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Biosorption of hexavalent chromium by chemically modified seaweed, *Cystoseira indica*

Shaik Basha [a,b], Z.V.P. Murthy [b,*], B. Jha [a]

[a] *Marine Biotechnology & Ecology Division, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364002, Gujarat, India*
[b] *Department of Chemical Engineering, S.V. National Institute of Technology Surat, Surat 395007, Gujarat, India*

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Abstract

The sorption of hexavalent chromium by marine brown algae *Cystoseira indica*, which was chemically-modified by cross-linking with epichlorohydrin (CB1, CB2), or oxidized by potassium permanganate (CB3), or only washed by distilled water (RB) was studied with variation in the parameters of contact time, pH, initial metal ion concentration and solid/liquid ratio. They were used for equilibrium sorption uptake studies with Cr(VI). The results indicate that biosorption equilibriums were rapidly established in about 2 h. The Cr(VI) adsorption was strictly pH dependent, and maximum removal of Cr(VI) on biosorbents were observed at pH 3.0. The maximum Chromium uptakes were 22.7, 24.2, 20.1 and 17.8 mg g^{-1}, respectively, for CB1, CB2, CB3 and RB. The order of maximum Cr(VI) uptakes for various biomasses was CB2 > CB1 > CB3 > RB. A comparison of different isotherm models revealed that the Dubinin–Radushkevich (D–R) isotherm model fitted the experimental data best based on R^2, $q_{\max}$ and standard error (S.E.) values and the mean energy of the sorption values indicated that biosorption of Cr(VI) by *C. indica* may be an ion exchange reaction.

Keywords: Hexavalent chromium; *Cystoseira indica*; Chemical modifications; Sorption isotherm models

1. Introduction

The presence of toxic heavy metals in water resulting from rapid industrialization and technological advances is a world wide environmental problem. Removal of these pollutants from aqueous effluents has conventionally been accomplished through a range of abiotic processes [1–3]. However, these processes can be expensive and not fully effective. Recently, increasing interest in the application of materials of biological origin in heavy metals removal from diluted, large volume solutions has been observed. Sorption with bio-materials has become an alternative to traditional methods of industrial wastewaters treatment, such as precipitation, adsorption, coagulation, etc. [4–6] and it is relatively inexpensive, non-hazardous, and may permit recovery of the metals from the sorbing biomass [6,7]. The potential of nonviable brown seaweeds in the recovery of heavy metal ions from aqueous effluents has been well demonstrated [8,9].

Chromium is one of the key contaminant in the wastewaters of industrial dyes and pigments, film and photography, galvanometry and electric, metal cleaning, plating and electroplating, leather and mining. While hexavalent (CrO_2^{4-} and $Cr_2O_2^{7-}$) and trivalent (Cr^{3+} and $CrOH^{2+}$) species of chromium are prevalent in industrial waste solutions, the hexavalent form has been considered more hazardous to public health due to its mutagenic and carcinogenic properties [10,11].

Recent investigations by various groups have shown that selected species of brown seaweeds possess impressive sorption capacities for the removal of hexavalent chromium due to their high uptake capacities and availability in enormous amounts from oceans [12–17]. *Cystoseira indica*, abundantly available seaweed along Suarashtra–Kutchchh coast of India, may be economically used as a potential biosorbent for heavy metal removal from aqueous solutions. It was pretreated in order to enhance the sorption performance and also to strengthen it for sorption process applications. To enhance the removal efficiency of metal ions by the biomass, various pretreatments can be used. Pretreatment may be in terms of hardening the cell wall structure through

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[*] Corresponding author. Tel.: +91 261 2201641/2223371–4; fax: +91 261 2201641/2227334.
E-mail addresses: zvpm2000@yahoo.com, zvpm@ched.svnit.ac.in (Z.V.P. Murthy).

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Nomenclature

b	Langmuir isotherm equilibrium binding constant ($\mathrm{L\,mg^{-1}}$)
C_e	equilibrium concentration of sorbate in solution ($\mathrm{mg\,L^{-1}}$)
C_i	initial concentration of sorbate in solution ($\mathrm{mg\,L^{-1}}$)
e	Polanyi potential ($\mathrm{kJ\,mol^{-1}}$)
E	mean free energy ($\mathrm{kJ\,mol^{-1}}$)
K	Freundlich isotherm constant ($\mathrm{L\,g^{-1}}$)
n	exponent in Freundlich isotherm
q_e	amount of sorbate sorbed at equilibrium ($\mathrm{mg\,g^{-1}}$)
q_{max}	maximum sorption capacity ($\mathrm{mg\,g^{-1}}$)
R	universal gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$)
R^2	correlation coefficient
R_L	Langmuir separation factor
S.E.	standard error
t	sorption time (min)
V	volume of metal solution (L)
W	mass of sorbent (g)

a cross-linking reaction using epichlorohydrin [18], or increasing the negative charge on the cell surface by NaOH treatment [19], or opening of the available sites for the adsorption by acid treatment [16,20], and enhancing ion exchange by Ca^{2+} solution treatment [12]. However, the studies on the use of chemically modified seaweed for Cr(VI) removal from wastewater are very limited [12,16,18–20].

The aim of the present investigation is to enhance the Cr(VI)-reducing capacity of the *C. indica* biomass by various chemical treatments. In this study, first, raw brown algae, *C. indica* was modified by potassium permanganate. The raw alga was also pretreated with epichlorohydrin to improve the surface characteristics and enhance the metal uptake capacity. The influence of various parameters like adsorption time, pH and solid/liquid ratio on metal sorption has been investigated. Various isotherm models including Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) are applied to fit experimental data.

2. Experimental

2.1. Biomass and chemical modification

The brown alga *C. indica* was collected from the Suarashtra coast of Gujarat (Veraval), India in December 2005. The alga was washed twice with running water and five times with deionized water. The washed biomass was oven-dried at 60 °C for 24 h, crushed with an analytical mill, sieved (size fraction of 0.35–0.50 mm) and stored in polyethylene bottles until use. The resulting dried biomass was designated as the raw biomass (RB) in the present study, and subjected to various chemical treatments.

2.1.1. Epichlorohydrin cross-linking

A 10 g of raw biomass was taken into a flask together with 150 mL of dimethyl sulphoxide (DMSO) and stirred for 24 h at room temperature. This mixture was subjected to undergo the cross-linking reaction at 20 °C for 2 h after adding 20 mL of epichlorohydrin. Further, 20 mL of 5 M NaOH solution was added and stirred for 5 h at 50 °C. After attaining room temperature, the solution was filtered and washed with 70% aqueous 2-propanol followed by 0.5 M HCl and finally with 70% aqueous 2-propanol to neutral pH. The sample was dried in an oven at 70 °C for 8 h and stored in polyethylene bottle until use, hereafter abbreviated as CB1.

Another biomass sample was obtained by repeating the above procedure only with one change of 20% aqueous 2-propanol instead of 70% aqueous 2-propanol, to reduce the cost of the treated sorbent, hereafter abbreviated as CB2.

2.1.2. Oxidation with potassium permanganate

A 10 g raw biomass was oxidized in 10 mM solution of potassium permanganate at 30 °C for 30 min and the mixture was separated by centrifugation and washed thoroughly with distilled water [21]. It was dried in an oven at 70 °C for 8 h and stored in polyethylene bottle until use, hereafter abbreviated as CB3. The surface area, pore volume and pore size of various forms of *C. indica* are measured by surface area analyzer (Micromeritics, ASAP 2010) and are given in Table 1.

2.1.3. Fourier transform infrared analysis (FTIR)

Infrared spectra of the raw as well as chemically modified biomass were obtained using a Fourier transform infrared spectrometer (FTIR GX 2000, Perkin-Elmer). For the FTIR study, 30 mg of finely ground biomass was encapsulated in 300 mg of KBr (Sigma) in order to prepare translucent sample disks.

2.2. Sorption experiments and analytical method

All the experiments were conducted at a constant temperature of 25 ± 1 °C to be representative of environmentally relevant conditions. Batch equilibrium sorption experiments were carried out in 250 mL Erlenmeyer flasks containing Potassium dichromate solutions (100 mL) of known concentrations, which varied from 10 to 100 $\mathrm{mg\,L^{-1}}$. Known amounts of biomass were added to each flask and the mixtures were agitated on the rotary shaker. The solution pH was adjusted to the required value by using HCl or NaOH. After the sorption equilibrium was reached, the solution was separated from the biomass by membrane filtration (Millipore 0.45 mm pore size). The change in Cr(VI) concentration due to sorption was determined colorimetrically (Shimadzu spectrophotometer) according to Standard Methods [22]. A purple-violet colored complex was developed in the reaction between Cr(VI) and 1,5-diphenylcarbazide in acidic condition. Absorbance was measured at wavelength (λ) 540 nm.

Kinetics experiments were conducted in continuously stirred (200 rpm) beakers containing 100 mL of solution and 0.05 g of each type of biomass. Samples were drawn from the mixture at pre-determined time intervals for analysis. The pH of the solution was monitored continuously with a pH electrode

Table 1
Characteristics of chemically modified and raw seaweeds

Parameter	Seaweed biomass			
	CB1	CB2	CB3	RB
Surface area				
Single point surface area ($m^2\,g^{-1}$)	0.9011 at P/P_0 0.200527	1.0020 at P/P_0 0.200499	0.7241 at P/P_0 0.214547	0.3062 at P/P_0 0.219549
BET surface area ($m^2\,g^{-1}$)	1.1562	1.3864	0.9843	0.4257
BJH adsorption cumulative surface area of pores between 17.000000 and 150.000000 Å diameter ($m^2\,g^{-1}$)	0.4026	0.5124	0.3657	0.1488
BJH desorption cumulative surface area of pores between 17.000000 and 150.000000 Å diameter ($m^2\,g^{-1}$)	0.0186	0.0169	0.0122	0.0154
Pore volume				
Single point adsorption total pore volume of pores ($cm^3\,g^{-1}$)	0.001126 of pores less than 1004.7057 Å at P/P_0 0.98032	0.001438 pores less than 866.8675 Å at P/P_0 0.97714	0.000915 pores less than 3082.9371 Å at P/P_0 0.97500	0.000779 pores less than 794.1870 Å at P/P_0 0.99370
Pore size				
Adsorption average pore diameter (4 V/A by single point) (Å)	56.458	60.245	52.462	28.676
BJH adsorption average pore diameter (4 V/A by single point) (Å)	28.497	30.5113	28.6674	24.012
BJH desorption average pore diameter (4 V/A by single point) (Å)	40.2567	78.2665	128.4604	114.6566

and adjusted with HCl or NaOH solution, if deviations were observed. All the biosorption experiments were repeated twice to confirm the results. The data were the mean values of two replicate determinations.

2.3. Chromium uptake capacities and sorption isotherm

The amount of Cr(VI) sorbed at equilibrium, q ($mg\,g^{-1}$), which represents the metal uptake, was calculated from the difference in metal concentration in the aqueous phase before and after adsorption, according to the following equation:

$$q = \frac{V(C_i - C_e)}{W} \tag{1}$$

where V is the volume of Cr(VI) solution (L), C_i and C_e are the initial and equilibrium concentration of Cr(VI) in solution ($mg\,L^{-1}$), respectively, and W is the mass of dry seaweed (g).

To examine the relationship between sorbed and aqueous concentration at equilibrium, sorption isotherm models, Langmuir, Freundlich and Dubinin–Radushkevich were used for fitting the data.

2.3.1. Freundlich adsorption model

The Freundlich model [23] habitually gives a better fit particularly for adsorption from liquids and can be expressed as:

$$q = KC_e^{1/n} \tag{2}$$

In this model, the mechanism and the rate of adsorption are functions of the constants $1/n$ and K ($L\,g^{-1}$). For a good adsorbent, $0.2 < 1/n < 0.8$, and a smaller value of $1/n$ indicates better adsorption and formation of rather strong bond between the adsorbate and adsorbent. Many researchers have used this model to interpret their sorption data for various systems [24–27].

2.3.2. Langmuir adsorption model

The Langmuir adsorption isotherm [28,29] is given by the following equation:

$$q = \frac{q_{max} b C_e}{1 + bC_e} \tag{3}$$

In this model, q_{max} ($mg\,g^{-1}$) is the amount of adsorption corresponding to complete monolayer coverage, i.e., the maximum adsorption capacity and b ($L\,mg^{-1}$) is the Langmuir constant. A host of research workers have applied this model to interpret their sorption data [24–27,30]. For Langmuir type adsorption process, to determine if the adsorption is favorable or not, a dimensionless separation factor is defined as [31]:

$$R_L = \frac{1}{1 + bC_i} \tag{4}$$

If $R_L > 1$, the isotherm is unfavorable, $R_L = 1$, the isotherm is linear, $0 < R_L < 1$, the isotherm is favorable, $R_L = 0$, the isotherm is irreversible.

2.3.3. Dubinin–Redushkevich (D–R) model

This adsorption isotherm [32] is given as:

$$q = q_{max}\exp(-Be^2) \tag{5}$$

where e (known as Polanyi potential) is given as:

$$e = RT\ln\left(1+\frac{1}{C_e}\right) \tag{6}$$

where R is the gas constant, T is temperature and the constant B ($\mathrm{mol^2\,kJ^{-2}}$) given by the following equation [33], the mean free energy E ($\mathrm{kJ\,mol^{-1}}$) of adsorption per molecule of adsorbate, when it is transferred to the surface of the solid from infinity in the solution, is

$$E = \frac{1}{\sqrt{2B}} \tag{7}$$

The linear form of D–R equation is:

$$\ln q = \ln q_{\max} - Be^2 \tag{8}$$

A plot of ln q versus e^2 should yield a straight line.

3. Results and discussion

3.1. Fourier transform infrared analysis

Numerous chemical groups have been proposed to be responsible for biosorption metal binding by algae (carboxyl, hydroxyl, amide, ether, etc.); their importance for metal uptake depends on factors such as the quantity of sites, its accessibility, chemical state or affinity between site and metal [34]. FTIR was used to analyze the functional groups in the raw as well as chemically modified *C. indica* and is shown in Fig. 1. The biomasses CB1 and CB2 showed almost similar spectra, while CB3 and RB showed different absorption peaks. However, the absorption peak at 2929 $\mathrm{cm^{-1}}$, which was observed in all biomasses, is indicative of the existence of CH_2 asymetric stretching vibration. The broad absorption peaks at 3397 $\mathrm{cm^{-1}}$ (CB1 and CB2), 3429 $\mathrm{cm^{-1}}$ (CB3) and 3428 $\mathrm{cm^{-1}}$ (RB) are due to O–H and N–H stretching [35–38]. The absorption peaks at 2358, 2359, 2364 and 2362 $\mathrm{cm^{-1}}$ for CB1, CB2, CB3 and RB, respectively, were assigned to P–H group [39]. The moderate absorption peak at 1729 $\mathrm{cm^{-1}}$ for CB1 and CB2 may be assigned to C=O stretching, and those at 1625 $\mathrm{cm^{-1}}$ and 2362 $\mathrm{cm^{-1}}$C=O chelate stretching of carboxylic groups for CB3 and RB, respectively [40]. The absorption peaks at 1112 $\mathrm{cm^{-1}}$ for CB1 and CB2 were due to the –C–O stretching of ether groups, while the –C–O stretching of alcoholic groups was assigned at 1032 $\mathrm{cm^{-1}}$ and 1031 $\mathrm{cm^{-1}}$ for CB3 and RB, respectively. Although other absorption peaks were observed, it was difficult to interpret all.

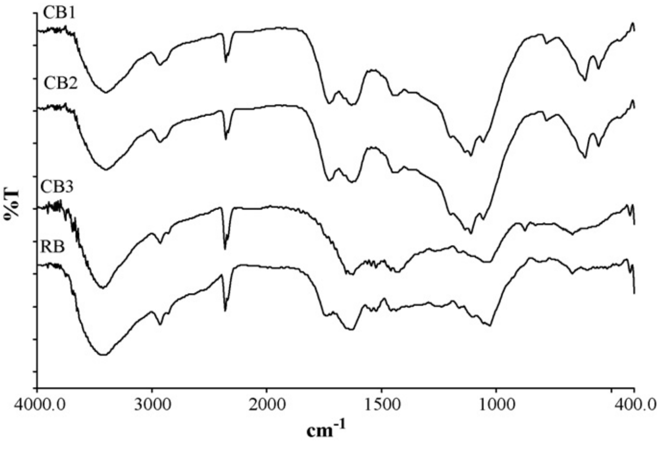

Fig. 1. FT-IR spectra of various forms of *C. indica*.

3.2. Cr(VI) biosorption kinetics

Various chemical modifications were applied to enhance the Cr(VI) reduction by the *Cystosiera* biomass, and a series of batch experiments carried out with the raw and chemically-treated biomasses. Information on the kinetics Cr(VI) of uptake is required for selecting the optimum operating conditions for further experiments.

The uptake of heavy metal ions by seaweeds has often been observed to occur in two stages; an initial rapid uptake due to surface adsorption on the cell walls and a subsequent slow uptake due to membrane transport of the metal ions on the cytoplasm of the cells [41–43]. Cr(VI) biosorption by various forms of *C. indica* algae exhibited the same behavior (see Fig. 2). As contact time increases, Cr(VI) uptakes also increase initially, then become almost stable, indicating attainment of equilibrium. The equilibrium could be achieved after having been shaking more than 2 h. These changes in Cr(VI) uptake may be due to the fact that, initially, all adsorbent sites were vacant and the solute concentration was high. After that period, only a very low increase in the Cr(VI) uptake was observed because there are few surface active sites on the cell wall of alga. The quick equilibrium time may be attributed to the particle size. The effective surface area is high for small particles. This result is typical for biosorption of metals involving no energy-mediated reactions, where metal removed from solution is due to purely physico/chemical interactions between the biomass and metal in solution. Luo et al. [44] observed same results in case of biosorption of lead with chemically modified *Laminaria japonica*. The rapid kinetics has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy. All the further

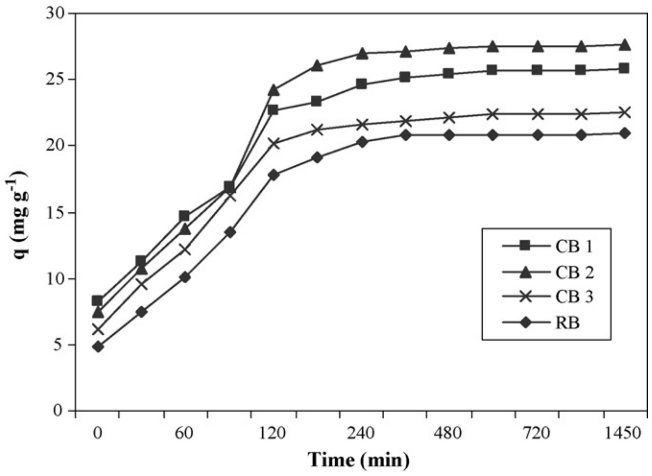

Fig. 2. Kinetics of Cr(VI) sorption by chemically modified and raw *C. indica* (initial Cr(VI) concentration: 30 $\mathrm{mg\,L^{-1}}$, pH: 3.0, solid to liquid ratio (s/l): 0.5 $\mathrm{g\,L^{-1}}$).

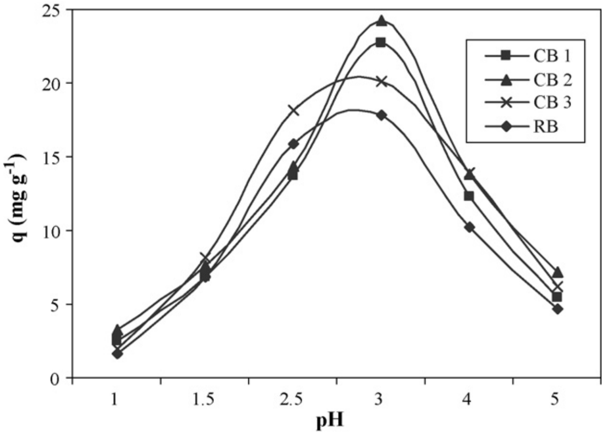

Fig. 3. Effect of pH on Cr(VI) sorption by chemically modified and raw *C. indica* (initial Cr(VI) concentration: 30 mg L^{-1}, contact time: 180 min, solid to liquid ratio (s/l): 0.5 g L^{-1}).

sorption experiments were carried out over 2 h to make sure true equilibrium is established.

3.3. *Effect of pH on Cr(VI) sorption*

Earlier studies on heavy metal biosorption have showed that pH is an important parameter affecting the biosorption process [16,45–47]. The adsorption characteristics of Cr(VI) with various pH in the range of 1.0–5.0 are studied at initial concentration of 30 mg L^{-1}, using four biomasses as shown in Fig. 3. The biosorption of Cr(VI) for all the biomasses increased with pH and then declined with further increase in pH. As seen from the Fig. 3, the Cr(VI) equilibrium uptakes by CB1 and CB2 biomasses increase with the pH values increase from 2.0 to 3.0. The highest uptake capacity of Cr(VI) is 22.7 and 24.2 mg g^{-1} for CB1 and CB2, respectively, at pH 3.0. This increase in chromium uptake could be due to the ionization of carboxyl groups present in the seaweeds at this pH, which can result in higher interaction with chromium. With further increase in pH to about 4.0, the chromium uptake of CB1and CB2 decreased. For CB3 and RB the Cr(VI) equilibrium uptakes increase as the pH increase from pH 1 to 2.5, then marginal increase with the pH from 2.5 to 3.0. The maximum Cr(VI) uptakes for CB3 and RB are 20.1 and 17.8 mg g^{-1}, respectively, obtained at pH 3.0. The cell wall of brown algae, *C. indica* species contains a large number of surface functional groups, in which carboxyl is generally the most abundant acidic functional group. The pH dependence of metal adsorption can largely be related to type and ionic state of these functional groups and also on the metal chemistry in solution [47,48]. Cr(VI) and some other metals such as arsenic, depending on the pH, are known to exist as anions. At low pH values, cell wall ligands are protonated and compete significantly with metal binding. With increasing pH, more ligands such as amino and carboxyl groups, would be exposed leading to attraction between these negative charges and the metals and hence increases in biosorption on to the cell surface [49]. As the pH increased further, the overall surface charge on the cells could become negative and biosorption decreased [50].

3.4. *Effect of chemical modification*

Three different chemical modifications were applied to *C. indica* to enhance the uptake of Cr(VI) and these methods also can improve the mechanical stability and pressure resistance of the seaweed. Epichlorohydrin modification facilitates chemical cross-linking between various polysaccharides via the hydroxylic groups in alkaline conditions and DMSO will expose the hidden metal binding groups before cross-linking [18,47]. The excess epichlorohydrin and DMSO was removed by washing with 2-propanol. The unique mixture of polysaccharides, mainly alginate and fucoidan, is largely responsible for the excellent metal sequestering ability of the brown algae [8,42,46]. Alginic acid makes up 14–40% of the dry weight of brown algae [43]. Brown seaweed also contains about 5 to 20% sulfated polysaccharide fucoidan [51], about 40% of which is sulfate esters. Carboxylate groups of alginate have been identified as the main metal binding site.

Jeon et al. [21] reported that oxidation with potassium permanganate, which intern results in carboxylated alginic acid, had a high uptake capacity to heavy metals. In the present study, *C. indica* was oxidized with potassium permanganate to increase carboxylic groups. The results indicate that the maximum uptakes of Cr(VI) for CB1 and CB2 have increased respectively by 21% and 26% compared to RB. Epichlorohydrin modified biomasses have been showed a high uptake capacity for Cr(VI). The Cr(VI) uptake capacity of CB3 increases by 11.4% as compared with raw seaweed, RB. Based on the maximum uptake capacity and cost effect, CB2 is the best sorbent than CB1 and CB3 for Cr(VI) removal applications.

3.5. *Effect of initial Cr(VI) concentration on biosorption*

The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases. The biosorption of Cr(VI) was carried out at different initial Cr(VI) ion concentrations ranging from 10 to 100 mg L^{-1} at pH 3.0 for four biosorbents and isotherms are shown in Fig. 4. The equilibrium sorption capacity

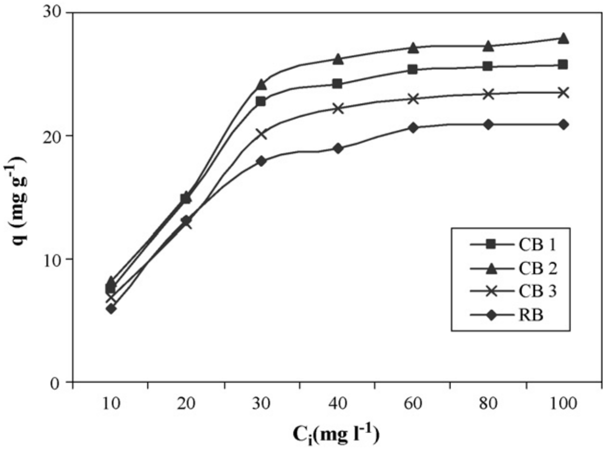

Fig. 4. Sorption of Cr(VI) by chemically modified and raw *C. indica* (contact time: 180 min, pH: 3.0, solid to liquid ratio (s/l): 0.5 g L^{-1}).

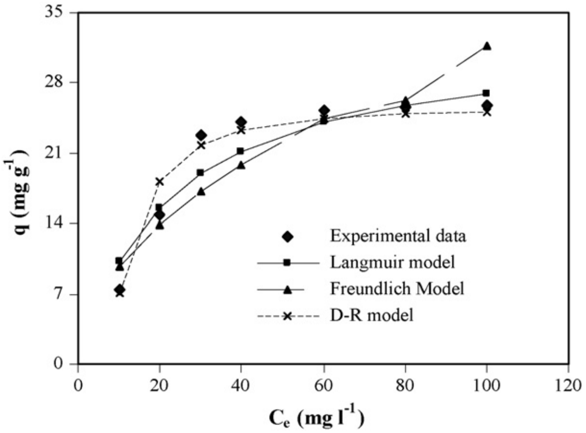

Fig. 5. Experimental and adjusted isotherms for sorption of Cr(VI) with sorbent CB1 (contact time: 180 min, pH: 3.0, solid to liquid ratio (s/l): 0.5 g L^{-1}).

of all the sorbents increased with increasing initial Cr(VI) concentration from 10 to 30 mg L^{-1}, due to the increase in the number of ions competing for the available binding sites in the biomass. The uptake of Cr(VI) by all the four sorbents gave a plateau at 30–100 mg L^{-1} showing the saturation of binding sites at higher concentration levels. The maximum amounts of Cr(VI) adsorbed are 22.7, 24.2, 20.1 and 17.8 mg g^{-1}, respectively for CB1, CB2, CB3 and RB. The order of Cr(VI) uptakes for different pretreated and raw alga is CB2 > CB1 > CB3 > RB. The higher initial concentration provides increased driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases resulting in higher probability of collision between Cr(VI) ions and sorbents. This results in higher metal uptake. Moreover, cell membranes of *C. indica* contain polysaccharides as basic building blocks which have ion exchange properties, and also proteins and lipids and therefore offer a host of functional groups capable of binding to Cr(VI) ions. These functional groups, mainly carboxylic and amino groups, differ in their affinity and specificity for Cr(VI) uptake due to the properties of the algae [8,52].

3.6. Equilibrium models to fit experimental data

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. To examine the relationship between sorption and aqueous concentration at equilibrium, various sorption isotherm models are widely employed for fitting the data. Langmuir, Freundlich and Dubinin–Radushkevich models were used to describe the equilibrium between the Cr(VI) sorbed on the four pretreated biomasses of *C. indica* (q) and Cr(VI) ions in the solution (C_e) as shown through Figs. 5–8 for all the sorbents used. The main reason for the extended use of these isotherm models is that they incorporate constants that are easily interpretable. The model constants along with correlation coefficients (R^2) and standard error (S.E.) of the estimate obtained from the three isotherm models are listed in Table 2. All the model parameters were evaluated by least square fitting method using SYSTAT 11® software.

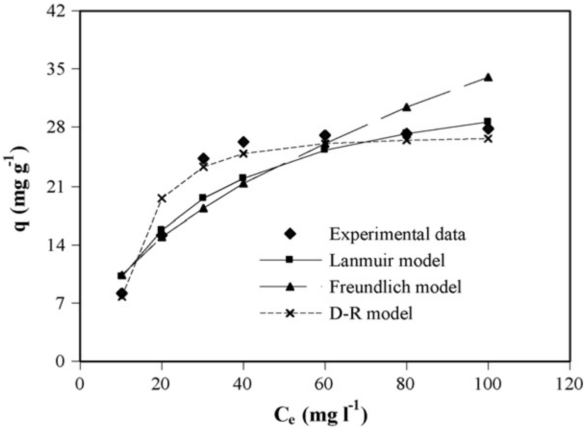

Fig. 6. Experimental and adjusted isotherms for sorption of Cr(VI) with sorbent CB2 (contact time: 180 min, pH: 3.0, solid to liquid ratio (s/l): 0.5 g L^{-1}).

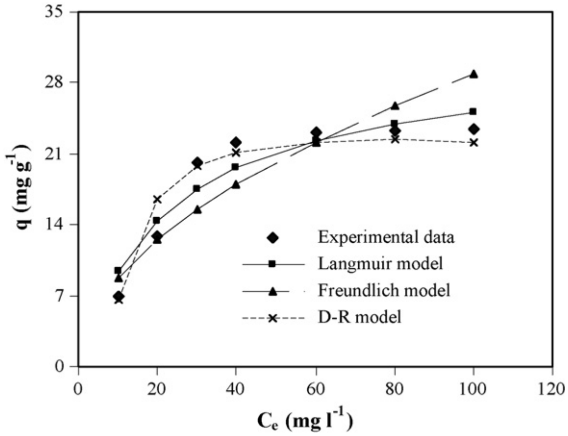

Fig. 7. Experimental and adjusted isotherms for sorption of Cr(VI) with sorbent CB3 (contact time: 180 min, pH: 3.0, solid to liquid ratio (s/l): 0.5 g L^{-1}).

The Langmuir model served to estimate the maximum metal uptake values where they could not be reached in the experiments. The experimental data fitted satisfactorily with the shape of the Langmuir isotherms showing high values of the correlation coefficients R^2. The constant b represents affinity between

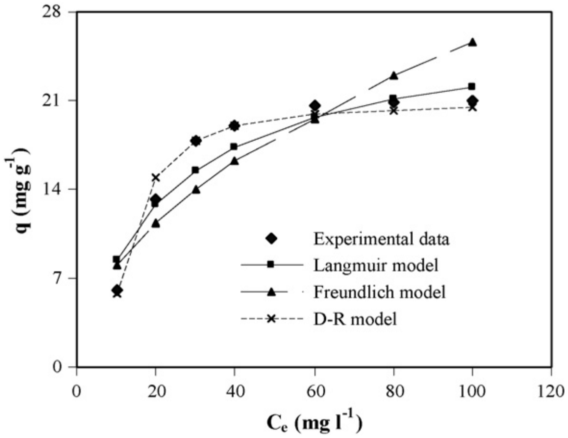

Fig. 8. Experimental and adjusted isotherms for sorption of Cr(VI) with sorbent RB (contact time: 180 min, pH: 3.0, solid to liquid ratio (s/l): 0.5 g L^{-1}).

Table 2
Langmuir, Freundlich and D–R models parameters for Cr(VI) sorption on various biomasses of *Cystoseira indica*

Model Parameters	Biomass			
	CB1	CB2	CB3	RB
Langmuir				
$q_{\max}$ (mg g^{-1})	31.96	34.74	29.81	26.03
b (L mg^{-1})	0.046	0.040	0.045	0.047
R^2	0.951	0.992	0.996	0.996
S.E.	0.0981	0.1204	0.1212	0.6121
Freundlich				
K	0.480	0.50	0.427	0.402
n	1.960	1.937	1.934	1.984
R^2	0.805	0.819	0.825	0.806
S.E.	0.0968	0.0938	0.0917	0.0955
Dubinin–Radushkevich				
$q_{\max}$ (mg g^{-1})	25.40	27.11	22.91	20.71
B (mol^2 kJ^{-2})	2.27×10^{-3}	2.255×10^{-3}	2.25×10^{-3}	2.26×10^{-3}
E (kJ mol^{-1})	14.82	14.90	14.92	14.85
R^2	0.962	0.941	0.943	0.985
S.E.	0.2468	0.0917	0.0718	0.0877

S.E.: standard error of the estimate.

the sorbent and sorbate. Maximum Cr(VI) uptakes of 31.96, 34.74, 29.81 and 26.03 mg g^{-1} were obtained for biomasses CB1, CB2, CB3 and RB, respectively. High values of b are reflected in the steep initial slope of a sorption isotherm, indicating desirable high affinity. The essential characteristics of Langmuir isotherm can be explained [31] in terms of the dimensionless separation factor, R_L, as explained earlier. Table 2 shows that Cr(VI) sorption with all types of biosorbents used in this study is favorable.

The Freundlich isotherm is originally empirical in nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities and has been used widely to fit experimental data [53,54]. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. Fig. 5 indicates that the Freundlich model does not fit the experimental data well. In the low concentration range the calculated Freundlich uptakes are lower, whereas in the high concentration range it is higher than the experimental uptake values. Hence, the Freundlich model is not the suitable model for describing the sorption process with sorbents used in the present study, as R^2 values are lower than other models, as shown in Table 2.

Another popular model for the analysis of isotherms of a high degree of regularity is the Dubinin–Radushkevich model, whose constants and mean free energy are given in Table 2. It is found that the D–R isotherm model gives a best fit for all Cr(VI) sorption isotherms. The constant $q_{\max}$ agrees well with experimental data and the maximum value of 27.11 mg g^{-1} was observed for biomass CB2. The magnitude of E is useful for estimating the type of sorption reaction. The E values obtained were around 15 kJ mol^{-1}, which are in the energy range of an ion-exchange reaction, i.e., 8–16 kJ mol^{-1} [55]. This supports the fact that biosorption of Cr(VI) by *C. indica* may be an ion exchange reaction.

Table 3 lists some reported sorption capacity values for Cr(VI) uptake by brown seaweeds. In general, the three brown seaweeds tested in this study exhibited sorption capacity values comparable or less than to those reported elsewhere for various brown seaweed species.

3.7. Effect of solid/liquid ratio on biosorption

The effect of the solid/liquid ratio (s/l) on the Cr(VI) sorption is studied at room temperature and at pH 3.0. Various s/l ratios including 0.25, 0.5, 1.5, 2.0, 2.5, 3.0 g L^{-1} are used, while keeping the volume and the initial concentration of the metal solution constant and the results are shown in Fig. 9. The results indicate that all the four biosorbents have a similar behavior. At the beginning, the removal rate increases as s/l ratio increases then the quantity of Cr(VI) adsorbed slightly increased when s/l ratio varied from 1.5 to 2.5 g L^{-1}. The maximum uptake rate is obtained at 1.5 g L^{-1} and further increase in s/l ratio not caused much increase in uptake rate. Hence, for all the biosorbents, 1.5 g L^{-1} would be the optimum s/l that would be required for cost effective treatment of hexavalent chromium.

Table 3
Sorption capacities for Cr(VI) using different brown seaweeds

Brown seaweed	Sorption capacity (mg g^{-1})	Refs.
Padina sp.	54.60	[17]
Ecklonia	4.49 mmol g^{-1}	[16]
Pilayella littoralis	4.68	[13]
Sargassum siliquosum	66.4	[56]
Turbinaria ornate	31.0	[57]
Sargassum sp.	31.72	[17]
Cystoseira indica	20.9–27.9	Present study

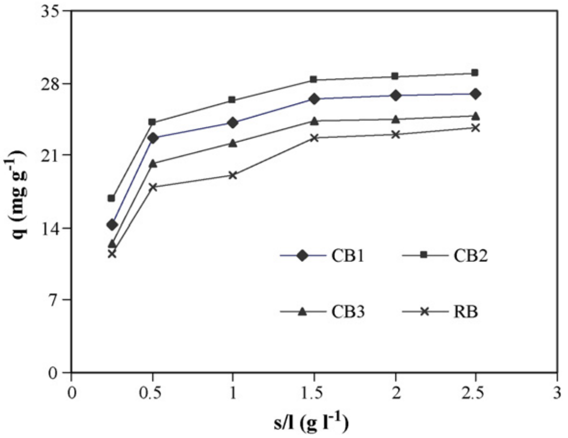

Fig. 9. Effect of solid to liquid ratio on Cr(VI) sorption by chemically modified and raw *C. indica* (initial Cr(VI) concentration: 30 mg L^{-1}, contact time: 180 min, pH: 3.0).

4. Conclusions

Biosorption performances of the various forms of pretreated brown seaweed, *C. indica* are studied for the removal of hexavalent chromium from aqueous solutions. The kinetic experiments show that the biosorption on all the sorbents is rapid and maximum sorption capacities achieved in 2 h. The removal of Cr(VI) increases with an increasing pH, and an optimum pH of about 3.0 is observed. The optimum s/l ratio is 1.5 g L^{-1} in terms of high uptake rate and the cost efficiency. Epichlorohydrin modified biomasses (CB2, CB1) have showed a high uptake capacity for Cr(VI). Dubinin–Radushkevich isotherm model is in good agreement with all the experimental data as compared to Langmuir and Freundlich isotherm models. The Dubinin–Radushkevich model effectively described the biosorption equilibrium of Cr(VI) in the studied conditions. Assuming the batch biosorption as a single-staged equilibrium operation, the separation process can be mathematically defined using these isotherms constants to estimate the residual concentration of metal ions or amount of biosorbent for desired purification. The study revealed that pretreated seaweed has much potential as a biosorbent for the removal of Cr(VI) from wastewaters.

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References

[1] A.P. Padilla, E.L. Tavani, Treatment of industrial effluent by reverse osmosis, Desalination 126 (1999) 219–226.
[2] M.J.S. Yabe, E. de Oliveira, Heavy metals removal in industrial effluents by sequential adsorbent treatment, Adv. Environ. Res. 7 (2003) 263–272.
[3] J.U.K. Oubagaranadin, N. Sathyamurthy, Z.V.P. Murthy, Evaluation of Fuller's earth for the adsorption of mercury from aqueous solutions: a comparative study with activated carbon, J. Hazard. Mater. 142 (2007) 165–174.
[4] H.S. Regime, F. Viera, B. Volesky, Biosorption: a solution to pollution, Int. Microbiol. 3 (2000) 17–24.
[5] S.K. Mehta, J.P. Gaur, Use of algae for removing heavy metal ions from wastewater: progress and prospects, Crit. Rev. Biotechnol. 25 (2005) 113–152.
[6] S. Basha, Z.V.P. Murthy, Seaweeds for engineering metal biosorption: a review, in: L.G. Mason (Ed.), Focus on Hazardous Materials Research Nova Science Publishers Hauppauge, New York, 2007, pp. 165–209.
[7] R. Jalali, H. Ghafourian, Y. Asef, S.J. Davarpanah, S. Sepehr, Removal and recovery of lead using nonliving biomass of marine algae, J. Hazard. Mater. 92 (2002) 253–262.
[8] T.A. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, Water Res. 37 (2003) 4311–4330.
[9] Y.S. Yun, Characterization of functional groups of protonated *Sargassum polycystum* biomass capable of binding protons and metal ions, J. Microbiol. Biotechnol. 14 (2004) 29–34.
[10] M. Costa, Potential hazards of hexavalent chromate in our drinking water, Toxicol. Appl. Pharm. 188 (2003) 1–5.
[11] A. Baral, R.D. Engelken, Chromium-based regulations and greening in metal finishing industries in the USA, Environ. Sci. Pol. 5 (2002) 121–133.
[12] D. Kratochvil, P. Pimentel, B. Volesky, Removal of trivalent and hexavalent chromium by seaweed biosorbent, Environ. Sci. Technol. 32 (1998) 2693–2698.
[13] E.N. Carrilho, T.R. Gilbert, Assessing metal sorption on the marine algae *Pilayella littoralis*, J. Environ. Mon. 2 (2000) 410–415.
[14] A.M. Hayashi, W. Amorim, D.M. Pereira, P.F. Pimentel, M.G.C. da Silava, Biosorption of Cr(VI) in algae biomass: kinetic study, in: Proceedings of Biohydrometallurgy Symposium – IBS 2001, Biohydrometallurgy and Environment, part B, 2001, pp. 199–206.
[15] J.A. Cavalcante, S.C.S. Rocha, M.C.G. da Silva, Influence of the marine algae drying on the capacity of removal of the chromium, in: Drying 2004 – Proceedings of the 14th International Drying Symposium (IDS 2004), Sao Paulo, Brazil, 22–25 August 2004, vol. B, 2004, pp. 844–851.
[16] D. Park, Y.S. Yun, J.M. Park, Reduction of hexavalent chromium with the brown seaweed *Ecklonia* biomass, Environ. Sci. Technol. 38 (2004) 4860–4864.
[17] P.X. Sheng, L.H. Tan, J.P. Chen, Y.P. Ting, Biosorption performance of two brown marine algae for removal of chromium and cadmium, J. Disper. Sci. Technol. 25 (2004) 679–686.
[18] Y.H. Kim, J.Y. Park, Y.J. Yoo, J.W. Kwak, Removal of lead using xanthated marine brown alga, *Undaria pinnatifida*, Process Biochem. 34 (1999) 647–652.
[19] E. Gurisik, M.Y. Arica, S. Bektas, O. Genc, Comparison of the heavy metal biosorption capacity of active, heat-inactivated and NaOH-treated *Phanerochaete chrysosporium* biosorbents, Eng. Life Sci. 4 (2004) 86–89.
[20] J. Yang, B. Volesky, Modeling uranium–proton ion exchange in biosorption, Environ. Sci. Technol. 33 (1999) 4079–4085.
[21] C. Jeon, J.Y. Park, Y.J. Yoo, Characteristics of metal removal using carboxylated alginic acid, Water Res. 36 (2002) 1814–1824.
[22] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, American Water Work Association, and Water Environment Federation, Washington, DC, 1998.
[23] H. Freundlich, Über die adsorption in Lösungen, Z. Phys. Chem. 57 (1907) 385–470.
[24] T.V.N. Padmesh, K. Vijayaraghavan, G. Sekaran, M. Velan, Application of *Azolla rongpong* on biosorption of acid red 88, acid green 3, acid orange 7 and acid blue 15 from synthetic solutions, Chem. Eng. J. 122 (2006) 55–63.
[25] S. Kundu, A.K. Gupta, Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization, Chem. Eng. J. 122 (2006) 93–106.
[26] A.K. Golder, A.N. Samanta, S. Ray, Anionic reactive dye removal from aqueous solution using a new adsorbent – sludge generated in removal of heavy metal by electrocoagulation, Chem. Eng. J. 122 (2006) 107–115.
[27] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[28] I. Langmuir, The constitution and fundamental properties of solids and liquids. I. Solids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[29] I. Langmuir, The constitution and fundamental properties of solids and liquids. II. Liquids, J. Am. Chem. Soc. 39 (1917) 1848–1906.

[30] M.A.M. Khraisheh, Y.S. Al-Degs, W.A.M. Mcminn, Remediation of wastewater containing heavy metals using raw and modified diatomite, Chem. Eng. J. 99 (2004) 177–184.

[31] 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. Fund. 5 (1966) 212–223.

[32] M.M. Dubinin, L.V. Radushkevich, Equation of the characteristic curve of activated charcoal, Proc. Acad. Sci. Phys. Chem. Sect. USSR 55 (1947) 331–333.

[33] J.P. Hobson, Physical adsorption isotherms extending from ultrahigh vacuum to vapor pressure, J. Phys. Chem. 73 (1969) 2720–2727.

[34] P. Lodeiro, J.L. Barriada, R. Herrero, M.E. Sastre de Vicente, The marine macroalga *Cystoseira baccata* as biosorbent for cadmium(II) and lead(II) removal: kinetic and equilibrium studies, Environ. Pollut. 142 (2006) 264–273.

[35] D.L. Pavia, G.M. Lampman, G.S. Kaiz, Introduction to spectroscopy: a guide for students of organic chemistry, W.B. Saunders Company, 1987.

[36] J. He, W. Ma, J. He, J. Zhao, J.C. Yu, Photooxidation of azo dye in aqueous dispersions of H_2O_2-α-FeOOH, Appl. Catal. B: Environ. 39 (2002) 211–220.

[37] M. Arami, N.Y. Limaee, N.M. Mahmoodi, N.S. Tabrizi, Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull, J. Hazard. Mater. B 135 (2006) 171–179.

[38] M. Arami, N.Y. Limaee, N.M. Mahmoodi, Investigation on the adsorption capability of egg shell membrane towards model textile dyes, Chemosphere 65 (2006) 1999–2008.

[39] D.H. Williams, I. Fleming, Spectroscopic Methods in Organic Chemistry, Tata McGraw-Hill Book Company Ltd, New Delhi, 1991.

[40] Y.S. Yun, D. Park, J.M. Park, B. Volesky, Biosorption of trivalent chromium on the brown seaweed biomass, Environ. Sci. Technol. 35 (2001) 4353–4358.

[41] E. Fourest, B. Volesky, Contribution of sulfonate groups and alginate to heavy metal biosorption by the dry biomass of *Sargassum fluitans*, Environ. Sci. Technol. 30 (1996) 277–282.

[42] T.A. Davis, B. Volesky, R.H.S.F. Vieira, *Sargassum* seaweed as biosorbent for heavy metals, Water Res. 34 (2000) 4270–4278.

[43] S. Schiewer, M.H. Wong, Ionic strength effects in biosorption of metals by marine algae, Chemosphere 41 (2000) 271–282.

[44] F. Luo, Y. Liu, X. Li, Z. Xuan, J. Ma, Biosorption of lead ion by chemically-modified biomass of marine brown algae Laminaria japonica, Chemosphere 64 (2006) 1122–1127.

[45] Z.R. Holan, B. Volesky, Biosorption of lead and nickel by biomass of marine algae, Biotechnol. Bioeng. 43 (1994) 1001–1009.

[46] E. Fourest, C. Canal, J.C. Roux, Improvement of heavy metal biosorption by mycelial dead biomasses (*Rhizopus arrhizus*, *Muchor miehei*, and *Pencillium chrysogenum*): pH control, and cationic activation, FEMS Microbiol. Rev. 14 (1994) 325–332.

[47] J.T. Matheickal, Q. Yu, Biosorption of lead from aqueous solutions by marine alga *Ecklonia radiate*, Water Sci. Technol. 34 (1996) 1–7.

[48] J.T. Matheickal, Q. Yu, G.M. Woodburn, Biosorption of cadmium from aqueous solutions by pretreated biomass of marine alga *Durvillaea potatorum*, Water Res. 33 (1999) 335–342.

[49] Z. Aksu, Equilibrium and kinetic modelling of cadmium(II) biosorption by *C. vulgaris* in a batch system: effect of temperature, Sep. Purif. Technol. 21 (2001) 285–294.

[50] Z. Aksu, D. Akpinar, Competitive biosorption of phenol and chromium(VI) from binary mixtures onto dried anaerobic activated sludge, Biochem. Eng. J. 7 (2001) 183–193.

[51] V.J. Chapman, Seaweeds and Their Uses, Chapman & Hall, London, 1980.

[52] R.H. Crist, K. Oberholster, N. Shank, M. Nguyen, Nature of binding between metallic ions and algal cell walls, Environ. Sci. Technol. 15 (1981) 1212–1217.

[53] Z. Aksu, T. Kutsal, A bioseparation process for removing lead(II) ions from waste water by using *C. vulgaris*, J. Chem. Technol. Biotechnol. 52 (1991) 109–118.

[54] A.A. Koelmans, F. Gillissen, L. Lijklema, Influence of salinity and mineralization on trace metal sorption to cyanobacteria in natural waters, Water Res. 30 (1996) 853–864.

[55] F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962.

[56] L.K. Cabatingan, R.C. Agapay, J.L.L. Rakels, M. Ottens, L.A.M. van der Wielen, Potential of biosorption for the recovery of chromate in industrial wastewaters, Ind. Eng. Chem. Res. 40 (2001) 2302–2309.

[57] R. Aravindhan, B. Madhan, J.R. Rao, B.U. Nair, Recovery and reuse of chromium from tannery wastewaters using *Turbinaria ornata* seaweed, J. Chem. Technol. Biotechnol. 79 (2004) 1251–1258.