



BIOSORPTION OF METALS IN BROWN SEAWEED BIOMASS

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Abstract—Biosorption of Cd by biomass of the brown seaweeds *Durvillaea*, *Laminaria*, *Ecklonia* and *Homosira* presaturated with Ca, Mg or K was coupled with the release of these light ions. The feasibility of biomass pre-treatment to develop a better biosorbent was evaluated by its biosorption performance, the degree of its component leaching (measured by the weight loss and TOC) as well as by the number of ion-exchange sites remaining in the biomass after the pre-treatment. Multicomponent Langmuir and ion exchange models applied to the equilibrium sorption data for pH 4.5 confirmed the ion exchange mechanism involved in the biosorption of metals. Both models fitted well the experimental data and their parameters can be used in the derivation of dimensionless ion-exchange isotherms which are instrumental in predicting the behavior of the biosorbents in dynamic flow-through biosorption systems. The sequence of biomass affinities established for the selected heavy metals can be correlated with the chemical pretreatment of the biomass. © 1999 Elsevier Science Ltd. All rights reserved

Key words—biosorption, brown seaweed, heavy metal, ion exchange

NOMENCLATURE

| | |
|-----------------------------|---|
| B | biomass binding site |
| C_0 | normality of the solution (meq/l) |
| C_{FM} , C_{FH} | equilibrium final concentration of species M, H in liquid phase |
| C_M | equilibrium concentration of species M in liquid phase (meq/l) |
| C_{ML} | concentration of species M in liquid phase (meq/l) |
| k | constant defined in equation (9) |
| K_M | constant in the multicomponent Langmuir model |
| $K_{M/I}$ | ratio of constants for M/I in the multicomponent Langmuir model |
| K_{MI} | ion-exchange selectivity coefficient |
| M | metal species in the liquid |
| \underline{M} | metal species in the solid sorbent phase |
| m , n | metal ion respective valences |
| q_{M1} , q_{M2} , q_M | uptake of species M1 or M2 or M (meq/l) |
| Q | concentration of binding sites in the biomass (meq/g) in equations (3)–(5) and equilibrium uptake of M at $C_{ML} = C_{M0} \cdot C_0$ (meq/g) in equation (8) |
| x_{M1} , x_{M2} | equivalent fractions of species M1 and M2, respectively, in liquid phase |
| y_{M1} , y_{M2} | equivalent fractions of species M1 and M2, respectively, in solid phase |

INTRODUCTION

Aqueous heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain. The main sources of heavy metal pollution are mining, milling and surface finishing industries, discharging a variety of toxic metals such as Cd, Cu, Zn and Pb into the environment (Moore and Ramamoorthy, 1984).

While the removal of toxic heavy metals from industrial wastewaters has been practiced for several decades, the effectiveness, and particularly the cost effectiveness, of the most common physical–chemical processes is limited. Biological materials have shown potential for heavy metal removal, but only low-cost biological materials with sufficiently high metal-binding capacity and selectivity for heavy metals are suitable for use in a full-scale biosorption process (Volesky and Holan, 1995; Kratochvil and Volesky, 1998a).

Various bio-materials have been examined for their biosorptive properties and different types of biomass have shown levels of metal uptake high enough (in the order of 1 mmol/g) to warrant further research (Volesky and Holan, 1995). Among the most promising types of biosorbents studied is algal biomass. The abundance of algae can hardly

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be overestimated. The world harvest of seaweeds for food and algal products (e.g. agar, carrageenan, alginate, that can be employed as thickeners) already exceeds 3 million tons annually and potential harvests are estimated as 2.6 million tons for red algae and 16 million tons for brown algae (Schiewer and Volesky, 1998). Biosorption in algae has mainly been attributed to the cell wall, composed of fibrillar skeleton and an amorphous embedding matrix. Both electrostatic attraction and complexation of metals in the biomaterial can play a role. While the skeleton of the cell wall is formed by cellulosic material, in the brown algae group Pheophyta the largest amount of amorphous matrix consists of mainly alginic acid and some sulfated polysaccharides such as fucoidan (Lee, 1989).

Although not all of the potentially applicable biosorbents have yet been systematically examined, substantial evidence identifies ion exchange as the main mechanism of metal biosorption. Recent studies revealed that uptakes of divalent metals by algal biomass (Crist *et al.*, 1994; Schiewer *et al.*, 1995; Schiewer and Volesky, 1995) and by filamentous fungi (Treen-Sears *et al.*, 1984; Fourest and Roux, 1994) are accompanied by the release of ionic species from the biosorbents.

The objective of the present work was to determine the cadmium uptake capacity of brown algal biomass types, *Durvillaea*, *Laminaria*, *Ecklonia* and *Homosira*, considering the ion exchange mechanism. Although metal-sorbing potential of these biomass types has been indicated (Aderhold *et al.*, 1996; Matheickal and Yu, 1996; Sandau *et al.*, 1996), there is no systematic study of the mechanism involved in the process. Pre-treatment of the selected biomass has been also examined in order to identify ways of optimizing the biomass metal-sorbing performance for its potential use in multiple cycles of sorption and desorption/regeneration.

MATERIALS AND METHODS

Preparation of the biomass

The brown algae *Laminaria*, *Durvillaea*, *Ecklonia* and *Homosira* were collected and sun dried in Victoria (Australia) in October. Analytical grades of Cd nitrate (BDH, Toronto) and of nitric acid and hydroxides (Ca-, Mg-, K-) (Anachemia, Montreal) were used for all the experiments. Atomic absorption standards (1000 mg/l) for all metals, as well as Na hydroxide 0.1 M standard solution, were purchased from Fisher Scientific (Montreal).

Particles (0.5–0.84 mm) of the disintegrated raw biomass were treated with 0.2 N HNO₃ solution in a batch for 3 h at the biomass concentration of 10 g/l, followed by a rinse with distilled water until the solution reached pH 4.5 and, finally, dried in the oven overnight at 60°C. The resulting biomass is called protonated biomass in this work.

The conversion of the protonated biomass to Ca-, Mg- or K-biomass was carried out using a 20 mM solution of Ca(OH)₂, Mg(OH)₂ or KOH, until the pH of the spent hydroxide supernatant solution reached 6.5. The solution was kept for total organic carbon (TOC) analyses. Separated biomass was dried overnight and used in exper-

iments. Its weight loss was determined based on the final dry weight as compared to the initial weight before each pretreatment.

Metal ion binding experiments

Twenty mg of biomass was put in contact with 10 ml of a Cd nitrate solution in a test tube for 6 h (1–10 mM of Cd, pH adjusted to 4.5). Mixing was promoted by mild bubble aeration. Samples were taken of the initial metal solution, and of the supernatant solution after the sorption equilibrium was reached. The samples were analyzed for metal content using atomic absorption spectroscopy (AAS, Perkin-Elmer 3100). The metal uptake was determined from the difference of metal concentrations in the initial and final solutions. No significant change in the pH values was observed throughout the equilibrium contact experiments which was one of the purposes of the biomass chemical pretreatment.

Total organic carbon (TOC) determination

The TOC of the biomass pretreatment supernatants was measured using the TOC analyzer (Dohrman DC-80) by both combustion and UV-persulfate methods. Aliquots of the samples were first filtered through 0.45 µm pore size chromatographic filter membrane and subsequently acidified with HNO₃ prior to analysis. The TOC analyzer was calibrated using 200 mg/l solution of K-phthalate prepared from a standard solution containing 1000 mg/l of the chemical. The TOC in samples whose acidified liquors produced precipitate was determined as follows: first, the TC (total carbon) was determined by analyzing aliquots of these samples without pH adjustment. Second, the TIC (total inorganic carbon) in these samples was determined using the TIC mode of the DC-80 analyzer. Finally, the TOC was calculated as the difference between the TC and the TIC values.

Titration of the biomass samples

Potentiometric titrations of protonated biomass were conducted as described by Fourest and Volesky (1997). Typically, 100 mg of algal biomass, converted to the hydrogen form (protonated) with 0.1 M HCl and washed with deionized water to constant conductance, was dispersed in 100 ml of 1 mM NaCl solution prepared with deionized water. Titration was carried out in the automatic titrator (Autotitrator Mettler DL25) by stepwise additions of not more than 0.1 ml of a 0.1 M NaOH solution. The suspension was kept under nitrogen atmosphere and constantly stirred. The pH of the suspension was registered after each NaOH solution addition. The total number of sites was determined from the second inflection point read off the curve of pH vs the amount of NaOH added/g biomass.

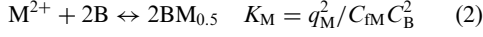
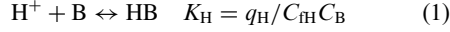
THEORETICAL BACKGROUND

This study presents unique quantitative results of screening several biomass types for selected heavy metal biosorption which is best evaluated by expressing sorption equilibrium constants. The methodology of doing so is described which could become a more standard approach for others. The essential background information presented in this section serves only as a convenient brief reference.

Multicomponent Langmuir model

A mathematical model of biosorption by *Sargassum* biomass has been developed and tested by Schiewer and Volesky (1995). The model defines

equilibrium binding constants K_H and K_M for protons H^+ and divalent metal cations M^{2+} , respectively, sorbing onto binding sites in the biomass B according to the following reactions:



where q_H and q_M are the equilibrium uptakes of H and M , respectively, and C_{fH} and C_{fM} represent the equilibrium concentrations of protons and metals in solution, respectively. C_B denotes the concentration of free, unoccupied, binding sites in the biomass.

By rearranging equations (1) and (2), the following expressions can be obtained for equilibrium uptakes of metals in proton-metal ($H^+ - M^{2+}$) and Metal1-Metal2 ($M1^{2+} - M2^{2+}$) binary systems:

$$q_M = \frac{Q\sqrt{K_M C_{fM}}}{1 + K_H C_{fM} + \sqrt{K_M C_{fM}}} \quad (3)$$

$$q_{M1} = \frac{Q\sqrt{K_{M1} C_{fM1}}}{1 + \sqrt{K_{M1} C_{fM1}} + \sqrt{K_{M2} C_{fM2}}} \quad (4)$$

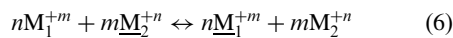
$$q_{M2} = \frac{Q\sqrt{K_{M2} C_{fM2}}}{1 + \sqrt{K_{M1} C_{fM1}} + \sqrt{K_{M2} C_{fM2}}} \quad (5)$$

where Q represents the total concentration of sites in the *Sargassum* biomass.

These equations represent the explicit sorption isotherms whereby uptakes of metals M , $M1$ and $M2$ are expressed as explicit functions of the equilibrium composition in the liquid. With the above equations it is possible to determine the equilibrium binding constants K of metal ions and protons as a function of pH and/or metal final concentrations.

Ion exchange model and isotherms

As ion exchange is the predominant metal-ion binding mechanism in biosorption (Kratochvil and Volesky, 1998a) the classical ion-exchange concept based on ion-exchange equilibrium constants (Vermeulen *et al.*, 1973; Shallcross *et al.*, 1988) can be thus applied to this case. That was the approach used by Kratochvil and Volesky (1998b) to study biosorption of heavy metals by *Sargassum* biosorbent in a multicomponent solution. The generalized ion-exchange reaction for dissolved species $\underline{M1}$ (of valence $+m$) exchanging for a bound species $\underline{M2}$ (of valence $+n$), is considered as follows (solid-bound species is underlined):



The equilibrium constant K_{M1M2} is defined in equation (7) for the case of ideal behavior of the exchanging species (1:1 ion exchange, activity = 1) in both of the phases:

$$K_{M1M2} = \frac{q_{M1}^n C_{fM2}^m}{C_{fM1}^n q_{M2}^m} = \frac{y_{M1}^n x_{M2}^m C_0^{m-n}}{x_{M1}^n y_{M2}^m Q^{m-n}} \quad (7)$$

where x is the fraction of one of the components in the solution and y is the fraction of one of the components in the exchanger.

For the binary ion-exchange system, the constant K_{M1M2} represents in a quantitative way the relative ionic compositions in the solid ion-exchanger and solution phases. Values of K_{M1M2} that are different from unity indicate the relative difference in preference of the solution and exchanger phases for the two competing ions. K_{M1M2} can be determined from the slope of the plot of q_{M1}/q_{M2} vs C_{fM1}/C_{fM2} . When plotting q_{M1}/q_{M2} vs C_{fM1}/C_{fM2} in order to determine the value of K_{M1M2} from the slope, one very frequently finds that the individual points do not align in a straight line, this approach leading to a large error. Thermodynamically based activity can cause deviations from the plot linearity and can be neglected for ideal solutions, however, often not so for the ions in the exchanger phase (Reichenberg, 1966). Freeman (1961) presented a solution to this problem: the fraction of one of the components in the exchanger (y_M) is plotted vs the K_{M1M2} values which are calculated from individual experimental data using the first part of equation (7). The measurements are integrated in an empirical expression to calculate the average K_{M1M2} values. The error is seldom very large and a number of examples of use of this method can be found in the literature (Reichenberg, 1966). This approach has also been applied in the current work.

Ion exchange isotherms are usually displayed using dimensionless forms of the uptake and concentration and they vary in shape depending on the total normality of the solution C_0 :

$$\frac{q_M}{Q} = f \frac{C_{ML}}{C_0} \quad (8)$$

where C_{ML} is the concentration of species M in the liquid phase.

The overall binding capacity Q for a binary system is given by the sum of the functional groups in the sorbent ($q_{M1} + q_{M2}$) and the total normality of the solution C_0 is given by the sum of the equilibrium concentrations of M_1 and M_2 ($C_{fM1} + C_{fM2}$). By eliminating q_{M2} through substitution, a useful expression for q_{M1}/Q can be obtained:

$$\frac{q_{M1}}{Q} = \frac{1}{1 + (C_{fM2}/K_{M1M2}C_{fM1})} = \frac{1}{1 + kC_{fM2}} \quad (9)$$

$$\text{where } k = \frac{1}{K_{M1M2}C_{fM1}}$$

Equation (9) shows that, for a fixed value of C_{fM1} , q_{M1}/Q is a hyperbolic function of C_{fM2} that may also be described using simple dimensionless concentration fractions as variables:

$$x_{M1} = \frac{C_{fM1}}{C_0}; \quad x_{M2} = \frac{C_{fM2}}{C_0}; \quad y_{M1} = \frac{q_{ML}}{Q} \quad (10)$$

yielding equation (11), which represents an ion-exchange isotherm for a binary sorption system:

$$y_{M1} = \frac{1}{1 + (x_{M2}/K_{M1M2}x_{M1})} \quad (11)$$

Fitting the models

The binary biosorption equilibrium data sets for Cd/Ca, Cd/Mg and Cd/K sorption systems, where the first element indicates the sorbing species and the second element specifies the ionic form of the biomass, provided the experimental basis for the fitting of the biosorption models. The multicomponent Langmuir model was fitted and the constants K_{Cd} and K_{M2} ($M_2 = \text{Ca, Mg or K}$) were obtained by minimizing the objective function F_M represented by equation (12):

$$F_M = \text{sum} \left\{ \frac{q_{Cd}^{\text{exp}} - q_{Cd}^{\text{theor}}}{q_{Cd}^{\text{exp}}} \right\}^2 \quad (12)$$

Due to the different valence of the ions used in the pretreatment of the biomass, equations (4) and (5) were used for calculating the affinity constants of divalent ions exchanging in the biomass, whereby equation (3) was applied in the calculation of constants for heterovalent (Cd with K) ions exchanging in the biosorbent. The computer program MATLAB 4.0 was used for this purpose.

The same data sets were used for the determination of the relative affinity constant K_{M1M2} by the ion exchange model. The fraction of Cd in the exchanger (y_{Cd}) was plotted vs the K_{CdM2} values which were calculated from individual experimental data using the first part of equation (7). The measurements were integrated in an empirical polynomial expression to calculate the average K_{M1M2} values. The goodness of fit was evaluated by the R^2 values obtained for each set of data. The error between the calculated and experimental uptake was calculated by the objective function F_M [equation (12)]. The ion exchange equilibrium isotherm was calculated using equations (10) and (11).

RESULTS AND DISCUSSION

Pre-treatment of the biomass

The loss of biomass components during the biomass pretreatment is summarized in Table 1. The supernatant liquid total organic carbon (TOC) content demonstrated that most of the biomass leaching occurred during the acidic wash with nitric acid solution. This leaching is also reflected in the reduction of the biomass dry weight reaching up to 49%. The acidic wash released a substantial portion of soluble biomass material, smaller organic molecules and ions. It replaced Ca, Mg, Na and K bound to available active sites with protons. This behavior was similar to that reported for another type of acid pretreated seaweed biomass (Lee and Volesky, 1997; Kratochvil and Volesky, 1998b). The largest difference in the effect of pretreatment observed in this work was that between the Ca(OH)_2 wash which resulted in the least biomass leaching (weight loss) and the KOH exposure which led to weight losses varying from 7 to 20%. A different behaviour was observed with *Homosira* biomass which lost at least 10% of its weight, even during Ca(OH)_2 pretreatment. At this point, one can observe similarities in the leaching behavior between *Durvillaea* and *Laminaria*, with weight losses increasing with the pretreatment of $\text{Ca} > \text{Mg} > \text{K}$. This relationship is somewhat different for *Ecklonia* and *Homosira*, where the least leaching was observed with Mg pretreatment.

The biomass weight loss during pretreatment can be used as an indication of the chemical stability of the biomass which is enhanced by its treatment with different ion solutions. Ca-saturation pretreatment was proposed by Kratochvil and Volesky (1998b) for the stabilization of *S. fluitans* because Ca^{2+} keeps the alginate, an important molecule for the ion exchange phenomenon, locked inside the biomass in the form of crosslinked Ca-alginate (Thom *et al.*, 1982). Once alginate is entrapped inside the biomass, fewer ion exchange sites may be lost during biosorption column regeneration cycles. However, determination of the biosorbent material weight loss cannot be feasibly carried out for a biosorption column. The TOC leached into the solution can be used as a coarse way of monitoring the biomass organic content lost during regeneration cycles. However, the results in Table 1 do not

Table 1. The loss of brown algae biomass components during different treatments: total organic carbon (TOC, mg/g of biomass) leached into solution and dry weight biomass loss (% of the raw biomass). Biomass loaded with Ca-, Mg- or K was produced by contacting the acid washed biomass respectively with hydroxide solutions of Ca, Mg or K (see Materials and methods section)

| Treatment type | Biomass | | | |
|----------------|------------------|-------------------|-----------------|-----------------|
| | <i>Laminaria</i> | <i>Durvillaea</i> | <i>Ecklonia</i> | <i>Homosira</i> |
| Acid wash | 37.99 (39.72%) | 73.36 (43.00%) | 58.68 (48.54%) | 76.41 (48.54%) |
| Ca-loading | 4.42 (0.01%) | 5.75 (0.02%) | 4.15 (1.02%) | 17.10 (13.56%) |
| Mg-loading | 1.83 (1.59%) | 3.56 (0.81%) | 3.40 (0.84%) | 7.74 (12.59%) |
| K-loading | 6.87 (6.60%) | 10.20 (11.76%) | 16.89 (15.26%) | 25.59 (19.21%) |

suggest a good correlation between the TOC and lost dry weight analyses. This could particularly be due to different forms of alginate present in each biomass type which would be more or less soluble depending on its ionic form. Smidsrod and Haug (1965) showed that properties of alginate samples varied depending on the raw material from which they were prepared. Guluronic acid had a higher selectivity for Ca and other divalent ions in exchange with Na than mannuronic acid (Haug and Smidsrod, 1965). This can be explained by the zig-zag structure of guluronic acid which can accommodate the Ca ion more easily (Lobban *et al.*, 1985). In addition, guluronic acid has generally higher selectivity for divalent metal ions (Ca, Mg, Cu, Sr, Ba, Co: selectivity factors between 0.17 and 150), while the selectivity of mannuronic acid for the same ions is smaller (selectivity factors between 1.1 and 12) (Haug and Smidsrod, 1970).

Potentiometric titration of the biomass

The mathematical model for biosorption developed by Schiewer *et al.* (1995) allows the calculation of both equilibrium constants for each metal present in the system as well as the total number of metal or active binding sites Q in the biomass. However, the model could not accurately predict the concentration of active sites which had to be estimated based on the titration of protonated biomass with a single-metal solution accompanied by the displacement of protons. Another approach to determine the concentration of sulfonate and carboxyl groups in *Sargassum* biosorbent was used by Fourest and Volesky (1996): the protonated biomass was titrated with NaOH solution. The concentrations of both sites in the biomass was determined through estimating the position of inflection points on the resulting titration curve.

The procedure described by Fourest and Volesky (1996) was used in the present work in order to determine the overall concentrations of metal-binding sites in the biomass types examined. Moreover, because of the weight losses observed, the concentration of sites was corrected in the model for each biomass as it was differently pretreated. Table 2 exhibits the concentration of active sites for each biomass type after every pretreatment. The active site concentration determined for each acid washed biomass was between 2.0 and 2.4 meq/g. A re-

duction in the number of sites as low as 18% (*Ecklonia* treated with K) and as high as 41% (*Laminaria* treated with K) was observed after the pretreatment with different hydroxide solutions. The diverse constitution of molecules present in the biomass can once again be the reason for the different concentrations found by titration of the biomass sites: distinct composition of the molecules that form the metal-binding sites would lead to varied degrees of solubility. The fact that there seemed to have been no reasonable correlation between the biomass weight loss and the reduction in the number of metal-binding sites could at this point only be attributed to the broad variety of the leached compounds.

Modeling of the batch equilibrium data

Ion exchange was previously demonstrated as the main mechanism involved in heavy metal uptake by algal biosorbent materials (Crist *et al.*, 1994; Schiewer *et al.*, 1995; Kratochvil and Volesky, 1998b). In order to confirm the phenomenon in the present experiments, the batch equilibrium data were fitted with multicomponent Langmuir and ion exchange models described earlier.

The calculated equilibrium constants K obtained by fitting the experimental data with the multicomponent Langmuir model are presented in Table 3. The model, developed from the Langmuir sorption isotherm model, assumes that all sites are initially free and does not consider any reverse reaction of a displaced ion with the site. The value of unity in the denominator of equations (3)–(5) is related to the amount of free sites still available in the biomass at a given equilibrium concentration of the metal. By dividing the values obtained for individual K_{Cd} by those for each 'light metal' ion present in the biomass one can determine the relative equilibrium constant for a bi-component sorption system (K_{Cd/M_2} ; $M_2 = \text{Ca, Mg or K}$). This value can be then compared to those of the ion exchange selectivity coefficient K_{CdM_2} obtained for the ion exchange model fitting.

The procedure used by Kratochvil and Volesky (1998b) to calculate the values of $K_{M_1M_2}$ for a given sorption system was based on obtaining a linear equation to describe the relationship between q_{M_1}/q_{M_2} vs C_{M_1}/C_{M_2} . However, this approach was not feasible for the present systems since no linear re-

Table 2. Total concentration of sorption sites (meq/g) in brown algae biomass after different pre-treatment. Ca-, Mg- and K-loaded biomass was protonated with 0.1 M HCl solution prior to their potentiometric titration

| Treatment type | Biomass | | | |
|----------------|------------------|-------------------|-----------------|-----------------|
| | <i>Laminaria</i> | <i>Durvillaea</i> | <i>Ecklonia</i> | <i>Homosira</i> |
| Protonation | 2.40 | 2.24 | 2.00 | 2.10 |
| Ca-loading | 1.46 | 1.65 | 1.60 | 1.57 |
| Mg-loading | 1.56 | 1.45 | 1.57 | 1.49 |
| K-loading | 1.42 | 1.69 | 1.65 | 1.57 |

Table 3. Equilibrium sorption model parameter values: constants K (l/mmol) and K_{Cd}/K_M ratios

| Biomass | Treatment | | | | | | | | |
|-------------------|-------------------|----------|-----------------|-------------------|----------|-----------------|------------------|-------|--------------|
| | Ca-loaded biomass | | | Mg-loaded biomass | | | K-loaded biomass | | |
| | K_{Cd} | K_{Ca} | K_{Cd}/K_{Ca} | K_{Cd} | K_{Mg} | K_{Cd}/K_{Mg} | K_{Cd} | K_K | K_{Cd}/K_K |
| <i>Laminaria</i> | 1.28 | 2.04 | 0.63 | 0.72 | 1.42 | 0.51 | 1.66 | 0.58 | 2.86 |
| <i>Durvillaea</i> | 34.18 | 15.77 | 2.17 | 2.69 | 0.83 | 3.24 | 2.86 | 0.49 | 5.84 |
| <i>Ecklonia</i> | 1.18 | 1.35 | 0.87 | 0.64 | 0.23 | 2.78 | 1.66 | 0.98 | 1.69 |
| <i>Homosira</i> | 98.67 | 32.34 | 3.05 | 0.77 | 1.59 | 0.48 | 1.72 | 0.68 | 2.53 |

relationship was observed for any set of data. An alternative approach (Freeman, 1961) of fitting the data with an empirical expression was applied to all data sets. Figure 1 shows the experimental profile for K_{Cd}/K_{Ca} obtained with *Durvillaea* biomass pretreated with Ca. This profile was fitted with a polynomial expression ($y = -10.73x^2 + 8.40x + 2.49$, $R^2 = 0.929$). Similar polynomials, one for each biomass type, can be easily integrated and values for the average selectivity coefficients K_{CdM} were obtained by this procedure (Freeman, 1961) (Table 4). Fitting of all the experimental data sets was obtained with a high confidence, as seen from the values of R^2 , for polynomial expressions of the second order.

The ion exchange model assumes that all sites to which metal ions are sorbed are initially occupied, i.e. the number of free sites stays constant. The variation of the selectivity constant K_{CdM2} with ionic composition has been attributed to numerous non-uniformity factors even for synthetic resins (Marcus, 1966; Reichenberg, 1966; Marinsky, 1976; Buffle, 1988). In complex biomaterials these non-uniformities could play an even more important role (Schiewer *et al.*, 1995). By comparing the

results obtained with both models, the sequence of biomass affinity toward the metals examined can be established for each biomass type:

By the multicomponent Langmuir model:

Ca > Mg > Cd > K for *Laminaria*.

Cd > Ca > Mg > K for *Durvillaea*.

Ca > Cd > K > Mg for *Ecklonia*.

Mg > Cd > K > Ca for *Homosira*.

By the ion exchange model:

Ca > Mg > Cd > K for *Laminaria*.

Cd > Mg > Ca > K for *Durvillaea*.

Ca > Cd > K > Mg for *Ecklonia*.

Mg > Cd > K > Ca for *Homosira*.

All the sequences of affinity established are the same for both models, except for *Durvillaea* biomass where there is a change of sequence between Ca and Mg. Even in this case, the difference in the values of Ca and Mg constants was small enough so that they could be considered as practically the same. The varied sequence of affinity observed for the different types of biomass tested could be explained by their chemical constitution, since distinct types of polysaccharides would present different affinities for the ions. Several authors studied

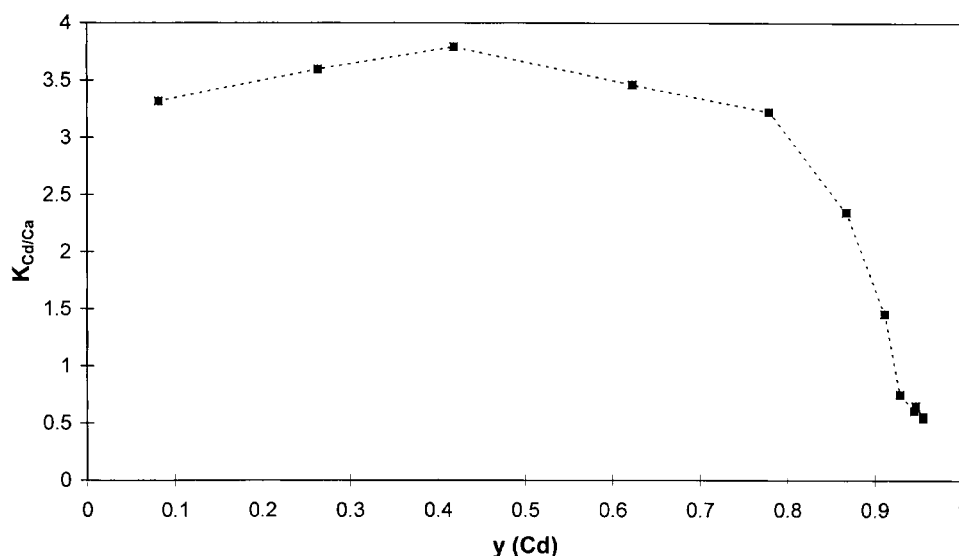


Fig. 1. Biosorption of Cd by Ca-loaded *Durvillaea* biomass: measured distribution of Cd and Ca in *Durvillaea* biomass at varying fractional Cd content in the biomass. The distribution is not constant.

Table 4. Ion exchange model selectivity coefficient K_{CdM} (by integration of polynomial fitting) and the "goodness-of-fit" evaluation (R^2)

| Biomass | Treatment | | | | | |
|-------------------|------------|-------|------------|-------|-----------|-------|
| | Ca-loaded | | Mg-loaded | | K-loaded | |
| | K_{CdCa} | R^2 | K_{CdMg} | R^2 | K_{CdK} | R^2 |
| <i>Laminaria</i> | 0.62 | 0.94 | 0.45 | 0.98 | 2.82 | 0.96 |
| <i>Durvillaea</i> | 3.31 | 0.923 | 2.96 | 0.95 | 5.06 | 0.94 |
| <i>Ecklonia</i> | 0.65 | 0.99 | 6.98 | 0.96 | 1.72 | 0.93 |
| <i>Homosira</i> | 3.28 | 0.92 | 0.48 | 0.90 | 2.08 | 0.88 |

the ion binding properties of algal polysaccharides. As a general rule, there is a preferential binding of heavier ions to alginate which could be due to stereo-chemical effects, larger ions might better fit a binding site with two distinct active groups (Haug and Smidsrod, 1970). Studying the ion binding to alginate from *Laminaria digitata*, Haug and Smidsrod (1965) reported that the amount of protons released into solution decreased in the order $Pb > Cu > Cd > Ba > Sr > Ca > Co > Ni > Zn > Mg$. In binding by fucoidan, however, the affinity sequence $Pb > Ba > Cd > Sr > Cu > Co > Zn > Mg > Ni > Ca$ was reported (Paskins-Hurlburt *et al.*, 1976). The affinity sequences observed for the biomass types studied here would be a net result of individual affinities of their polysaccharides to the ions, as well as the relevant contribution of those molecules to the overall ion exchange sites.

In order to confirm the goodness of fit of the models, the calculated uptakes at the experimental equilibrium normality of the solution C_0 were compared to the experimental ones using equation (12). Table 5 displays the values of the objective function F_M as well as the percentage of experimental data

that are within 5% error band around the fit. Both models considered in this work fit the experimental data relatively well. In all systems studied, the greater error was observed for the data points at lower equivalent fractions of Cd in the liquid (not shown).

Ion exchange isotherms

Figure 2 shows an example of ion-exchange isotherms for the Ca-*Durvillaea*-Cd system calculated from the parameters obtained by each model. In general, the multicomponent Langmuir model under-predicts uptakes in the lower concentration range. Crist *et al.* (1994) compared the fit of the Langmuir sorption isotherm and the ion exchange models. The difference between the two models was especially pronounced at low metal ion concentrations because of the effect of reverse reaction involving the displaced ion. Correspondingly, it was postulated that the Langmuir model applies better at higher metal concentrations where binding of the displaced ion is low. Schiewer *et al.* (1995) assumed that this deficiency loses significance for the multicomponent Langmuir model, used in this study, since the effect of competing ions, which is high at

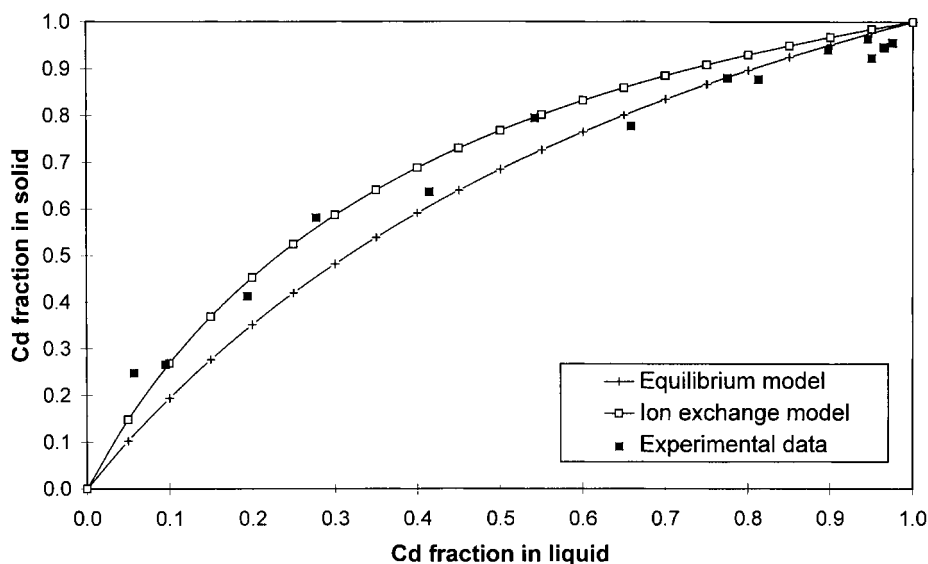


Fig. 2. Biosorption of Cd by Ca-loaded *Durvillaea* biomass: predictions by the two models and experimental points at a given normality C_0 .

Table 5. Results of minimization of errors (F_M) for equilibrium and ion exchange models based on the metal uptake at the experimental equilibrium concentration C_0 (normality)

| Biomass | Treatment | Equilibrium model | | Ion exchange model | |
|-------------------|-----------|-------------------|--|--------------------|--|
| | | Value of F_M | Percentage of data within the 5% error band around the fit | Value of F_M | Percentage of data within the 5% error band around the fit |
| <i>Durvillaea</i> | Ca-loaded | 0.0296 | 90.00 | 0.0098 | 95.00 |
| | Mg-loaded | 0.0744 | 80.00 | 0.0194 | 95.00 |
| | K-loaded | 0.0919 | 75.00 | 0.0837 | 80.00 |
| <i>Laminaria</i> | Ca-loaded | 0.0786 | 80.00 | 0.0503 | 80.00 |
| | Mg-loaded | 0.0259 | 90.00 | 0.0372 | 90.00 |
| | K-loaded | 0.0636 | 85.00 | 0.0549 | 85.00 |
| <i>Ecklonia</i> | Ca-loaded | 0.0105 | 90.00 | 0.0112 | 90.00 |
| | Mg-loaded | 0.0240 | 90.00 | 0.0313 | 90.00 |
| | K-loaded | 0.0973 | 75.00 | 0.0829 | 80.00 |
| <i>Homosira</i> | Ca-loaded | 0.0559 | 85.00 | 0.0437 | 85.00 |
| | Mg-loaded | 0.0163 | 90.00 | 0.0233 | 90.00 |
| | K-loaded | 0.0792 | 75.00 | 0.0689 | 80.00 |

low metal ion concentrations, is taken into consideration. The authors demonstrated the applicability of the model to systems containing heavy metals and protons. However, the model seems to have the same shortcoming observed for the conventional Langmuir sorption model for both divalent-divalent (Cd with Ca or Mg) and divalent-monovalent (Cd with K) ion exchange.

The concave shape of those curves (operation-favorable) depicts the situation when $y_{Cd} > x_{Cd}$, revealing that Cd is preferred by *Durvillaea* biomass over the pre-loaded Ca. This is demonstrated by the ratio of the equilibrium constants obtained by the multicomponent Langmuir model as well as by the selectivity coefficient obtained by the ion exchange model which have values higher than 1 (2.17 and 3.31, respectively). Although a knowledge of biosorbent mass transfer properties is important for sizing of sorption columns, the equilibrium behavior often determines the feasibility of the process (deVault, 1943). For this reason, it is important to determine the relative equilibrium affinities of pre-saturating ions and heavy metals to be sorbed by the biomass and illustrate the affinity with equilibrium isotherms.

Metal-loading capacities of different biosorbents can be conveniently compared by determining the number of sites available in the biomass for ion exchange. This can be done by titrating the biomass active sites, as described in the present work. While several studies involving the biosorption of heavy metals by brown seaweeds were analyzed by non-mechanistic approaches (Aderhold *et al.*, 1996; Matheickal and Yu, 1996; Sandau *et al.*, 1996; Matheickal *et al.*, 1997), Sargassum biosorbent, appearing as a superior one (Holan *et al.*, 1993; Matheickal and Yu, 1996; Figueira *et al.*, 1997), involves the ion exchange mechanism (Schiewer and Volesky, 1996; Lee and Volesky, 1997).

Complete desorption of most heavy metals cations from seaweed biosorbents can usually be achieved simply by using small amounts of a suit-

able elutant, usually a mineral acid. The cost effectiveness of the biosorption process depends on high stability of biosorbents in the desorption cycles (Tsezos, 1988; Ehrlich and Brierley, 1990; Huber *et al.*, 1990; Maranon and Sastre, 1991). While solubilities of Ca or Mg limit the strength of their respective hydroxides if they were to be used for a combined desorption-activation sequence, highly soluble potassium in KOH tested in the present work allows a cost-effective pretreatment providing for the strongest desorbing solution possibly even obviating the acidic biomass regeneration step.

CONCLUSIONS

An example methodology has been demonstrated in this work for screening different biosorbents (brown seaweeds) for the uptake of heavy metals. The comparison of metal biosorption performance was based on expressing the key equilibrium biosorption parameters such as the total number of active sites (by titration), two types of equilibrium constants according to two mathematical models capable of reflecting well experimental metal biosorption data: the multicomponent Langmuir and ion exchange models. The models can also assist in establishing biosorption metal affinity sequences for materials studied which is of importance for selecting an optimum pretreatment of the biosorbent for process applications. For brown seaweed biomass, pretreatment with potassium hydroxide appears to be very cost-effective.

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