

# Ionic Strength and Electrostatic Effects in Biosorption of Divalent Metal Ions and Protons

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This study is concerned with passive biosorption of metal ions by biomass of the brown alga *Sargassum*, a process that may eventually be used for the treatment of industrial wastewaters. This work provides a mathematical model for predicting the equilibrium of proton and metal ion binding as a function of metal ion concentration, pH, and ionic strength. Since the presence of sodium significantly influenced Cd binding, it is recommended to use models that incorporate ionic strength effects. Although swelling of the biomass particle was observed, a simple Donnan model that assumed a rigid particle already yielded good prediction of the experimental data. A combined Donnan-Biosorption-Isotherm equation was derived that allowed for direct calculation of cation binding without iterations. Only one parameter, the binding constant, had to be determined each for Cd and Ca. The intrinsic binding constant was several orders of magnitude lower than the apparent one. Using the parameters (amount of binding sites, proton binding constant, and specific particle volume) obtained from pH titrations in an earlier study, it was possible to predict the effect of pH, ionic strength, and Ca concentration on Cd binding.

## Introduction

Biosorption, the process of passive cation binding by dead or living biomass, represents a potentially cost-effective way of eliminating toxic heavy metals from industrial wastewaters. Industrial effluents usually contain a mixture of cations, among those harmless ions such as Na or Ca. The removal of such ions is not a primary focus of biosorption, but their presence (and binding) may interfere with the binding of targeted heavy metal ions such as Cd.

Na as a typical "hard" ion is not expected to form strong coordinate bonds but rather to be electrostatically attracted to the negatively charged biomass particle. Nevertheless, the presence of Na can reduce the amount of other electrostatically bound counterions that balance the negative charge of the biomass. Thereby, it can affect the intraparticle concentration and, consequently, the binding of other ions. Calcium, which may form specific, coordinate bonds, might have an even stronger influence on heavy metal ion binding. It is known that the presence of light metal ions can affect heavy metal ion binding in humic and fulvic acids as well as alginate (1-4). Similarly, a reduction of heavy metal biosorption was observed in the presence of light metals (5-8). In modeling biosorption of protons, the effect of ionic strength was recently taken into account (9), but in modeling the equilibrium of heavy metal biosorption, the influence of

alkaline (earth) metals has until now been neglected (10). Therefore, in order to be able to predict biosorption performance, it is necessary to investigate the influence of light metal ions in heavy metal binding and to account for this phenomenon in biosorption modeling.

A useful compilation of different modeling approaches was presented by Buffle (11). In the modeling of electrostatic effects on cation binding to humic and fulvic acids, double-layer models (Helmholtz or Gouy-Chapman) have been used for example by Bartschat et al. for binding of H and Cu (12); by Tipping for H, Cu, Cd, Ca, and Mg (13); and by Xue et al. for Cu and Cd (14). Donnan models have extensively been applied by the Marinsky research group for interpretation (but not really prediction) of H and Cu sorption to humic and fulvic acids (1, 15) or H, Ca, Cd, Ni, Zn, and Co binding to alginic acid and chondroitin sulfate (16). A rare case of actual prediction of the metal binding with the Donnan model is the very recent work of Kinniburgh et al. (17) where the effect of H, Ca, and Na on Cd or Cu binding by humic acids was modeled.

Biosorption by algal particles is different from humic and fulvic acids in that the particles are large and heterogeneous. This work investigates how far similar concepts as those used in humic and fulvic acid modeling can be applied for biosorption.

## Materials and Methods

**Materials.** Beach-dried brown alga biomass of the genus *Sargassum*, collected in Natal, Brazil, was chopped manually and sieved. After washing with distilled deionized water, the biomass of the size fraction 0.5-1.7 mm was first washed twice with 1 N HCl (50 g of biomass/L) for protonation, then 10 times in the same volume of distilled deionized water, and finally dried in an oven at 60-80 °C. Protonation of the biomass was performed to eliminate any other exchangeable ions that were present in the raw biomass, thereby enabling the study of a simple sorption system, one involving only a limited number of cations. It has been shown earlier (10) that acid washing is effective in removing light metal ions from the binding sites of *Sargassum* biomass.

**Experiments.** The 0.1-1.0 g *Sargassum* biomass [the higher sorbent masses were generally applied at low pH values (pH 3) and at high Ca concentrations ( $[Ca]_i > 100$  ppm) in order to avoid large experimental errors (18)] was contacted with 50 mL of solution containing sodium (0 or 100 mM, referred to as low and high ionic strength, respectively, in the discussion and in the figure legends), calcium (initial concentrations 1-400 ppm), and cadmium nitrate (initial concentrations 3-900 ppm) in 125-mL Erlenmeyer flasks on a gyrotory shaker (New Brunswick Scientific, Model G2) at 2 Hz for 12 h. The kinetics of metal biosorption is controlled by mass transfer. With small sorbent particles (0.5-1.5 mm diameter), the equilibrium is reached in approximately 2 h, a substantial fraction of the equilibrium binding is actually achieved after a few minutes. Therefore, 12 h is ample time to ensure equilibrium. Different known amounts of NaOH (0.1-1 M) were added to the samples in order to achieve different final pH values (pH 3 or pH 4.5) that were measured (ORION Ionalyser Model 407A). In order to determine the specific particle volume, the biomass was filtered off (using previously weighed Whatman no. 4 filter paper), weighed immediately, oven-dried at 60 °C, and weighed again after equilibrating at room atmosphere. Due to an unknown amount of water adhering to the biomass particles, these measurements of the particle volume are only semiquantitative. Both initial and final cadmium and calcium concentrations were determined by atomic absorption spectrometer (Thermo Jarrel Ash, Model Smith-Hieftje II).

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Previous work showed that though sulfate groups are present in *Sargassum* (19) their amount of binding sites and their binding constants are much smaller than the respective values for carboxyl groups (10). Therefore their contribution in metal binding is negligible as compared to carboxyl groups except for pH < 3 where carboxyl groups become protonated. In order to keep the model as simple as possible, it was thus assumed that only one type of binding site C (carboxyl groups) is responsible for most of the metal binding. The binding of ions (protons = H, divalent metal ions = M) is defined as the sum of the coordinately (as  $CX_{1/z_x}$ ) and electrostatically (as  $[X_p] - [X]$ ) bound ions:

$${}^Hq = CH + ([H_p] - [H]) V_m \quad (\text{mequiv/g}) \quad (1)$$

$${}^Mq = CM_{0.5} + 2([M_p] - [M]) V_m \quad (\text{mequiv/g}) \quad (2)$$

For any ionic species "X" with the charge  $z_x$ , the concentrations  $[X]$  without subscript are the ones in the bulk solution, and  $[X_p]$  is the average concentration of X in the particle (of the specific volume  $V_m$  which is a fitting parameter). As shown in Figure 1, the intraparticle concentrations  $[X_p]$ , which cannot be measured, are calculated using eq 10 for known values of  $\lambda$  (eq 11) and  $[X]$ . The final metal ion binding in the experiments can be calculated from the mass balance for M:

$${}^Mq = {}^Mq_i + 2 \frac{[M]_i V_i - [M] V}{m} \quad (\text{mequiv/g}) \quad (3)$$

with  $m$  being the mass of the sorbent and  $V$  the volume of the solution. The subscript  $i$  denotes initial values. For the experimental data in this study  ${}^Mq_i$  was zero because the biomass was initially completely protonated.

The concentration of the anion in solution (in this case  $\text{NO}_3^-$ , which was added with the metal salts) can be calculated from the mass balance:

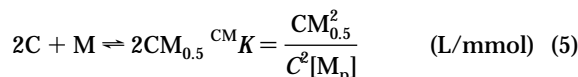
$$L = \frac{([NaL]_i + 2[CdL_2]_i + 2[CaL_2]_i) V_i + ([L_p]_i - [L_p]) V_m m}{V} \quad (\text{mmol/L}) \quad (4)$$

Contrary to the cations, the intraparticle concentration of the anion,  $[L_p]$ , is lower than its bulk concentration,  $[L]$ , because the negatively charged biomass repels anions.

## Model

**Reactions and Isotherm Models.** Since this work is an extension of a previous study on simple proton binding, only the equations relating to metal ion binding that have not yet been given in the preceding work (9) will be listed here.

The reaction for the complexation of divalent metal ions M to a binding site C is



Since the total number of binding sites stays constant

$${}^tC = C + CH + CCd_{0.5} + CCa_{0.5} \quad (\text{mequiv/g}) \quad (6)$$

the isotherm for the proton and metal ion binding can be derived from the binding constants for metal ions (eq 5) and protons (see preceding work (9) by substituting  ${}^tC/C$  using eq 6. Then

$$CH = \frac{{}^tC {}^{CH}K[H_p]}{1 + {}^{CH}K[H_p] + \sqrt{{}^{CCd}K[Cd_p]} + \sqrt{{}^{CCa}K[Ca_p]}} \quad (\text{mequiv/g}) \quad (7)$$

$$CM_{0.5} = \frac{{}^tC \sqrt{{}^{CM}K[M_p]}}{1 + {}^{CH}K[H_p] + \sqrt{{}^{CCd}K[Cd_p]} + \sqrt{{}^{CCa}K[Ca_p]}} \quad (\text{mequiv/g}) \quad (8)$$

This isotherm is a specific case of the general multicomponent isotherm for any number of bound ions and several sites that was described earlier (20). M refers to either Cd or Ca. The appropriateness of assuming  $CM_{0.5}$  complexes as opposed to  $C_2M$  complexes (as commonly done) is discussed in the section Stoichiometry Plot and illustrated in Figure 8, both in the Supporting Information.

**Donnan Model.** The equations for charge neutrality in the particle are for  $[L] \gg [OH]$ :

$$C = V_m \sum (z_x [X_p]) = V_m \frac{([H_p] + 2[Cd_p] + 2[Ca_p] + [Na_p] - [L_p])}{[Na_p] - [L_p]} \quad (\text{mmol/g}) \quad (9)$$

The commonly known equation for the concentration factor  $\lambda$  in an electrolytic gel according to the Donnan theory (21) is

$$\lambda = \frac{[X_p]^{1/z_x}}{[X]^{1/z_x}} = \frac{[H_p]}{[H]} = \frac{[Na_p]}{[Na]} = \sqrt{\frac{[M_p]}{[M]} \frac{[L]}{[L_p]}} \quad (-) \quad (10)$$

With  $[X_p]$  being the concentration of any ionic species X with the charge  $z_x$  in the gel. It is not necessary to include the activity coefficient  $\gamma$  in the model equations since electrostatic effects are already accounted for by the concentration factor  $\lambda$  and since any changes in the activity coefficient would be much smaller than the effect of  $\lambda$ . Expressing all intraparticle concentrations in terms of  $\lambda$  (eq 10) and substituting into the charge balance of the particle (eq 9) yields after replacing  $([Cd] + [Ca])$  by  $[\Sigma M]$  and  $([H] + [Na])$  by  $(I - 3[\Sigma M])$  (using the charge balance in solution and the definition of the ionic strength):

$$\lambda = \frac{[H_p]}{[H]} = -\frac{I - 3[\Sigma M]}{4[\Sigma M]} + \sqrt{\frac{(I - 3[\Sigma M])^2}{16[\Sigma M]^2} + \frac{C/V_m + I - [\Sigma M]}{2[\Sigma M]}} \quad (\text{mmol/L}) \quad (11)$$

The equation is also valid if more than two divalent and/or more than two monovalent ions are present.  $[\Sigma M]$  generally stands for the sum of the concentrations of all divalent ions;  $(I - 3[\Sigma M])$  stands for the sum of the concentrations of all monovalent ions. In the derivation of eq 11, it was assumed that  $C/V_m + L/\lambda \sim C/V_m + L$  since at high ionic strength values  $\lambda$  approaches 1.0 and at low ionic strength (i.e., low L and  $\lambda > 1$ )  $\lambda C/V_m \gg L$ .

The apparent C site metal ion binding constant is

$${}^{CM}K_{app} = \frac{(CM_{0.5})^2}{C^2[M]} = {}^{CM}K \lambda^2 \quad (\text{L/mmol}) \quad (12)$$

Or, if C is unknown, the apparent binding constant can be defined as

$${}^{CM}K_{app}^* = \frac{{}^Mq^2}{C_{app}^2[M]} = {}^{CM}K \lambda^2 \frac{{}^Mq^2}{CM_{0.5}^2 C_{app}^2} \quad (\text{L/mmol}) \quad (13)$$

with  $C_{app} = {}^tC - {}^Hq - {}^{Cd}q - {}^{Ca}q$ .

**Modeling the Swelling of *Sargassum* Particles.** The particle volume  $V_m$  is the fitting parameter that takes care of electrostatic effects for the rigid Donnan (DORI) model.

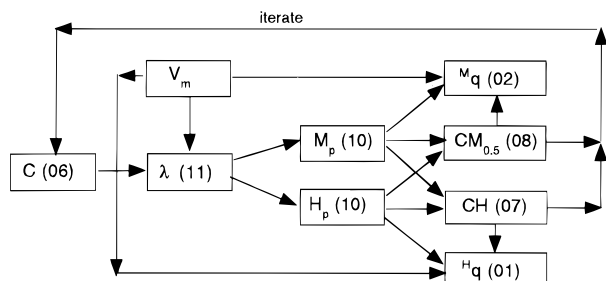


FIGURE 1. Calculation algorithm for the extended Donnan model. Depending on the assumption made for particle swelling,  $V_m$  is defined in different ways. The figure shows the algorithm for the DORI model where  $V_m$  is constant. For the DOSWa model, no iteration is necessary, and  $\lambda$  is the first variable calculated. For the DOSWb model,  $V_m$  is a function of  $C$  and  ${}^Mq$  (eq 15).

Swelling changes the concentration of charged sites per volume and therefore also the concentrations of ions in the gel. Since it was observed (see below) that swelling of *Sargassum* increased with the number of free sites  $C$ , the following simple linear relationship between the specific particle volume and  $C$  was assumed:

$$V_m = Y_v C \quad (\text{L/g}) \quad (14)$$

$Y_v$  is a constant that has to be determined from the experimental data. For  $C$  approaching zero (i.e., all sites are occupied), electrostatic effects and therefore the volume are irrelevant (i.e., it does not matter that the value calculated for  $V_m$  approaches zero). Equation 14 expresses that the charge density per volume is constant, independent of the degree of site occupation.

Since, however, the swelling did not only strongly increase with  $C$  but, *additionally*, it decreased with  ${}^Mq$ , the following alternative swelling correlation was considered:

$$V_m = 1 + 0.5(C^2 - {}^Mq) \quad (\text{L/g}) \quad (15)$$

Three versions of the Donnan model are considered in the following: one that assumes a rigid particle (DORI), one (DOSWa) that accounts for swelling by a linear correlation (eq 14), and one (DOSWb) that accounts for swelling by a more complex relation (eq 15).

The algorithm for the calculation of the cation binding and other variables is shown in Figure 1. It is necessary to perform the calculations iteratively unless eqs 18 and 19 are used, which is only possible for the DOSWa model. It has proven a reliable, stable method to start the iteration by assuming that the concentration of free sites is equal to the experimentally determined value of apparently free sites  $C \sim C_{app} = {}^tC - {}^Hq - {}^{Cd}q - {}^{Ca}q$ .

**Combination of the Isotherm and Donnan Models.** The general calculation algorithm shown in Figure 1 can be used in conjunction with any type of sorption isotherm. Specifically for the isotherm model used here, the calculation process can be further simplified. Upon substituting the amount of coordinately bound metal (eq 8) into eq 2, replacing  $[X_p]$  in terms of  $[X]$  and  $\lambda$  (eq 10) after dividing denominator and numerator of the left-hand term by  $\lambda$  the following relationship is obtained:

$${}^Mq = \frac{{}^tC \sqrt{{}^{CM}K[M]}}{\frac{1}{\lambda} + {}^{CH}K[H] + \sqrt{{}^{CCd}K[Cd]} + \sqrt{{}^{CCa}K[Ca]}} + \frac{2[M](\lambda^2 - 1)Y_v {}^tC/\lambda}{{}^tC/(\lambda C)} \quad (\text{mequiv/g}) \quad (16)$$

Though this equation is already more "compact", it still requires iterative calculation of  $\lambda$  and  $V_m$ . For the specific

case that swelling linearly increases with the number of free sites (i.e., for the DOSWa model), the isotherm can be further simplified so that  ${}^Mq$  can be calculated directly without iterations. Substituting  $V_m$  according to eq 14 into eq 16 yields

$${}^Mq = \frac{{}^tC \sqrt{{}^{CM}K[M]}}{\frac{1}{\lambda} + {}^{CH}K[H] + \sqrt{{}^{CCd}K[Cd]} + \sqrt{{}^{CCa}K[Ca]}} + \frac{2[M](\lambda^2 - 1)Y_v {}^tC/\lambda}{{}^tC/(\lambda C)} \quad (\text{mequiv/g}) \quad (17)$$

The second term was expressed in such a way that its denominator equals the denominator of the first term. This way the two numerators can easily be added:

$${}^Mq = \frac{{}^tC(\sqrt{{}^{CM}K[M]} + 2[M]Y_v(\lambda - 1/\lambda))}{\frac{1}{\lambda} + {}^{CH}K[H] + \sqrt{{}^{CCd}K[Cd]} + \sqrt{{}^{CCa}K[Ca]}} \quad (\text{mequiv/g}) \quad (18)$$

Analogously, an equation for proton binding can be derived as

$${}^Hq = \frac{{}^tC({}^{CH}K[H] + [H]Y_v(1 - 1/\lambda))}{\frac{1}{\lambda} + {}^{CH}K[H] + \sqrt{{}^{CCd}K[Cd]} + \sqrt{{}^{CCa}K[Ca]}} \quad (\text{mequiv/g}) \quad (19)$$

Now it is possible to calculate the binding of both metal ions and protons without iteration. First,  $\lambda$  is calculated according to eq 11, with the constant  $1/Y_v$  substituted for the term  $C/V_m$ . Then  ${}^Mq$  (eq 18) and  ${}^Hq$  (eq 19) are calculated. Theoretically, eq 11 could be substituted into eq 18 and 19 so that only one equation is necessary, but the resulting equation would be rather complicated and "inelegant". Further simplifications of the above equations are discussed in the section Model Simplifications in the Supporting Information.

## Results and Discussion

**Specific Particle Volume.** For all selected experimental series (different pH,  $I$ , combination of divalent ions), it was observed that the specific particle volume per dry biomass (the ratio between wet and dry weight of the particle, assuming a density  $\sim 1$  g/mL for wet biomass) decreased with increasing  $M^{2+}$  concentration, approaching a value of 2.5–3 mL/g for  $[Cd] \geq 1$  mM and  $[Ca] \geq 5$  mM (data not shown). At low metal concentrations, the different series diverge from each other. For low pH and low  $I$  the specific particle volume remains about constant (at 2.5–3 mL/g). For high pH and high  $I$ , on the other hand, the particle swells considerably, and a specific volume of up to 4.5–5 mL/g is reached for  $M < 0.3$  mM. This volume change by a factor of 2 means that swelling can still be significant in the presence of heavy metals at low to intermediate concentration. The observation that swelling is most pronounced at high pH and  $I$  can be explained by the fact that under these conditions the number of free sites is high. It was noticed before (9) that swelling increased with pH because protonated alginic acid has a smaller volume than dissociated alginic acid. The fact that swelling does not only decrease with pH but also with the increasing Cd or Ca concentration indicates that Cd-alginate or Ca-alginate also has a smaller volume than dissociated alginic acid (Na-alginate). This phenomenon may be enhanced by the possibility that divalent ions may cross-link alginate when bound to it (22, 23). For a comparison of the model predicted

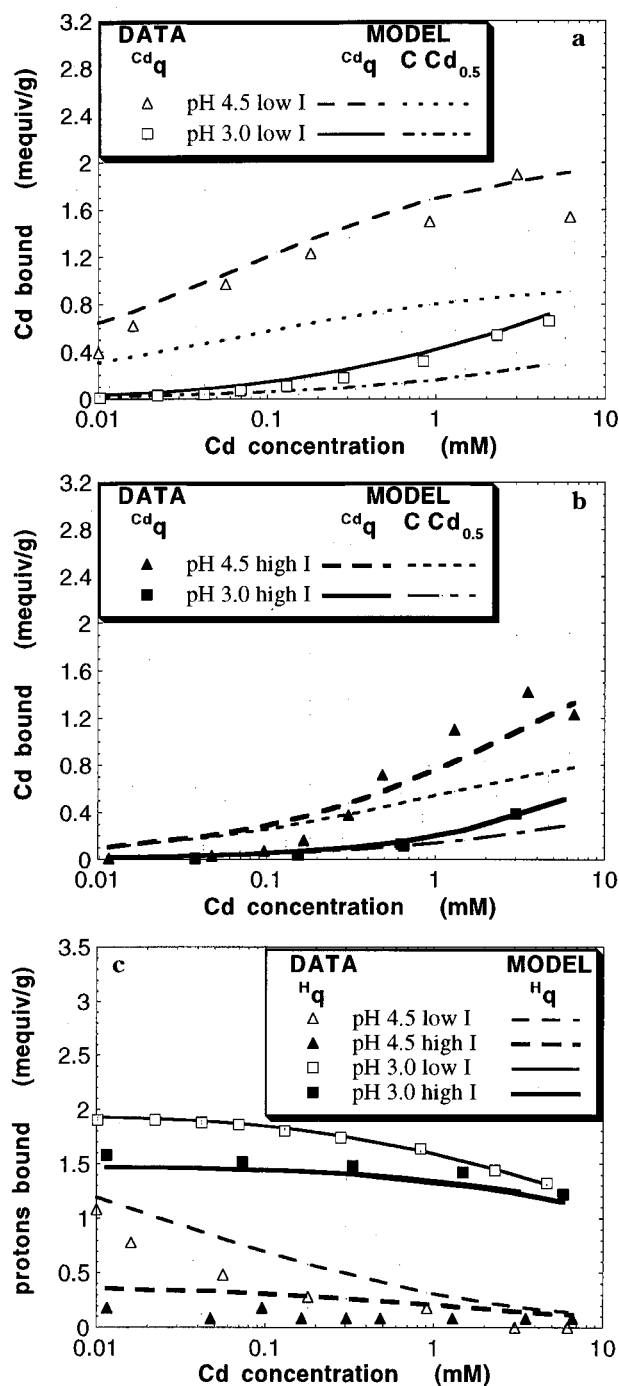


FIGURE 2. Cadmium and proton binding by *Sargassum* biomass at different ionic strength  $I$  and pH (experimental data and predictions by the Donnan model for rigid particles): (a) total ( $C^{Cd}$ ) and coordinate ( $CCd_{0.5}$ ) cadmium binding at low ionic strength; (b) total ( $C^{Cd}$ ) and coordinate ( $CCd_{0.5}$ ) cadmium binding at high ionic strength; (c) total ( $H^q$ ) proton binding.

active volume (eqs 14 and 15) with the measured total particle volume, please refer to the section Modeling the Particle Swelling and Figure 7, both in the Supporting Information.

**Cadmium and Proton Binding.** As shown in Figure 2, panels a and b, respectively, Cd binding increases with pH and Cd concentration, while H binding decreases. This once again illustrates the well-known competition of heavy metal ions and protons for the same binding sites (10). The sum of the binding of both ions changes, however, indicating that not only ion exchange between these two ions occurs but also a variable amount of free sites is present (Figure 3). The binding of Cd and H decreases with increasing ionic strength

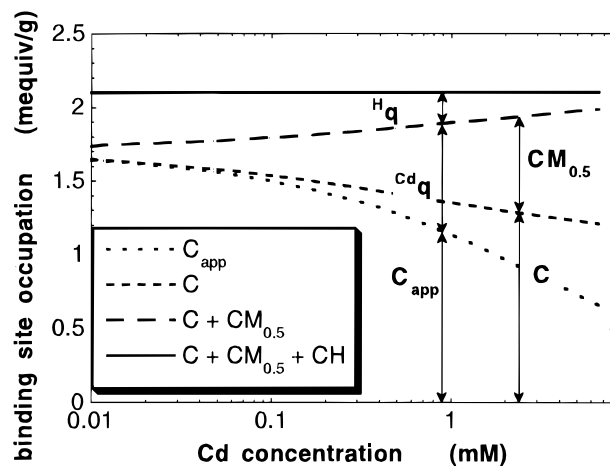


FIGURE 3. Change of *Sargassum* biomass binding sites occupation with increasing metal concentration for pH 4.5 and  $I = 100$  mM.  $C$  is the number of free binding sites,  $C_{app}$  is the number of apparently free binding sites ( $C - H^q - Cd^q - Ca^q$ ) (predictions by the Donnan model for rigid particles).

(1). This can be explained by lower intraparticle concentrations of Cd and H at high  $I$ , because Na contributes to balancing the negative charge of the free sites of the biomass. At low  $I$ , the intraparticle concentrations are much larger than the bulk concentration because of electrostatic attraction of cations by the negatively charged biomass. Since binding of each ion obviously increases with its concentration (or more correct: activity) near the binding site, these elevated concentrations also contribute to a higher amount of coordinately bound H or Cd. The effect of  $I$  is most pronounced at high pH and low  $[Cd]$ . Under these conditions the binding of both ions at low  $I$  is several times higher than the binding at high  $I$  (Figure 2). This observation can be explained by the large charge due to a larger number of free sites at high pH and low  $[Cd]$ .

**Model Parameters and Fit.** In each modeling case, the values for the total number of binding sites ( $C = 2.1$  mequiv/g) and the binding constant for protons (for the Donnan model for rigid particles:  $-p^{CH}K = 2.8$ , for the Donnan model with swelling  $-p^{CH}K = 2.65$ ) were adopted from preceding work (9). For the rigid Donnan model (DORI), the following cases were distinguished: (a) Only  $CM^K$  was optimized. The value for  $V_m$  was adopted from preceding work (9). (b) Both  $V_m$  and  $CM^K$  were optimized simultaneously.

For the Donnan model with swelling (DOSW), two alternative swelling correlations were considered: (a) A linear relation between active volume and number of free binding sites (eq 14) where the parameter  $Y_v$  was optimized in addition to  $CM^K$ . With this model version eqs 18 and 19 can be used. (b) A more complex correlation (eq 15) that in itself can already be regarded as an optimization for  $V_m$  (see section Modeling the Particle Volume of the Supporting Information) so that only  $CM^K$  was optimized.

The model parameters for systems without Ca are all listed in Table 1, those that have been optimized in this work are marked. The average absolute deviations of model predictions from experimental data, expressed in percent of the total binding capacity  $C$ , range from 5.8 to 6.5%. They can be considered rather similar so that it is not necessary to include swelling in the modeling for obtaining a good average fit of the experimental data.

In addition, it is possible to use  $V_m$  determined in preceding work (9). As shown in Table 1, the value obtained for  $V_m$  when both  $CCd^K$  and  $V_m$  were optimized (DOR1b) is identical to the one obtained earlier in pH titrations (DOR1a) (9). This means that the effect of electrostatic attraction in metal binding can be predicted from results obtained from proton

TABLE 1. Model Parameters for Mono-Metal Systems with Cd

model type	parameters			
	$I^C$ (mequiv/g)	$-p^{CH}K$ (-)	$^{Cd}K$ (L/mol)	$V_m$ (mL/g)
DOR1a	2.1	2.8	2.0 <sup>a</sup>	1.4
DOR1a	2.1	2.8	2.1 <sup>a,b</sup>	1.4
DOR1b	2.1	2.8	2.0 <sup>a</sup>	1.4 <sup>a</sup>
DOSWa	2.1	2.65	3.4 <sup>a</sup>	1.5 C <sup>a</sup>
DOSWb	2.1	2.65	3.1 <sup>a</sup>	1 + 0.5(C <sup>2</sup> - M <sub>q</sub> ) <sup>a</sup>

<sup>a</sup> Parameters optimized in this work. <sup>b</sup> Determined only from selected data at pH 4.5, low  $I$ ,  $M_q < 0.75^C$ .

binding experiments. For that reason the DOR1a model may be considered the best model because it is the conceptually simplest one and requires a minimum number of fitting parameters to be determined (i.e., the relation between the model complexity and results is most advantageous). The results of the DOR1a model application are depicted in Figures 2–4, 7, and 9, using  $^{Cd}K$  determined only from the data at pH 4.5 and low ionic strength. The choice of these conditions for determining the parameters is explained in the section Conditions Suitable for Parameter Determination in the Supporting Information. In order to also show the performance of the combined Donnan isotherm for the DOSWa model, which is conceptually a little more complicated, but which, on the other hand, has the advantage of being the most user-friendly, eq 18 was used for calculating the metal binding presented in Figures 5 and 6.

A comparison of the intrinsic and apparent binding constants is made in the section Change of Apparent Binding Constant and in Figure 9 in the Supporting Information.

**Modeling the Cadmium and Proton Binding.** Using the DOR1a model, which was the simplest model tested, the metal binding (Figure 2a) was very well predicted for all but the pH 4.5,  $I = 100$  mM series. For the latter conditions, swelling is of strong importance, and therefore a “rigid model” yields worse predictions than the “swelling models”. Especially for DOSWb the predictions of this series are much better than for DOR1a. Under most conditions, however, the DOR1a model is adequate, its average fit is comparable to that of the DOSW models. The proton binding (Figure 2b) is reasonably well predicted, though with a tendency of overestimating the proton binding. This again improves when using the DOSW models for which  $^{CH}K$  is lower.

Additionally to the total binding of Cd and H, the extents to which these ions are coordinately bound are also shown in Figure 2ab. For protons the two lines coincide ( $CH \sim Hq$ ), i.e., practically all binding is coordinate. For Cd, however, a significant portion of the binding is electrostatic: especially at low  $I$ , ~50% of  $^{Cd}q$  is bound electrostatically. The increasing amount of electrostatic binding with an increasing Cd concentration for the high ionic strength data is due to the fact that the intraparticle ionic strength becomes dominated by Cd, i.e.,  $[Cd_p] \gg [H_p] + [Na_p]$ . That means that the charge of the biomass particles is mostly balanced by Cd. If, however, the Cd concentration were to be increased further, all sites would eventually be occupied by Cd until “no” free sites are left and then, of course, the Cd binding would be exclusively coordinative and not electrostatic.

The generally higher direct contribution of electrostatic binding to  $^{M}q$  as compared to  $^{H}q$  is due to the fact that divalent ions are preferably accumulated near the charged interface. But apart from the direct contribution of electrostatic effects to binding (as  $[M_p]$  or  $[H_p]$ ) there is an indirect contribution:  $CM_{0.5}$  or  $CH$  are increased because of intraparticle activities that are higher than the bulk activities. This is also very strongly visible for protons: the change of  $CH$  with changing  $I$  is a consequence of elevated intraparticle activities for low  $I$ , with increasing  $I$  electrostatic effects become diminished.

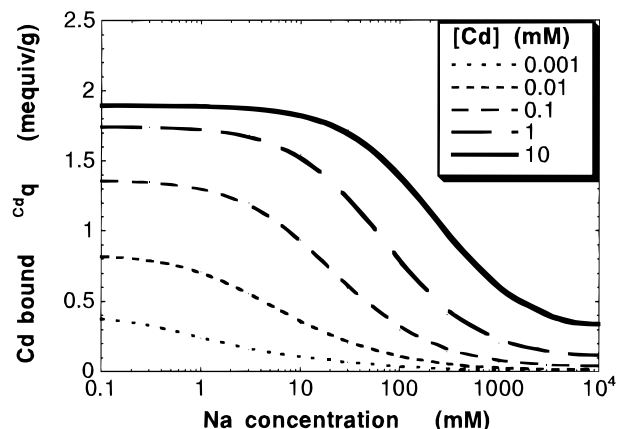


FIGURE 4. Importance of Na in Cd binding by *Sargassum* biomass at pH 4.5 (predictions by the Donnan model DOR1a assuming rigid particles).

This indirect contribution to cation binding shows in the change of the apparent binding constant, which will be discussed in the section Change of Apparent Binding Constant in the Supporting Information. It is possible to conclude that, while electrostatic effects contribute to H binding mainly in an indirect way, a significant direct contribution (~50%) exists for Cd binding.

**Importance of the Na Concentration for Cd Binding.**

First of all, it is necessary to make a distinction between conditions where (a) electrostatic effects are important or (b) the influence of changes in the Na concentration on Cd binding is noticeable.

Electrostatic effects are only negligible at a very high ionic strength, i.e., at a high concentration of Na or other ions. The Na concentration has no influence on Cd binding either if electrostatic effects are negligible (i.e., if  $I$  is very high) or if the Na concentration is very low.

An example of how the Na concentration affects Cd binding is given in Figure 4. The metal uptake at pH 4.5 predicted by the DOR1a model is plotted for different final Cd concentrations as a function of the Na concentration. A noticeable effect of the presence of Na (10% reduction in Cd binding as compared to Cd binding in Na-free system) is, for example, observed at Na = 0.6 mM for [Cd] = 0.01 mM (1 ppm) or at Na = 2.5 mM for [Cd] = 0.1 mM (10 ppm). These or even lower final metal concentrations can be regarded as typical for practical applications of biosorption as a ‘polishing’ step in the treatment of industrial wastewaters. Although in either of those cases  $[Na] \gg [Cd]$  was necessary to exert a noticeable effect, significant amounts of Na are usually present in wastewater. In the experiments performed in this study, for example, the final Na concentration resulting from pH adjustment (no additional NaL added) was already > 4 mM for [Cd] = 0.01 or 0.1 mM. This means that even without a deliberate salt addition the effect of Na is already noticeable.

A complete elimination of electrostatic effects (i.e., a leveling out of the curves, so that any further increase of Na does not reduce the Cd binding) only occurs at Na ~ 1000 mM. As a consequence, ionic strength effects should always be considered in the modeling of biosorption unless it is ensured that either (a)  $I$  is constant in all experiments, (b)  $[Na]$  is not too much larger than  $[M]$  (e.g.,  $[Na] < 0.1$  mM for [Cd] = 0.001 mM,  $[Na] < 10$  mM for [Cd] = 1 mM), or (c)  $I > 1000$  mM.

Only at a very high  $I$  is the use of a purely chemical binding model theoretically justified. In cases a and b electrostatic effects still affect the binding, but it is possible to model the binding as a function of the pH and Cd concentration alone. However, if the data points were obtained for different amounts of biomass added per solution volume (i.e. different “S/L” ratios), then the ionic strength in the samples may (even

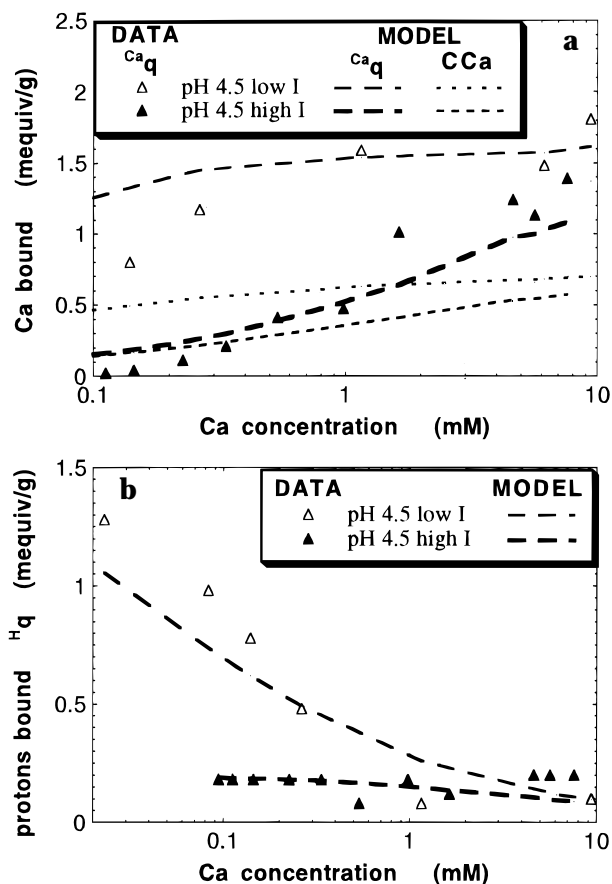


FIGURE 5. Calcium and proton binding by *Sargassum* biomass at different ionic strength levels and pH 4.5 (experimental data and predictions by the combined Donnan isotherm model): (a) total ( $Ca_q$ ) and covalent ( $CCa$ ) calcium binding; (b) total ( $H_q$ ) and covalent ( $CH$ ) proton binding.

at identical amounts of Na salt added, final pH and concentration of divalent metal ions) vary substantially as a consequence of pronounced differences in the amount of base added for pH adjustment. In conclusion, it is recommended to use a model that incorporates the influence of  $I$  due to electrostatic effects for most practically relevant conditions (i.e.,  $[M] \ll [Na] < 1000$  mM).

**Binding of Calcium in Mono-Metal Systems.** The binding of Ca and H in systems with Ca as the only divalent ion is depicted in Figure 5. The general behavior is similar to the Cd system (Figure 2a,b) except that Ca binding is lower and to a lesser degree coordinative. This is reflected in the binding constant  $^{Ca}K$  for Ca, which is much lower than the one for Cd (Table 1). The constant  $^{Ca}K = 0.84$  L/mol was determined from Ca binding data at pH 4.5 and  $I \sim 100$  mM only. Though this value is different from the one determined from all Ca binding data in monometal system  $^{Ca}K = 0.20$  L/mol, the average absolute errors for both constants in modeling all data, being 9.7 and 9.6% of the total binding capacity, respectively, do not differ widely. Since all models fitted the Cd binding data similarly well, only the DOSWa model, which is the most user-friendly one, was used for predicting Ca systems, including the two-metal system Cd–Ca (see below).

Though a significant portion ( $\sim 40\%$  for low  $I$ ,  $> 60\%$  for high  $I$ ) of the Ca binding is coordinative, the total Ca binding at pH 4.5 and low  $I$  according to the DORiA model would only be reduced by  $\sim 15\text{--}20\%$  if  $^{Ca}K = 0$  (i.e., purely electrostatic binding) was assumed (data not shown). This means that for obtaining a preliminary estimate of light metal binding before any experiments are conducted one can assume that it binds only electrostatically and use the data from pH titrations at different  $I$  in order to predict the Ca binding. Also, this was

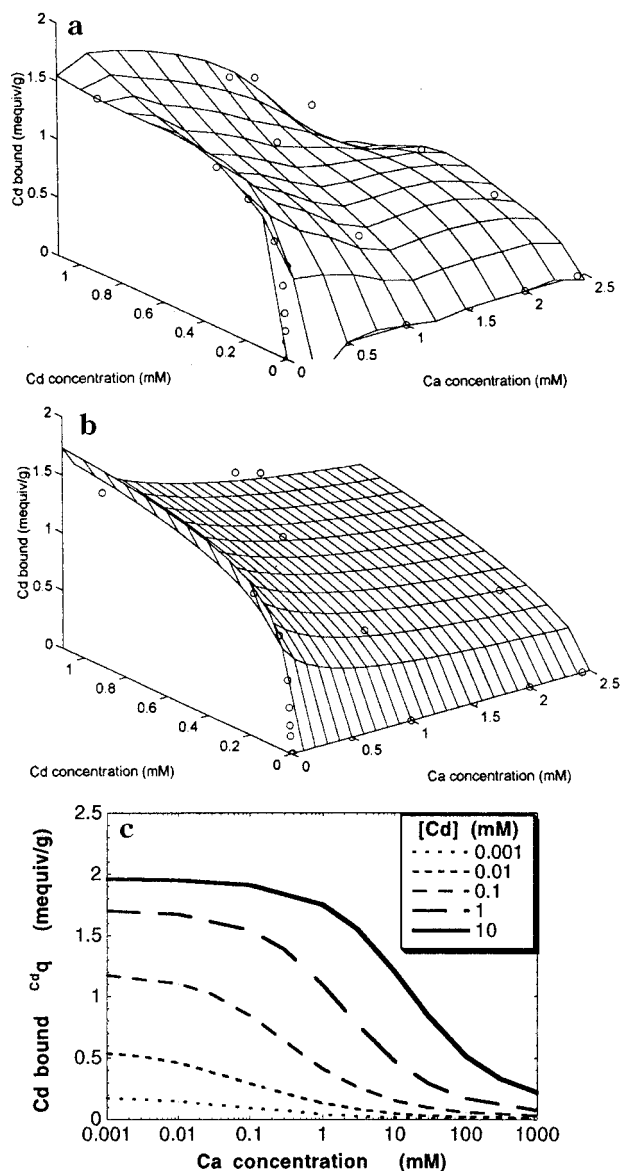


FIGURE 6. Cadmium binding by *Sargassum* biomass in the two-metal system Cd–Ca as a function of both metal concentrations at pH 4.5 and low ionic strength: (a) 3D plot of the Cd binding (experimental data); (b) 3D plot of the Cd binding (predictions by the combined Donnan isotherm model); (c) 2D plot of the Cd binding (predictions by the combined Donnan isotherm model).

the reason for choosing the high  $I$  data for determining  $^{Ca}K$ , since the binding at low  $I$  is very insensitive to changes in  $^{Ca}K$ .

**Influence of Ca on Cd Binding in Di-Metal Systems.** The combined Donnan isotherm (eqs 18 and 19) with the parameters  $Y_v = 1.5$  mL/mequiv,  $^{Cd}K = 3.4$  L/mol (determined for the DOSWa model in systems with Cd alone), and  $^{Ca}K = 0.84$  L/mol (determined only from the data at  $I \sim 100$  mM for Ca mono-metal systems) was used in order to predict the Cd binding in the two-metal system Ca–Cd at different ionic strength levels. The modeling errors were similar to the ones determined in the modeling of Cd binding in mono-metal systems (5.8–6.5% of  ${}^tC$ , depending on the model used): the average absolute error of Cd binding in the two-metal system was 5.8% of the total binding capacity  ${}^tC$  for low  $I$  and 6.7% for  $I \sim 100$  mM. This means that the behavior of two-metal systems can be predicted from one-metal systems without losing precision. Similar prediction possibilities had been shown to exist for the competition among heavy metals (20).

As an example, Figure 6 shows the Cd binding at pH 4.5

and low  $I$  as a function of both Ca and Cd concentrations. The experimental data are depicted as a 3D plot in Figure 6a. One can see that the Cd binding is visibly reduced with the increasing Ca concentration. The same trend is reflected in Figure 6b, which shows the model predictions with the DOSWa model, using the convenient combined Donnan isotherm (eq 18). For easier quantitative evaluation of the Ca influence on the Cd binding, Figure 6c shows a series of 2D "cuts" through the 3D surface of Figure 6b at constant [Cd] values. It can be seen that a 10% reduction of the Cd binding is reached when [Ca] is ~5–10% of the [Cd]. For a 50% reduction, [Ca] has to be between 2 (for [Cd] = 10 mM) and 100 (for [Cd] = 0.001 mM) times higher than [Cd].

Comparing the influence of Ca and Na on the Cd binding (Figures 6c and 4), one can see that a Ca concentration of ~0.4 mM has a similar effect as a Na concentration of ~20 mM, e.g., by reducing the Cd binding at [Cd] = 0.1 mM by 50%. As expected, the divalent ion Ca has a higher effect on the Cd binding both due to its higher electrostatic accumulation and because it partially binds coordinately. Given a fixed ratio of light metal per heavy metal in solution, the influence of the light metals is more pronounced at higher concentrations. For the one-site model presented here, an explanation is that fewer free binding sites are available and ion competition is therefore more severe. The results of the work presented here are compared with those from the literature in the sections Comparison with Ca Competitions Results in the Literature and Comparison with Donnan Models in the Literature in the Supporting Information.

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## Supporting Information Available

Text, a table, and three figures detailing model simplifications, particle swelling, conditions for parameter determination, stoichiometry plot, change of apparent binding constant, and comparison with Ca competition results and with Donnan models in the literature (13 pp) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for \$27.00 for photocopy (\$29.00 foreign) or \$12.00 for microfiche (\$13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is also available via the World Wide Web at URL <http://www.chemcenter.org>. Users should select Electronic Publications and then Environmental Science and Technology under Electronic Editions. Detailed instructions for using this service, along with a description of the file formats, are available at this site. To download the Supporting Information, enter the journal subscription number from your mailing label. For additional information on electronic access, send electronic mail to [sihelp@acs.org](mailto:sihelp@acs.org) or phone (202)872-6333.

## Glossary

### Model Abbreviations

DORI	Donnan model assuming rigid particle
DOSW	Donnan model assuming particle swelling

## Variables

${}^tC$	total amount of binding sites $C$ , mequiv/g
$I$	ionic strength, mmol/L
${}^c_jK$	equilibrium constant (formation) for binding of cation $j$ , L/mmol
$m$	dry weight of biomass, g
$p^c_jK$ , $pX$	$-\log$ of ${}^c_jK$ (in L/mol) or of concentration (in mol/L), (–)
$j_q$	binding (coordinative plus electrostatic) of cation $j$ , mequiv/g
$V$	volume of solution, L
$V_m$	specific cation binding volume per dry weight, L/g
${}^tV_m$	specific total particle volume per dry weight, L/g
$Y_v$	fitting parameter for $V_m$ , mL/mequiv
$z_j$	charge of species $j$ , –
$\lambda$	concentration factor, –
[X]	concentration (of molecular species X), mmol/L
$\sum[M]$	sum of the concentrations of all divalent cations, mmol/L

## Indices

app	apparent, bottom right
i	initial, bottom right
p	average in particle, bottom right
t	total, top left

## Molecular Species

C	free binding sites
$CM_{0.5}$ , $C_2M$	binding site occupied by divalent cation (Cd, Ca)
H	protons
L	anion
M	divalent cation, e.g., Cd, Ca
Na	sodium
X	any ionic species

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