Biosorption of cadmium by biomass of brown marine macroalgae

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Abstract

Five different brown seaweeds, *Bifurcaria bifurcata*, *Saccorhiza polyschides*, *Ascophyllum nodosum*, *Laminaria ochroleuca* and *Pelvetia caniculata* were studied for their ability to remove cadmium from aqueous solution.

Kinetic of cadmium adsorption by all the algae was relatively fast, 90% of total adsorption occurring in less than one hour. These experiments could be accuracy described by a pseudo-second order rate equation, obtaining for the rate constant sorption, *k*, values between $1.66 \cdot 10^{-3}$ and $9.92 \cdot 10^{-3}$ g/mg·min.

The equilibrium adsorption isotherms of Langmuir, Langmuir-Freundlich, Tóth and Freundlich were obtained for the quantitative description of the cadmium uptake. The maximum metal biosorption capacity (q_{max}) and the affinity constant (*b*) for all the algae were evaluated employing the Langmuir isotherm. The values for q_{max} were between 64 and 95 mg/g, whiles *b* was included between 0.036 and 0.094 L/mg. Moreover, a dimensionless constant separation factor, R_s, was calculated founding a favourable condition for the sorption system.

The effect of pH on biosorption was studied at values ranging from 1 to 6, demonstrating the importance of this parameter for the removal of cadmium. Equilibrium studies were carried out at pH 4.5.

Acid-base properties of algae were studied by potentiometry, leading to *pK* values (from 3.54 to 3.98), which are comparable with typical values associated to the ionization of carboxyl groups of alginates. Furthermore, the total number of these acid groups was estimated.

Keywords: Biosorption, cadmium, marine macroalgae, kinetics, equilibrium, acid-base properties.

1. Introduction

The study of biosorption has a great importance from an environmental point of view, as it can be considered as an alternative technique of removing toxic pollutants from wastewaters (Vegliò and Beolchini, 1997; Vieira and Volesky, 2000). Interest has recently been focused on marine biomass because of its high metal-sorbing capacity, low cost and also their ready abundance (Davis et al., 2003).

Due to its acute toxicity, cadmium, lead and mercury are the heavy metals with the greatest potential hazard to humans and the environment. Cadmium poses a serious threat to human health as it accumulates on the environment throughout the food chain. Besides, the industrial uses of cadmium are widespread and increasing in electroplating, paint pigments, plastics, alloy preparation, mining, ceramics and silver-cadmium batteries (Volesky, 1990; Wase and Forster, 1997).

There are different methods for the removal of heavy metal pollutants from wastewaters when they are present in high concentrations, such as chemical-

precipitation, evaporation, solvent extraction, electroplating, ion exchange and membrane processes. However, identifying practical and cost-effective means of removing such contaminants at very low concentrations is much more difficult. Processes suitable at high concentrations are often either ineffective or cost prohibitive when applied to dilute wastes with low heavy metal concentrations.

For these reasons, alternative metal removal and/or recovery methods are being considered, all based on metal-sequestering properties of several natural materials of biological origin. Certain types of biomass can retain relatively high quantities of metal ions by “passive” sorption and/or complexation. This process is known as biosorption in contrast to bioaccumulation, an active mode of metal accumulation by living cells which depends on the metabolic activity of the cell (Volesky, 1990; Wase and Forster, 1997).

The sequestering behaviour of biological materials for cationic or anionic species has been well accepted and reported during the past few decades and the idea has been potentially applied to the removal of some pollutant ions from aqueous wastes and industrial effluents (Bailey et al., 1999; Kapoor and Viraraghavan, 1995; Volesky, 1994). Numerous chemical groups have been suggested to contribute to biosorption metal binding such as carboxyl, hydroxyl, carbonyl, sulfhydryl, thioether, sulfonate, amine, imine, amide, imidazole, phosphonate, and phosphodiester groups (Crist et al., 1981). Biosorption capacity of any given group depends on several factors: the number of sites in the biosorbent material, its accessibility, its chemical state (i.e. availability), and the affinity between site and metal (i.e. binding strength) (Vieira and Volesky, 2000).

The algal cell wall is made of a multilayer microfibrillar framework generally consisting of cellulose and amorphous material. Most of the algal cells are also often

covered by mucilaginous layers characterized by a significant metal sorption capacity due to the presence of alginate that is present in a gel form in the algal cell walls.

Marine algae contain a high proportion of alginate constituting 14-40% of the dry weight of the biomass. The major component of the alginate is alginic acid, a polymer composed of unbranched chains of 1,4-linked β-D-mannuronic and α-L-guluronic acids (Percival and McDowell, 1967). Other negatively charged functional groups, such as the sulphonate groups of fucoidan, also contribute to heavy metal complexation although it is difficult to evaluate the absolute role that these polymers play in determining the heavy metal uptake. Fucoidan is a branched polysaccharide sulfate ester with L-fucose building blocks which are predominantly $\alpha(1\rightarrow2)$ linked (Davis et al., 2003).

In this paper the authors have studied the adsorption kinetics and the adsorption equilibrium of cadmium by several seaweed biomass types originated from the Galician coast. Also the acid-base properties of these algae have been studied as they are related to their capacity of binding to metals.

2. Materials and methods

Samples of marine algae *Bifurcaria bifurcata*, *Saccorhiza polyschides*, *Ascophyllum nodosum*, *Laminaria ochroleuca* and *Pelvetia caniculata* were collected from A Coruña coast, Galicia, Spain. They were washed twice with running water and once with deionized water. After dried, at 60 ºC for 24 hours, they were crushed with an analytical mill (IKA A 10) and ground in a blender to granules of 0.5-1 mm.

The chemicals used in this work were HNO_3 (Merck suprapur and Merck pro analysis), $NaNO_3$ (Merck pro analysis), $Cd(NO_3)_2 \cdot 4H_2O$ (Merck pro analysis), cadmium atomic absorption standard solution (1.000 ± 0.002 g/L) (Panreac), NaOH (Merck pro

analysis), HCl (Merck pro analysis), N_2 C-55 from Carburos Metalicos and cellulose nitrate membrane filters (Whatman and Albet).

For equilibrium studies, eight cadmium solutions with concentrations ranging from 10 to 350 mg/L were prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ in deionized water. The experiments were performed in 100 mL conical flasks containing 0.1 g of algae and 40 mL of cadmium solution. The mixtures were agitated on a rotary shaker at 175 rpm for 3 hours at constant room temperature. NaOH and HNO_3 were used for pH adjustment. The algae biomass was filtered through a 0.45 μm pore size cellulose nitrate membrane filter and the cadmium concentration in the filtrates was determined by differential pulse anodic stripping voltammetry (DPASV) by use of 757 VA Computrace (Metrohm) with a conventional system of three electrodes: hanging mercury drop electrode as working electrode, Pt auxiliary electrode and 3M Ag/AgCl reference electrode. Adsorption isotherms were achieved at pH 4.5 ± 0.1 for all algae. The effect of pH on cadmium uptake has also been studied.

Kinetic experiments were done by adding 0.25 g of algae to 100 mL of cadmium solution (250 mg/L) at constant temperature (25.0 ± 0.1 ºC). The ionic strength was adjusted to 0.05 M with $NaNO_3$. Cadmium concentration was analyzed with a cadmium selective electrode (CdISE) previously calibrated in cadmium concentration. All kinetic experiments were done at natural pH (between 4.8 and 5.6 for all the algae studied).

For potentiometric titrations, the algae were subjected to acid treatment in two steps. The biomass was initially protonated by soaking in a 0.1 M HCl solution at a 1:50 (w/v) ratio and it was subsequently washed with deionized water and dried at 50ºC for 12 hours. Afterwards, 1 g of the biomass was resuspended in 200 mL of a 0.1 M HCl solution for two hours and rinsed with deionized water until constant conductivity was achieved (Davis et al., 2000). The algae was titrated at constant temperature (25.0 ± 0.1

ºC) with an automatic burette CRISON model BU 1S connected to a Hamilton syringe (10 mL) and to a Crison micropH 2000 meter equipped with a Radiometer GK2401C combination glass membrane electrode (Ag/AgCl sat. as reference). The glass electrode was calibrated in proton concentration at a constant ionic strength following the procedure described elsewhere (Brandariz et al., 1998; Fiol et al., 1992). For each titration, ca. 0.5 g of dry biomass was suspended in a 0.05 M $NaNO_3$ solution (100 mL) and accurate volumes of 0.05 M NaOH were added stepwise. The suspension was shaked and purged continually with nitrogen gas to remove O_2 and CO_2.

3. Results and discussions

3.1. Kinetics of adsorption

The main objective of the kinetic study is to determine equilibrium contact time. In order to obtain mechanistic conclusions additional studies would be required.

Experimental data of cadmium adsorption by seaweed were fitted to different kinetic models as Elovich, first order, second order, and diffusion. The best equation representing sorption of cadmium onto algae during agitation was based in a pseudo-second order process. The kinetic rate equation is given by (Ho and McKay, 2000; Ho et al., 1996).

$$\frac{dq_t}{dt} = k \cdot (q - q_t)^2 \qquad (1)$$

where k (g/mg·min) is the rate constant of sorption, q (mg/g) is the amount of cadmium ion sorbed at equilibrium and q_t (mg/g) is the amount of cadmium ion on the surface of the sorbent at any time, t (min). q, cadmium sorbed at equilibrium, represents the metal uptake and is given by Eq. (2):

$$q = \frac{V \cdot (C_i - C)}{1000 \cdot w} \tag{2}$$

where V is the volume of cadmium solution (mL), C_i and C are the initial and equilibrium concentration of Cd^{+2} in the solution (mg/L) respectively, and w is the mass of algae (g).

Separating the variables in Eq. (1) and integrating for the boundary conditions $q_t = 0$ at $t = 0$ and q_t at time t, the following equation is obtained

$$\frac{t}{q_t} = \frac{1}{k \cdot q^2} + \frac{1}{q} \cdot t \tag{3}$$

which is the linear form equation for a pseudo-second order reaction. The constants (k and q) can be experimentally determined by plotting t/q_t against t.

CdISE was employed for kinetic studies since this technique allows to obtain a great number of experimental points easily and fast, so the time needed to achieve the adsorption equilibrium can be determined accurately.

Fig. 1 shows the kinetics of cadmium adsorption onto the algae. The plots represent the amount of metal adsorbed, q_t, versus time for an initial cadmium concentration of 250 mg/L.

The cadmium uptake is relatively fast for all the algae studied. In general, the system reaches over 50% of the total biomass cadmium uptake within 10 minutes of contact and it is observed that over 90% of the total soluble cadmium is removed from solution within 60 minutes of agitation for all the algae.

Saccorhiza polyschides produces the fastest uptake process whereas *Bifurcaria bifurcata* corresponds to slowest one. Similar values for the kinetic rate constant were found with other marine macroalgae (Cordero et al., 2004). The fast cadmium uptake observed for the entire marine algal biosorbents suggests a practical use, as it will facilitate shorter adsorption columns ensuring, in principle, efficiency and economy. However, this implies a previous pretreatment step in order to improve the biomass stability avoiding clog effects (Lodeiro et al., 2004).

For all the algae it was observed that 3 hours were enough to reach the adsorption equilibrium with cadmium, so this time was used for the equilibrium studies.

Comparable equilibrium times are obtained for other algae. For instance, Aksu reported 4 hours with the microalgae *Chlorella vulgaris* (Aksu, 2001) whereas similar times were employed with macroalgae (Cordero et al., 2004; Lodeiro et al., 2004).

The rate law for a pseudo-second order fits the experimental data with a very high correlation coefficient indicating that the sorption of cadmium onto algae agrees with a chemisorption process as the rate-controlling mechanism (Ho, 2003). 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.

Table 1 shows the kinetic parameters of Eq. (3) for cadmium adsorption onto the algae. As it is shown in this table, excellent regression coefficients and low errors in parameters q and k demonstrate the goodness of fits, plotted in Fig. 1. No comparison was included with the other tested kinetic models because pseudo-second order model was definitively better.

3.2. Adsorption equilibrium

Effect of pH on metal uptake

The pH of the solution is an important parameter affecting biosorption of heavy metals. Fig. 2 shows the removal of cadmium from a 250 mg/L solution at different pH values by *Pelvetia caniculata*. All the different algae studied in this work show the same behaviour with the change of pH as *Pelvetia caniculata.*

From Fig. 2, it is seen that sorption of cadmium increases from pH 1.0 to pH 4.0 reaching a plateau at pH around 4.0. However, at pH lower than 2.0, the cadmium uptake capacity is almost negligible. At pH values higher than 9, different hydroxyl low-soluble species can be formed, i.e. $Cd(OH)_2$ and $Cd(OH)_3^-$. The speciation of Cd^{+2} in the working solutions was obtained by means of MINEQL+ programme (Schecher and McAvoy, 1992) which showed that free Cd^{+2} was the only species formed in the pH interval studied.

All equilibrium studies were carried out at pH 4.5 where the maximum metal uptake obtained was 95 mg/g for the alga *Saccorhiza polyschides*. This pH value was chosen since the adsorption maximum is reached and problems associated to the formation of low-soluble species of cadmium that appear at higher pH values are avoided.

The pH dependence of cadmium uptake is closely related to the acid-base properties of various functional groups on the algal cell surfaces, mainly carboxyl groups, and to the metal solution chemistry. At pH values less than 4.0, 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 have a pKa value around 3.7 (Table 5). The cadmium biosorption depends on the extend of protonation of these carboxyl groups. At pH values lower than pKa, carboxylate groups are mainly protonated and

resulting in a low cadmium uptake. At pH values higher than pKa, more functional groups carry negative charge and the positively charged cadmium ions will be bound, increasing the cadmium uptake.

At pH values below 2 the cadmium uptake is very small, but not negligible, which can be a result of the presence of a relatively low amount of very strong acid groups like sulfonic groups from fucoidans (Fourest and Volesky, 1996) in percentages lower than 10% of total amount of titratable groups. Crist et al. (Crist et al., 1992) reported the pK of biomass sulfate groups to be between 1 and 2.5. Hydroxyl groups are also present in the polysaccharides of the brown algae, but they only become negatively charged at pH >10, so their contribution to metal uptake is secondary (Schiewer and Volesky, 2000).

Adsorption isotherms

The adsorption of a substance from one phase to the surface of another in a specific system leads to a thermodynamically defined distribution of that substance between the phases as the system reaches equilibrium. This distribution can be expressed in terms of adsorption isotherms. The metal uptake (q) values are calculated by use of Eq. (2).

Table 2 shows the different adsorption isotherm equations used in this work to fit the experimental data obtained for all the algae. q_{max} represents the maximum adsorption and b is an affinity constant: a high value indicates a steep desirable beginning of the isotherm reflecting the high affinity of the biosorbent for the sorbate (Davis et al., 2000). n is an empirical parameter that varies with the degree of heterogeneity and K_f relates to biosorption capacity.

Fig. 3 shows the experimental data fitted to Langmuir, Freundlich, Langmuir-Freundlich and Tóth models for cadmium adsorption by *Pelvetia caniculata* at a solution pH of 4.5 ± 0.1. The adjustable parameters obtained for the different isotherms are given in Table 3 with the corresponding coefficients of correlation.

As it is shown in Table 3, the estimate of q_{max} varies with the isotherm model used because the adjustable parameters may not always be well-defined due to the limited range of experimental data available, which implies extrapolations depending on isotherm model (Kinniburgh, 1986). The results also demonstrate that in this case the isotherms with three adjustable parameters have slightly higher errors associated to them. As a consequence, Langmuir isotherm has been chosen to fit the data of this work since it involves only two adjustable parameters and it exhibits lower errors and better fits than Freundlich isotherm.

The experimental data of the cadmium adsorption for all the algae fitted to the Langmuir isotherm at pH 4.5 are given in Fig. 4. The curves drawn use the adjustable parameters, q_{max} and b, showed in Table 4.

The maximum uptake of cadmium (q_{max}) for all the algae is rather similar, although *Saccorhiza polyschides* has the highest one, whereas *Ascophyllum nodosum* lead to the maximum value of b for cadmium adsorption and shows the highest cadmium uptake in low metal concentration ranges with a value of q_{10} = 38 mg/g at C = 10 mg/L.

Hall (Hall et al., 1966) showed that the essential characteristics of a Langmuir isotherm equation could be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_s, which is defined by:

$$R_s = \frac{1}{(1 + bC_i)} \quad (4)$$

where R_s is the dimensionless constant separation factor; b is the Langmuir constant as defined earlier (L/mg), and C_i is the initial concentration of Cd^{+2} in the solution (mg/L). The separation factor yields the type of isotherm which was described by Weber (Weber and Chakravorti, 1974) as shown below: R_s>1: unfavourable; R_s=0: linear; 0<R_s<1: favourable; R_s<0: irreversible. R_s was calculated for the Langmuir isotherm and was found to be lower than 1 for all the algae (Fig. 5) which is a favourable condition.

Cadmium adsorption capacities (q_{max}) obtained for the algae studied are similar to those obtained with other brown algae (Cordero et al., 2004; Davis et al., 2003; Lodeiro et al., 2004) and similar or clearly better than sorption capacities published for other materials, usually employed as commercially sorbents (Bailey et al., 1999; Chamarthy et al., 2001; Wase and Forster, 1997).

3.3. Acid-base properties of algae

The maximum amount of acid functional groups was calculated from the volume at the equivalence point of the potentiometric titration curve for protonated algae, after addition of a NaOH solution.

Sulfate groups are known to be present in marine macroalgae (Percival and McDowell, 1967), however, no evidence of their presence was found in the titration curves. The total number of weak acid groups ($q_{max,H}$) found varies from 2.43 to 3.33 mmol/g for *Pelvetia caniculata* and *Laminaria ochroleuca* respectively, determined in 0.05M $NaNO_3$ (Table 5). This amount is between 3 and 6 times greater than the maximum cadmium uptake capacities obtained with raw biomass. This fact can be

explained as a combination of factors. First, since the raw biomass is stabilized with Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} ions present in seawater, cadmium ions must compete with these major ions for the active binding sites, and therefore not all the binding sites are occupied by the heavy metal. Second, it can be expected a certain degree of multidentism in the binding mechanism, i.e., more than one acid group can be involved in the binding to a single metal ion. Similar number of acid groups were found with other brown seaweed species (Cordero et al., 2004; Lodeiro et al., 2004; Rey-Castro et al., 2003).

Acid sites play a key role in biosoption by macroalgae, since ion exchange takes place between metals when binding to them. However, the term ion exchange does not explicity identify the metal uptake mechanism, this may range from physical (electrostatic or London-van de Waals forces) to chemical binding (ionic and covalent).

A physicochemical model that accounts for the effects of pH and ionic strength on the proton binding equilibria of algae was recently proposed by Rey-Castro et al. (Rey-Castro et al., 2003). The proton binding active zone of the algal biomass is supposed to be constituted of a polyelectrolyte that forms a charged, three-dimensional structure. Moreover, surface charge models also reproduced with similar accuracy experimental equilibrium data (Rey-Castro et al., 2004b).

Katchalsky (Katchalsky et al., 1954) found that the titration curve of a polyacid could be empirically described by two constants, *pK* and *n*, according to the equation:

$$pH = pK - n \cdot log \frac{1-\alpha}{\alpha} \qquad (5)$$

where α represents the degree of dissociation which is defined in Eq. (6), and *n* is a empirical parameter that accounts for the chemically heterogeneous nature of the algal biomass, and whose value is greater than one,

$$\alpha = \frac{\left[COO^{-}\right]}{\left(C_0 \cdot V_0\right)/\left(V_0 + V_{NaOH}\right)} \tag{6}$$

C_0 is the initial concentration of the carboxylic acid, V_0 is the initial volume and V_{NaOH} is the volume of NaOH added. *pK* and *n* values can be obtained by the fit of experimental data to Eq. (5). The empirical parameters obtained with Katchalsky linear fit for every algae are shown in Table 5 together with their regression coefficients.

It can be observed that the *pK* values are very similar for all the algae. Besides, these values agree rather well with the values corresponding to carboxyl groups from mannuronic and guluronic acids (3.38 and 3.65) of alginate (Haug, 1961) or to the recently calculated *pK* values for alginic acid (Rey-Castro et al., 2004a), so these groups are likely to be responsible for cadmium sorption.

4. Conclusions

The kinetics of cadmium adsorption by all the algae is relatively fast with 90 % of total adsorption occurring in less than one hour.

A pseudo-second order process can describe the adsorption of cadmium by algae. The rate-limiting step may be a chemisorption process.

The equilibrium adsorption studies carried out indicate that marine macroalgae can be used as an excellent biosorbent material for cadmium recovery with a cadmium adsorption capacity comparable or higher than other commercial materials. A Langmuir

isotherm allows to calculate the maximum cadmium uptake values and an affinity parameter indicative of the binding energy between the adsorbed solute molecules and the adsorbent.

Solution pH is an important parameter affecting biosorption of cadmium by algae, being the uptake almost negligible at pH ≤ 2.0 and reaching a plateau at around 4.0. This behaviour is interesting to consider in order to use algal biomass as a sorbent. pH change can be used to regenerate columns filled with these sorbents.

Potentiometric titrations used to study the acid-base properties of algae in water solution allow to calculate the number of acidic groups and the apparent pK by use of Katchalsky´s model. The pK values obtained are in good agreement with those corresponding to carboxyl groups from alginate that is likely to be responsible for cadmium sorption.

Acknowledgments

The authors wish to thank Xunta de Galicia through project PGIDT02TAM10302PR and Ministerio de Ciencia y Tecnología through project BQU 2002-02133 for financial support. The authors would like to thank Dr. I. Bárbara and Dr. J. Cremades (University of A Coruña) for the collection and classification of the species.

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Figure Captions

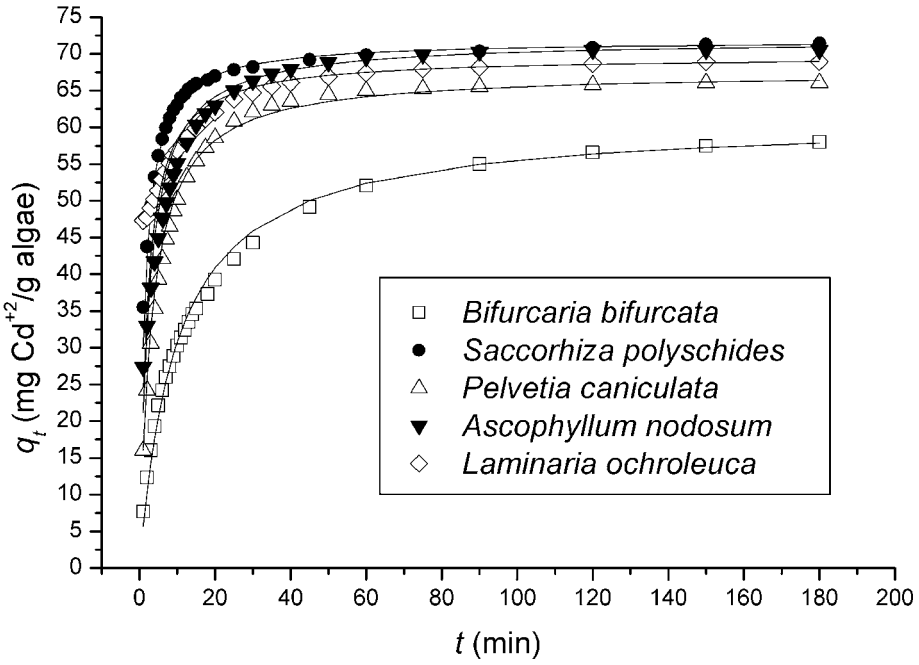
Fig. 1. Kinetics of cadmium uptake by different algae. Lines represent fitting using the pseudo-second order equation model (algae concentration: 2.5 g/L; initial cadmium concentration: 250 mg/L; temperature: 25.0 ± 0.1 ºC; pH between 4.8 and 5.6).

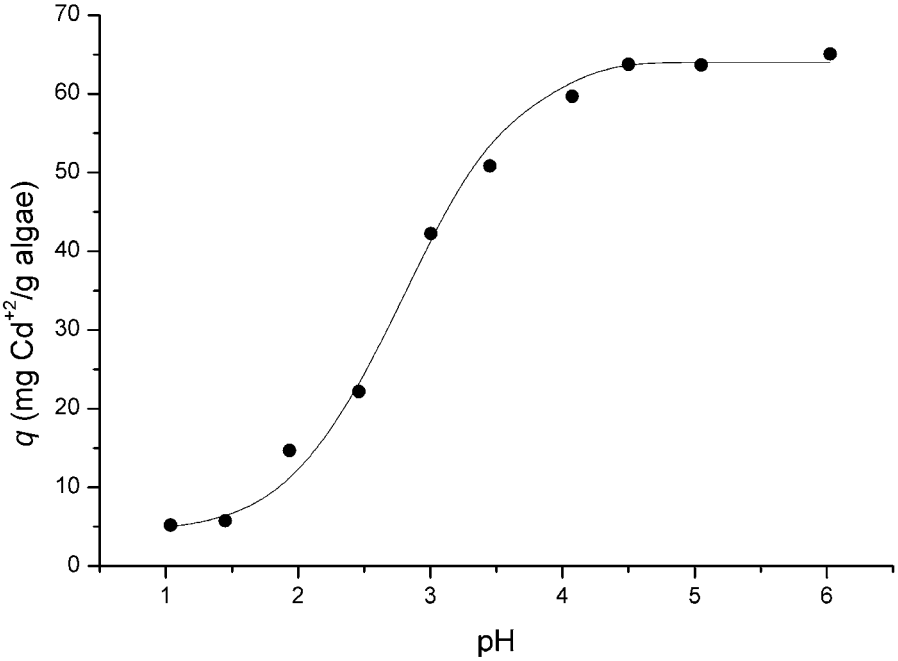
Fig. 2. Effect of pH on cadmium adsorption by *Pelvetia caniculata* (alga concentration: 2.5 g/L; initial cadmium concentration: 250 mg/L; temperature: 25.0 ± 0.1 ºC).

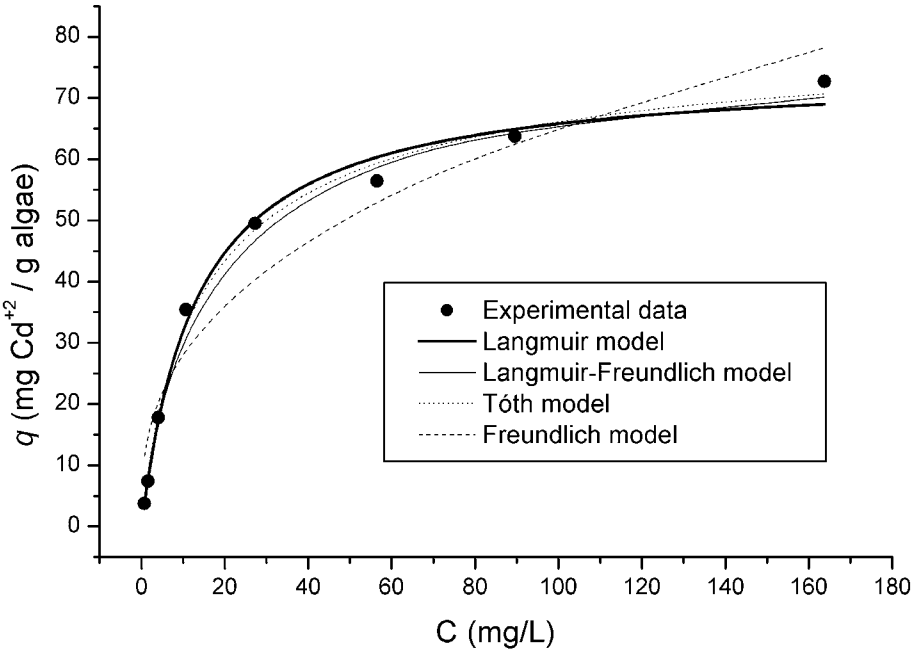
Fig. 3. Fit of the Langmuir, Freundlich, Langmuir-Freundlich and Tóth isotherms for cadmium adsorption by *Pelvetia caniculata* (alga concentration: 2.5 g/L; equilibrium pH: 4.5 ± 0.1; temperature 25.0 ± 0.1 ºC).

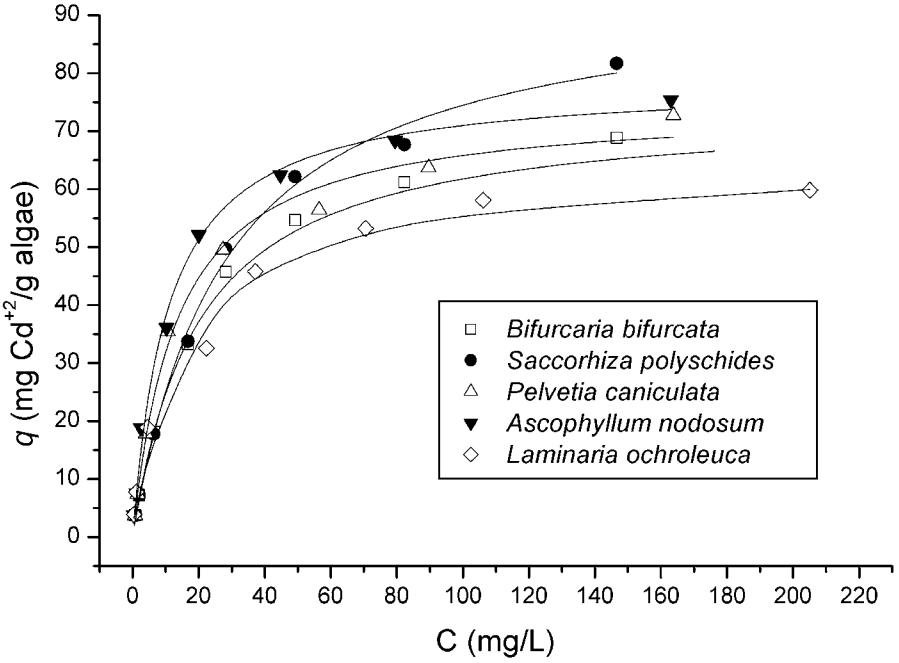
Fig. 4. Cadmium sorption isotherms for *Bifurcaria bifurcata*, *Saccorhiza polyschides*, *Pelvetia caniculata*, *Ascophyllum nodosum* and *Laminaria ochroleuca* (algae concentration: 2.5 g/L; equilibrium pH: 4.5 ± 0.1; temperature: 25.0 ± 0.1 ºC).

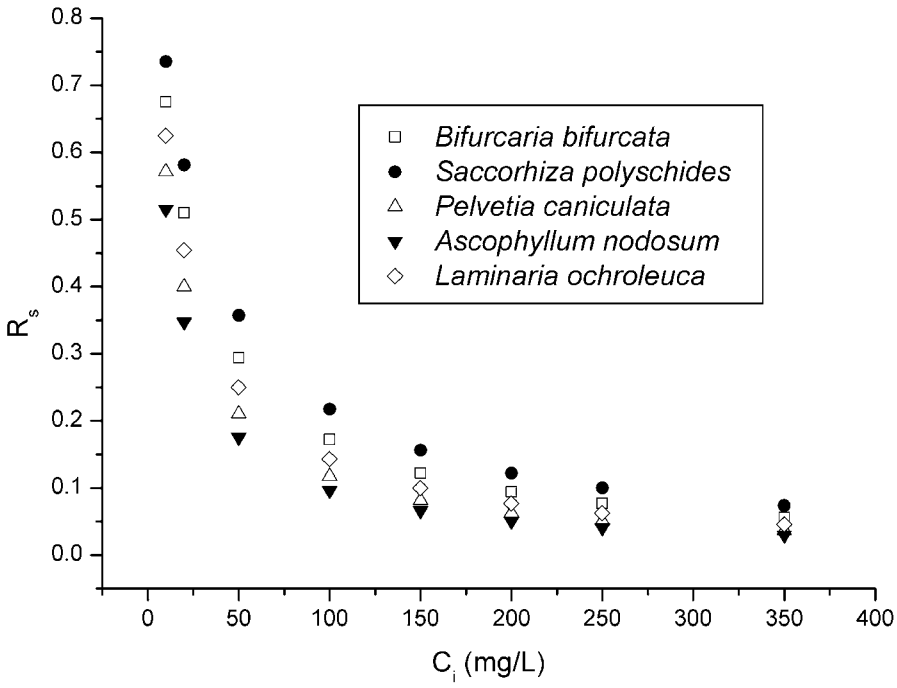
Fig. 5. Variation of R_s for all the algae with initial concentrations between 10 and 350 mg/L.


q_t (mg Cd^{+2}/g algae)
t (min)
Bifurcaria bifurcata
Saccorhiza polyschides
Pelvetia caniculata
Ascophyllum nodosum
Laminaria ochroleuca


70
60
50
40
30
20
10
0
q (mg Cd+2/g algae)
1
2
3
4
5
6
pH


q (mg Cd+2 / g algae)
C (mg/L)
Experimental data
Langmuir model
Langmuir-Freundlich model
Tóth model
Freundlich model
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100
120
140
160
180


q (mg Cd+2/g algae)
C (mg/L)
Bifurcaria bifurcata
Saccorhiza polyschides
Pelvetia caniculata
Ascophyllum nodosum
Laminaria ochroleuca


0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
R_s
0
50
100
150
200
250
300
350
400
C_i (mg/L)
Bifurcaria bifurcata
Saccorhiza polyschides
Pelvetia caniculata
Ascophyllum nodosum
Laminaria ochroleuca

Tables

Table 1. Kinetic parameters for cadmium adsorption onto the algae.

Algae	r^2	q (mg/g)	k (g/mg·min)
Bifurcaria bifurcata	0.9994	61.02 ± 0.3	$1.66 \cdot 10^{-3} \pm 0.06 \cdot 10^{-3}$
Saccorhiza polyschides	0.9999	71.82 ± 0.06	$9.92 \cdot 10^{-3} \pm 0.37 \cdot 10^{-3}$
Pelvetia caniculata	0.9999	67.62 ± 0.13	$4.60 \cdot 10^{-3} \pm 0.19 \cdot 10^{-3}$
Ascophyllum nodosum	0.9999	71.90 ± 0.14	$5.22 \cdot 10^{-3} \pm 0.25 \cdot 10^{-3}$
Laminaria ochroleuca	0.9999	69.68 ± 0.14	$7.43 \cdot 10^{-3} \pm 0.51 \cdot 10^{-3}$

Table 2. Adsorption isotherm equations.

Isotherm	Equation	Number of adjustable parameters
Langmuir	$q = \frac{q_{max} \cdot b \cdot C}{1 + b \cdot C}$	2
Freundlich	$q = K_f \cdot C^{1/n}$	2
Langmuir-Freundlich	$q = \frac{q_{max} \cdot (b \cdot C)^{1/n}}{1 + (b \cdot C)^{1/n}}$	3
Tóth	$q = \frac{b \cdot C \cdot q_{max}}{\left[1 + (b \cdot C)^{1/n}\right]^n}$	3

Table 3. Adjustable parameters for the isotherms models showed in Table 2 for cadmium adsorption by *Pelvetia caniculata* at pH 4.5 ± 0.1.

Model	q_{max} (mg/g)	b (L/mg)/ K_f	n	r^2
Langmuir	75 ± 2	0.075 ± 0.009		0.992
Langmuir-Freundlich	79 ± 5	0.06 ± 0.01	1.1 ± 0.1	0.994
Tóth	83 ± 8	0.09 ± 0.02	1.3 ± 0.3	0.994
Freundlich		13 ± 3	2.8 ± 0.4	0.94

Table 4. Langmuir parameters for cadmium adsorption by different algae at pH 4.5. q_{10} q_{200}: uptakes of cadmium at chosen respective final concentrations: C = (10; 200 mg/L).

Algae	q_{10} (mg/g)	q_{200} (mg/g)	q_{max} (mg/g)	b (L/mg)
Bifurcaria bifurcata	24	67	74 ± 3	0.048 ± 0.008
Saccorhiza polyschides	25	83	95 ± 3	0.036 ± 0.003
Pelvetia caniculata	32	70	75 ± 2	0.075 ± 0.009
Ascophyllum nodosum	38	75	79 ± 2	0.094 ± 0.009
Laminaria ochroleuca	25	60	64 ± 3	0.06 ± 0.01

Table 5. Total number of weak acid groups ($q_{max,H}$) and parameters obtained with Katchalsky representation for every algae.

Algae	$q_{max,H}$ (mmol/g)	*pK*	*n*	r^2
Bifurcaria bifurcata	2.85	3.84 ± 0.01	1.96 ± 0.02	0.996
Saccorhiza polyschides	3.00	3.98 ± 0.02	1.44 ± 0.02	0.992
Pelvetia caniculata	2.43	3.63 ± 0.01	1.12 ± 0.04	0.990
Ascophyllum nodosum	2.81	3.54 ± 0.01	1.51 ± 0.02	0.996
Laminaria ochroleuca	3.33	3.62 ± 0.01	1.36 ± 0.02	0.994