

# Modeling Multi-Metal Ion Exchange in Biosorption

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Some types of dead microbial or seaweed biomass are capable of effectively binding heavy metals often through ion exchange. This biosorption can be used for purification of metal-bearing effluents. A recently developed two-site model for the ion exchange between divalent metal ions and protons in biosorption was extended to describe multi-site and multi-ion system behavior. A model case for two ion exchange sites and three ions was compared to the experimental data for the sorption of Cd, Cu, and Zn by protonated *Sargassum fluitans* biomass in systems containing two metal ions and protons at different pH values. The equilibrium constants were comparable to those obtained for systems where, in addition to protons, only one metal ion was present. This opens the possibility of predicting the sorption performance for three-cation systems from equilibrium constants determined in two-cation systems. There was no interference between the sorbed species except for competition for the same sorption sites. The model was able to predict the equilibrium binding of all three ions as a function of pH and of the final metal concentrations. Only two equilibrium constants, which were valid for any pH and in the presence of any competing ion, were necessary for predicting the binding of each metal ion. The complete equilibrium state (final concentration and binding) can be predicted as a function of the initial state for a pH titration in the simultaneous presence of two metal ions when the equilibrium constants are used in the chemical equilibrium program MINEQL+.

## Introduction

Biosorption, the passive non-metabolically mediated process of metal ion binding by living or dead biomass, may serve as a means for purifying industrial wastewaters that contain toxic heavy metal ions. Compared to other technologies, the advantages of biosorption are the high purity of the treated wastewater and the cheap raw material: waste products from other industries (e.g., fermentation byproducts) or naturally abundant biomass (e.g., marine algae) may be used as biosorbents.

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The metal ion binding mechanism in biosorption may involve different processes such as complexation, coordination, electrostatic attraction, or microprecipitation whereby ion exchange plays a major role in the binding of metal ions by algal biomass (1-3). Therefore, the use of ion exchange reaction constants instead of Langmuir- or Freundlich-type sorption isotherm relationships has been recommended for describing the process (2). The latter simplistic isotherms do not account for the effect of the back reaction of the displaced ion. This makes them unsuitable for modeling sorption processes where there is still significant binding of the displaced ion, e.g., at low concentrations of the sorbed metal.

Often the prediction of sorption equilibria is complicated by the presence of several sorbed ions, requiring the use of multicomponent isotherm equations (4). This is especially relevant when the sorption of one ion influences the binding of another, as is the case when different ions compete for the same binding site.

Another factor is the effect of pH on metal ion binding. Most cations sorb better at a higher pH (5, 6). This is largely due to a lowered competition by protons for the same binding sites that metal cations may use (7). The modeling of this effect is rendered more difficult in the case of biosorption because the biomass may contain several acidic groups active in metal sorption. The  $pK_a$  value, site quantity, and binding constants for the metal ions must be known for each of those sites. For the metal ion biosorption by the brown alga *Sargassum fluitans*, which contains the carboxyl groups of alginate and the sulfate groups of fucoidan (8), an ion-exchange-based two-site model has been developed (7). This model opened the possibility of predicting the pH effect on binding by protonated biomass in one-metal systems.

The purpose of the present work was to extend this model so that ion exchange in multi-metal systems involving multiple binding sites could be described. The sorption performance prediction by the resulting model has been examined for a specific typical multi-metal system.

## Materials and Methods

**Preparation of Sorbent.** Beach-dried *Sargassum fluitans*, collected in Naples, FL, was ground in a homogenizer and sieved. To eliminate weight loss and leaching of soluble biomass components such as alginate, the size fraction 0.84-1 mm was cross-linked with formaldehyde (9). After being washed with distilled deionized water, the biomass was protonated in 0.1 N HCl (10 g of biomass/L), washed 10 times in the same volume of distilled deionized water, and oven-dried at 60-80 °C. The protonation of the biomass was performed to eliminate any other exchangeable ions that were present on the raw biomass. This elimination was complete: in contrast to the non-protonated biomass, analysis of the equilibrated solution, even for high heavy metal binding, showed that no light metal ions such as Mg, Ca, Na, or K were released.

**Metal Binding Experiments.** The sulfate salts  $3CdSO_4 \cdot 8H_2O$  (AESAR),  $CuSO_4 \cdot 5H_2O$  (ACP Chemicals), and  $ZnSO_4 \cdot 7H_2O$  (J. T. Baker Chemical) were dissolved in distilled deionized  $H_2O$ . A total of 0.1 g of biomass was contacted with 50 mL of metal ion solution in 125-mL Erlenmeyer

flasks on a gyrotory shaker (New Brunswick Scientific, Model G2) at 2 Hz for 12 h. The initial concentrations ranged from 10 to 1000 ppm for Cd and from 10 to 500 ppm for Cu and Zn. The pH was constantly controlled using a pH controller (Cole Parmer, Model 5997-20). Blanks and duplicates were run as appropriate.

**Determination of Binding.** The initial and final metal concentrations were determined using an atomic absorption spectrometer (Thermo Jarrel Ash, Model Smith-Hieftje II), calibrated with standard solutions prepared from 1000 mg/L certified reference solutions (Fischer).

The metal ion binding was calculated from the mass balance:

$$q = ([M]_i - [M]_f)V/m \quad (\text{mol/g}) \quad (1)$$

with  $V$  being the solution volume,  $m$  being the mass of sorbent, and  $[M]_i$  and  $[M]_f$  being the initial and final metal ion concentrations, respectively.

Some experiments were performed with  $[M]_i \sim [M]_f$ , so that a desired final concentration was obtained. This was achieved by choosing a liquid volume of  $\geq 1$  L. Since the binding could not be determined from the concentration difference, the biomass was collected in a Buchner funnel and dried, and the metal ions were desorbed in 50 mL ( $V_{\text{des}}$ ) of 1 M HCl. After contacting overnight on a rotary shaker, the solution was filtered and analyzed for the metal concentration ( $[M]_{\text{des}}$ ). A correction was made for metal in the water volume ( $V_{\text{ad}}$ ) adhering to the biomass ( $m$ ) after filtering:

$$M^d q = ([M]_{\text{des}} V_{\text{des}} - [M]_f V_{\text{ad}})/m \quad (\text{mol/g}) \quad (2)$$

The change in the proton binding  $\Delta^H q$  was calculated as the difference between the quantity of protons added ( $[H]_{\text{add}} V_{\text{add}}$ ) for pH adjustment and the protons that accumulated in the solution ( $([H]_f - [H]_i)V$ ). For pH near 7, an additional term for water dissociation may be added which was however negligible under the conditions of the study:

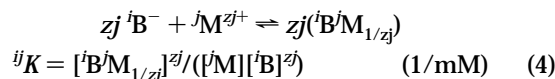
$$\Delta^H q = ([H]_{\text{add}} V_{\text{add}} - ([H]_f - [H]_i)V)/m \quad (\text{mol/g}) \quad (3)$$

The consumption or release of protons due to reactions in the aqueous phase is negligible because modeling with MINEQL+ (10) showed that no hydrolyzed species occur up to pH 7 or even higher, except for Cu where precipitation may occur at around pH 5. Since protonated biomass was used, it was assumed that the initial proton binding was equal to the total number of sorption sites.

**Modeling of the Metal Ion Binding.** Multicomponent Langmuir isotherms for one binding site and formation of 1:1 sorbate/sorbent complexes have been described by Hill (11). A case including one gaseous species that occupies two sites after dissociation was also considered by that author.

These multicomponent isotherms were adapted for the case of multi-site and multi-ion biosorption for different ion valences. Since biosorption by seaweed biomass is largely an ion-exchange phenomenon, it was assumed that each cationic species sorbs to the number of monovalent ionized groups, which is equal to the valence of the cation, such that the overall charge is preserved. The equation for a cation  $M$  of the charge  $z_j$  sorbing to a binding site  $B$  is

for ideal behavior (all activity coefficients equal to unity):



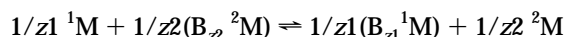
The first character of the upper left index of the equilibrium constant (or of the metal binding  $q$ ) refers to the binding site, the following to the sorbed ion. Protons are treated as one of the monovalent species with  $z_j = 1$ . Divalent ions form  ${}^i B/M_{0.5}$  complexes.

Note that the term  $z_j {}^i B^j M_{1/z_j}$  has been chosen instead of  ${}^i B_{z_j} {}^j M$  because it implies that a number of bonds equal to the charge  $z_j$  of the ion have to be broken for the release of an  $z_j$ -valent ion, i.e., the dissociation reaction is of the order  $z_j$  and not of the order one as this would be the case for the dissociation of a  ${}^i B_{z_j} {}^j M$  species. According to Buffle (12), the former version should be preferred over the latter when specific complexation instead of nonspecific electrostatic attraction is the binding mechanism. In biosorption, selectivity for specific ions is high (7) and therefore  ${}^i B/M_{1/z_j}$  complexes were assumed. This choice is in agreement with the experimental data (see discussion of Figure 4).

Although eq 4 expresses sorption to free sites, ion exchange can be modeled when the corresponding equations for all exchanged ions are included because the ion exchange constant is obtained by simply dividing the  $z_j$ th root of the binding constant (eq 4) for one ion by the respective root for the other ion:

$$K_{\text{exch}} = \frac{B_1 K^{1/z_1}}{B_2 K^{1/z_2}} = \frac{[B {}^1 M_{1/z_1}]^{1/z_1} [{}^2 M]^{1/z_2}}{[B {}^2 M_{1/z_2}]^{1/z_2} [{}^1 M]^{1/z_1}} \quad (\text{mM}^{z_1/z_2}) \quad (5)$$

If the term  $B_{z_j} {}^j M$  were chosen (i.e.,  $B_2 {}^2 M$  complexes form for divalent ions), the exchange constant for the reaction



would be

$$K_{\text{exch}} = \frac{[B_{z_1} {}^1 M]^{1/z_1} [{}^2 M]^{1/z_2}}{[B_{z_2} {}^2 M]^{1/z_2} [{}^1 M]^{1/z_1}} \quad (-) \quad (6)$$

This corresponds to the commonly known ion exchange constant in the literature (13), which has also been used for the description of biosorption of multivalent ions (1, 2).

Instead of using ion exchange constants where the binding of each metal ion can only be obtained by repeated iterations, it is useful to have an isotherm expression that relates the binding of a species to the concentrations of all species such that the binding can be calculated directly. It is assumed that secondary interactions are negligible and that there is no other influence of the other cation than competition for the same binding sites. For the reaction of the ion  $M$  in a system with  $n$  cations and  $m$  binding sites, it follows then from eq 4

$${}^j q = \sum_{k=1}^m [{}^k B^j M_{1/z_j}] = \sum_{k=1}^m K^k B \frac{({}^k K [M])^{1/z_j}}{1 + \sum_{h=1}^n ({}^h K [M])^{1/z_h}} \quad (\text{mequiv/g}) \quad (7)$$

TABLE 1

Model Parameters and Deviations between Model Predictions and Experimentally Determined Metal Ion Binding<sup>a</sup>

parameter set	equilibrium constants (L/mmol)						(% av absolute errors <sup>b</sup> predicting)		
	<sup>CCd</sup> K	<sup>CCu</sup> K	<sup>CZn</sup> K	<sup>SCd</sup> K	<sup>SCu</sup> K	<sup>SZn</sup> K	1-met syst	2-met syst	all data
1	80	200	10	0.8	3.7	0.5	5.4	6.4	6.1
2	40	210	7.6	0.5	5.2	0.1	6.3	6.1	6.1
3	65	190	10	0.5	6.3	0.1	5.6	6.2	6.0

<sup>a</sup> Parameter set 1 was derived from one-metal systems; set 2 was from two-metal systems; and set 3 was from all data. For all parameter sets, the amounts of binding sites were <sup>1</sup>C = 2 mequiv/g and <sup>1</sup>S = 0.25 mequiv/g with the apparent proton binding constants <sup>CH</sup>K = 10<sup>4.8</sup> L/mol and <sup>SH</sup>K = 10<sup>2.5</sup> L/mol. <sup>b</sup> Expressed in % of total binding capacity.

If only one site is present (i.e.,  $m = 1$ ) eq 7 can be regarded as a specific case of the Fritz–Schlender isotherm (14), which however needs  $n(2n + 3)$  parameters in order to describe a  $n$ -solute system (i.e., 14 for a two-solute system). The model presented here needs only  $(n + 1)$  parameters (i.e., 3 for a two-solute system) for the one-site case and  $(2n + 2)$  for the two-site case. Since the exponents  $1/z_j$  are related to the ion valence, they do not constitute adjustable parameters. Since the Fritz–Schlender isotherm needs such a high number of constants, it has frequently been used in different simplified forms (15, 16), which include the so called Langmuir-Freundlich isotherm (17).

The binding sites in *Sargassum* biomass are believed to be mostly the carboxyl groups of alginate (signified by C) and the sulfate groups of fucoidan (referred to as S sites) (7, 8). Therefore, the model case including these two sites, C and S groups, was chosen for the sorption system presently considered. In a system of two divalent metal ions <sup>1</sup>M and <sup>2</sup>M as well as protons (H), eq 7 is reduced to

$${}^1q = {}^tC \frac{(C^1 K^1 M)^{1/2}}{1 + {}^{CH}K[H] + (C^1 K^1 M)^{1/2} + (C^2 K^2 M)^{1/2}} + {}^tS \frac{(\delta^1 K^1 M)^{1/2}}{1 + {}^{SH}K[H] + (\delta^1 K^1 M)^{1/2} + (\delta^2 K^2 M)^{1/2}} \quad (\text{mequiv/g}) \quad (8)$$

$${}^Hq = {}^tC \frac{({}^{CH}K[H])}{1 + {}^{CH}K[H] + (C^1 K^1 M)^{1/2} + (C^2 K^2 M)^{1/2}} + {}^tS \frac{{}^{SH}K[H]}{1 + {}^{SH}K[H] + (\delta^1 K^1 M)^{1/2} + (\delta^2 K^2 M)^{1/2}} \quad (\text{mequiv/g}) \quad (9)$$

In order to predict final concentrations and binding from the initial conditions, the equilibrium program MINEQL was used (for a review of different equilibrium programs see ref 18). As input parameters, it is necessary to specify the total concentrations of all species and the equilibrium constants. The model iteratively computes the final speciation of each component in solution as well as the formation of solid compounds.

## Results

**Equilibrium Constants.** For each of the two-metal systems Cd–Cu, Cd–Zn, and Cu–Zn, experiments were performed at pH 2.5, 3, and 4.5. In order to quantify the effect of one metal ion on the binding of the other, the constants <sup>CM</sup>K and <sup>SM</sup>K for eqs 8 and 9 were determined by minimizing the average absolute deviations between the model predictions and experimental data points for the metal ion binding using the computer program MATLAB 4.0. The values <sup>1</sup>C

= 2 mequiv/g, <sup>1</sup>S = 0.25 mequiv/g, <sup>CH</sup>K = 10<sup>4.8</sup> L/mol, and <sup>SH</sup>K = 10<sup>2.5</sup> L/mol were derived earlier (7). As mentioned above, the competitive effect of Na, which was added during pH adjustment, was assumed to be negligible. The concentration of Na was of the same order of magnitude (<5 mM) as those of the other ions; however, its binding was much weaker because it is monovalent and can be expected to bind only electrostatically as has been confirmed for other acids of biological origin (19).

The determined constants for binding site–metal complexes are summarized in Table 1. Parameter set 1 consists of the values determined by Schiewer (7) in one-metal systems for the same protonated biomass as used in this work. Parameter set 2 is the constants determined for true two-metal systems. Parameter set 3 was obtained using both the one-metal and the two-metal systems data. It can be observed that the magnitude of the constants determined from one-metal systems is similar to those determined from two-metal systems.

Table 1 also lists the average discrepancies between the data points and the model predictions. For the modeling of one-metal systems, the error was smallest for parameter set 1 and largest for set 2. For the two-metal system data, set 2 fit better than set 1. Set 3 was intermediate in both cases. When both one- and two-metal systems were considered, the error for each metal species in each system (metal combination and pH) was weighed equally to form an average. Thus, for all the data, set 3 gave the best fit. This means that the experimental data were in each case (one-metal system, two-metal system or all data) best described by the parameter set derived from these data (set 1, 2, and 3, respectively). In general, however, the absolute deviations between model predictions and experiments were similar for all data sets, averaging around 6% of the total binding capacity.

In general, larger amounts of free sites exist only at high pH and low metal concentrations. Protons occupy the majority of sites at low pH. At high pH, and medium or high metal concentrations, most sites are complexed with metal ions. Metal ions alone occupy between 0 and ~100% of the sites; metal ions and protons together occupy between 50 and ~100%. Since the ratio of binding of the two metal ions still changes when a plateau value for the total binding is reached (Figures 1 and 2c), data near the saturation level are still interesting for competition modeling.

The average experimental errors in the determination of the binding of each metal ion are listed in Table 2. These values were estimated using the method described by Schiewer and Volesky (20) with most of the errors resulting from inaccuracies of the determination of the initial and final metal concentrations using the atomic absorption

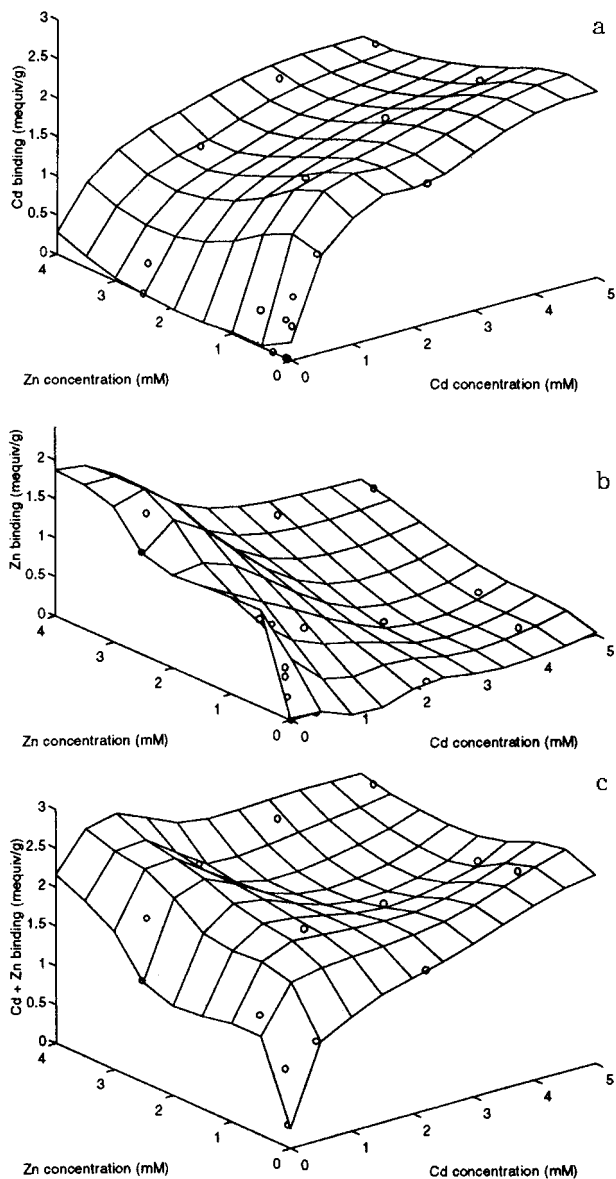


FIGURE 1. Two-metal (Cd+Zn) biosorption by *Sargassum fluitans* biomass at pH 4.5. (a) Experimental Cd binding in the interpolated sorption isotherm surface; (b) Experimental Zn binding in the interpolated sorption isotherm surface; (c) Experimental total metal ion binding in the interpolated sorption isotherm surface.

spectrophotometer. While the instrument calibration error affects the accuracy of the measurement, the drift and fluctuation errors affect the precision of the measurement. The error of the metal uptake modeling that occurred due to errors in the determination of the final pH (estimated 0.05 pH unit) are also listed. Overall, the experimental errors are of a similar magnitude as the modeling errors (Table 1).

**Influence of the Metal Ion Concentrations on the Metal Ion Binding at Fixed pH: Experimental Data and Model Predictions.** As an example for one of the nine investigated systems, the binding of the metal ions in the Cd–Zn system at pH 4.5 was plotted in a 3D graph (Figure 1). The grid surface is simply an interpolation between the individual points. For the total binding of both metal ions (Figure 1c), a plateau value of  $q \sim 2$  mequiv/g is reached at high concentrations ( $[Cd] > 2$  mM,  $[Zn] > 2$  mM). Although the proportion of the binding of the two metal ions may vary

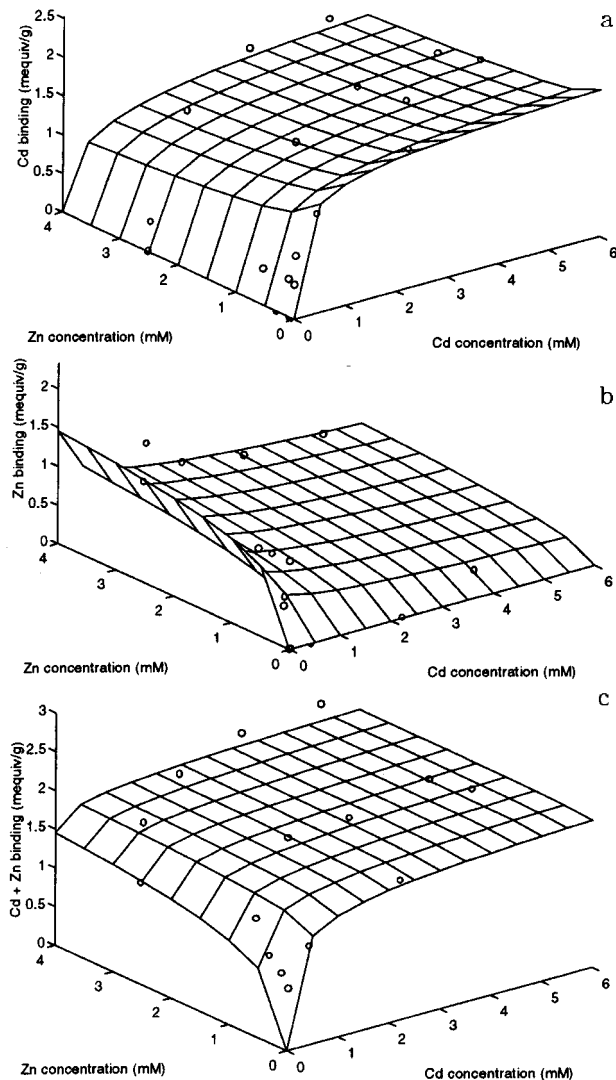


FIGURE 2. Two-metal (Cd+Zn) biosorption by *Sargassum fluitans* biomass at pH 4.5. (a) Experimental Cd binding data and the model-predicted sorption isotherm surface; (b) Experimental Zn binding data and the model-predicted sorption isotherm surface; (c) Experimental total metal ion binding data and the model-predicted sorption isotherm surface.

TABLE 2

**Experimental Errors in Determination of Metal Ion Binding: Average Absolute Errors in Percent of Total Binding Capacity**

metal	pH	calibration	drift & fluct.	pH reading	total
Cd	4.5	0.64	0.45	0.50	1.91
	3.0	0.73	0.51	0.75	2.12
	2.5	0.75	0.52	0.51	1.83
Cu	4.5	0.91	0.62	0.82	2.87
	3.0	0.81	0.69	0.74	2.68
	2.5	0.77	0.67	0.44	2.31
Zn	4.5	1.21	1.94	0.05	3.45
	3.0	1.79	2.61	0.35	4.85
	2.5	2.00	2.71	0.12	4.86

with the concentrations, the total metal ion binding stays constant. In addition, it is clear that the binding of Zn (Figure 1b) is more strongly affected by the presence of Cd than vice versa (Figure 1a). In general, a preference of sorption  $Cu > Cd > Zn$  was observed at all pH values and for all metal combinations.

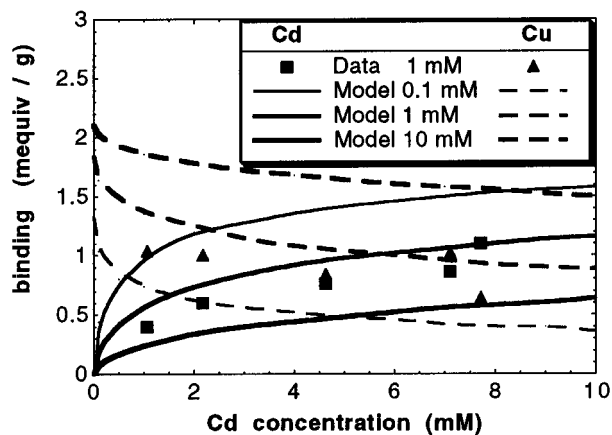


FIGURE 3. Biosorption of Cd and Cu by *Sargassum fluitans* biomass at pH 4.5 at different Cu concentrations: Binding data and model predictions.

Using the constants from parameter set 3, the model predictions and experimental data for the total metal ion binding in the Cd–Zn system at pH 4.5 are plotted in Figure 2. The plateau phenomenon is reflected in the model.

**Influence of the Cd Concentration on the Binding of Both Metals. For Different Cu Concentrations at a Fixed pH.** Since the quantitative interpretation of 3D graphs is difficult, it is recommendable to evolve them into a series of 2D graphs that represent isoconcentration cuts of the 3D plot (4). Figure 3 shows the binding of Cd and Cu at pH 4.5 as a function of both concentrations. In general, the experimental methodology used does not allow for the adjustment of the final concentration as an independent variable, it is dependent on the initial concentration and cannot be predicted beforehand unless the equilibrium constants are already known. Therefore, the direct comparison between the measurements and the model predictions for the binding of one metal ion at a specific concentration of the competing ion is not feasible. In order to render such a comparison possible, a limited number of experiments were performed in a liquid volume large enough so that the concentration of metal ions in the liquid phase remained constant (and known) throughout the experiment. With this approach, however, the binding cannot be determined from the concentration difference in the solution (initial – final) but was determined by metal ion elution from the sorbent instead. Some experimental data obtained by this methodology are included in Figure 3. The model predicts the tendency displayed by these additional data that had not been used in the determination of the model parameters.

**Influence of the Metal Concentration Ratio on the Relative and Total Metal Ion Binding at a Constant Total Metal Concentration and pH.** While Figure 3 represents cuts of the sorption isotherm “surface” at constant Cu concentrations, Figure 4 is composed of diagonal cuts at constant total metal ion concentration. The ratio of the Cd/Cu binding and their sum are depicted as a function of the concentration ratio [Cd]/[Cu]. Although the total binding is almost independent of the concentration ratio at pH 4.5 for [Cd] + [Cu] = 5 mM, it decreases with increasing Cd portion when ionic strength or pH are lower.

The ratio between the Cd and Cu bindings also varied with pH but not significantly with the total metal concentration. The relationship between the relative binding and the relative concentration is linear with the slope of 1/2.

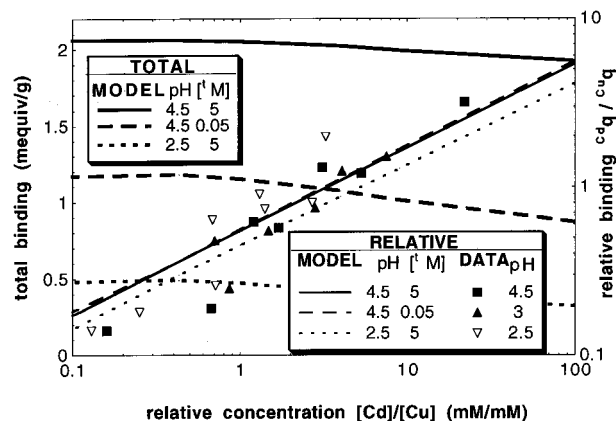


FIGURE 4. Biosorption of Cd, Cu, and H by *Sargassum fluitans* biomass for different total metal concentrations and pH values: Model predictions.

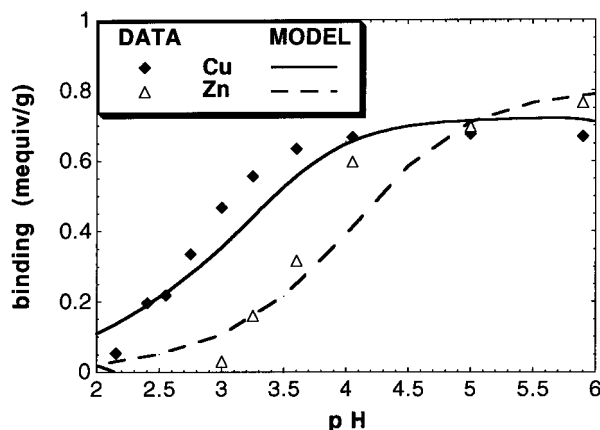


FIGURE 5. Titration of *Sargassum fluitans* biomass in the simultaneous presence of Cu and Zn at constant total concentrations of each metal: Biosorption binding data and MINEQL+ model predictions.

This slope is also visible in the experimental data. Since the total concentration has no significant influence on the relative binding (when the pH is constant and both metal ions have the same valence), the data points were obtained at different total concentrations. The slope of the line that best fits the data points ( $R = 0.93$ ) in Figure 4 is 0.65.

**pH Titration for a Constant Total Concentration of Each of the Two Metals.** Figure 5 demonstrates the sorption behavior of a Cu–Zn system at changing pH values for a constant total concentration (solid + liquid phase) of each metal. At a higher pH, the binding of the two metals is similar. With decreasing pH, however, Zn gets released much more readily than Cu. At pH 3.6, the Zn binding is already reduced to less than half of its maximum value, while the binding of Cu is still almost unchanged.

The system was modeled by incorporating the equilibrium constants into the chemical equilibrium program MINEQL+. The complete final state (concentrations in solution and binding values) was predicted from the known initial conditions. The model predicted a similar trend as observed from the experimental data.

## Discussion

**Influence of Metal Ion Concentrations on the Metal Ion Binding at Fixed pH: Experimental Data and Model Predictions.** The occurrence of a plateau value (Figures 1c and 2c) for high metal ion concentrations where the total

binding is independent of the concentration indicated that both metal ions compete for the same limited number of sites: with an increased concentration of one metal ion the increase in the binding of this metal is accompanied by a corresponding decrease in binding of the other metal such that the total binding is constant when it is at its maximum value. This is reflected in the model, which assumes competition of all ions for the same binding sites.

**Equilibrium Constants.** *Comparison between Constants Obtained in One- and Two-Metal Systems.* In general, the constants determined in two-metal systems (set 2) and one-metal systems (set 1) (7) are similar to the ones determined for all the data (set 3), which may be regarded as the most reliable.

As Table 1 indicates, the data in two-metal systems are described best by parameter set 2, which was derived exactly from these data. However, the error in the prediction of two-metal system sorption behavior increased only by 5% (from 6.2 to 6.4% of the maximum binding) when the constants derived from one-metal systems (set 1) were used. This means that the prediction of the two-metal system behavior by using results from one-metal systems is possible. Therefore, the amount of experimental work needed to provide a basis for modeling multi-metal systems can be greatly reduced. Instead of a systematic investigation of the influence of each metal ion, only spot-checks may be necessary in order to confirm the applicability of the constants derived from one-metal systems. For those spot-checks, the modeling may already help to design the experiments in such a way that the desired final concentrations are reached and that the experimental error is kept low (20).

From a theoretical modeling perspective, this similarity in the different sets of constants indicates that secondary interactions in the ion-exchange-based metal biosorption systems are probably weak. The influence of the presence of one metal on the binding of another one is mainly due to competition for sorption sites.

*Number of constants, Predictive Power.* A major advantage of the presented model, as compared to earlier multi-metal isotherms (4), is that only two constants  $^{SM}K$  and  $^{CM}K$  were necessary to predict the binding of each metal ion at different pH values and in the presence of different concentrations of either of the two other competing ions. Previously, it was necessary to determine a new set of constants for each pH and each combination of metal ions. The presented model reduces the amount of experimental work since the prediction, e.g., of binding, at other pH values is possible.

**Influence of the Cd Concentration on the Binding of Both Metals for Different Cu Concentrations at a Fixed pH.** The predictive power of the model is shown in Figure 3. Although the data points were not used in the determination of the binding constants, the general trend is well predicted. A tendency of the experimental binding to be lower than the modeled binding can, however, be observed for both metals. This may be due to the experimental methodology: specifically for the data points in Figure 3, desorption was used in order to determine the binding. This elution of the metal ions may not have been 100% complete, resulting in an underestimation of the binding.

**Influence of the Metal Concentration Ratio on the Relative and Total Metal Ion Binding at a Constant Total Metal Concentration and pH.** *Effect on Total Binding.* As seen in Figure 4, the effect of the concentration ratio on the

total metal ion binding is most pronounced at low pH or low total metal ion concentrations. Under these conditions, the presence of the more strongly binding Cu instead of Cd can contribute to increased total metal ion binding by competing more effectively for sites occupied by protons (at low pH) or by occupying additional free sites (at low metal concentrations). At high pH and metal ion concentrations this is not possible because even Cd can occupy almost all sites and nearly no protonated or free sites remain.

*Effect on Relative Binding.* The constant slope (0.5) in the relationship between the relative binding and the relative concentration (Figure 4) corresponds to the exponent of the metal ion concentration ratio in eq (5) which, expressed in logarithmic terms, becomes for  $z_1 = z_2 = 2$ :

$$\log ({}^1q/{}^2q) = \log ([B {}^1M_{0.5}]/[B {}^2M_{0.5}]) = \log K_{\text{exch}} + 0.5 \log ({}^1M/{}^2M) \quad (-) \quad (10)$$

The expected slope of 0.5 is also reflected in the experimental data for which the line of the best fit has a slope of 0.65. Consequently, the  $BM_{0.5}$  assumption that yields a slope of 0.5 fits the Cd-Cu data better than the  $B_2M$  assumption, which would predict a slope of 1.0. For the other two-metal systems (Cd-Zn and Cu-Zn), however, the experimentally observed slope of 0.97 and 0.77, respectively (data not shown), was larger, favoring the  $B_2M$  assumption. It can be concluded that both electrostatic attraction (corresponding to a slope of 1.0) and covalent bonds may contribute to biosorption, resulting in the formation of both  $BM_{0.5}$  and  $B_2M$  complexes.

**pH Titration for a Constant Total Concentration of Each of the Two Metals.** The difference between the inflection points (Figure 5) of the curves for Cu and Zn binding is due to the fact that the more strongly binding Cu can better resist the competition from protons than the weakly binding Zn. This effect can be used in practice for selective metal ion desorption. Desorption with acids is a promising technique for the regeneration of the sorbent material (21). When the difference between the binding constants of the sorbed metal ions is large enough, not only the biomass can be regenerated by acidic desorption but also partial selective recovery of the sorbed metal may be possible. The data in Figure 5 were not used for the determination of the binding constants. This demonstrates the predictive power of the model, being able to even describe metal ion binding at pH values different from those at which the model parameters were determined.

## Glossary

${}^iB, {}^iC, {}^iS$	amount of binding sites ${}^iB, C,$ and $S$ (mequiv/g)
${}^iK$	equilibrium constant of complex formation site $i$ - cation $j$ (L/mol)
$m$	dry weight of biomass (g)
$q$	binding (mequiv/g)
$V$	volume of solution (L)
[ ]	concentration (of species within brackets) (mol/L or mequiv/g)

## Indices

$z_j$	charge (valence) of ion $j$ , stoichiometric factor
$1/z_j$	stoichiometric factor for ion $j$

f	final
i	initial (if referring to M species)
B, C, S, <i>i</i> , <i>k</i>	(running) index of binding site
H, M, <i>j</i> , <i>h</i> , 1, 2	(running) index of ionic species
t	total

### Molecular Species

B, C, S	binding sites
H	protons
$M^{zj}$	ionic species <i>j</i> of valence <i>zj</i>
CH, SH	protonated sites
$BM_{1/zj}$ , $B_2M$ , $CM_{0.5}$ , $SM_{0.5}$	metal–biomass complexes

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