater. 137 (2006) 899–908.
[50] A.H. Hawari, C.N. Mulligan, Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass, Bioresour. Technol. 97 (2006) 692–700.