# Biosorption Column Performance with a Metal Mixture

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The biosorption of Cu, Cd, and Zn from multicomponent
mixtures was studied in equilibrium systems and in a flow-
through column packed with potassium-saturated
*Sargassum* algal biosorbent. Pretreatment of the biomass
with calcium-, sodium-, magnesium-, and potassium-
hydroxides was examined. KOH washing resulted in a
stable biosorbent with an improved affinity for Zinc. Two-
metal sorption resulted in Zn breaking through the
column faster than Cd due to its low affinity. The sharp
favorable Zn breakthrough curve can be explained by its
affinity toward the biomass which is higher than that of K.
An overshoot of the Zn exit concentration was observed
and explained by the ion exchange between Cd and Zn,
whereby the higher-affinity Cd from the solution displaces
Zn already bound to the biosorbent. The same effect was
observed for Zn, and to a lesser extent Cd, in three-
metal sorption (Zn, Cd, Cu). The Cd exit concentration
also exceeded its feed level as Cu displaced it on the binding
sites of the biomass in the bed. The time interval between
Zn and Cd breakthroughs was much shorter than that
between the breakthrough points of Cd and Cu. This is
because the relative affinities of Zn and Cd, determined from
batch equilibrium experiments, are much closer to each
other ($Zn/K = 1.96$ and $Cd/K = 3.71$) than to Cu ($Cu/K = 16.51$).
The application of experimental IMPACT computer
software examined was only partially successful in exactly
simulating the biosorption column performance.

## Introduction

Biosorption is a process which utilizes inexpensive dead
biomass to sequester heavy metals from aqueous solutions.
Toxic heavy metals pose an environmental threat and need
to be removed from usually large volumes of industrial
effluents. The metal-laden biosorbent can accumulate metal
to levels that can be an order of magnitude higher than those
in the liquid phase. Thus, biosorption can serve to reduce
the waste volume. Instead of having to deal with a large
volume of liquid waste, only a small volume of solid waste
could be disposed of by incineration or deposition in landfills
(*1*). As compared to conventional methods for removing toxic
metals from industrial effluents, such as precipitation with
lime, and/or ion exchange, the biosorption process offers in
addition low operating costs and high efficiency in detoxi-

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fication of very diluted effluents. These advantages serve as
the primary incentives for developing full-scale biosorption
processes to cleanup heavy metal pollution (*2*).

Biosorbents are prepared from the naturally abundant
and/or waste biomass of algae, moss, fungi, or bacteria which
is inactivated and usually pretreated by washing with acids
and/or bases before final application (*3*). While simple cutting
and/or grinding of the dry biomass may yield stable bio-
sorbent particles (*4*), some types of biomass have to be either
immobilized in a synthetic polymer matrix (*5*), and/or grafted
on an inorganic supporting material such as silica in order
to yield particles with the required mechanical properties
(*6*). Biosorbent particles can then be packed in sorption
columns which are perhaps the most effective device for the
continuous removal of heavy metal (*7*).

In light of recent studies, biosorbents can be viewed as
natural ion-exchange materials that primarily contain weakly
acidic and basic groups (*8–10*). Thus, the well-developed
and structured knowledge of ion exchange can now be
applied in the study of biosorption, to describe both the
mechanism(s) involved as well as to predict the performance
of the biosorption process on a large scale. That was the
approach used by Kratochvil and Volesky (*11*) when studying
the biosorption of Cd, Cu, Zn, and Fe from multicomponent
mixtures in a flow-through column packed with *Sargassum*
biomass based algal biosorbent in the Ca-form. The authors
observed an overshoot of the Zn exit concentration upon the
Zn early breakthrough which they attributed to the lower
affinity of Zn toward the biosorbent than that of Ca. The
authors suggested that the biomass should be pretreated by
loading it with a cation with a lower affinity for the biomass
than all the influent ions, thus decreasing the undesirable
premature breakthrough of Zn in the column effluent.

The first objective of the present work was to evaluate the
Zn biosorption performance of *Sargassum* biomass pretreated
with several cations, Mg, Na, and K, and compare the results
with the Ca-form biomass studied earlier (*11*). Similar
pretreatment of the biomass was tested in earlier work (*12*)
with other types of seaweeds where the pretreatment
procedure was discussed in terms of the number of active
sites present in the biomass as well as its further ability to
uptake Cd. The second objective was to examine the
performance of the selected biomass in flow-through column
experiments with multiple metal bearing solutions.

## Materials and Methods

**Preparation of the Biomass.** The brown seaweed *Sargassum*
was collected in Naples (Florida) in March. A 10 g/L batch
of raw, sun-dried biomass was treated with a 0.2 N HCl
solution under gentle shaker agitation for 3 h, followed by
a rinse with distilled water until the pH of the solution reached
the value of 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-, Na-, or K-biomass was carried out using a 20 mM
solution of $Ca(OH)_2$, $Mg(OH)_2$, NaOH, or KOH, respectively.
The biomass was soaked several times in fresh hydroxide
solution under gentle mixing with a magnetic stirrer until
the pH of the final spent solution remained constant at about
pH 5.5. Only small amounts of hydroxide were added at a
time in order to avoid pH exceeding pH 6.0 to prevent biomass
leaching. The spent hydroxide supernatant solutions were
eventually analyzed for the total organic carbon (TOC).
Following decantation, biomass was dried overnight and used
in the experiments. Its weight loss was determined based on

the final dry weight as compared to the initial weight before each pretreatment.

**Metal Binding Experiments.** A total of 20 mg of biomass was put in contact with 10 mL of a single heavy metal sulfate solution in a test tube for 6 h (1−10 mM of the heavy metal, pH initially adjusted to 5.0). 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. Blanks, represented by either biomass in distilled water or metal solutions without biomass, were run as required. The samples were analyzed for metal content using inductively coupled plasma atomic spectrometer (ICP-AS Thermo Jarel Ash, Trace Scan). The metal uptake was determined from the difference of metal concentrations in the initial and final solutions to obtain full single-metal isotherms. No significant changes in pH values were observed throughout the equilibrium contact experiments (final pH 4.8−5.0).

**Total Organic Carbon (TOC) Determination.** The TOC of the biomass pretreatement 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 $\mu$m pore size chromatographic filter membrane and subsequently acidified with $HNO_3$ prior to analysis. The TOC analyzer was calibrated using 200 mg/L solution of potassium-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. A 5% error was expected in the analyses over the concentration range dealt with in this work.

**Titration of the Biomass Samples.** Potentiometric titrations of protonated biomass were conducted as described by Fourest and Volesky (*13*). 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 with an automatic titrator (Metler) 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 versus the amount of NaOH added/g biomass.

**Column Experiments.** Dry K-biomass was packed into a 50 cm long column of 2.5 cm in diameter, yielding an approximate packing density of 100 g $L^{-1}$. The column was then slowly flooded with distilled water from the bottom. The metal solutions (3 mequiv $L^{-1}$ of total metal: Zn alone, equal Zn + Cd, or equal Zn + Cd + Cu) were fed into the column from the top, at a rate of approximately 8 $cm^3 min^{-1}$, and samples of the column effluent were collected every 30 min from the bottom by means of a fraction collector (FC203 Gilson). The pH in the effluent as well as the pressure at the column inlet were continuously monitored using a flow-through cell and a pressure transducer (PX602, Omega), respectively. The data acquision card (PCL 711S, Omega) was used in combination with a PC computer to convert the analogue signals corresponding to the effluent pH and the pressure to a digital format and to store them on a computer hard disk. The computer also served for the remote control of the fraction collector.

The samples obtained from the column effluent were analyzed for K and the heavy metals used in the feed solution.

To compare the different systems studied, the dimensionless concentration ($C/C_0$) was plotted against the dimensionless time (*T*), calculated according to the equation:

$$T = \frac{C_0 F t}{\rho_b Q V_c} \tag{1}$$

where $C_0$ is the total normality of the solution (or the sum of all ions in solution) (mequiv $L^{-1}$), $F$ is the volumetric flowrate ($cm^3 h^{-1}$), $t$ is time (h), $\rho_b$ is the packing density of the dry biomass in the packed-bed (g $m^{-3}$), $Q$ is the concentration of binding sites in the biosorbent (mequiv $g^{-1}$), and $V_c$ is the volume (L) of the packed-bed in the column.

**Column Performance Simulation by IMPACT.** IMPACT is a computer program written at the Laboratoire des Sciences du Genie Chimique, Centre National de la Recherche Scientifique, Ecole Nationale Superieure des Industries Chimiques in Grenoble, France (*14*). The IMPACT code and the associated modeling methodology are especially adapted for describing the transient transport of chemicals for various flow patterns with arbitrary chemical reactions. The basic assumptions in general include either instantaneous local equilibrium or mass transfer kinetic limitations, steady flow, constant temperature, pressure, and pore geometry.

For modeling purposes, IMPACT accounts for the flow structure in the sorption bed by assuming a series of ideal mixing cells (continuous stirred-tank reactors, CSTRs) of uniform composition. The user has to define the parameters of the series (number and volume of cells, flow rate between them). Chemical interactions are described by a restricted set of elementary reactions (homogeneous and heterogeneous).

The user must first define the elementary reactions. These are, in the present case, eqs 2 and 3. The computer code requires the name of species, their stoichiometric coefficients and the equilibrium constant. The data are stored in files of reactants for subsequent use. For a specific ion-speciation problem, a "mechanism" needs to be defined which is composed of a set of elementary reactions. The user has to choose among the reactions proposed by IMPACT code. A data file of mechanisms is thus generated. The flow arrangement is eventually chosen from a program menu and the key physical operating parameters are specified. The user also supplies the reference composition of the stationary phase(s). Finally, IMPACT code generates and solves the system of algebraic and differential equations automatically, computing equilibrium states of batch systems or establishing breakthrough curves and/or concentration profiles of flow systems.

In this work, IMPACT was tested to establish its ability to predict biosorption in packed-bed reactors. It was made to predict the performance of the three experimental column runs carried out, i.e., (1) Zn and K-biomass, (2) Cd, Zn, and K-biomass, and (3) Cu, Cd, Zn, and K-biomass. To run a sorption process simulation, all elements, reactions and mechanisms present in the biosorption system had to be inputed into the program. The program performed the simulations and provided the concentration breakthrough profiles of the ionic species chosen.

## Theoretical Approach

**Multicomponent Langmuir Model.** A mathematical model of biosorption by *Sargassum* biomass has been developed and tested by Schiewer and Volesky (*10*). 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 biomass B according to the following

reactions:

$$H^+ + B \leftrightarrow HB; \quad K_H = q_H/C_{fH}C_B \qquad (2)$$

$$M^{2+} + 2B \leftrightarrow 2BM_{0.5}; \quad K_M = q_M{}^2/C_{fM}C_B{}^2 \qquad (3)$$
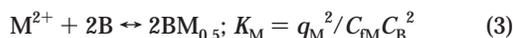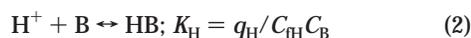
By rearranging eqs 2 and 3, the following expressions can be obtained for equilibrium uptakes of metals in proton-metal ($H^+ - M^{2+}$) and Metal1 $-$ Metal2 ($M1^{2+} - M2^{2+}$) binary systems:

$$q_M = \frac{Q\sqrt{K_M C_{fM}}}{1 + K_H C_{fH} + \sqrt{K_M C_{fM}}} \qquad (4)$$

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

$$q_{M2} = \frac{Q\sqrt{K_{M2}C_{fM2}}}{1 + \sqrt{K_{M1}C_{fM1}} + \sqrt{K_{M2}C_{fM2}}} \qquad (6)$$

where eq 3 has been used twice, once with M1 instead of M and once with M2 instead of M. These resulting 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 predict the equilibrium bindings constants $K$ of metal ions and protons as a function of pH and/or metal final concentrations.

**Fitting the Models.** Equilibrium data sets for Zn/Mg, Zn/Ca, Zn/Na, 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. Using the binary systems data, the multicomponent Langmuir model was fitted and the constants $K_{Zn}$ and $K_M$ (M = Ca, Mg, Na, or K) were obtained by minimizing the objective function $F_M$ represented by

$$F_M = sum\left\{ \frac{q_M^{exp} - q_M^{theor}}{q_M^{theor}} \right\}^2 \qquad (7)$$

The objective function was minimized considering both light and heavy metals in each system. One should notice that, due to the different valence of the ions used in the pretreatment of the biomass, eqs 5 and 6 were used for calculating the affinity constants of divalent ions exchanging in the biomass, whereby eq 4 was applied in the calculation of constants for heterovalent (Zn with K or Na) ions exchanging in the biosorbent, and putting values for K and Na for those of H in eq 4.

Another set of data obtained by exposing K-biomass to solutions containing Cd, Cu, and Zn at varied concentration combinations (0.1−5 mM of each heavy metal) was fitted by the multicomponent Langmuir model as described above. The computer program MATLAB 4.0 was used for this purpose.

## Results and Discussion

**Pretreatment of Sargassum Biomass: Leaching of Organic Material and Active Sites.** Table 1 shows the total organic carbon (TOC) leached from the biomass during its pretreatment with acid followed by Ca, Mg, Na, or K hydroxide solution wash, as well as its dry weight loss after each of these procedures. While the major biomass leaching observed was when it was washed with acid (~43 mg/g, corresponding to 39% of the raw biomass), much lower values of spent

### TABLE 1. Characteristics of Pretreated *Sargassum* Biomass

| treatment type | TOC in the wash (mg of TOC/g of biomass) | dry weight loss (%)[a] | total concentration of sites (mequiv/g biomass) |
|---|---|---|---|
| protonated, acid wash | 42.68 ± 2.23 | 38.79 ± 1.7 | 2.23 |
| Ca-loaded | 9.45 ± 0.76 | 0.82 ± 0.1 | 1.80 |
| Mg-loaded | 11.95 ± 0.88 | 1.72 ± 0.1 | 1.12 |
| Na-loaded | 10.58 ± 1.02 | 1.87 ± 0.1 | 1.55 |
| K-loaded | 10.22 ± 1.10 | 1.29 ± 0.1 | 1.71 |

[a] Calculated based on the total dry weight minus the mass of the metal present in the biomass. Results based on duplicates. Protonation was a common pretreatment of the biomass before Ca, Mg, Na, and K treatments. Ca, Mg, Na, and K biomass: % dry weight loss based on protonated biomass.

solution TOC values resulted from the alkaline treatment procedures (from 9.45 to 11.95 mg/g of biomass). Only low weight losses were also observed after the calcium-, magnesium-, sodium-, or potassium-hydroxide treatment, up to 1.87%, observed for the sodium-hydroxide treatment. The acid wash released a substantial portion of soluble biomass material, smaller organic molecules and ions. It replaced with protons ions such as Ca, Mg, Na, and K randomly bound to available active sites. This behavior was also reported for acid pretreated *Sargassum* biomass by other authors (*11*, *15*).

The major difference observed among the different types of pretreated biomass was in the total concentration of sites determined by titration with NaOH (Table 1). While the concentration of sites was 2.23 mequiv/g of biomass after the acid wash [this value is in agreement with the one reported by Fourest and Volesky (*16*)], some of these sites were leached out of the biomass after application of each pretreatment solution used. The percentage of active sites lost after each pretreatment was approximately 19% with calcium-, 23% with potassium-, 30% with sodium-, and 50% with magnesium-hydroxide pretreatment. This fact could be particularly explained by the different forms of alginate present in each biomass type which would be more or less soluble depending on its ionic form. Smidsrod and Haug (*17*) 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 (*18*). Fourest and Volesky (*13*) correlated the ion binding capacity of different seaweeds with their respective total carboxyl group content and related it to the electronegativity of the elements investigated (Ca, Zn, Cd, Cu, and Pb). These authors also reported that alginate leaching, due to its solubilization by Na ions, was observed to decrease with increasing intrinsic viscosity of extracted alginate (related to its molecular weight) and with increasing apparent acid dissociation constant (related to the alginate density inside the biomass). Alginate from *Sargassum* features higher $pK_a$ value (5.2) and a relatively high molecular weight (around 400 000) and high amounts of NaOH (1.0 mmol of NaOH/g) were required to release this alginate from the biomass.

**Stability of the Biomass Types during Heavy Metal Uptake.** An important factor influencing the performance of a biosorption process is the stability of the biosorbent which enables multiple sorption/desorption cycles of the material. This stability can be "measured" by the TOC analysis of the leachate as described above. It is important to determine whether the biomass would keep leaching out molecules during the biosorption of the heavy metals of interest, since this behavior could dramatically reduce the maximum load of metals in the biosorbent. Metal ions can, in many cases, cross-link the biomass active sites and thus decrease the leaching. This seems to be the case for *Sargassum* biomass

**TABLE 2. Behavior of Modified _Sargassum_ Biomass during Zn Biosorption[a]**

| | water (control) | | 0.075 mM Zn solution | | 7.5 mM Zn solution | |
|---|---|---|---|---|---|---|
| biomass type | TOC loss (mg of TOC/g of biomass) | dry weight loss (%)[b] | TOC loss (mg of TOC/g of biomass) | dry weight loss (%)[b] | TOC loss (mg of TOC/g of biomass) | dry weight loss (%)[b] |
| Ca-loaded | 7.47 ± 0.59 | 12.5 ± 1.0 | 6.96 ± 0.52 | 12.0 ± 0.9 | 6.79 ± 0.55 | 10.2 ± 0.8 |
| Mg-loaded | 9.48 ± 0.72 | 14.0 ± 1.2 | 7.59 ± 0.62 | 13.2 ± 0.8 | 7.30 ±0.65 | 11.5 ± 0.7 |
| Na-loaded | 6.86 ± 0.58 | 11.2 ± 1.1 | 5.69 ± 0.42 | 11.0 ± 0.8 | 5.23 ± 0.38 | 9.0 ± 0.7 |
| K-loaded | 6.50 ± 0.50 | 8.6 ± 0.9 | 5.65 ± 0.38 | 8.5 ± 0.7 | 4.17 ± 0.29 | 6.2 ± 0.6 |

[a] Results based on duplicate experiments. [b] Calculated based on the total dry weight minus the mass of the metal present in the biomass

**TABLE 3. Multicomponent Langmuir Model Parameters: Equilibrium Constants $K$ (L/mequiv), $K_{Zn}/K_M$ Ratios and Error Function $F_M$**

| biomass type | $K_{Zn}$ ($N = 16$) | $K_M$ ($N = 16$) | $K_{Zn}/K_M$ | error $F_M$ |
|---|---|---|---|---|
| Ca-loaded | 5.68 | 6.46 | 0.88 | 0.083 |
| Mg-loaded | 0.82 | 1.30 | 0.63 | 0.093 |
| Na-loaded | 10.96 | 4.22 | 2.60 | 0.051 |
| K-loaded | 12.18 | 5.13 | 2.37 | 0.049 |

**TABLE 4. Multicomponent Langmuir Model Parameters: Equilibrium Constants $K$ (L/mequiv), $K_M/K_K$ Ratios[a]**

| metal ion | $K^b$ | $K_M/K_K$ |
|---|---|---|
| K | 2.16 | |
| Zn | 4.26 | 1.96 |
| Cd | 8.02 | 3.71 |
| Cu | 35.35 | 16.51 |

[a] Values obtained from multimetal system experiments ($N = 36$) in which the metal concentrations varied independently. [b] Error function $F_M$ for the system = 0.092.

treated with the respective Ca, Mg, Na, and K hydroxides (Table 2). While a higher dry weight loss for biomass contacted with distilled water (as a control) or a low Zn concentration solution (0.075 mM) was observed, it was reduced when the biomass was contacted with a high-concentration Zn solution (7.5 mM). The TOC analyses showed the same trend.

As seen in Table 2, major weight losses were observed for biomass treated with magnesium-, calcium-, and sodium-hydroxides (up to 14, 12.5, and 11.2%, respectively), whereby lower losses resulted for K treatment (only up to 8.6%). These results reveal that K-biomass was the most stable one during the uptake of Zn, when compared to the other biomass types. Both TOC and dry weight loss values were higher in these experiments than the values determined after the pretreatment, indicating that none of the biomass types are completely stable after the pretreatment stage and can still leach some material out of the biomass structure during the uptake of heavy metals. However, for process feasibility purposes, it is important that this leaching is not significant enough to affect the biosorption process performance, e.g., by losing a portion of the major ion-exchange component and/or by plugging the column flow with fine solids particles.

Some reduction of the sorption performance of calcium-_Sargassum_ biomass was observed in the first three cycles of sorption/desorption in column 2. This can be explained by some leaching of the biomass components by both metal-bearing and acidic regenerating solutions. Depending on the degree of leaching of these components, operational problems such as flow plugging can occur due to the presence of very small, disintegrated biomass particles.

**Modeling of the Batch Equilibrium Data.** Ion exchange was previously demonstrated as the main mechanism involved in heavy metal uptake by _Sargassum_ biosorbent in protonated (_19_) or Ca-form (_11_). This can be confirmed in the present work through ion mass balances drawn for each set of batch equilibrium for biosorption of Zn by Mg-, Na- and K-biomass forms.

The calculated equilibrium constants $K$ obtained by fitting the experimental data with the multicomponent Langmuir model are presented in Table 3. Reverse reactions are considered by including a term for the displaced ion in the denominator of eqs 4−6. By dividing the values obtained for individual $K_{Zn}$ by those for each 'light metal' ion present in the biomass one can determine the relative equilibrium constants for bi-component sorption systems ($K_{Zn/M}$; M = Ca, Mg, Na, or K). The values of $F_M$ objective function reveal

that the model fitted the experimental data well within a deviation expected for this type of nonuniform sorption systems.

While the values of the relative equilibrium constant $K_{Zn/M}$ were smaller than 1 for Ca and Mg biomass types (0.89 and 0.63, respectively), the values for Na and K types were 2.6 and 2.4, respectively. These results show that Zn can bind more easily to the biomass pretreated with monovalent ions. This would make them the most suitable for biosorption process applications involving Zn. The value obtained for $K_{Zn/Ca}$ was very close to that obtained by Kratochvil and Volesky (_11_). Moreover, a similar ascending sequence of affinity: Na < K < Mg < Ca was observed by Kratochvil et al. (_20_) in the biosorption of Cu in a biosorption column containing raw _Sargassum_ biomass.

Because of the stability and relative selectivities presented by the biomass types tested, the K-biomass was selected for further experiments for both the determination of relative affinity for Cu, Cd, and Zn in multimetal solutions and in a flow-through column. Another advantage of using potassium in the pretreatment is in the fact that the solubility of KOH is much higher than that for Ca and Mg hydroxides. It is more effective to use higher concentrations of the solution for pretreating columns after the acid-wash desorption cycles.

Table 4 shows the values of the calculated equilibrium constants $K$ obtained by fitting the multimetal system experimental data with the multicomponent Langmuir model. The values of function $F_M$ show that the model fitted well the experimental data. The relative affinities of all the metals tested toward the K-form biomass were higher than that of K, confirming the feasibility of biomass K-pretreatment for sorption of those metals. While the relative affinity of Zn and Cd were of the same order of magnitude ($K_{Zn/K} = 1.96$ and $K_{Cd/K} = 3.71$), the one for Cu was much higher ($K_{Cu/K} = 16.51$).

The difference in the values of $K_{Zn/K}$ obtained for one-metal and multimetal systems (2.37 and 1.96 respectively) could be explained by the interference of other ions in assessing accurately the affinity of Zn for the biomass. This is specially true for systems exchanging heterovalent ions (mono- and divalent in this case), where the electrostatic interactions play an important role.

While it is probably true in general that Na and K binding in the biomass examined here is weaker than that of Ca and

Mg, it is not so obvious to deduce this solely from the fact that $K_{Zn/M}$ is larger for the monovalent ions. The resulting $K_{Zn/M}$ (dividing eq 3 by eq 2) for the monovalent K inserted in place of H would be

$$K_{Zn/M} = (q_{Zn}{}^2 C_{fK})/(C_{fZn} q_K C_B) \tag{8}$$

while dividing eq 3 for Zn by eq 3 for the divalent Ca yields

$$K_{Zn/M} = (q_{Zn}{}^2 C_{fCa})/(C_{fZn} q_{Ca}{}^2) \tag{9}$$

For exchange between two divalent cations such as Zn and Ca it is easy to grasp the meaning of $K_{Zn/M}$: for equal concentrations of $C_{fCa}$ and $C_{fZn}$, $q_{Zn}$ will be larger than $q_{Ca}$ if $K_{Zn/M} > 1$. For heterovalent exchange no such easy statement is possible.

For equal concentrations and $K_{Zn/M} > 1$, we obtain $q_{Zn}{}^2 > q_K C_B$.

It is apparent that the heterovalent exchange equilibrium is a function of the number of free binding sites $C_B$. High values of $K_{Zn/K}$ or $q_{Zn}{}^2/q_K C_B$ do not necessarily indicate high Zn binding. They could, for example, be due to low values of $C_B$ instead of high values of $q_{Zn}$ compared to $q_K$. Therefore the values of heterovalent exchange constants, e.g., $K_{Zn/K}$, are not directly comparable to values for exchange constants between divalent cations such as $K_{Zn/Ca}$. It is possible to obtain an exchange constant for heterovalent exchange that is not dependent on the number of free sites by dividing eq 3 by the square of eq 2, yielding

$$K_{Zn/M} = (q_{Zn}{}^2 C_{fK}{}^2)/(C_{fZn} q_K{}^2) \tag{10}$$

which is not exactly analogous but maybe better comparable to eq 9 above.

Although the description of a mathematical model that considers these interactions in the calculations appears in the literature (21, 22), this was not applied in the present work. Such variations become more pronounced when the normalities of the solutions are very low, which was not the case in the multimetal system studied here (concentrations range from 5 to 10 mequiv L$^{-1}$ in order to achieve a complete exchange of K in the biomass by the heavy metals).

**Dynamic Biosorption in the Fixed Bed.** The major advantage of choosing packed bed columns as a reactor for biosorption is that it combines an optimum exploitation of the sorption capacity with achieving very low effluent concentrations. The biosorbent is equilibrated at the relatively high incoming concentration of the metal bearing solution so that high uptake values are obtained, whereas the low-concentration effluent encounters fresh and powerful sorbent material.

In the biosorption of toxic heavy metals, unlike in nonselective ion-exchange processes such as water softening, the elution order and the maximum overshoot concentrations of the toxic species in the column effluent may determine the overall efficiency of the water treatment process. To determine the sequence of elution for two-, three-, and multimetal systems as well as the presence of effluent concentration overshoots when more than one metal is present, experiments were carried out in a flow-through column packed with K-*Sargassum* biomass. The operating conditions were kept the same for each set of experiments so that the data could be compared.

Figure 1 shows the concentrations of Zn and K in the column effluent as a function of dimensionless time ($T$). The throughput parameter $T$ is very useful when comparing the performance of flow-through columns for different concentrations of metals $C_0$ in the feed and/or different ionic forms of the biomass. The model simulations were based on eqs 2 and 3. As it can be seen from Figure 1, the removal of Zn
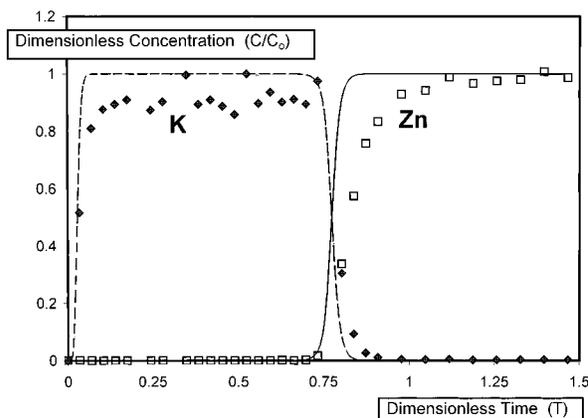


**FIGURE 1.** Biosorption column breakthrough profiles. Experimental data and IMPACT model simulations for K-*Sargassum* biosorbent. Feed solution pH 4.5; [Zn] = 3 mequiv/L; feed rate: 8 cm$^3$ min$^{-1}$. K outlet concentration (♦) experimental points; (---) IMPACT simulation. Zn outlet concentration (■) experimental points; (—) IMPACT simulation.
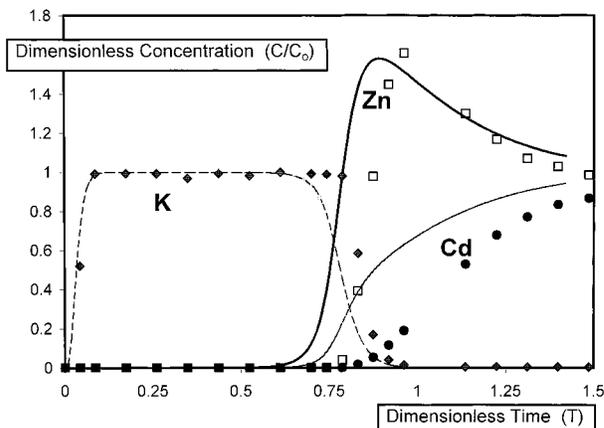


**FIGURE 2.** Biosorption column breakthrough profiles. Experimental data and IMPACT model simulations for K-*Sargassum* biosorbent. Feed solution pH 4.5; [Zn] = [Cd] = 1.5 mequiv/L; feed rate: 8 cm$^3$ min$^{-1}$. K outlet concentration (♦) experimental points; (---) IMPACT simulation. Zn outlet concentration (■) experimental points; (—) IMPACT simulation. Cd outlet concentration (●) experimental points; (— · —) IMPACT simulation. (IMPACT calculations ceased at $T = 1.4$).

from the continuous column feed was accompanied by the elution of K ions from the packed-bed. At approximately $T = 1.0$, the concentration of Zn in the column effluent reached the level in the feed, i.e., ($X_M$ or $C/C_0$) = 1. The fact that the breakthrough curve of Zn and the elution curve of K formed a mirror image of each other indicates that Zn is exchanged for K in the biomass. IMPACT model simulation predicted the breakthrough time of zinc very well. The model-simulated, somewhat steeper breakthrough curve is not quite an important deviation since in practice the column operation would have to be invariably halted soon after the heavy metal appears in the effluent.

The natural selectivity of the biomass for Cd over Zn is well exhibited by the results obtained using the flow-through column for the two-metal solution. Figure 2 displays the concentrations of Zn and Cd in the column effluent as a function of time for the sorption experiment during which the column packed with *Sargassum* biosorbent in K-form was fed with an equimolar mixture of Cd and Zn (1.5 mequiv/L). As can be seen in Figure 2, Zn, due to its low affinity, broke through the column faster than Cd (at $T$ approximately 0.75). A sharp favorable breakthrough curve observed for Zn
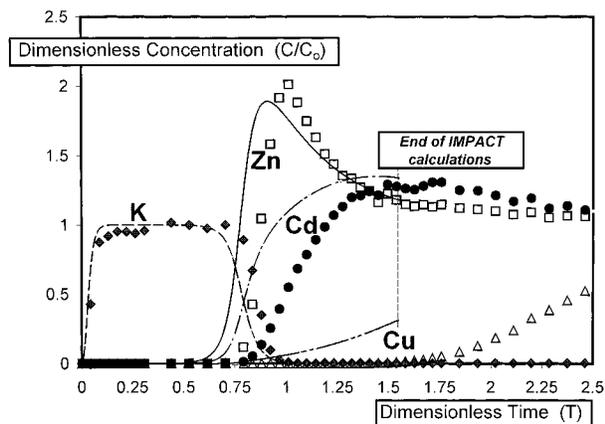
**FIGURE 3.** Biosorption column breakthrough profiles for a three-metal mixture. Experimental data and IMPACT model simulations for K-*Sargassum* biosorbent. Feed solution pH 4.5; [Zn] = [Cd] = [Cu] = 1.0 mequiv/L; feed rate: 8 cm³ min⁻¹. K outlet concentration (♦) experimental points; (---) IMPACT simulation. Zn outlet concentration (■) experimental points; (—) IMPACT simulation. Cd outlet concentration (●) experimental points; (− · −) IMPACT simulation. Cu outlet concentration (▲) experimental points; (− · · −) IMPACT simulation (IMPACT calculations ceased at $T = 1.6$).

is explained by its higher affinity toward the biomass when compared to the preloaded K and represents an effective utilization of the biosorbent material inside the column. At $T > 0.8$, the concentration of Zn in the column effluent plotted in Figure 2 reached the level of Zn in the feed. Subsequently, thereafter, Zn was no longer uptaken by the biosorbent, hence trickled down the packed-bed as an inert. The fact that the $C/C_0$ for Zn continued rising above 1 even after the $0.8T$ mark can be explained by the ion exchange between Cd and Zn, whereby Cd from the solution was displacing Zn already bound to the biosorbent. Since no more Zn was being sorbed from the liquid beyond this mark, the released Zn increased the overall concentration of Zn in the liquid above the level present in the column feed (up to 1.6 times the feed concentration). This phenomenon is commonly referred to as effluent concentration "overshooting" and was well exemplified by Kratochvil and Volesky (*11*) in a multicomponent flow-through column system. The overshooting of Zn is caused by a chromatographic effect, whereby the high affinity Cd desorbs the low affinity Zn which had previously sorbed onto the biosorbent in the bed. When the effluent concentration of Zn, as well as Cd, reaches the feed concentration (around $T > 1.3$), the column feed is completely in equilibrium with both Zn and Cd ions sorbed on the biomass.

The process simulation by IMPACT was not very accurate in the case of combined Cd−Zn biosorption. It predicted the breakthrough for both metals (for dimensionless time used) almost 20% shorter. Although the simulation did show correctly the magnitude of the exit concentration overshoot for zinc, its prediction was shifted forward in time. The case was similar for the Cd breakthrough curve which also came steeper than the experimental one. There was no Cd overshoot expected.

The exit concentration overshoot chromatographic effect can also be seen in Figure 3, representing the breakthrough curves of Zn, Cd, and Cu sorbing onto K-*Sargassum* biomass which was fed with equimolar concentrations of the metals (1.0 mequiv/L). An overshoot of even greater magnitude ($C/C_0 > 2$ at $T > 1$) was observed for Zn. A slight increase in the effluent concentration of Cd followed the overshoot of Zn for a period that lasted until the breakthrough of Cu was complete. In this system, the overshoot of Zn was caused mainly by its exchange for Cd ions in the biosorbent. When

that exchange was complete, Cd overshot up to ~1.25 times its feed concentration due to its exchange with Cu on the binding sites of the biomass in the bed. The time interval between Zn and Cd breakthroughs was much shorter than that between the breakthrough points of Cd and Cu. This is because the relative affinities of Zn and Cd are much closer to each other (Zn/K = 1.965 and Cd/K = 3.706) than to Cu (Cu/K = 16.514).

According to Kratochvil (*2*), the condition under which overshoots occur can be formulated as follows. Low-affinity species present in the feed overshoot in the column effluent only if the species with the highest affinity in the feed is bound to the biosorbent more strongly than the species with which the biosorbent had been presaturated. Consequently, a metal species may or may not overshoot in the column effluent depending on the ionic form of the biosorbent. This is the explanation for the overshoots of both Zn and Cd in K-*Sargassum* column: K being the species with the lowest affinity, all the metals in the feed solution would overshoot in the presence of Cu, the species with the highest affinity among the metals studied. IMPACT program predicted breakthrough times (dimensionless time) for zinc and cadmium shifted ahead by approximately 20% when compared with the experimental data. While shifting it slightly ahead, IMPACT predicted 90% overshoot of Zn and 25% overshoot of Cd which agrees very well with the experimental results. The latest Cu breakthrough time could not be judged properly since the simulation stopped prematurely due to simulation calculation problems. With the lack of support for the experimental software from its developers this problem could not be rectified. Further attempts to elucidate the reasons for the model algorithm malfunction and to further fine-tune IMPACT simulations was outside the scope of this work.

It was encouraging to see that, to a certain degree, IMPACT could reasonably simulate the complex column biosorption performance within the limited scope of the present work. While other mathematical models have been used for this purpose, they are invariably only experimental and their computer versions are proprietary and difficult to use. There is no readily available sorption column performance simulation model which would incorporate all aspects of sorption, including equilibrium sorption relationships, mass transfer, and fluid flow characteristics—and all this for multicomponent sorption systems. Work has been underway in this laboratory to develop biosorption process simulation models which are more structured and thus responsive to the key process parameters. Sophisticated process modeling software packages such as IMPACT would be extremely useful for biosorption performance estimation and process design. Needless to say, further testing and improvement of these packages is essential for their reliably successful, broader and easy application.

## Acknowledgments

## Nomenclature

$B$    biomass

$C_0$    total normality of the solution (meq L⁻¹)

$C_{fM}$    final, equilibrium concentration for metal M

$F$    volumetric flowrate (cm³ h⁻¹)

$F_M$    objective function defined by eq 7

$K_M$  Langmuir equilibrium constants for metal M (or protons − subscript H)

$q_M$  equilibrium uptake of metal M (or protons − subscript H)

$Q$  concentration of binding sites in the biosorbent (meq g$^{-1}$)

$t$  time (h)

$T$  dimensionless time calculated according to eq 1

$V_c$  volume (L) of the packed-bed in the column.

$\rho_b$  packing density of the dry biomass in the packed-bed (g m$^{-3}$)

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