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Evaluation of Native and Chemically Modified *Sargassum glaucescens* for Continuous Biosorption of Co(II)

Mina Ebrahimi · Reza Panahi · Reza Dabbagh

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Abstract In the present study, biosorption of stable cobalt was studied in an up-flow fixed-bed column using the brown alga *Sargassum glaucescens* treated with formaldehyde (FA) or $MgCl_2$. Notable increase in cobalt removal was observed for FA-treated biosorbent with 2.7 and 1.4 times higher dynamic capacity (DC) and uptake capacity (UC) than native alga, respectively. Consequently, FA-treated *S. glaucescens* was selected for further investigations. In particle size experiments, the DCs of 0.5–1 and 1–2 mm particles were both equal to 27.6 mg/g, and corresponding UCs were 34 and 38 mg/g, respectively. The maximum DC was obtained at residence time of 2.5 min. Studying the effect of additional ions indicated partial effect of Na^+ and K^+ ions on DC and UC, Mg^{2+} reduced highly the DC and slightly the UC while heavy metal ions (Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cr^{3+}) caused decrease in both DC and UC about 1.5–4.7 and 1.8–3.2 times, respectively. Moreover, the column regeneration studies were carried out for four sorption–desorption cycles. The DC and the UC highly decreased in the second cycle, partially decreased or remained constant in the third and in the fourth one.

Keywords Biosorption · Chemical modification · Waste-water treatment · Fixed-bed column · *Sargassum glaucescens* · Cobalt

Introduction

Heavy metals including cobalt are major pollutants in marine, ground, industrial and even treated wastewaters [1, 2]. Conventional methods used to remove dissolved heavy metal ions from wastewaters include chemical precipitation, chemical oxidation and reduction,

M. Ebrahimi
Department of Microbiology, Alzahra University, Tehran, Iran
e-mail: minaebra@gmail.com

R. Panahi (✉)
Department of Chemical Engineering, Tarbiat Modares University, Tehran, Iran
e-mail: r58panahi@yahoo.com

R. Dabbagh
Faculty of Environment, University of Tehran, Tehran, Iran
e-mail: rdabagh@yahoo.com

electrochemical treatment, ion exchange/chelating, filtration and reverse osmosis [3–5]. Recently, biosorption of heavy metals has been introduced as one of the most promising technologies involved in the removal of toxic metals from industrial waste streams as it offers the advantages of low operating costs, possibility of metal recovery, regeneration of biosorbent, minimization of the volume of chemical and/or biological sludge and high efficiency in detoxifying very dilute effluents [3, 6, 7].

Among the many types of biosorbents used by several researchers, algae have proved to be the most efficient and practical biomass for the removal of heavy metal ions from aqueous solutions. Amongst three major groups of algae, brown algae have been extensively used for biosorption [8].

Alginic acid constitutes 10–40% of dry weight of brown algae, and consists β-1,4-D-mannuronic (M) and α-1,4-L-glurunic acid (G) residues arranged in a non-regular, blockwise order along the chain. The residues typically occur as (–M–)*n*, (–G–)*n*, and (–MG–)*n* sequences or blocks. (Figure 1) [9–11]. It has become one of the most important groups of adsorbents among the biological materials and has great affinity to divalent cations. The presence of key functional groups such as carboxyl groups is responsible for its outstanding metal-sorbing properties. Various mechanisms have been reported for binding of metals to alginates. Some studies have mentioned mainly ion exchange and others have described sorption through complexation mechanism [9, 12].

In order to enhance mechanical and sorption properties of raw biomass for potential technological use, several types of modification techniques have been developed [10]. Treatments which improve ionic interactions generally imply one of two chemical alterations. The first is protonation of the biomass with a strong acid such as HCl whereby the proton displaces the light metal ions from the binding sites (i.e., carboxylic, sulfonic, and others). The second is biomass reaction with an aqueous solution of a given ion at high concentration so that the majority of binding sites are occupied by, for example, calcium, potassium [9] or magnesium. Other modifications such as crosslinking with aldehydes which reinforces the biosorbent particles by bridging—binding of their own molecules cause physical changes [10].

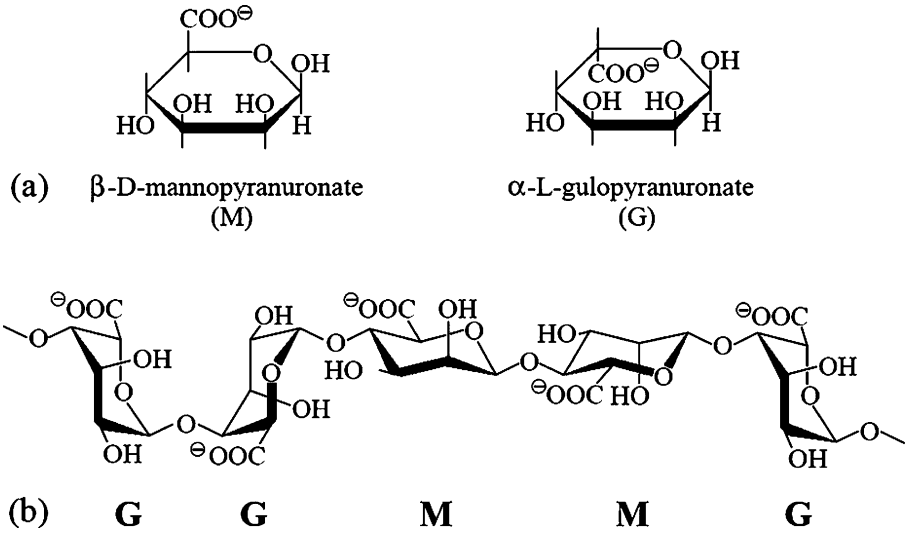

Fig. 1 Alginate structural data: **a** alginate monomers (M vs. G); **b** the alginate polymer [9]

Recently, native or treated biosorbents with salts and/or acids have been vastly employed [4, 7, 13–20]. However, fewer reports of crosslinking have been published, [21–26].

Since one of the most important aspects of crosslinking (biosorbent swelling behavior) is ignored in batch systems, studying the treated biosorbent in the packed bed column is necessary.

On the other hand in preparation for the biosorption process design the sorption/desorption performance and characteristic properties (mass transfer, pressure and attrition resistance, chemical stability, etc) of the biosorbent should be reasonably well known. Although equilibrium sorption tests yield some basic information, the sorption system behavior is invariably examined under continuous-flow conditions. The fixed-bed sorption column arrangement is usually the most effective process configuration [27].

Various species of the genus *Sargassum* have been studied. Jalali-Rad et al. studied cesium biosorption by brown alga *Sargassum glaucescens* which had been harvested from the Oman Sea in batch system and obtained good results [24]. They also investigated batch biosorption of cobalt by this alga. In their study, most of the cobalt ions were sequestered from solution within 15 min and equilibrium was established in 3 h, the highest removal of cobalt occurred at pH 4 and the biosorption of Co(II) increased with increase of initial cobalt concentration (unpublished data).

In the present study, biosorption of cobalt by chemically treated *S. glaucescens* in an up-flow fixed-bed column was investigated. Then the effect of residence time and particle size on the dynamic capacity (DC) and uptake capacity (UC) of biosorbent were investigated by "one factor at a time method". Furthermore, the effect co-ions and adsorption–desorption behavior on DC and UC of the modified biomass were examined.

Materials and Methods

Chemicals and Instrumentation

Formaldehyde (CH_2O), Na_2CO_3, $CoCl_2{\cdot}6H_2O$, NaCl, KCl, $MgCl_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $CdCl_2{\cdot}H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Pb(NO_3)_2$, $CrCl_3{\cdot}6H_2O$, $ZnCl_2$ and $CaCl_2$ were from Merck (Germany). The pH of solutions was adjusted with 0.1 M HCl (Merck, Germany). AS200 analytical sieve shaker (RETCH, Germany) was used for sieving biosorbents. All solutions were passed through the column by means of a 205U peristaltic pump (Watson-Marlow, UK). The amount of cation in the outlet solution was analyzed using an AA-220 atomic absorption spectrophotometer (VARIAN, Australia).

Biomass and Treatments

Brown alga *S. glaucescens* was harvested from Oman Sea on the coast of Chabahar, Iran. The alga was washed with distilled water, subsequent washing with tap water several times and then sun-dried on the beach. Eventually, the resulted biomass was utilized for preparation of chemically modified biosorbents.

Treatment with Formaldehyde (FA) To obtain FA-treated biomass, a mixture of 17 ml formalin 30% and 33 ml HCl 0.1 M was added to 2.5 g smoothly crushed biomass. The mixture was left at room temperature with gentle mixing. After 1 h, the biomass was filtered and washed with distilled water. Subsequently, the biosorbent was incubated with 50 ml sodium carbonate solution (0.2 M) for 15 min, filtered, washed with distilled water

and dried overnight at 80 °C [10, 24]. Finally, the dried biomass was ground gently and sieved to achieve 0.5–1 and 1–2 mm particles.

Treatment with $MgCl_2$ Treatment with $MgCl_2$ was done by passing 1 l $MgCl_2$ solution (0.1 M) through a packed column with native biosorbent for 1 h.

Column Biosorption Experiments

Column biosorption experiments were performed for native, formaldehyde-treated and magnesium chloride-treated biomass separately.

The continuous biosorption system included a glass column with 2.75 cm inner diameter and 30 cm height, connected to a peristaltic pump and a thermostatic bath. The column was packed by 5 g dry biomass using an adjustable plunger. The biomass was maintained in contact with distilled water overnight to complete the hydration process (biosorbent swelling). Then, the residual water was drained and the bed height was fixed to the desired length by moving the adjustable plunger until neither loose particles nor pressure was observed in the bed. Finally, void volume was measured.

Different biosorbents showed different bed heights and swelling behaviors. In order to keep constant the 2.5-min residence time, different flow rates were used. The void volume of native, magnesium chloride-treated and formaldehyde-treated biomass was 14.8 ml, 15.5 ml and 17.5 ml, respectively. The bed height of different biosorbents and the flow rate used at different residence times for FA-treated biosorbent have been shown in the appropriate table.

The biosorbent was washed with 600 ml distilled water using continuous flow for 30 min in order to accommodate the packed bed [13]. Subsequently, 72 mg/l cobalt solution (pH 4) was pumped upward through the column by a peristaltic pump at 27 °C. Samples were collected from outlet of the column at defined time intervals and analyzed for determination of cobalt concentration by atomic absorption spectrophotometer.

To evaluate the biosorption performance, cobalt ion concentration in the outlet (Co_{out}) was plotted versus the treated volume. The amount of removed cobalt ion by the pre-treated biomass was calculated from experimental breakthrough curve using the following formula:

$$q = \frac{1}{5,000} \int_0^{V_t} (C_0 - C)\, dV \tag{1}$$

where q is the amount of adsorbed cobalt per gram of biosorbent (mg/g), V_t is the volume passed through the column at a given time (ml), C_0 is the initial cobalt concentration (ppm), and C is the outlet cobalt concentration (ppm). The amount of q is equal to DC when V_t is referred to breakthrough point; and also, it is UC when V_t is considered as the total passed volume. The integral part of Eq. (1) was solved numerically using the experimental data from the breakthrough curve.

The total metal removal percent was calculated from the total metal mass adsorbed divided by the total amount of metal ions passed through the column up to saturation point, multiply by 100 [19].

The Effect of Co-ions

The effect of additional ions on cobalt biosorption was examined by adding 1 mM Na^+, K^+, Mg^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cr^{3+} to the 1 mM cobalt solution, individually.

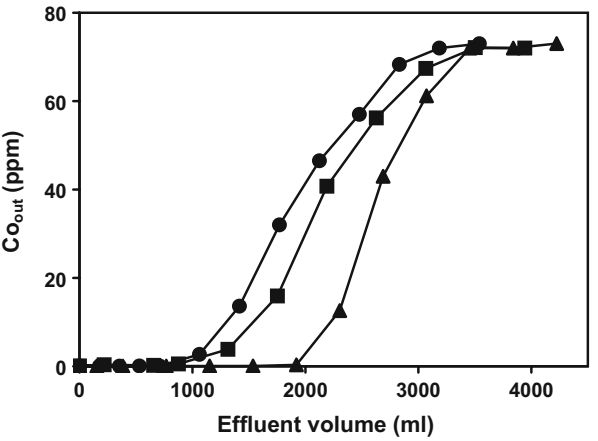

Fig. 2 Breakthrough curves as a function of treated volume for cobalt biosorption by native (*filled circle*) and treated *S. glaucescens* with $MgCl_2$ (*filled square*) and formaldehyde (*filled upright circle*). Feeding cobalt concentration, 72 mg/l; residence time, 2.5 min; biomass dry weight, 5 g; particle size, 1–2 mm; inlet pH, 4 and temperature, 27 °C

Sorption–Desorption Cycle Study

Having been used in column sorption experiments, the biosorbent was regenerated by passing 0.1 M $CaCl_2$ solution (pH 3) through column at the residence time equal to 2.5 min. After elution, distilled water was used to wash the bed until the pH in the wash effluent stabilized near 7.0 [19].

Biosorption studies were carried out again by passing cobalt solution through the regenerated column. The sorption–desorption cycle was repeated four times to evaluate the biomass sorption capacity. To determine the weight loss after four cycles, the biomass was washed with distilled water and dried overnight at 80 °C.

Results and Discussion

The Effect of Chemical Treatment

Various chemically modified biosorbents with particle size of 1–2 mm originated from *S. glaucescens* were studied in the up-flow fixed-bed column system at 2.5-minute residence time. The biosorption column breakthrough curves have been shown in Fig. 2, where the cobalt concentration in the column outlet is plotted vs. the passed solution volume. In comparison with native *S. glaucescens*, treatment with $MgCl_2$ caused a little increase in cobalt removal, while FA treatment increased the DC and the UC to 2.7 and 1.4 times, respectively. Moreover, the breakthrough time did not change after treatment with $MgCl_2$, but it increased 2.5 times after formaldehyde treatment (Table 1).

Table 1 Dynamic capacity, uptake capacity, breakthrough time and bed height for native and chemically modified *S. glaucescens* for Co(II) removal.

Treatment	Dynamic capacity (mg /g of dry biomass)	Uptake capacity (mg /g of dry biomass)	Breakthrough Time (hour)	Bed height (cm)
Native	10.2	27.7	2	7.8
$MgCl_2$	12.6	31.1	2	7.8
FA	27.6	38	5	10.2

FA modification is a chemical crosslinking neighboring chemical groups, preferably hydroxyl groups of two adjacent polysaccharide molecules of the cell wall. In reaction of formaldehyde with alginic acid, ethers could be formed. Formaldehyde forms a single carbon atom bridges between two different hydroxyl groups of two adjacent polysaccharide molecules. The reaction occurs in two steps. The generation of chemically unstable hemiacetal in the first step is followed by the reaction of hemiacetal to an acetal which completes the formation of the formaldehyde crosslinks [10]. As it can be seen in Table 1, the bed height of $MgCl_2$-treated biosorbent is the same as native one. But it has increased about 1.3 times after treatment with FA, which shows more swelling of biosorbent. These results show that FA treatment causes reinforcement and improves the ion-exchange activity of biosorbent because of exposing more chemical groups to the environment.

The treatment with $MgCl_2$ improved the ion-exchange activity. However, it caused less cobalt removal than FA treatment. Therefore, FA-treated *S. glaucescens* with the percent removal of 76.3% was selected for further experiments.

Particle Size Effect

Since decreasing particle size increases the contact surface, the FA-treated *S. glaucescens* with the particle size of 0.5–1 mm was also evaluated in the biosorption column. The breakthrough curve for 0.5–1 and 1–2 mm particles were similar. The DCs calculated for 0.5–1 and 1–2 mm particles were both 27.6 mg/g, while corresponding UCs were 34 and 38 mg/g, respectively. The bed height of 0.5–1 mm particles (9 cm) was lower than that of 1–2 mm particles (10.2 cm) which could cause pressure drop in the column because of smaller diffusion distance and consequently higher mass transfer resistance. Since 0.5–1 mm particles showed lower UC and could cause pressure drop in the column, the particles with 1–2 mm size were chosen for subsequent studies.

Effect of Residence Time

The effect of residence time on the DC and UC of FA-treated *S. glaucescens* has been shown in Fig. 3. The results in Table 2 show that the DC of the biosorbent at the residence time of 2.5 min is the highest, although corresponding UC is almost equal to that of 0.8 and 1.4 min residence times. In addition, the residence time of 4.9 min showed higher DC than

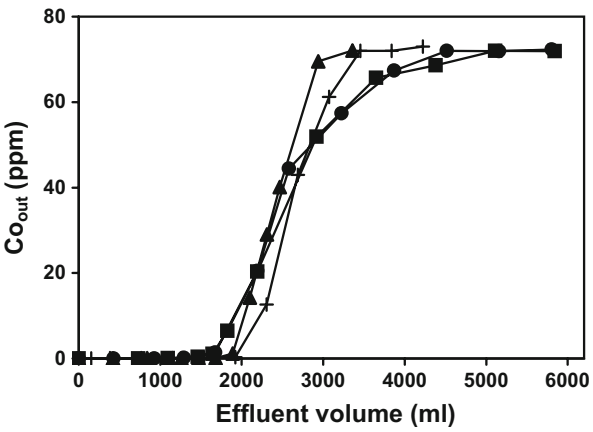

Fig. 3 Breakthrough curves as a function of treated volume for cobalt biosorption by FA-treated *S. glaucescens* at different residence times: 0.8 min (*filled circle*), 1.4 min (*filled square*), 2.5 min (*plus sign*) and 4.9 min (*filled upright triangle*). Feeding cobalt concentration, 72 mg/l; biomass dry weight, 5 g; particle size, 1–2 mm; inlet pH, 4; temperature, 27 °C; bed height, 10.2 cm

Table 2 The effect of residence time on the dynamic capacity and uptake capacity of FA-treated *S. glaucescens* for Co(II) removal.

Flow rate (ml/min)	Residence time (min)	Dynamic capacity (mg /g of dry biomass)	Uptake capacity (mg /g of dry biomass)
21.8	0.8	24.1	37.7
12.5	1.4	23.6	38.5
7	2.5	27.6	38
3.6	4.9	27.2	34.9

that of the 0.8 and 1.4 min residence times, while the UC was lower. It can be related to activation of sorption sites on biosorbent at adequate turbulence.

At high residence time there is not adequate turbulence. Consequently, particle-to-liquid mass transfer resistance is higher and intraparticle diffusion decreases [10]. As a result, the UC of 4.9 min residence time is less. On the other hand, at low residence time, the metal solution will leave the column before the equilibrium occurs. In other words, the solute does not have sufficient time to diffuse onto the active sites of the biosorbent. Therefore, the adsorbed metal ion concentration decreases as the residence time decreases [28].

Therefore, the experiments were followed with the residence time of 2.5 min because of the best performance.

Effect of Additional Ions

The effect of Na^+, K^+, Mg^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cr^{3+} ions, present in industrial waste waters [1, 7], on cobalt biosorption by FA-treated *S. glaucescens* was examined. The cation solutions (pH 4) were passed through the column with 1–2 mm biosorbent particles and the residence time of 2.5 min, at 27 °C. The results in Fig. 4 indicate that Na^+ and K^+ ions have partial effects on cobalt biosorption, although the other additional ions caused a noticeable decrease in breakthrough volume. The presence of Mg^{2+} reduced highly the DC and slightly the UC (Table 3).

Heavy metal ions caused decrease in both DC and UC about 1.5–4.7 times and 1.8–3.2 times, respectively. The highest decrease of DC and UC was due to Cd^{2+} and Pb^{2+}. These results indicate the existence of a competition behavior between divalent ions to gain access to the active sites of FA-treated *S. glaucescens*.

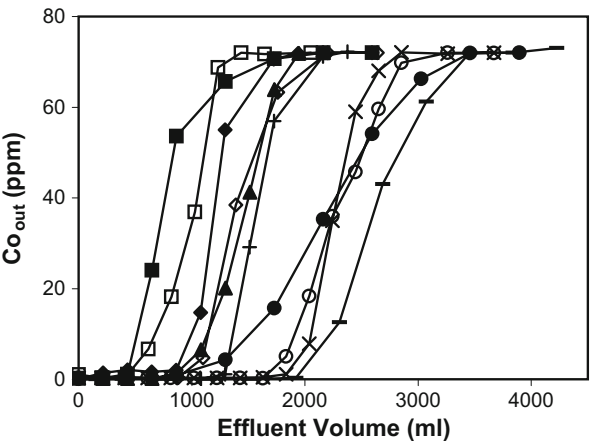

Fig. 4 Breakthrough curves as a function of treated volume for cobalt biosorption by FA-treated *S. glaucescens* in the presence of additional ions: Cd^{2+} (*filled square*), Pb^{2+} (*empty square*), Cr^{3+} (*filled diamond*), Cu^{2+} (*empty diamond*), Ni^{2+} (*filled upright triangle*), Zn^{2+} (*plus sign*), Mg^{2+} (*filled circle*), Na^+ (*empty circle*), K^+ (*x symbol*), None (control) (*dash*). Feeding cobalt concentration, 72 mg/l; residence time, 2.5 min; biomass dry weight, 5 g; particle size, 1–2 mm; inlet pH, 4; temperature, 27 °C; bed height, 10.2 cm

Table 3 The effect of additional ions on the dynamic capacity and uptake capacity of FA-treated *S. glaucescens* for Co(II) removal.

Additional ions	Dynamic capacity (mg Co /g of dry biomass)	Uptake capacity (mg Co /g of dry biomass)
None (control)	27.6	38
Pb^{2+}	5.9	13.8
Cd^{2+}	6.2	11.7
Zn^{2+}	18.7	23
Cu^{2+}	12.7	20.5
Ni^{2+}	12.5	20.7
Mg^{2+}	12.5	31.4
Cr^{3+}	12.4	17.3
K^{+}	26.4	32.5
Na^{+}	23.5	32.9

It has been reported that most *Sargassum* alginates have M:G (mannuronic acid:glurunic acid) ratios ranging from 0.8 to 1.5. Low M:G ratios (i.e., <1.0) are indicative of higher G content and are, therefore, deemed highly advantageous for the implementation of the biosorption process. This reflects the established selectivity for divalent cations of the guluronic block sections, in accordance with the "egg-box" model of Rees and coworkers [9]. According to our results (Table 3) divalent cations were more effective on cobalt biosorption than monovalent ones. This can be because of stronger divalent cations interaction with biosorbent. Consequently *S. glaucescens* alginates may consist lower M:G ratio.

Generally, according most studies, binding strength trends follow the pattern for monovalent ions—Cs>Rb>K>Na>Li—and for divalent ions—Ba>Sr>Ca>Mg; Cu>Ni>Co>Mn; Pb>Cd>Zn. While the preceding expresses basic trend, no fixed relation between these series can be established. Whether, for example, Cu or Cd happens to be more strongly bound depends on the sorbent material [27]. Similar results were obtained in this study. According to the decreasing cobalt UC (Table 3), binding strength trends followed the pattern Cd>Pb>Cr>Cu>Ni>Zn>Mg>K>Na. As it can be seen, monovalent cations showed less binding strength than divalent ones.

More over, the size of the cation appears to be an important variable in metal binding to alginates, both due to the rigid nature of the GG-linkages, as well as to the steric

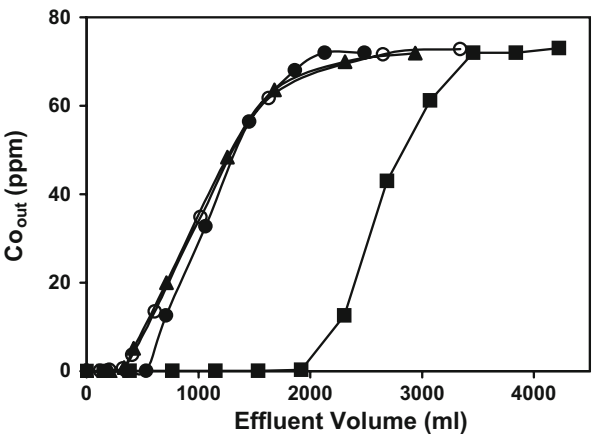

Fig. 5 Sorption breakthrough curves as a function of treated volume for cobalt biosorption during four regeneration cycles: cycle 1 (*filled square*), cycle 2 (*filled circle*), cycle 3 (*filled upright triangle*) and cycle 4 (*empty circle*). Feeding cobalt concentration, 72 mg/l; residence time, 2.5 min; biomass dry weight, 5 g; particle size, 1–2 mm; inlet pH, 4; temperature, 27 °C

Table 4 Cobalt sorption and elution results for four sorption–desorption cycles.

Cycle no.	Bed height (cm)	Dynamic capacity (mg /g of dry biomass)	Uptake capacity (mg /g of dry biomass)	Cobalt concentration at the pick of elution curve (mg/l)
1	10.2	27.6	38	1,062.8
2	9.0	7.7	16.5	1,095.7
3	9.0	4.8	15.7	1,102.6
4	9.0	4.7	16.3	1,123.5

arrangement of the electronegative ions surrounding the divalent cation [9]. According to our results, the highest decrease of DC and UC was due to Cd^{2+} and Pb^{2+} which have the highest ionic radii 0.95 Å and 1.19 Å, respectively. The ionic radii of other divalent cations are in the range of 0.65–0.74 Å [27]. On the other hand Cr^{3+} with the ionic radius of 0.615 Å showed a high increase of UC which can be because of trivalent charge.

Sorption–Desorption Experiments

In biological wastewater treatment, biomass regeneration is important to recover metal ions and to reuse biosorbents. The column regeneration studies were carried out for four sorption–desorption cycles. The column was packed with 5 g FA-treated *S. glaucescens* and the residence time was 2.5 min.

Breakthrough curves of all sorption cycles have been shown in Fig. 5. Up to breakthrough point, the treated effluent volume and the DC highly decreased in the second cycle and partially decreased in the third and in the forth one. The UC was also decreases by 56.5% after the first cycle but remained constant during other cycles (Table 4). Yang (1999) used a *Sargassum fluitans* loaded fix-bed column to study uranium biosorption. The column was maintained continuously for 1 month over which time five biosorption–desorption cycles were carried out. Their results was different since the decrease of uranium biosorption was low after the first cycle (7%), but it was higher at the end of the fifth cycle (20%) [9].

The elution curves of all four cycles in Fig. 6 show that 0.1 M $CaCl_2$ solution at pH 3 has properly regenerated the column. All cycles exhibited a similar trend, a sharp increase in the beginning followed by a gradual decrease. However, cycle 1 shows slower slope after the pick than other cycles that ascribes to higher DC of this cycle.

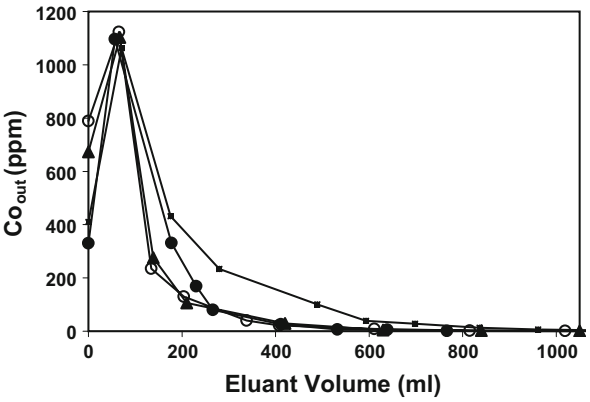

Fig. 6 Elution breakthrough curves as a function of eluant volume for cobalt desorption during four regeneration cycles: cycle 1 (*filled square*), cycle 2 (*filled circle*), cycle 3 (*filled upright triangle*) and cycle 4 (*empty circle*). Eluant, 0.1 M $CaCl_2$; pH, 3; biomass dry weight, 5 g; particle size, 1–2 mm; residence time, 2.5 min; temperature, 27 °C

About 3.8 g of the dry biomass was left in the column at the end of the first sorption process. The same amount of biosorbent was achieved after measuring biomass dry weight left in the column at the end of the fourth cycle. Therefore, biomass weight loss only occurred during the first sorption and before the first desorption process which can be because of escaping loose particles during operation. On the other hand, the UC remained constant in the third and fourth cycles. These results show that the biosorbent reaches physical stability after the first cycle.

Totally, a high decrease of cobalt biosorption after the first cycle in our study can be related to incomplete reduction of active sites, losing sodium carbonate which has been used during FA treatment, and escaping loose particles. Consequently, biosorbent treatment with sodium carbonate after each desorption is a promising way to achieve higher DC for more cycles.

Conclusions

In this research, biosorption of cobalt by different chemically modified *S. glaucescens* in an up-flow fixed-bed column was investigated. It was found that at the similar conditions, FA-treated *S. glaucescens* was the best biosorbent with the DC equal to 27.6 mg Co/g and UC of 38 mg Co/g for initial feed concentration of 72 mg/l. Also, the bed height of biosorbent increased about 1.3 times after treatment with FA which showed more biosorbent swelling and could improve the ion-exchange activity of the biosorbent

Acceptable results were obtained for 1–2 mm particles and the residence time of 2.5 min. Remarkable effect of Mg^{2+} and heavy metal ions on biosorption were observed while Na^{+} and K^{+} ions had no significant influences. The column regeneration studies for four sorption–desorption cycles demonstrated a noticeable decrease in dynamic capacity and uptake capacity. High decrease of cobalt biosorption after the first cycle could be related to both losing sodium carbonate which has been used during FA treatment and escaping loose particles. Consequently, biosorbent treatment with sodium carbonate after each desorption is a promising way to achieve higher DC for more cycles.

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