Biosorption of Cadmium by the protonated Macroalga *Sargassum muticum*: binding analysis with a non-ideal, competitive and thermodynamically consistent adsorption (NICCA) model

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ABSTRACT

Protonated biomass of the seaweed *Sargassum muticum* was investigated for its ability to remove cadmium(II) from aqueous solutions. In this work, a non-ideal, semi-empirical, thermodynamically consistent (NICCA) isotherm was proposed to fit the experimental ion binding data obtained in $NaNO_3$ 0.05 mol·L^{-1}. This model describes satisfactorily the competition between protons and metal ions. Moreover, it reflects the complexity of the macromolecular systems that take part in biosorption considering the heterogeneity of the sorbent. It was demonstrated in this work that NICCA isotherm constitutes a great improvement with respect to a simpler Langmuir competitive equation, which was not able to describe satisfactorily all the experimental data. Potentiometric acid-base titrations in absence of cadmium were made to estimate the maximum amount of acid functional groups (2.61 mmol·g^{-1}), and the conditional proton binding parameters, $\log \widetilde{K}_H$ (3.8) and m_H (0.54). The values of the binding parameters for the cadmium ion were chosen to provide the best simultaneous description of the isotherm at pH 4.5, as well as the dependence of cadmium adsorption on pH. Values of $\log \widetilde{K}_{Cd}$ (3.1), n_{Cd} (1.8) and p (0.19) in the case of NICCA isotherm or $\log K_{Cd}$ (2.94-3.4) for Langmuir competitive models were obtained. Kinetic experiments were performed at two different pH values (3.0 and 4.5), establishing the time dependence that represents the sorption of cadmium with a pseudo-second-order kinetic model. It was observed that 4 hours are enough to ensure that the equilibrium uptake was reached.

Keywords: Biosorption, algae, cadmium, *Sargassum muticum*, cross-link, NICCA.

INTRODUCTION

Sargassum muticum has been considered an invasive species in European waters, making its obliteration very important. Biosorption, the passive removal of contaminants (metallic cations, anions, colorants, etc.) by inert biomass, could be a powerful alternative to attempt the alga eradication. This marine macroalga came from Japanese and Chinese waters mainly due to aquaculture industry, and it is now playing a conspicuous role in the recipient ecosystems, taking the place of keystone species and being economically and ecologically harmful, i.e. a pest.

The employment of this alga as a useful biosorbent for heavy metal removal has been previously studied [1-4]. However, the use of protonated *S. muticum* alga (proposed in this paper), which results in a great increase in adsorption capacity, biomass stabilization and attrition characteristics compared with native biomass, was not systematically studied for its practical application.

The development of mathematical models that reflect the influence of variables such as pH, ionic strength or presence of competing cations is very useful for the quantitative description of the biosorption process in order to predict metal adsorption. Langmuir and Freundlich models have been widely used to describe biosorption data, although they were developed under many assumptions that are well known not to be meet in the case of biosorption. Other improved models accounting for pH or ionic strength effects were proposed by different authors [5,6].

In this work NICCA competitive isotherm is proposed to fit experimental data. It addresses heterogeneity and stoichiometry effects, and it was initially developed for humic and fulvic acids [7]. This model was able to describe different types of experiments (metal sorption isotherms, acid-base titrations and influence of pH on biosorption) simultaneously with great accuracy and a relatively small number of

parameters. This constitutes a great improvement with respect to the simpler Langmuir or Freundlich models.

The results obtained in a previous paper [2], dealing with the physical chemistry of cadmium biosorption on the native and pretreated seaweed *S. muticum*, encouraged further studies focusing on the suitability of the protonated algae for cadmium recovery process. The acid treatment led to an increase close to 50% for the cadmium uptake, compared with the raw biomass and a greater stabilization of the biomaterial. Moreover, it allows the release of metal and regeneration of the alga using a mineral acid in only one step.

MATERIALS AND METHODS

1. Biomass

Samples of the brown marine alga *Sargassum muticum* were collected from the coast of A Coruña (Galicia, NW Spain). The seaweed was washed with tap and deionized water to eliminate impurities. After drying at 60 ℃ for 12 hours, it was crushed and ground in an analytical mill (IKA A 10) to granules of 0.5-1 mm and stored in polyethylene bottles until use.

This algal raw biomass was protonated [8] by soaking and shaking it in a 0.2 mol·L^{-1} HNO$_3$ (Merck p.a.) solution in a rotary shaker (175 rpm) for 4 h, at a biomass concentration of 10 g·L^{-1}. Afterwards, the material was rinsed thoroughly with deionized water until pH 4.5 was attained. Following filtration, treated biomass was dried in an oven at 60℃ overnight.

2. Experiments

2.1. Kinetic studies

The experiments were carried out in a glass cell at constant temperature (25.0 ± 0.1 °C) adding 0.25g of the biomass to 100 ml of a 2.2 mmol·L^{-1} solution of cadmium(II) prepared by dissolving accurately weighed samples of $Cd(NO_3)_2 \cdot 4H_2O$ (Merck p.a.) in deionized water. Two series of experiments were performed at pH values of 3.0 (natural pH) and 4.5 (the same value employed in the equilibrium studies). The ionic strength was adjusted to 0.05 mol·L^{-1} with $NaNO_3$ (Merck p.a.). A cadmium ion selective electrode (CdISE, Orion) with a Ag/AgCl reference electrode (Orion), previously calibrated as a function of the free cadmium concentration at the same ionic strength, was used to follow the reaction kinetics.

The cadmium uptake at each moment was calculated from the equation:

$$q_{Cd,t} = \frac{V \cdot (c_{Cd,i} - c_{Cd,t})}{m_s} \qquad (1)$$

where V is the volume of cadmium solution, $c_{Cd,i}$ is the initial cadmium concentration, $c_{Cd,t}$ is the concentration of cadmium in solution at a given time, and m_s is the mass of sorbent (dry weight).

2.2. Potentiometric titrations

The proton binding equilibria were studied through potentiometric titrations of the protonated biomass using glass electrodes (GK2401C Radiometer). Electromotive force measurements were done with a Crison micropH 2000 meter. For each titration, ca. 0.5 g of protonated algal biomass were placed in a thermostated titration cell at 25.0 ± 0.1 °C, with 100 mL of 0.05 mol·L^{-1} $NaNO_3$ solution. Inert gas (nitrogen 99.9995%) was bubbled into the solution. A certain amount of HNO_3 (standardized with *di*-Sodium tetraborate decahydrate, Merck p.a.) was also added to yield an initial pH

value ca. 2. The titrating solution (0.05 mol·L^{-1} NaOH, Merck p.a., prepared with boiled deionized water and standardized with potassium hydrogen phthalate, Carlo Erba PRE) was added from a Crison microBu 2031 automatic burette.

The procedure followed for the titrations and glass electrode calibrations was described in greater detail elsewhere [9].

The amount of proton bound was calculated from the acid and base additions by means of charge balance considerations:

$$Q_H = Q_{max,H} - \frac{V_T}{m_s}\left([H^+] + \frac{V_b C_b - V_a C_a}{V_T} - \frac{K_w}{[H^+]}\right) \qquad (2)$$

where V_i, C_i are the volume and concentration of the acid and base added (subscripts a and b refer to acid and base, respectively), V_T is the total volume in the titration vessel, K_W is the ionic product of water, and $Q_{max,H}$ is the total amount of titratable groups, calculated from the equivalence point of the titrations.

2.3. Adsorption isotherms

A volume of 40 mL of eight cadmium(II) solutions of several concentrations (from 0.089 to 3.11 mmol·L^{-1}), was placed in 100 mL Erlenmeyer flask containing 0.1 g of alga. Each solution was prepared by dissolving the appropriate amount of $Cd(NO_3)_2 \cdot 4H_2O$ in $NaNO_3$. The mixtures were stirred in a rotary shaker at 175 rpm for 4 hours until equilibrium was reached; a NaOH solution (0.3 mol·L^{-1}) was used for pH adjustment to a value of 4.5±0.1. After that, the algal biomass was filtered through a 0.45 μm pore size cellulose nitrate membrane filter and the filtrate was analysed for the remaining cadmium ion concentration by differential pulse anodic stripping voltammetry (DPASV) using a 757 VA Computrace (Metrohm) with a conventional

system of three electrodes: hanging mercury drop electrode as working electrode, a Pt auxiliary electrode and 3 mol·L^{-1} Ag/AgCl as reference electrode.

The amount of cadmium sorbed at equilibrium, Q_{Cd}, which represents the metal uptake, was calculated from the difference in metal concentration in the aqueous phase before and after adsorption, according to an equation formally identical to Eq. (1), but referred to the equilibrium concentration; where now c_{Cd}, the equilibrium concentration of cadmium in solution, substitutes $c_{Cd,t}$.

2.4. Influence of pH on metal adsorption

The dependence of the metal uptake on pH was studied following the procedure described for the adsorption isotherms, using a 2.22 mmol·L^{-1} cadmium concentration solution in the pH range from 1 to 6, with ionic strength adjusted to 0.05 mol·L^{-1} with NaNO$_3$. The pH adjustments were carried out using NaOH and HNO$_3$ solutions.

MODELS

The development of a technology based on biosorption implies the use of mathematical models for the quantitative description of the process. These models should be capable of predicting metal biosorption, reflecting the mechanism of the sorbate uptake and the influence of variables such as pH, ionic strength, presence of competing cations, etc.

The most commonly used model in biosorption is the Langmuir isotherm, Eq. (3). This model incorporates easily interpretable constants: $Q_{max,Cd}$, that represents the maximum biosorption capacity and b, the affinity for the sorbate, which can be used to compare the biosorption performance. The Langmuir isotherm assumes that all sites have the same affinity and the secondary effects between sorbed species are negligible.

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However, this equation may reproduce satisfactorily the experimental data if environmental parameters, such as pH, are controlled carefully during experiments.

$$Q_{Cd} = \frac{Q_{max,Cd}\,b\,c_{Cd}}{1 + b\,c_{Cd}}$$ (3)

In order to account for stoichiometry and pH effects, a modified competitive Langmuir sorption model, Eq. (4), was proposed by Schiewer et al. [10]. It describes the metal and proton binding at equilibrium as a function of pH and free metal ion concentration in solution.

$$Q_{Cd} = n\,Q_{max,H}\,\frac{\left(K_{Cd}\,c_{Cd}\right)^n}{1 + K_H c_H + \left(K_{Cd}\,c_{Cd}\right)^n}$$ (4)

where K_{Cd} and K_H are the equilibrium constants for the binding of cadmium and protons, respectively; c_H is the proton concentration in solution, and the parameter n defines the stoichiometry ratio, 1:1 ($n=1$) or 1:2 ($n=0.5$).

However, these isotherm models were developed under many assumptions that are often not met in complexation phenomena of macromolecular systems (and particularly in biosorption); for instance, they do not take into account the presence of functional groups with different acidities.

Carboxylic groups are the main functionalities involved in metal binding reactions in brown algae [11]. Nevertheless, a smaller amount of functional groups such as sulphonic groups from fucoidans and, to a lesser extent, N- and S- containing groups from proteins may also be important for metal ion binding. As a consequence of this chemical heterogeneity, there will be a more or less broad range of affinities for the inorganic ions.

Moreover, it is expected a polyelectrolytic effect as a consequence of the ionization of these functional groups at the experimental pH values, which influences

the apparent (overall) affinity for the charged species (protons or metal cations) and is responsible for what is called *non-specific binding*. This effect was previously studied for protons [9,12]. The study for cadmium will be undertaken in future works.

Finally, an important issue to consider in the biosorption phenomena are the conformational effects such as the swelling/shrinking behaviour of the biomass particles, the leaching of soluble organic matter from the biomass and what is of most interest in brown algae, the formation of the characteristic alginate arrangement known as the *egg-box* structure [13,14]. These effects involve alterations in the steric conformation of the sorbent polymers caused by changes in the chemical conditions of the medium, which may affect biosorption to a large extent.

These phenomenons reflect the complexity of macromolecular systems that take part in biosorption. As a consequence, the Langmuir competitive model could result too simple to describe all the experimental data with the desired accuracy. In this case, new models with additional parameters that reflect the complexity of the system would be required.

The literature about humic substances has paid much attention to the study of competitive ion binding. Very recently, a non-ideal competitive adsorption model (NICCA) was developed [7] (and references therein) for humic and fulvic acids. This model is a semi-empirical, thermodynamically consistent model, which addresses the effects of chemical heterogeneity and metal-ligand stoichiometry; yet, its application is fairly simple. The basic NICCA equation for the overall binding of species i in the competitive situation is:

$$\theta_i = \frac{\left(\tilde{K}_i c_i\right)^{n_i}}{\sum_i \left(\tilde{K}_i c_i\right)^{n_i}} \frac{\left[\sum_i \left(\tilde{K}_i c_i\right)^{n_i}\right]^p}{1 + \left[\sum_i \left(\tilde{K}_i c_i\right)^{n_i}\right]^p} \tag{5}$$

where θ_i is the coverage fraction of the species i, $\tilde{K}_i$ is the median value of the affinity distribution for species i, p is the width of the distribution (usually interpreted as a generic or intrinsic heterogeneity seen by all ions) and n_i is an ion-specific non-ideality term. Strictly speaking, c_i should be the local concentration of species i at the binding site, i.e., the bulk concentration (or activity) corrected for the double layer effect (for instance, the concentrations in the Donnan phase). In this work, the bulk concentrations will be used instead and, therefore, the metal binding constants calculated will be conditional parameters (referred to 0.05 mol·L^{-1} ionic strength).

The following normalization condition is used to calculate the amount of species i bound, Q_i:

$$Q_i = \theta_i \left(\frac{n_i}{n_H} \right) Q_{max,H} \qquad (6)$$

where $Q_{max,H}$ is the maximum binding capacity for protons, which has been calculated from the equivalence point of the acid-base titrations in absence of heavy metal.

The ratio n_i/n_H has been interpreted by Kinniburgh et al [7] in terms of stoichiometry and cooperativity. When this ratio is less than one, then the maximum binding of species i is lower than the total amount of sites (defined as the amount of titratable protons), which would be a consequence of some degree of multidentism. On the other hand, a value of n_i/n_H greater than one would reflect some degree of cooperativity. Finally, if $n_i/n_H =1$, it can be demonstrated that the maximum proton/metal exchange ratio is one.

If only the proton binding is considered (i.e., absence of competing ions), Eqs. (5) and (6) simplify to the Langmuir-Freundlich (LF) isotherm:

$$Q_H = Q_{max,H} \frac{\left(\tilde{K}_H c_H \right)^{m_H}}{1 + \left(\tilde{K}_H c_H \right)^{m_H}} \qquad (7)$$

where now the heterogeneity parameter m_H describes the combined effect of n_H and p ($m_H = n_H \cdot p$). In the case of a homogeneous system (where all the binding sites behave as independent, chemically equivalent sites) n_i and p are 1, and then the mono or multicomponent Langmuir isotherm is obtained.

RESULTS AND DISCUSSION

1. Kinetics of adsorption

Kinetic studies of cadmium adsorption by the acid-treated *Sargassum muticum* were accomplished to estimate the time required to reach the sorption equilibrium. Figure 1 shows the kinetics of cadmium adsorption for an initial cadmium concentration of 2.22 mmol·L^{-1}. The experiments were performed at natural pH (3.0) and at the same pH value (4.5) used in adsorption isotherm studies. It can be observed that the process is relatively fast, especially in the first case where 90% of the equilibrium uptake is achieved in the first 20 minutes of contact. When the pH value is adjusted, the system took over 75 minutes to adsorb identical percentage of metal; this increment is probably due to conformational effects that occur in the alga as cadmium is complexed when pH is adjusted to 4.5, which are reflected in the decrease in the rate constant. Therefore, a time of 4 hours was selected for the following adsorption experiments in order to ensure that the equilibrium uptake was reached. This equilibrium time is shorter than those usually employed for the adsorption of cadmium by other adsorbent materials [15-17], so it can constitute a great advantage when biosorption systems are designed, as it will facilitate shorter adsorption columns ensuring, in principle, efficiency and economy.

In order to establish the time dependence representing the sorption of cadmium in the alga during the kinetic experiments, a pseudo-second-order model proposed by Ho [18,19] was chosen among others (Elovich, first and pseudo-first order, second order

and diffusion) which can only reproduce with accuracy the first 5 or 10 minutes of experimental data. The kinetic rate equation, Eq. (8), can be considered a pseudo-second order chemical biosorption process with respect to the algal biosorption sites:

$$\frac{dq_{Cd,t}}{dt} = k \cdot (Q_{Cd} - q_{Cd,t})^2 \qquad (8)$$

where k (g·mmol^{-1}·min^{-1}) is the pseudo-second order constant of sorption.

Separating variables in Eq. (8) and integrating for the boundary conditions $q_{Cd,t} = 0$ at $t = 0$ and $q_{Cd,t}$ at time t, the following equation is obtained:

$$q_{Cd,t} = \frac{Q_{Cd}^2 k \cdot t}{1 + Q_{Cd} k \cdot t} \qquad (9)$$

which can be linearised to the following equation

$$\frac{t}{q_{Cd,t}} = \frac{1}{k \cdot Q_{Cd}^2} + \frac{1}{Q_{Cd}} \cdot t \qquad (10)$$

The equilibrium sorption capacity, Q_{Cd}, and the pseudo-second order rate constant, k, were experimentally determined from slope and intercept of straight-line plots of $t/q_{Cd,t}$ against t. The values obtained are shown in Table 1. These parameters can change depending on experimental conditions as it was found by Lodeiro et al. [2], who obtained simple empirical equations to derive the dependence of k and Q_{Cd} under different experimental conditions (ionic strength, algal mass and metal concentration). The fits show very good regression coefficients and good compliance between predicted curves and the experimental data points was found. However, the fact that experimental data may be fitted by a given rate expression is not sufficient evidence that the molecularity of the reaction is that implied by the rate expression [20].

2. Equilibrium studies

2.1. Description of H^+/Cd^{+2} binding data

The cadmium uptake capacity of the biomaterial was tested by means of batch sorption experiments performed with the protonated *Sargassum* biomass in $NaNO_3$ aqueous solutions of 0.05 mol·L^{-1} overall ionic strength. As a matter of comparison the experimental data obtained were fitted to a simple Langmuir isotherm (Figure 2). The maximum uptake ($Q_{max,Cd}$) obtained was 1.2 mmol·g^{-1} (Table 2), equivalent to 13% of the total dry weight of the alga. As it is expected, this value is higher than the obtained for the raw *Sargassum* (0.58 mmol·g^{-1}) [2]; however, the $Q_{max,Cd}$ value found for protonated biomass in the same conditions, but in absence of electrolyte addition, is slightly lower (0.85 mmol·g^{-1}) (Table 2). It is well known that light metal ions, such as sodium, compete with divalent cations for the electrostatic binding to the biomass [11]. Therefore, the cadmium sorption should decrease as the concentration of light metal ions increases. Indeed, at low metal concentration, the cadmium uptake is appreciably enhanced in absence of electrolyte, while as the metal concentration increases this effect decreases. This can be clearly observed in the comparison between the isotherms in presence and absence of $NaNO_3$ shown in Figure 2. Therefore, the fact that $Q_{max,Cd}$ was lower in deionized water than in presence of background salt is attributed to model fitting artifacts.

The acid-base titrations of protonated biomass samples allow the evaluation of the maximum amount of acid functional groups, $Q_{max,H}$ (Table 3) by estimation of the position of inflection point in the resulting titration curve [2]. This amount is 2.2 times greater than the maximum cadmium uptake capacities. This fact can be explained if a certain degree of multidentism in the binding mechanism is present; i.e., more than one acid group can be involved in the binding to a single metal ion.

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Figure 3 shows the proton binding data obtained from the potentiometric titrations. It has already been mentioned that the NICCA equation is reduced to a LF isotherm, Eq. (7), under these conditions (absence of heavy metal ions). As it can be observed, the fit of this equation to the experimental data is very good. Similar results have been obtained with other seaweed species [9]. On the other hand, the fit of proton binding data to a simple Langmuir isotherm is also shown in Figure 3. This equation is not able to describe satisfactorily the experimental data, due to the fact that it assumes an homogeneous ligand behaviour (i.e., an affinity distribution represented by a discrete value of the binding constant).

The procedure followed for the interpretation of proton and metal binding in terms of competitive adsorption isotherms was as follows. The proton binding data (in absence of cadmium) (Figure 3) was used to obtain the best fit values of the conditional parameters in Eq. (7) ($Q_{max, H}$, $\log \tilde{K}_H$ and m_H). These values were assumed to apply also in the presence of cadmium. The binding parameters for the cadmium ion were chosen to provide the best simultaneous description of the isotherm at constant pH (4.5), and the data of cadmium adsorption vs. pH. The values of $\log \tilde{K}_{Cd}$, n_{Cd} and p, in the NICCA isotherm or $\log K_{Cd}$ in the Langmuir competitive models, were first optimized by least squares fit for each data set, and then average values (see Table 3) were used to plot the model calculations showed in Figure 4 and Figure 5. In the NICCA model, the separation of n_H and p was made using the constraint $m_H = n_H \cdot p$.

As it is shown in Figure 4, an S shape curve centred at pH 3-4 was obtained from the plot of cadmium binding vs. pH. This curve is characteristic of other seaweeds and it is closely related to the acid-base properties of the functional groups on the algal cell surface, mainly carboxylic groups, and to the metal solution chemistry [21-23]. At pH values lower than 8.0, cadmium is present in its free ionic form, Cd^{+2}, so the

increase in cadmium adsorption from pH 2.0 to pH 4.0 cannot be explained by the change in cadmium speciation but by the type and ionic state of the carboxyl functional groups that present a dissociation constant (in log units) between 3 and 4 [24]. This implies that the metal biosorption depends on the protonation or deprotonation of the cell wall polymer functional groups. Above pH 4.5 the cadmium biosorption capacity levelled off at a maximum value reaching a plateau.

The inset of Figure 4 and the Figure 5 show the fits of the NICCA (Eq. (5-6)) and Langmuir competitive (Eq. (4)) models to the cadmium uptake data. In the latter case, K_H was fixed to the value obtained from the Langmuir fit of the proton binding data (dashed line in Figure 3).

The data obtained in the plots of cadmium(II) uptake vs. pH at pH values lower than pK_H were excluded from the model discussion. The carboxylate groups are closely associated with the hydrogen ions at these low pH values, restricting access to sites to cadmium ions and resulting in a low cadmium uptake. Therefore, the cadmium uptake is very small, but not negligible. It can be a result of the presence of a relatively low amount of very strong acid groups like sulfonic groups from fucoidans [25], that were not included in the model. Crist et al. reported the pK of biomass sulfate groups to be between 1 and 2.5 [26].

It can be observed that only the NICCA model can reflect adequately the experimental data, employing the same constants attained through proton binding studies, in both experiments (concentration and pH dependence of cadmium uptake). In fact, this model could constitute a powerful tool for the description of competition between metals and protons for the algae binding sites.

However, despite these encouraging results, the knowledge of the geometric parameters that determine the electrostatic description of the system would be required

in order to derive the intrinsic binding parameters (i.e., independent of the bulk ionic strength) [27].

Since the value of the ratio n_{Cd}/n_H is lower than one (in fact, 0.6), the maximum metal binding is somewhat lower than the total number of acid sites, which would reflect a certain degree of multidentism as it was explained before. In fact, FTIR analysis demonstrates the participation of carboxyl groups in the formation of chelates of different stoichiometries [28,29]. However, it must be pointed out that the NICCA isotherm does not require a priori assumptions about the binding stoichiometry [7].

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1

Sorption of cadmium as a function of contact time, for aqueous suspensions of the protonated *S. muticum* in 0.05 mol·L^{-1} NaNO$_3$ and 2.22 mmol·L^{-1} initial cadmium concentration. The symbols correspond to the experimental points at pH 4.5 (open squares) and pH 3.0 (open circles). The solid lines represent the best fits to Eq. (9).

Figure 2

Cadmium biosorption isotherms for suspensions of protonated *S. muticum* (2.5 g·L^{-1}) in deionized water (filled triangles) and in 0.05 mol·L^{-1} NaNO$_3$ (open triangles) at pH 4.5 ± 0.1 and 25 ºC. The lines represent the fits to the Langmuir equation, Eq. (3).

Figure 3

Proton binding by *S. muticum* (in absence of cadmium) in 0.05 mol·L^{-1} NaNO$_3$. Symbols represent experimental points, solid line corresponds to the best fit of a Langmuir-Freundlich isotherm, Eq. (7), and dashed line to a simple Langmuir isotherm. In both cases, the value of $Q_{max,H}$ was set equal to the total amount of titratable groups, determined from the equivalence point of the titrations.

Figure 4

Effect of pH on cadmium biosorption by 2.5 g·L^{-1} of protonated *S. muticum* in 0.05 mol·L^{-1} NaNO$_3$ at 25ºC, with initial cadmium concentrations of 2.22 mmol·L^{-1} (open rhombuses). The inset represents the fit of the data at the higher pH values to

different equations: NICCA isotherm (solid line), competitive Langmuir isotherm assuming 1:1 stoichiometry (dotted line) and assuming 1:2 stoichiometry (dashed line).

Figure 5

Cadmium binding by *S. muticum* at pH= 4.5 $\pm$ 0.1 in 0.05 mol$\cdot$L^{-1} NaNO$_3$. Symbols represent experimental points, solid line is the fitted NICCA isotherm, Eqs.(5-6), dotted line is the competitive Langmuir isotherm assuming 1:1 stoichiometry and dashed line assuming 1:2 stoichiometry, Eq. (4).
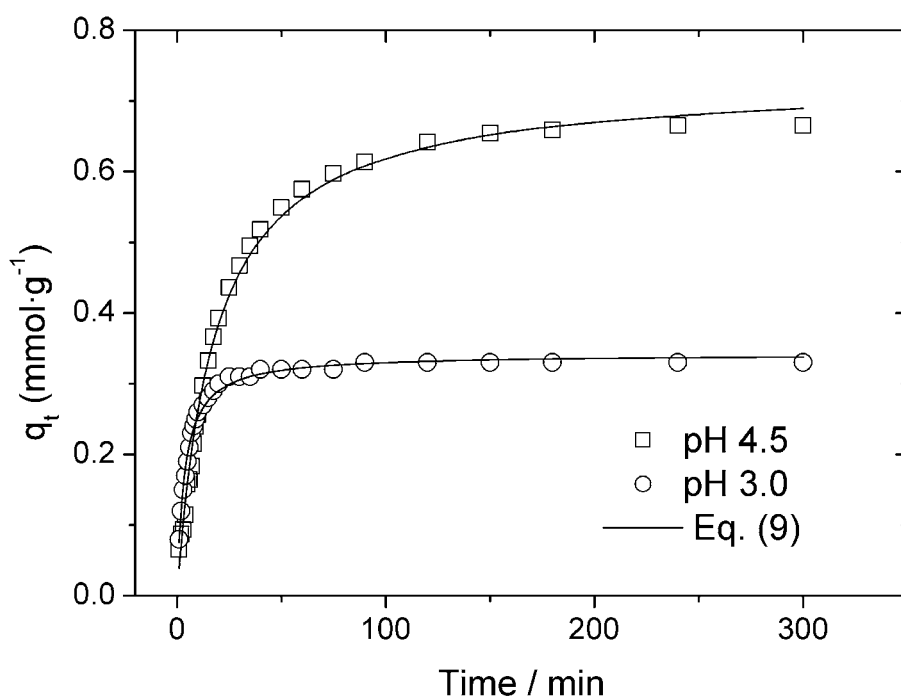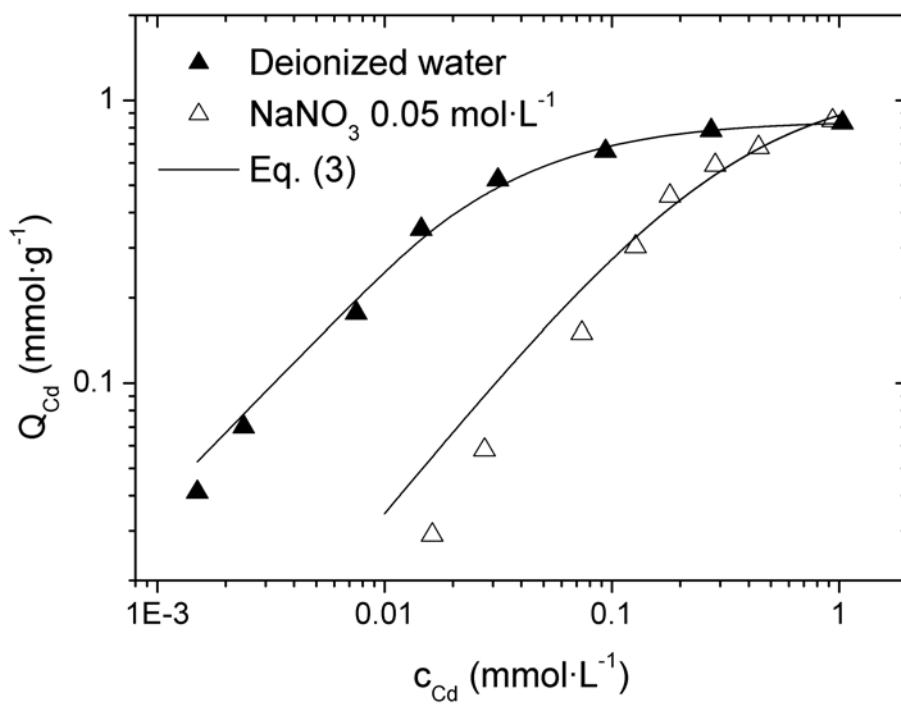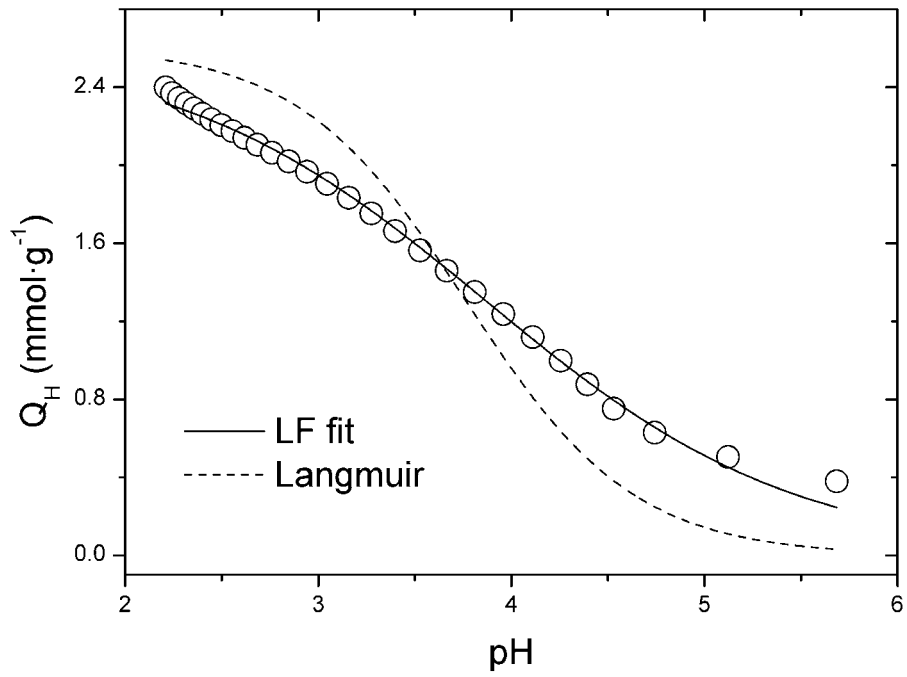
Figure 1
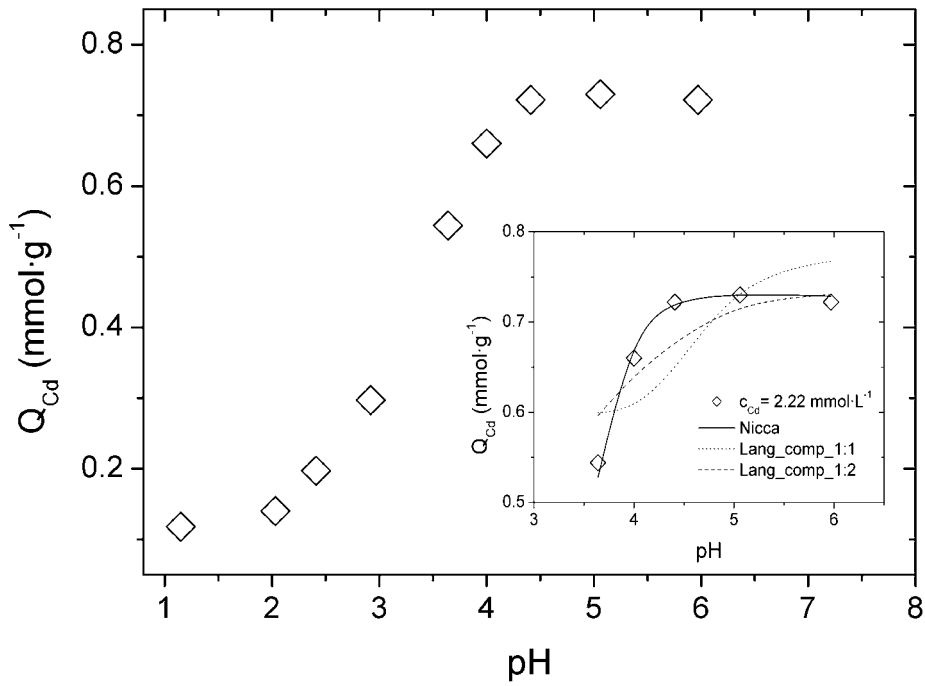

Figure 2

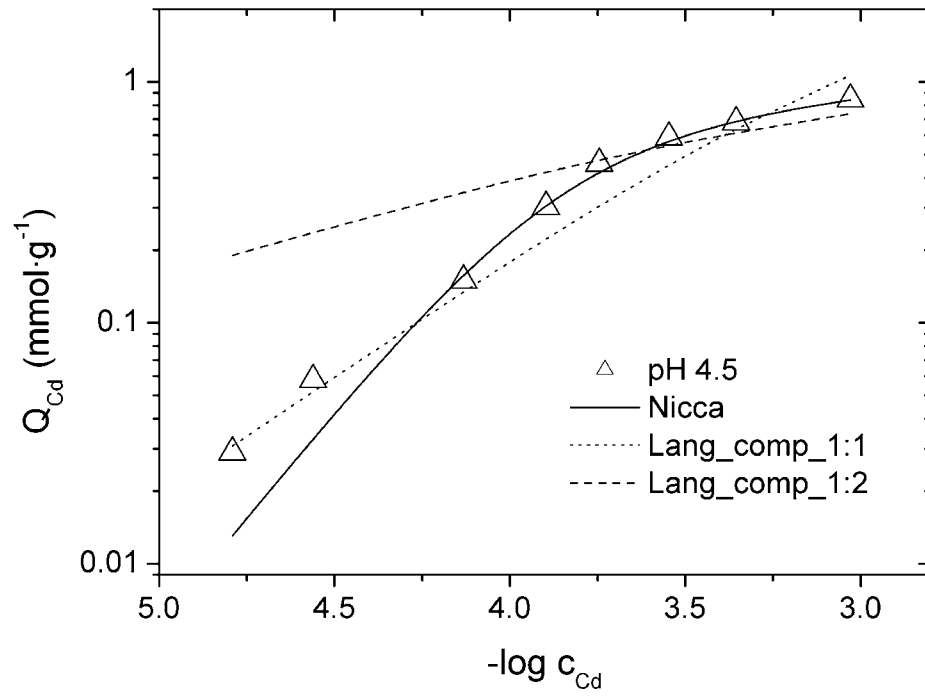**Figure 3**

Figure 4

Figure 5

TABLES

Table 1

Parameters obtained from the pseudo-second order rate reaction. 2.5 g·L^{-1} of algal dose (protonated *S. muticum*) with ionic strength adjusted to 0.05 mol·L^{-1} with NaNO$_3$ at 2.22 mmol·L^{-1} initial cadmium concentration. (Errors between brackets).

Final pH	Q$_{Cd}$ (mmol·g^{-1})	k (g·mmol^{-1}·min^{-1})	r^2
4.5	0.731 (0.007)	0.076 (0.003)	0.9962
3.0	0.342 (0.002)	0.83 (0.03)	0.9929

Table 2

Optimal Langmuir isotherm parameters, Eq. (3), estimated for cadmium binding by the protonated *Sargassum* biomass at pH 4.5 in deionized water and with ionic strength adjusted to 0.05 mol·L^{-1} with NaNO$_3$. (Errors between brackets).

	Q$_{max,Cd}$ (mmol·g^{-1})	Log b	r^2
Deionized Water	0.85 (0.02)	1.64 (0.04)	0.9955
NaNO$_3$	1.2 (0.1)	0.48 (0.08)	0.9831

Table 3

Optimal parameters estimated for proton and cadmium binding by the acid-treated biomass in 0.05 mol·L^{-1} NaNO$_3$.

Proton binding parameters		
Site density, Q$_{max,H}$ (mmol·g^{-1}) [a]	log $\tilde{K}_H$ /logK$_H$ [b]	m$_H$ = p·n$_H$ [b]
LF fit	2.61 (0.06)	3.8 (0.2)	0.54 (0.01)
Lang. fit	2.61 (0.06)	3.8 (0.1)	1
Cadmium binding parameters		
log $\tilde{K}_{Cd}$ /logK$_{Cd}$ [c]	n$_{Cd}$ /n [c]	Heterogeneity parameter, p [c]
NICCA fit	3.1 (0.1)	1.80 (0.2)	0.19 (0.01)
Lang. fit	2.94 (0.05)	1	
Lang. fit	3.4 (0.2)	0.5	

[a] Estimated from the equivalence point of the acid-base titrations performed in absence of heavy metal. [b] Calculated from least-squares fit of the LF isotherm (**log $\tilde{K}_H$**), Eq. (7), or Langmuir isotherm to the proton binding data (**logK$_H$**). [c] Calculated from least-squares fit of the NICCA isotherm (**log $\tilde{K}_{Cd}$, n$_{Cd}$, p**), Eqs. (5-6), or Langmuir isotherm (**logK$_{Cd}$, n**), Eq. (4), to the cadmium sorption data. (Errors between brackets).