Journal of Hazardous Materials B113 (2004) 223–230

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Removal of nickel(II) ions from aqueous solution using crab shell particles in a packed bed up-flow column

K. Vijayaraghavan[a], J. Jegan[a], K. Palanivelu[b], M. Velan[a,*]

[a] *Department of Chemical Engineering, Anna University, Chennai 600025, India*
[b] *Centre for Environmental Studies, Anna University, Chennai 600025, India*

Received 12 March 2004; received in revised form 18 June 2004; accepted 22 June 2004
Available online 31 July 2004

Abstract

This paper investigates the ability of crab shell to remove nickel(II) ions from aqueous solution in a packed bed up-flow column with an internal diameter of 2 cm. The experiments were performed with different bed heights (15–25 cm) and using different flow rates (5–20 ml/min) in order to obtain experimental breakthrough curves. The bed depth service time (BDST) model was used to analyze the experimental data and the model parameters were evaluated. The column regeneration studies were carried out for seven sorption–desorption cycles. The elutant used for the regeneration of the sorbent was 0.01 M EDTA (disodium) solution at pH 9.8 adjusted using NH_4OH. Due to continuous usage of crab shell, a performance loss was observed as the breakthrough curves become more flattened also indicated by the broadened mass transfer zone. The breakthrough time decreased uniformly from 28.1 to 9.5 h as the cycles progressed from one to seven, whereas nickel uptake remained approximately constant throughout the seven cycles. The life-factors for crab shell in terms of critical bed length and breakthrough time were found to be 1.1 cm/cycle and 0.17 per cycle, respectively. The elution efficiency was greater than 99.1% in all the seven cycles. The pH profiles during both sorption and desorption process were also reported. In sorption cycles, there was a sudden raise in pH in the early part of the process and then the pH decreased as the time progressed. In desorption cycles, pH decreased in initial stages and followed by gradual increase in pH, which eventually reached the pH of the inlet elutant.

Keywords: Crab shell; Nickel; Biosorption; Packed bed column; Regeneration

1. Introduction

Biosorption, a popular technique for metal removal/recovery from waste streams, utilizes the potential of microbial and waste biomass to sequester heavy metal ions from aqueous solution by physicochemical mechanisms. Biosorption usually comprises of several mechanisms, some mechanisms can be sub-mechanisms of the other overall mechanisms, such as ion exchange, complexation, coordination, chelation, microprecipitation or adsorption [1]. Heavy metal biosorption by biological materials, such as bacteria and fungi, presents few problems when operated in continuous mode of operation; among these, solid/liquid separation is a major constrain. Even though immobilization may solve this problem, chemical costs and mechanical strength should be taken into consideration [2]. For these reasons, recent research attention has focused on low-cost and waste materials [3]. Crab shell, widely employed as biosorbent, have shown in the past its unique ability to bind wide variety of heavy metals [4,5]. The most of the earlier investigations on heavy metal biosorption were restricted to batch equilibrium studies; the probable reason for this restriction is mainly due to the unavailability of bulk quantity of biomass. The rigidity of the biomass and its ability to withstand extreme pH conditions employed during regeneration (desorption) are the other important factors, which limit the biosorbent usage in column studies.

The practical application of biosorption of heavy metals is most economically carried out in a packed column operation [6,7]. Al-Asheh et al. [6] used a glass column of 1.2 cm i.d. packed with 21.5 g of spent animal bones to remove copper.

* Corresponding author.
E-mail address: velan@annauniv.edu (M. Velan).

0304-3894/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2004.06.014

Volesky et al. [7] employed a column of 2.5 cm i.d. and packed with 38 g of dry *Sargassum filipendula* biomass to remove copper.

The objective of the current investigation was to examine the sorption of nickel onto crab shell in an up-flow packed bed column arrangement. The effects of design parameters, such as bed height and flow rate, have been investigated. The breakthrough profiles for the sorption of nickel were analyzed using bed depth service time (BDST) model. The nickel sorption behavior of crab shell in seven consecutive sorption–desorption cycles has also been investigated.

2. Materials and methods

2.1. Biosorbent material

Waste shells of *Portunus sanguinolentus* commonly known as three spot crabs were collected from Marina beach, India and were sun dried and crushed to a particle size of 0.767 mm using ball mill. The pretreatment of crab shells were carried out by washing with 0.1 M HCl for 4 h to remove $CaCO_3$. The treated shells were then washed with distilled water and dried naturally and the weight loss was found to be approximately 50%. So prepared crab shell particles will be referred to as "CSP" in this paper.

2.2. Chemicals

Analytical grades of HCl, NaOH, $NiSO_4{\cdot}6H_2O$, EDTA (disodium) and NH_4OH were purchased from Ranbaxy Fine Chemicals Ltd., India. A stock solution of nickel ions (100 mg/l) was prepared by dissolving 0.4478 g of $NiSO_4{\cdot}6H_2O$ per liter of distilled water.

2.3. Column

Continuous-flow sorption experiments were conducted in a glass column. The column was designed with an internal diameter of 2 and 35 cm in length. Since the ratio of column diameter to particle diameter is high, the effects of channeling have a negligible effect. At the top of the column, an adjustable plunger was attached with a 0.5 mm stainless sieve. At the bottom of the column, a 0.5 mm stainless sieve was attached followed by glass wool. A 2 cm high layer of glass beads (1.5 mm in diameter) was placed at the column base in order to provide a uniform inlet flow of the solution into the column.

2.4. Experimental procedure

A known quantity of CSP was placed in the column to yield the desired bed height of the sorbent. Nickel(II) solution having initial concentration of 100 mg/l and pH of 4.5 (adjusted using 0.1 M HCl) was pumped upward through the column at a desired flow rate by a peristaltic pump (pp40, Miclins). Samples were collected from the exit of the column at different time intervals and analyzed for nickel concentration using Atomic Absorption Spectrophotometer (AAS 6VARIO; Analytik Jena, Germany). The pH of the influent and effluent were recorded. Operation of the column was stopped when the effluent nickel concentration exceeded a value of 99.5 mg/l or higher. Fig. 1 shows the experimental set-up used for the present study.

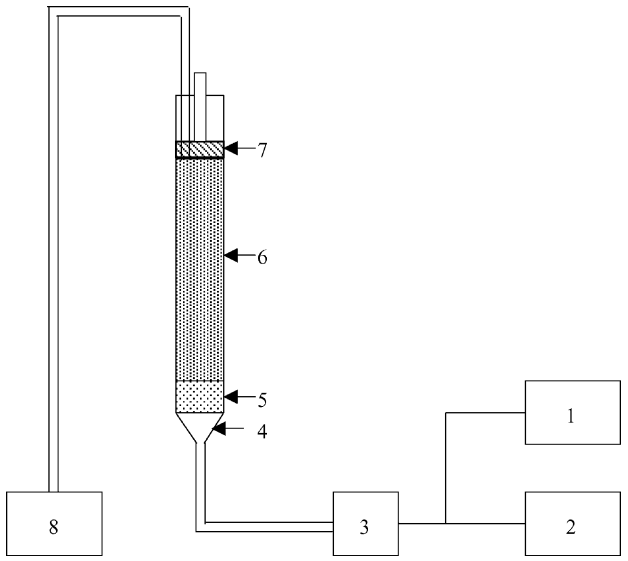

Fig. 1. Experimental set-up of up-flow packed bed column. (1) Nickel solution, (2) EDTA solution, (3) peristaltic pump, (4) glass wool, (5) glass beads, (6) crab shell particles, (7) adjustable plunger, (8) effluent storage.

After the column reached exhaustion, the loaded CSP with nickel ions was regenerated, using 0.01 M EDTA (disodium) solution adjusted to pH 9.8 with concentrated NH_4OH. The flow rate was adjusted to 10 ml/min. After elution, distilled water was used to wash the bed until the pH in the wash effluent stabilized near 7.0. Then, the column was fed again with nickel solution and the sorption studies were carried out. After bed exhaustion, elutant was fed into the column and the regeneration studies were conducted. These cycles of sorption followed by desorption were repeated for seven times to evaluate the CSP sorption capacity. To determine the weight loss after seven cycles, the CSP was washed with distilled water and dried naturally.

2.5. Modeling and analysis of column data

The analysis of breakthrough curve was done using BDST model. BDST is a simple model for predicting the relationship between bed height, Z, and service time, t, in terms of process concentrations and adsorption parameters [8], given by Eq. (1):

$$\ln\left(\frac{C_0}{C_b} - 1\right) = \ln(e^{K_a N_0 Z/\upsilon} - 1) - K_a C_0 t \quad (1)$$

Hutchins [9] proposed a linear relationship between bed height and service time given by Eq. (2):

$$t = \frac{N_0 Z}{C_0 \upsilon} - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \quad (2)$$

where C_0 is the initial nickel concentration (mg/l); C_b is the breakthrough nickel concentration (mg/l); N_0 is the sorption capacity of bed (mg/l); υ is the linear velocity (cm/h) and K_a is the rate constant (l/(mg h))

The quantity of metal retained in the column represented by the area above the breakthrough curve (C versus t), is obtained through numerical integration [7]. Dividing the metal mass (m_{ad}) by the sorbent mass (M) leads to the uptake capacity (Q) of the CSP.

The breakthrough time (t_b, the time at which nickel concentration in the effluent reached 1 mg/l) and bed exhaustion time (t_e, the time at which nickel concentration in the effluent exceeded 99.5 mg/l) were used to evaluate the overall sorption zone ($\triangle t$) as follows [7]:

$$\Delta t = t_e - t_b \quad (3)$$

The length of the mass transfer zone (Z_m) can be calculated from the breakthrough curve [7] given by Eq. (4):

$$Z_m = Z\left(1 - \frac{t_b}{t_e}\right) \quad (4)$$

Effluent volume (V_{eff}) can be calculated as follows [10]:

$$V_{eff} = Ft_e \quad (5)$$

where F is the volumetric flow rate (ml/min).

Total amount nickel sent to column (m_{total}) can be calculated as follows [10]:

$$m_{total} = \frac{C_0 F t_e}{1000} \quad (6)$$

Total nickel removal percent with respect to flow volume can be calculated as follows [10]:

$$\text{Total nickel removal (\%)} = \frac{m_{ad}}{m_{total}} \times 100 \quad (7)$$

The metal mass desorbed (m_d) can be calculated from the elution curve (C versus t). The elution efficiency (E) can be calculated as follows [7]:

$$E\,(\%) = \frac{m_d}{m_{ad}} \times 100 \quad (8)$$

3. Results and discussion

3.1. Effect of bed height

The sorption performance of CSP was tested at various bed heights (15–25 cm) at 5 ml/min flow rate and 100 mg/l initial nickel concentration. In order to yield different bed heights, 31, 41 and 51 g of CSP were added to produce bed heights of 15, 20 and 25 cm, respectively. Fig. 2 shows the breakthrough profile of nickel sorption at different bed heights. The nickel uptake capacity of CSP remained almost identical for different bed heights investigated, probably because uptake capacity strongly depends on the amount of sorbent available for the sorption. The breakthrough time (t_b) and exhaustion time (t_e) increased with the increase in bed height. The stoichiometric time (t_s) reflects the time at which complete (i.e., stoichiometric) saturation of the sorption capacity of the bed occurs [11]. By plotting C/C_0 versus time, the stoichiometric time can be calculated from the area above the curve and is shown in Table 1. The slope of the S-curve from t_b to t_e decreased as the bed height increased from 15 to 25 cm, indicating the breakthrough curve becomes steeper as the bed height decreased. As expected, an increased bed height resulted in high volume of metal solution treated and high percentage of nickel removal.

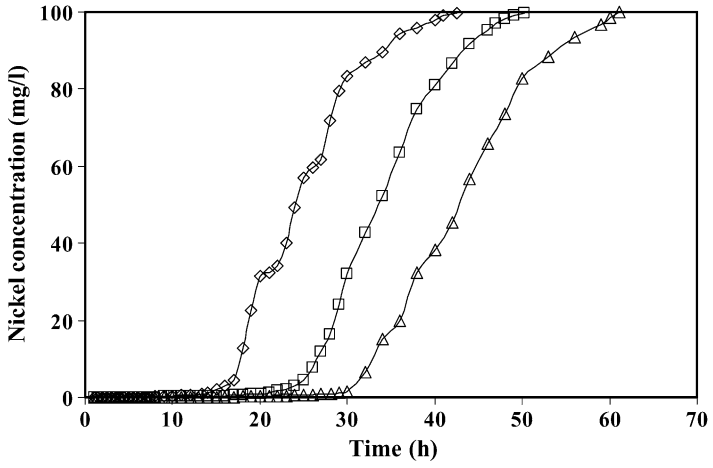

Fig. 2. Breakthrough curves for nickel sorption onto crab shell particles at different bed heights (flow rate = 5 ml/min, initial nickel concentration = 100 mg/l, pH = 4.5). Bed height: (◊) 15 cm; (□) 20 cm; (△) 25 cm.

Table 1
Column data and parameters obtained at different bed heights

Bed height (cm)	Uptake (mg/g)	t_b (h)	t_e (h)	$\triangle t$ (h)	t_s (h)	dc/dt (mg/l h)	V_{eff} (l)	Total nickel removal (%)
15	24.74	13.4	42.5	29.1	25.4	3.961	12.75	59.88
20	24.77	20.2	50.3	30.1	34.0	3.928	15.09	67.63
25	25.57	28.1	61.1	33.0	43.8	3.345	18.33	71.82

Conditions: flow rate = 5 ml/min, initial nickel concentration = 100 mg/l, pH 4.5.

The BDST model is based on physically measuring the capacity of the bed at different breakthrough values. The column service time was selected as time when the effluent nickel concentration reached 1 mg/l. The plot of service time against bed height at a flow rate of 5 ml/min (graph not presented) was linear (R^2 = 0.998) indicating the validity of BDST model for the present system. The sorption capacity of the bed per unit bed volume, N_0, was calculated from the slope of BDST plot, assuming initial concentration, C_0, and linear velocity, υ, as constant during the column operation. The rate constant, K_a, calculated from the intercept of BDST plot, characterizes the rate of solute transfer from the fluid phase to the solid phase [11]. The computed N_0 and K_a were 14044.59 mg/l and 0.0052 l/mg h respectively. If K_a is large, even a short bed will avoid breakthrough, but as K_a decreases a progressively longer bed is required to avoid breakthrough [11]. The BDST model parameters can be useful to scale up the process for other flow rates without further experimental data and analysis.

3.2. Effect of flow rate

The effect of flow rate on nickel sorption by CSP was studied by varying the flow rate from 5 to 20 ml/min, while the bed height and initial nickel concentration were held constant at 25 cm and 100 mg/l, respectively. The plots of effluent nickel concentration versus time at different flow rates are shown in Fig. 3. As the flow rate increased, the breakthrough curve becomes steeper, also resembled by the slope of the S-curve shown in Table 2. The breakthrough time, exhaustion time, stoichiometric time and uptake capacity decreased as the flow rate increased. The reason for this behavior can be explained in the following ways: (1) when the flow rate increased, the residence time of the solute in the column decreased, which causes the nickel solution to leave the column before equilibrium occurs; (2) when the process is intraparticle mass transfer controlled, a slower flow rate favors the sorption and when the process is subjected to external mass transfer control; a higher flow rate decreases the film resistance [12]. Even though the volume of nickel solution treated was higher at flow rates of 10 and 20 ml/min, the lowest flow rate of 5 ml/min displayed a relatively high nickel removal (%).

3.3. Regeneration

The column regeneration studies were carried out for seven sorption–desorption cycles. The column was packed with 51 g of CSP yielding an initial bed height of 25 cm and bed volume of 78.5 ml with packing density of 650 g/l. The flow rate was adjusted to 5 ml/min. The breakthrough time, exhaustion time, stoichiometric time and nickel uptake for all seven cycles are summarized in Table 3. At the end of seventh cycle, 39 g of dry CSP was left in the column indicating a weight loss of 23.4%.

The breakthrough time steadily decreased from 28.1 to 9.5 h as the cycle progressed from 1 to 7. This decreasing trend was also reflected in stoichiometric time. The bed ex-

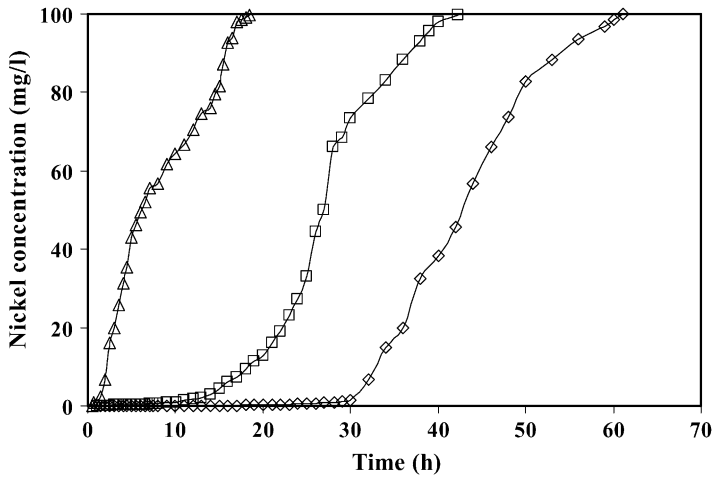

Fig. 3. Breakthrough curves for nickel sorption onto crab shell particles at different flow rates (bed height = 25 cm, initial nickel concentration = 100 mg/l, pH 4.5). Flow rate: (◊) 5 ml/min; (□) 10 ml/min; (△) 20 ml/min.

Table 2
Column data and parameters obtained at different flow rates

Flow rate (ml/min)	Uptake (mg/g)	t_b (h)	t_e (h)	$\triangle t$ (h)	t_s (h)	dc/dt (mg/l h)	V_{eff} (l)	Total nickel removal (%)
5	25.57	28.1	61.1	33.0	43.8	3.345	18.33	71.82
10	21.18	10.1	42.3	32.2	28.6	3.748	25.38	42.94
20	20.58	0.7	18.5	17.8	8.5	5.211	22.20	47.73

Conditions: bed height = 25 cm, initial nickel concentration = 100 mg/l, pH 4.5.

Table 3
Sorption process parameters for seven sorption–desorption cycles

Sorption cycle no.	Uptake (mg/g)	t_b (h)	t_e (h)	$\triangle t$ (h)	t_s (h)	dc/dt (mg/l h)	Z (cm)	Z_m (cm)	V_{eff} (l)	Total nickel removal (%)
1	25.57	28.1	61.1	33.0	43.8	3.345	25.0	13.5	18.33	71.82
2	20.62	22.8	57.6	34.8	35.4	3.159	24.8	15.0	17.28	61.43
3	21.65	20.4	59.5	39.1	38.5	2.618	24.6	16.2	17.85	62.44
4	22.40	19.1	61.3	42.2	38.4	2.764	24.5	16.9	18.39	62.70
5	22.61	15.2	59.3	44.1	41.6	2.337	24.2	18.0	17.79	65.44
6	22.03	12.4	61.6	49.2	37.8	2.231	24.1	19.2	18.48	61.36
7	23.99	9.5	65.4	55.9	41.2	2.048	23.8	20.3	19.62	62.95

Conditions: bed height = 25 cm, flow rate = 5 ml/min, initial nickel concentration = 100 mg/l, pH 4.5.

haustion time increased as the cycle progressed. The bed exhaustive limit was selected as 99.5 mg Ni/l in order to avoid the time delay normally occur for full bed saturation. The overall sorption zone (Δt) tends to increase as the cycle progressed, indicating the sorption sites were not easily accessible as they were still occupied by metal ions or destroyed by previous elution step. The breakthrough curves for all cycles (1–7) are presented in Fig. 4. The breakthrough curves tend to flattened as the cycles proceeded also represented by the slope of the breakthrough curve, which was around 3.3 mg/l h (1st cycle) and decreased to 2 mg/l h (7th cycle). The bed length actually decreased from 25 cm (1st cycle) to 23.8 cm (7th cycle), whereas the bed volume and the packing density decreased to 74.8 ml and 527 g/l, respectively, after seven sorption–desorption cycles. It may be due some soluble constituents of the sorbent dissolved in strong alkaline environment, which was provided to favor elution step. This deterioration was also reflected in metal uptake capacity of the CSP. The nickel uptake obtained in the first sorption cycle was never reached again in any of the subsequent cycles, even though uptake was slightly increased in the last cycle. The uptake was strongly depends upon the previous elution step. Since prolonged elution may destroy the binding sites or inadequate elution may allow metal ions to retain in the sites.

The minimum bed length (Z_m) required to obtain the breakthrough time t_b at $t = 0$ (also called critical bed length) was uniformly increased as the cycle progressed, indicating the broadening of the mass transfer zone. For biosorption, the activity-indicator can be calculated as "life-factors" based on the minimum bed length and the breakthrough time.

In order to calculate life-factor in terms of critical bed length, a linear regression was used [7],

$$Z_m = Z_{m,0} + k_L x \quad (9)$$

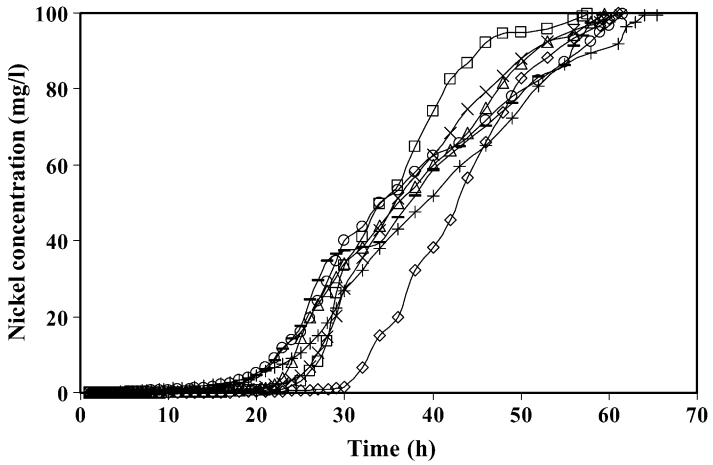

Fig. 4. Breakthrough curves for nickel sorption onto crab shell particles during seven sorption–desorption cycles (bed height = 25 cm, flow rate = 5 ml/min, initial nickel concentration = 100 mg/l, pH 4.5). Sorption cycle: (◊) cycle 1; (□) cycle 2; (△) cycle 3; (×) cycle 4; (–) cycle 5; (◯) cycle 6; (+) cycle 7.

where x is the cycle number, $Z_{m,0}$ is the initial critical bed length (cm) and k_L is the corresponding life factor (cm/cycle). From the plot of Z_m versus x (graph not presented), $Z_{m,0}$ and k_L values were found to be 12.6 cm and 1.103 cm/cycle respectively.

For life-factor in terms of breakthrough time, an exponential decay function regression was used [7],

$$t_b = t_{b,0} \exp(-k_b x) \quad (10)$$

where $t_{b,0}$ is the initial breakthrough time (h) and k_b is the corresponding life factor (per cycle). Eq. (10) was linearized to determine $t_{b,0}$ as 33.9 h and its corresponding life factor k_b = 0.1726 per cycle. Thus, the life-factors calculated in terms of critical bed length and breakthrough time serves as indicators to evaluate the decreasing sorption performance of crab shell.

For a system of continuous operation to work successfully, the desorption process and agents must be effective and should not cause much damage to the sorbent. Furthermore, the understanding of the mechanism responsible for metal sorption would be very helpful in selection of eluting agents. Crab shell comprises of mainly calcium carbonate, chitin along with some proteins. Chitin has been postulated as the main constituent responsible for metal coordination [4,13]. The mechanism involved is usually complex formation between dissolved metallic species and chitin. In order to retrieve the cations, which are physicochemically sequestered to the cell surface, a strong complexing agent might be helpful. A preliminary examination revealed that among several complexing agents (results not presented), 0.01 M EDTA (disodium) solution at pH 9.8 adjusted using conc. NH_4OH was found to be suitable for the present system. Also, Chui et al. [14] reported that 0.1 M EDTA recovered 80–100% of Cu(II) and Ni(II) from shrimp chitin in column experiments.

The elution curves obtained for all seven cycles are presented in Fig. 5. The elution curves observed in all the cycles exhibited a similar trend, a sharp increase in the beginning followed by a gradual decrease. The flow rate in the elution process was maintained at 10 ml/min to avoid the over contact of the elutant with the sorbent and also to obtain maximum nickel concentration in a shorter time [7]. The elution efficiency (E) was greater than 99.1% in all the seven cycles. In cycle 2, the elution efficiency was around 103.6%, this may be due to inadequate elution in the previous cycle. Also in cycle 1 at t = 45 min, 2058 mg Ni/l was present and this value was not reached in any of the other cycles. The time required for elution process and elution efficiencies of all cycles are presented in Table 4.

Table 4
Elution process parameters for seven sorption–desorption cycles

Elution cycle no.	Time for elution (h)	Elution efficiency (%)
1	8.9	99.1
2	9.0	103.6
3	8.8	99.8
4	8.4	99.7
5	7.9	99.8
6	7.8	99.6
7	7.4	100.0

Conditions: flow rate = 10 ml/min, EDTA concentration = 0.01 M, pH 9.8.

The pH profile during the course of sorption process for cycles 1, 3 and 7 are shown in Fig. 6. In all the cycles, it was commonly observed that there was a sudden raise in pH in the early part of the process and pH tends to decrease as the time progressed but never reached the initial pH of the influent (pH 4.5). The Amino and the hydroxyl groups of chitin are the major effective binding sites for metal ions, forming stable complexes by coordination [15]. The interaction between the functional groups in chitin and Ni^{2+} ions may be responsible for pH increase in the initial stages and as the saturation of the bed proceeds, the pH decreased. In addition, Ng et al. [16] observed the pH values of equilibrated solution of Cu(II) considerably increased from the pH values before chitosan addition. The pH profile during the course of the

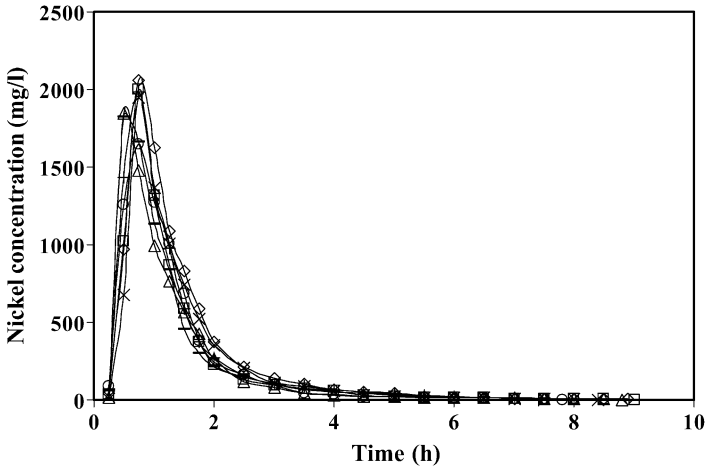

Fig. 5. Elution curves for desorption of nickel during seven sorption–desorption cycles (flow rate = 10 ml/min, elutant concentration = 0.01 M, pH 9.8). Elution cycle: (◊) cycle 1; (□) cycle 2; (△) cycle 3; (×) cycle 4; (–) cycle 5; (◯) cycle 6; (+) cycle 7.

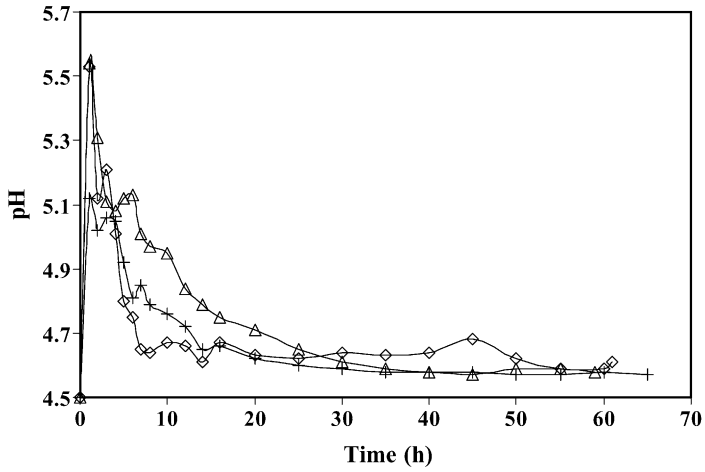

Fig. 6. Sorption pH profiles during seven sorption–desorption cycles (bed height = 25 cm, flow rate = 5 ml/min, initial nickel concentration = 100 mg/l). Sorption cycle: (◊) cycle 1; (△) cycle 3; (+) cycle 7.

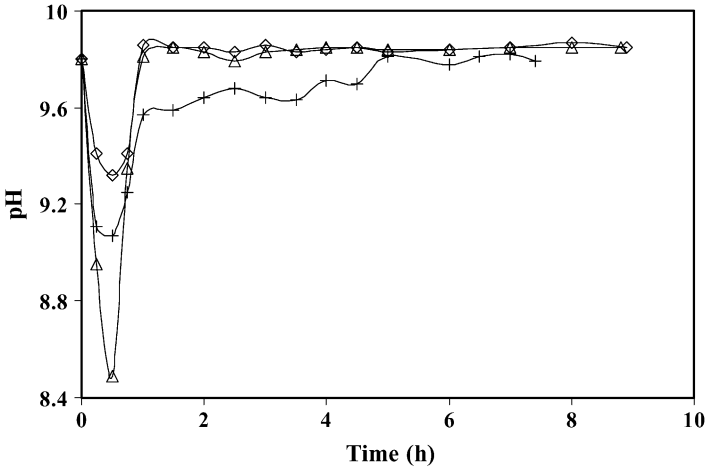

Fig. 7. Elution pH profiles during seven sorption–desorption cycles (flow rate = 10 ml/min, elutant concentration = 0.01 M). Elution cycle: (◊) cycle 1; (△) cycle 3; (+) cycle 7.

elution process for cycles 1, 3 and 7 are shown in Fig. 7. In all the cycles, it was generally observed that there was a decrease in pH in initial stages (which prolonged for around 30 min) and followed by gradual increase in pH. A certain decrease in effluent pH in the initial stages may be due to the combine effect of EDTA and NH_4OH in retrieving the nickel ions from the sorbent. As the nickel concentration in the effluent decreased, the pH increased and reached the pH of the inlet elutant (pH 9.8).

The total volume of nickel bearing solution (100 mg/l) treated during this regeneration study was around 127.74 l (in seven cycles) and the total volume of 0.01 M EDTA (pH 9.8, NH_4OH) utilized for elution process was nearly 34.92 l, which corresponds to approximately 20 days of continuous operation. Even after seven sorption–desorption cycles, CSP exhibited a relatively high percentage of nickel removal (62.95%) and nickel uptake of 23.99 mg/g, indicating the potential of CSP to withstand extreme conditions at the same time retaining its nickel sorption capacity.

4. Conclusions

This study identified crab shell as a suitable biosorbent to be utilized for continuous removal of nickel(II) ions from aqueous solution. An up-flow packed bed column was employed in the present study, as it allows a large volume of wastewater to be continuously treated using a defined quantity of sorbent in the column. Experimental data confirmed that the bed height influence was not pronounced in nickel uptake (based on initial weight of the sorbent loaded) by crab shell, as it remained relatively constant for all the bed heights (15–25 cm) investigated. The increase in flow rate (5–20 ml/min) resulted in decreased nickel uptake, probably due to insufficient residence time of the solute in the column.

A successful biosorption process operation required the multiple reuse of the sorbent, which greatly reduce the process cost as well as decrease the dependency of the process on continuous supply of the sorbent. The sorption performance

of crab shell was evaluated in seven sorption–desorption cycles. A loss of sorption performance was observed as the cycles progressed, which was equally indicated by a decrease in breakthrough time, broadening of mass transfer zone, loss in sorbent weight, decrease in nickel uptake and decline in % nickel removal at the end of seventh cycle. It is always desirable to select an elutant, which neither affects the physical condition of the sorbent nor alters the metal uptake. The process of identifying an efficient elutant for a particular sorbent is rather complicated and requires a complete understanding of the mechanism responsible for metal binding. For the present system, 0.01 M EDTA (disodium) solution at pH 9.8 adjusted using NH_4OH works well exhibited elution efficiencies of greater than 99.1% for the entire seven sorption–desorption cycles. The pH variations observed during the course of sorption and desorption process revealed that even though there was a pH shift in the initial stages of the process, in almost all the cases pH approaches steadily towards that of inlet solution. These observed pH variations could be useful for a simplified control of column sorption process. The economic and environmental advantages of reusing the shell particles and good sorption capacity makes crab shell as an attractive treatment option for nickel bearing solutions.

References

[1] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Prog. 11 (1995) 235–250.
[2] F. Veglio, F. Beolchini, Removal of metals by biosorption: a review, Hydrometallurgy 44 (1997) 301–316.
[3] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.
[4] M.Y. Lee, J.M. Park, J.W. Yang, Micro precipitation of lead on the surface of crab shell particles, Proc. Biochem. 22 (1997) 671–677.
[5] J.R. Evans, W.G. Davids, J.D. MacRae, A. Amirbahman, Kinetics of cadmium uptake by chitosan-based crab shells, Water Res. 36 (2002) 3219–3226.
[6] S. Al-Asheh, N. Abdel-Jabar, F. Banat, Packed-bed sorption of copper using spent animal bones: factorial experimental design, desorption and column regeneration, Adv. Environ. Res. 6 (2002) 221–227.
[7] B. Volesky, J. Weber, J.M. Park, Continuous-flow metal biosorption in a regenerable *Sargassum* column, Water Res. 37 (2003) 297–306.
[8] Z. Zulfadhly, M.D. Mashitah, S. Bhatia, Heavy metals removal in fixed-bed column by the macro fungus *Pycnoporus sanguineus*, Environ. Pollut. 112 (2001) 463–470.
[9] R.A. Hutchins, New method simplifies design of activated carbon systems, Chem. Eng. 80 (1973) 133–138.
[10] Z. Aksu, F. Gonen, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, Proc. Biochem. 39 (2003) 599–613.
[11] D.O. Cooney, Adsorption Design for Wastewater Treatment, CRC Press, Boca Raton, 1999.
[12] D.C.K. Ko, J.F. Porter, G. McKay, Optimised correlations for the fixed-bed adsorption of metal ions on bone char, Chem. Eng. Sci. 55 (2000) 5819–5829.
[13] M. Tsezos, B. Volesky, Biosorption of uranium and thorium, Biotechnol. Bioeng. 23 (1981) 583–604.
[14] V.W.D. Chui, K.W. Mok, C.Y. Ng, B.P. Luong, K.K. Ma, Removal and recovery of copper(II), chromium(II) and nickel(II) from solutions using crude shrimp chitin packed in small columns, Environ. Int. 22 (1996) 463–468.
[15] L. Zhang, L. Zhao, Y. Yu, C. Chen, Removal of lead from aqueous solution by non-living *Rhizopus nigricans*, Water Res. 32 (1998) 1437–1444.
[16] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies of the sorption of Cu(II) ions onto chitosan, J. Colloid Interf. Sci. 255 (2002) 64–74.