Characterization of the biosorption of cadmium, lead and copper with the brown alga *Fucus vesiculosus*

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Abstract

The recovery of cadmium, lead and copper with the brown alga *Fucus vesiculosus* was characterized and quantified. The biosorption data fitted the pseudo-second order and Langmuir isotherm models, but did not adjust to the intraparticle diffusion model. The metal uptakes deduced from the pseudo-second order kinetic model and the Langmuir isotherm model followed a similar sequence: $Cu > Cd \approx Pb$. The Langmuir maximum metal uptakes were: 0.9626 mmol/g, Pb 1.02 mmol/g, and Cu 1.66 mmol/g. According to the equilibrium constants of this isotherm model, the affinity of metals for the biomass followed this order: $Pb > Cu > Cd$. Biosorption was accomplished by ion exchange between metals in solution and algal protons, calcium and other light metals, and by complexation of the adsorbed metals with algal carboxyl groups. FTIR spectra showed a shift in the bands of carboxyl, hydroxyl and sulfonate groups.
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1. Introduction

Heavy metals are highly toxic elements that can accumulate and concentrate in live tissues. Lead, copper and especially cadmium can become a sanitary and ecological threat to drinking water resources, even at very low concentrations. Thus, clean alternatives must be developed in order to remove heavy metals from effluents. In the case of copper, its recovery can also be economically interesting based on high market prices.

The traditional methods for the removal of heavy metals from water are generally expensive or inadequate to treat highly dilute solutions. These methods include: chemical precipitation and filtration, electrochemical treatments, reverse osmosis, ion exchange, adsorption and evaporation. Biosorption is a cost effective alternative that can be appropriate for treating effluents with low metal concentrations and can also be used to remove other contaminants such as dyes and organic compounds. Metals in solution bind passively onto chemically active sites or functional groups of a certain biosorbent (biomass)

that becomes saturated at an equilibrium metal concentration [1]. Dead biomass has higher metal uptakes, being the process nutrient independent [2].

The type of biomass can affect the amount of metal recovered during biosorption. Algae present greater metal uptakes than bacteria and fungi. Of the different types of alga, brown algae have greater uptakes than green and red algae [3]. In addition, brown algae are low-cost and readily available biosorbents. They are commonly used as nutritional supplements, animal feed, fertilizers, and as a source of thickeners such as alginate. Brown algae have been used in numerous biosorption studies because of their high metal uptakes [4–7]. Nevertheless, biosorption with algae still represents less than 16% of the total studies in the field before June 2004. In fact, algae have been less employed as biosorbent material than other kinds of biomass, especially fungi and bacteria [8].

Metal biosorption with algae occurs mainly on functional groups present on the cell walls, which represents between 60 and 80% of the total dry weight. The cell wall structure of brown algae is complex compared to that of green and red algae. It contains a greater proportion of mucilaginous polysaccharides in the outer cell wall, including alginate and fucoidans (sulfated polysaccharides) that could explain the higher metal uptakes [6].

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Possible biosorption mechanisms are: chemisorption, complexation, surface adsorption–complexation, ion exchange and microprecipitation. Whereas physical sorption is due to weak Van der Waals forces, chemical sorption is due to electron exchange and formation of chemical bonds. Metals in solution can also be exchanged with protons or other cations of the biomass. Variables such as pH, biomass concentration, particle size and temperature can affect the biosorption process.

Different models can describe the biosorption kinetics: the pseudo-first order model proposed by Lagergren, the pseudo-second order model proposed by Ho and the intraparticle diffusion model proposed by Weber–Morris [9,10]. Biosorption generally fits the pseudo-first order model when diffusion through a boundary layer is the rate-controlling step. Nevertheless, biosorption involves several processes such as electrostatic phenomena and chemical reactions between binding sites and metals. Therefore, the pseudo-second order model fits most biosorption processes and theoretically is more correct. The maximum metal uptake and the biomass affinity for a certain metal can be obtained from the sorption isotherms. The Langmuir isotherm is the most applied in monometallic systems.

In this work, a systematic approach was used to characterize and quantify the biosorption of cadmium, lead and copper with the brown alga *F. vesiculosus*. This edible alga, also called bladderwrack for its distinct flotation bladders, is readily available and grows abundantly in the North Atlantic coasts. In order to obtain kinetic and isotherm parameters, biosorption data were analyzed using three different models: pseudo-second order, intraparticle diffusion and the Langmuir isotherm. The biomass was characterized with and without metal using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) to determine possible metal binding mechanisms.

2. Materials and methods

2.1. Biomass

The brown alga *F. vesiculosus* was collected by Algamar in the northern Atlantic coasts of Spain. The alga was washed, dried in an oven at $60\,^{\circ}\mathrm{C}$, ground with an agate mortar and sieved through <0.5 mm mesh size.

2.2. Batch biosorption

2.2.1. Kinetic studies

The experimental procedure and conditions were based on a previous study with different algae [8]. The biosorption experiments were performed with monometallic solutions prepared from stock solutions of 1000 mg/l using chemical reagents of analytical grade: $CdSO_4 \cdot 8/3H_2O$, $Pb(NO_3)_2$ and $CuSO_4 \cdot 5H_2O$. Nitrate instead of sulfate was used for lead to avoid metal precipitation. Previous studies have shown that the effect of the anion is negligible [11]. The initial pH of solutions (5 for copper and lead and 6 for cadmium) was adjusted with diluted H_2SO_4 for Cd and Cu, and with HNO_3 for Pb. These values were optimized in previous tests performed with the same alga [12]. Kinetic stud-

ies were carried out in an orbital shaker at 150 rpm with 75 ml of metal solution (100 mg/l) at room temperature ($23 \pm 1\,^{\circ}\mathrm{C}$) in contact with the algal biomass (1 g/l). Samples of the metal solution were removed at different times (0, 2, 5, 10, 30, 60 and 120 min) and the pH and metal concentration (using atomic absorption spectroscopy, AAS) were measured.

The metal uptake was calculated from the following expression:

$$q_t = \frac{C_0 - C_t}{B} \tag{1}$$

where q_t, metal uptake at time t (mmol/g of biomass); C_0, initial metal concentration (mmol/l); C_t, metal concentration at time t (mmol/l); B, biomass concentration (g/l).

Based on previous studies [11], the proton consumption during the kinetic experiments was calculated from the change in pH with respect to the initial pH values using the following expression:

$$H^+_{consumed}/g \text{ of biomass} = \frac{10^{-\text{initial pH}} - 10^{-\text{final pH}}}{g \text{ of biomass}} \tag{2}$$

The results were fitted to the pseudo-second order [9] and intraparticle diffusion kinetic models.

The pseudo-second order kinetics is given by this equation:

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \tag{3}$$

where q_2, maximum uptake for the pseudo-second order kinetics (mmol/g of biomass); k_2, rate constant of the pseudo-second order sorption (g/mmol min).

Assuming that the metal uptake is proportional to the number of biomass binding sites with sorbed metal and integrating at the limit conditions from $t = 0$ to t and from $q_t = 0$ to q_1, the pseudo-second order model can be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2}t \tag{4}$$

The values of q_2 and k_2 can be deduced from the linear plot of t/q_t versus t.

The Weber–Morris intraparticle diffusion equation reflects a two-step biosorption process: the metal binding to the biomass surface followed by the diffusion of the metal through its pores [10]:

$$q_t = k_p t^{1/2} + C \tag{5}$$

where k_p, intraparticle diffusion constant that can be calculated from the slope of the curve (mmol/g min$^{1/2}$).

The model applies when a linear representation of q_t versus $t^{1/2}$ is obtained. If the linear plot intercepts the origin, the intraparticle diffusion would be the rate-controlling step of the biosorption process [13]. Otherwise, other mechanisms, besides diffusion, would be involved.

2.2.2. Biosorption isotherms

These experiments were carried out with 0.5 g/l initial biomass concentration, at initial pH values similar to the kinetic experiments, and at different initial metal concentrations: 10, 25,
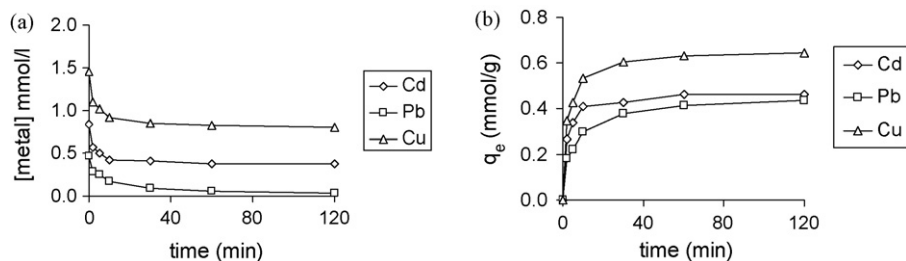
Fig. 1. Evolution of the metal concentration (a) and uptake (b) of Cd, Pb and Cu with *Fucus vesiculosus*.

50, 100 and 150 mg/l [11]. Tests were run for 120 min, enough time to reach equilibrium. The experimental results were fitted to the Langmuir model [14]:

$$q_e = \frac{bq_{max}C_e}{1 + bC_e} \qquad (6)$$

where q_e, metal uptake of the biomass (mmol metal/g of biomass); q_{max}, maximum metal uptake (mmol metal/g of biomass); C_e, final metal concentration at the equilibrium (mmol metal/l); b, equilibrium constant (l/mmol metal).

The equilibrium constant indicates the affinity between the biomass and a given metal, the greater its value the greater the affinity.

The sorption parameters can be calculated from the isotherm using the linear Langmuir plot of C_e/q versus C_e:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \qquad (7)$$

2.3. FTIR analysis

For FTIR (Fourier transform infrared spectroscopy) analyses, KBr discs with 2% finely ground sample were analyzed in a MIDAC Prospect-IR spectrophotometer. The spectral data were processed using Nicolet OMNIC E.S.P software. Infrared spectra were recorded in the region of 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.4. SEM and EDS analysis

The biomass particles, with and without adsorbed metal, were coated with a thin layer of gold, or graphite in the case of samples containing lead, and examined in a SEM microscope (JEOL JSM-6400).

3. Results and discussion

3.1. Kinetic studies

Fig. 1 shows the evolution of both metal concentration and uptake during the biosorption of cadmium, lead and copper with the brown alga *F. vesiculosus*. The biomass in contact with each metal solution decreased the metal concentration until an equilibrium concentration was reached after 2 h.

The experimental data were fitted to the pseudo-second order kinetic model (Fig. 2a). The corresponding kinetic parameters

derived from this model are shown in Table 1. The plots fit linearly to this model, indicating that the biosorption occurred in at least two steps (Fig. 2). Those steps could correspond to the dissociation of the complexes formed between metals in solution and water hydronium ions followed by the interaction of metals with algal functional groups [15]. The kinetic uptakes (q_2) followed the sequence: Cu > Cd ≈ Pb, which is inversely proportional to cation size (Cu^{2+} 0.072 nm, Cd^{2+} 0.097 nm and Pb^{2+} 0.120 nm) [16]. The sequence of kinetic rates (k_2) is consistent with metal uptakes: Cu > Cd > Pb.

Cochrane et al. also reported that the copper biosorption by *F. vesiculosus* fitted the pseudo-second order kinetic model, but no specific parameter values were given [17]. Absolute values of the kinetic parameters are difficult to compare, even with the same biomass, because of the great heterogeneity of experimental procedures used in the literature. For instance, Herrero et al., using the same initial metal concentration (100 mg/l) and a greater biomass concentration (5 g/l), found that the biosorption of cadmium by *F. vesiculosus* also fitted the pseudo-second order kinetic model and obtained a similar kinetic uptake
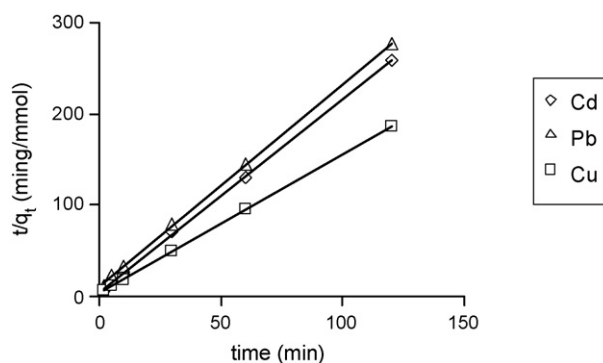

Fig. 2. Biosorption of Cd, Pb and Cu with *Fucus vesiculosus*. Adjustment to the pseudo-second order kinetic model.

Table 1
Kinetic and isotherm parameters for the biosorption of Cd, Pb and Cu with *Fucus vesiculosus*

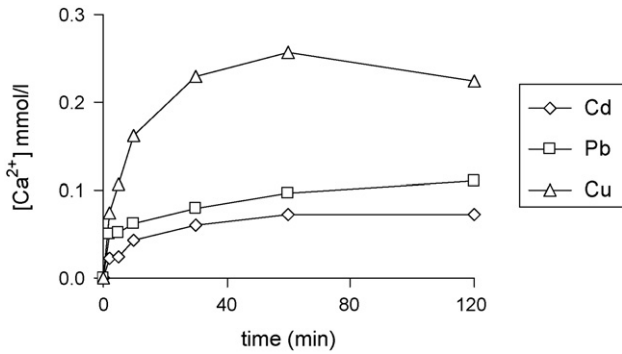|		Cd	Pb	Cu
Pseudo-second order kinetic model	q_2 (mmol/g)	0.4702	0.4496	0.6569
	k_2 (g/mmol min)	0.0569	0.0194	0.1204
	R^2	0.9998	0.9995	0.9999
Langmuir isotherm model	q_{max} (mmol/g)	0.9626	1.02	1.66
	b (l/mmol)	12.71	15.78	13.16
	R^2	0.9972	0.9735	0.9979

Fig. 3. Relationship between the amount of Ca in solution and the biosorption of Cd, Pb and Cu with *Fucus vesiculosus*.

Table 2
Amount of metals adsorbed and calcium released after the biosorption of Cd, Pb and Cu with *Fucus vesiculosus*

	Adsorbed Me (mmol/l)	Released Ca (mmol/l)	Ca/Me
Cd	0.4626	0.0724	0.1565
Pb	0.4343	0.1098	0.2528
Cu	0.6452	0.2246	0.3481
Alga	–	0.0250	–

(0.578 mmol/g), but a different rate constant (0.38 g/mmol min) [18].

The experimental results of the biosorption of cadmium, lead and copper with *F. vesiculosus* did not fit linearly to the intraparticle diffusion equation (data not shown). Therefore, diffusion was not a limiting factor during metal uptake. That was probably related to a large available surface area of the biomass because of the small particle size used (>0.5 mm).

The calcium concentration in solution increased during the kinetic experiments, as shown in Fig. 3. Table 2 compares the
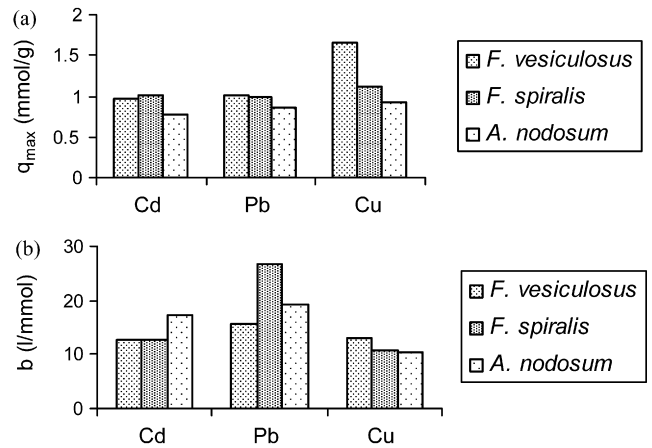

Fig. 6. Comparison between the Langmuir parameters of the biosorption of Cd, Pb and Cu with *Fucus vesiculosus* and other brown algae from the study by Romera et al. [8].

amount of calcium released after these experiments with respect to the amount of metal adsorbed. Those quantities were always greater than the calcium released in an experiment without the addition of metals in solution. Therefore, one of the mechanisms involved in the biosorption of cadmium, lead and copper with *F. vesiculosus* would be the exchange between metals in solution and calcium present in the alginate of the algal cell wall. Ion exchange has also been observed by other authors during the biosorption of these metals with brown algae [19,20]. This mechanism seems to be more important during the biosorption of copper, since a greater amount of calcium was released. The importance of ion exchange with calcium during the biosorption of copper with *F. vesiculosus* has also been documented [17]. In the case of cadmium, the ratio between calcium released and metal adsorbed was lower than for lead and copper. The presence
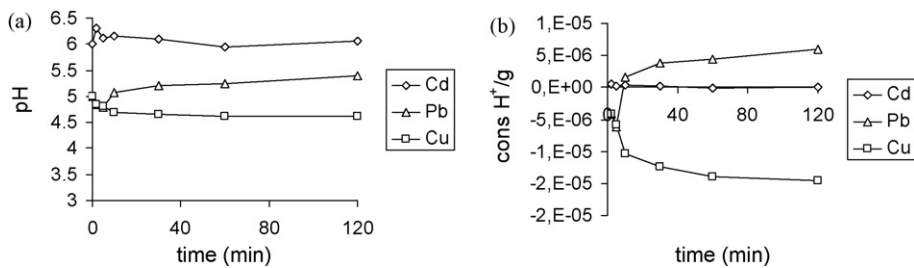

Fig. 4. Change of pH (a) and proton consumption (b) during the biosorption of Cd, Pb and Cu with *Fucus vesiculosus*.
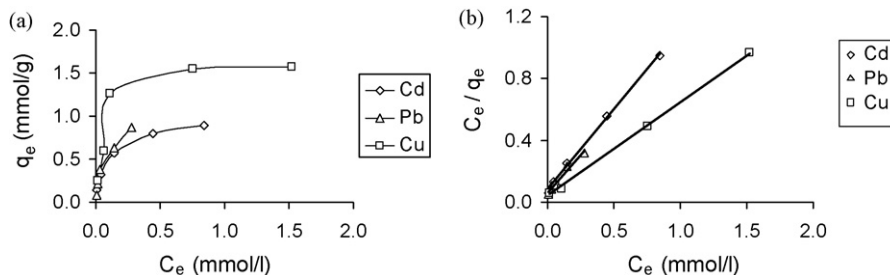

Fig. 5. (a) Biosorption isotherms of Cd, Pb and Cu. (b) Adjustment to the Langmuir model.
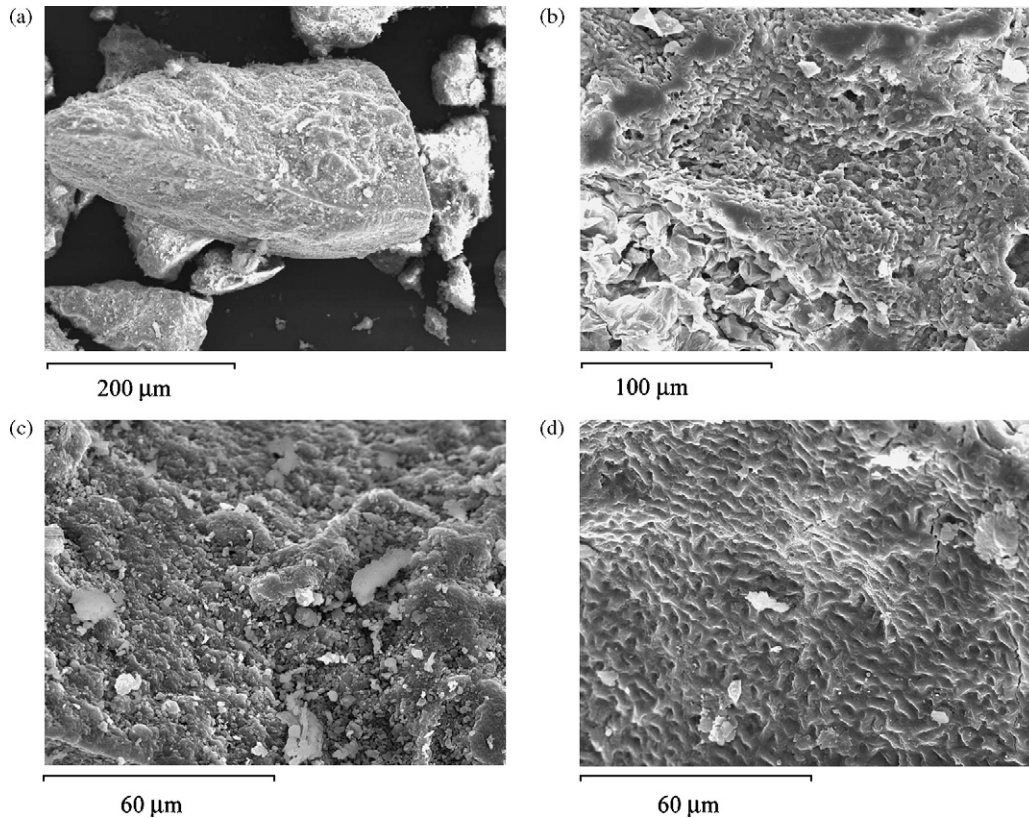
Fig. 7. SEM micrographs of *Fucus vesiculosus* particles.

of calcium in the algal biomass could interfere in the cadmium uptake. For instance, Hashim and Chu, using different types of algae, observed a reduction in the biosorption of cadmium with increasing calcium concentrations [5]. Cadmium and calcium can compete during biosorption because of their similar ionic radii: Cd^{2+} 0.097 nm and Ca^{2+} 0.099 nm [16,21].

During biosorption, metals in solution can also be exchanged with biomass protons, as was observed by Raize et al. using *Sargassum* [6]. Fig. 4 shows the change of pH and proton consumption during the biosorption of cadmium, lead and copper with *F. vesiculosus*. Although only the initial pH values of the metal solutions were adjusted, the final pH values (6.06 for Cd, 4.61 for Pb and 5.4 for Cu) were below the precipitation values for the corresponding final metal concentrations. Unlike during

the biosorption of lead and copper, little changes in pH were observed for cadmium.

Lead and copper uptakes showed an initial stage of proton release that could be related to the dissociation of metal–hydronium complexes and to the exchange between algal protons and metal in solution (Fig. 4) [15]. The initial pH (5) was above the pK_a value of the alginate in the algal cell wall. Therefore, dissociation of alginate carboxyl groups could also have contributed to the initial proton release (3.20 for guluronic and 3.38 for mannuronic) [22]. Such dissociation has also been documented during copper biosorption with brown algae by Crist et al. [19]. In the case of lead biosorption, the competition between protons and metal in solution for the binding sites of the biomass caused an increase of pH. Conversely, pH is stable during copper
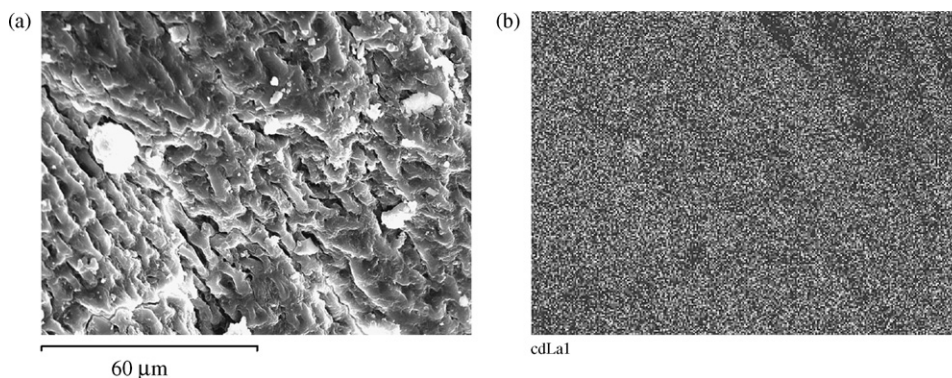

Fig. 8. SEM micrograph (a) and X-ray map (b) of Cd adsorbed on the surface of *Fucus vesiculosus*.

biosorption after the initial proton release, in accordance with Cochrane et al [17].

Other cations, aside from calcium, such as magnesium, sodium and potassium could also be exchanged with metals in solution during the biosorption process. The presence of those cations in the alga *F. vesiculosus* was confirmed by EDS analysis. Different authors observed an increase in the concentrations of these ions and calcium during the biosorption of cadmium, lead and copper with brown algae [6,17]. For instance, copper biosorption with *F. vesiculosus* was estimated to be 77% due to ion exchange, with 13, 9, 24 and 31% accounting for interchange with Ca^{2+}, Mg^{2+}, Na^+ and K^+, respectively [17]. Chen described the influence of these metals in solutions during the biosorption of cadmium, lead and copper with the brown algae *Sargassum* [23]. Ion exchange between cadmium and copper in solution and other light element cations of fungi has also been reported [24].

3.2. Biosorption isotherms

The biosorption isotherms of cadmium, lead and copper with the brown alga *F. vesiculosus* were adjusted to the Langmuir model (Fig. 5). The corresponding parameters are shown in Table 1. Similar values have been reported for two other brown algae, *Fucus spiralis* and *Ascophyllum nodosum*, as shown in Fig. 6 from a previous study using a similar experimental procedure [8]. *F. vesiculosus* has a greater copper uptake than the other two algae. Cochrane et al., using different experimental conditions, also fitted the copper biosorption with *F. vesiculosus* to the Langmuir model and obtained a similar metal uptake (1.81 mmol/g) but a different constant (3.11 l/mmol) [17].

The metal uptake sequence deduced from the Langmuir isotherm was: Cu > Pb ≈ Cd. Interestingly, in spite of the different approaches, this sequence is similar to that obtained from the pseudo-second order kinetic model. According to the equilibrium constants, the metals affinities for the alga followed the sequence: Pb > Cu > Cd. A similar order can be deduced from the rule of Irving Williams regarding the stability of complexes between metal cations and oxygen donor groups [25]. Such donor groups include carboxyl and hydroxyl groups which are involved in metal sorption. The equilibrium constant, related to the free energy of biosorption and the enthalpy change, increases with bond strength [26]. Thus, lead formed the most stable complex with alga while cadmium the weakest.

3.3. Biomass characterization

Fig. 7 shows SEM micrographs of *F. vesiculosus* particles. Two different morphologies can be distinguished: irregular (Fig. 7c) and regular (Fig. 7d) surfaces. Both types of surfaces are present in Fig. 7(b). The regular structure was not observed in previous studies with *F. spiralis*, and seems to be characteristic of *F. vesiculosus*. The main difference between both species is the flotation bladders. It is possible, therefore, that these regular structures, part of those bladders, were broken apart when the alga was ground.
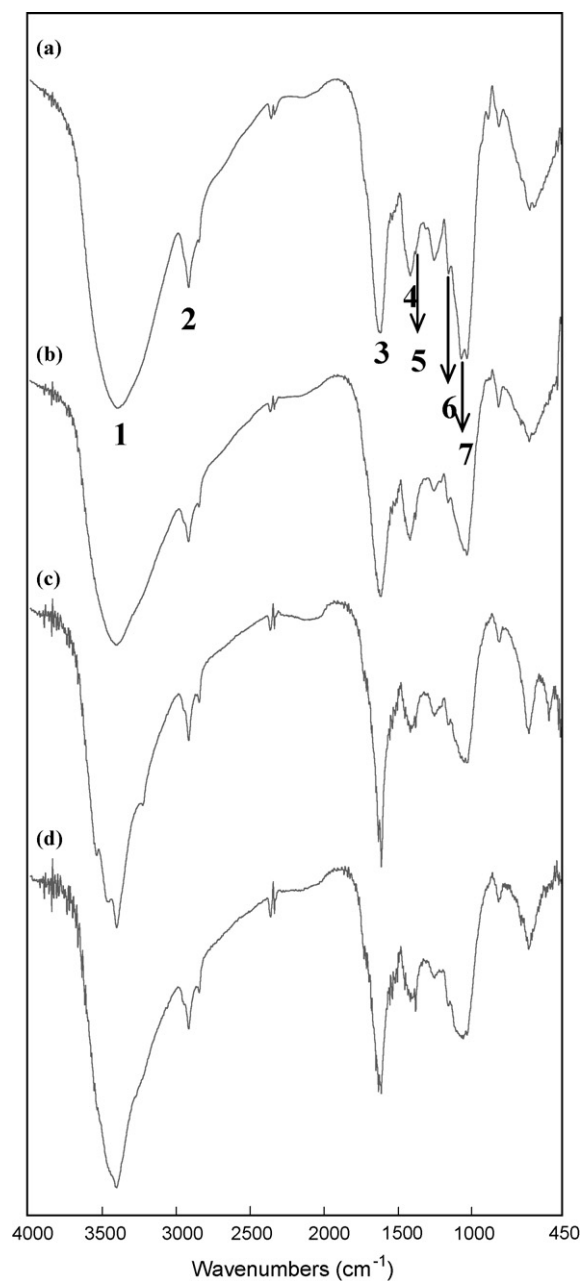

Fig. 9. FTIR spectra of *Fucus vesiculosus* without metal (a), with Cd (b), Pb (c) and Cu (d). The most relevant bands are numbered: (OH) stretching (1), (CH) stretching, asymmetric (3) and symmetric (4) (COOH) stretching, asymmetric (5) and symmetric (6) (SO$_3$) stretching, and (CO) stretching of the (COH) (7) (Refs. [7,24]).

After biosorption, cadmium, lead and copper were distributed uniformly over the alga surface independently of the initial morphology. No physical change was visible after metals were bound. Fig. 8 shows an X-ray map of the cadmium distribution on a representative sample of the algal surface.

FTIR spectra studies on brown and green algae *Sargassum* and *Cladophora fascicularis*, respectively, provided the basis to interpret the results with *F. vesiculosus* [7,27]. As shown in Fig. 9, the bands corresponding to carboxyl (COOH) groups shifted after the biosorption process. These changes in the FTIR

spectra have also been observed in other biosorption studies with marine algae [7,23,28].

After metal binding, the asymmetric carboxyl stretching band shifted from 1625 to 1618 cm^{-1}. The distance between this band and the symmetric stretching of the same groups (at 1421 cm^{-1}) decreased to lower wave numbers after biosorption, indicating that chelating complexes were formed [27,29]. Therefore, chelation was another important mechanism involved in the biosorption of cadmium, lead and copper with *F. vesiculosus*; as reported earlier by Raize et al. for *Sargassum* with FTIR and XPS spectroscopy studies [6]. Other studies using the alga *Sargassum* stated that cadmium biosorption was accomplished by the formation of ionic bridges between the metal and two carboxyl groups or a bidentate chelating complex with one carboxyl group [30,31]. The intensity of the symmetric carboxyl-stretching band decreased after lead and copper binding. In accordance to the sequence obtained from the equilibrium constants (Table 1), the alga formed stronger bonds with these two metals.

Carboxyl groups are the most abundant functional groups in polysaccharides and are the main functional groups involved in the biosorption of heavy metals with algae and other biomasses [1,2,4]. Cadmium biosorption with fungi and *Sargassum* diminished after blocking these groups with methanol [27,32]. The majority of these groups are located in the alginate of the algal cell wall and their negative charge can attract metal cations [5]. Raize et al. reported less nickel biosorption when alginate was extracted from the brown alga *Sargassum* [6].

Other functional groups, besides carboxyl groups, can participate to less extent in the biosorption, such as sulfyhdrils and sulfonates [27]. The FTIR bands corresponding to the asymmetric and especially symmetric stretching vibrations of sulfonate groups also shifted after biosorption from 1380 to 1385 cm^{-1} and from 1175 to 1165 cm^{-1}, respectively.

4. Conclusions

The biosorption of cadmium, lead and copper with the brown alga *F. vesiculosus* fitted linearly to the pseudo-second order kinetic model, indicating that the process occurred in at least two steps. Copper had the fastest biosorption kinetics and the highest metal uptake. The kinetic uptakes and rates were inversely proportional to the size of metal cations.

The biosorption isotherms of cadmium, lead and copper fitted the Langmuir model. The metal uptake sequence was similar to that obtained in the kinetic experiments: Cu > Pb ≈ Cd. The Langmuir parameters obtained were similar to other studies using brown algae and identical experimental conditions. Copper had the highest maximum metal uptake. According to the equilibrium constants, the affinity of metals for the biomass followed the sequence: Pb > Cu > Cd.

During biosorption of the three metals, ion exchange between metals in solution and algal protons and calcium took place. The ion exchange with calcium was higher for copper than for the other two metals tested. In addition, complexation and chelation reactions between metals and carboxyl groups are also possible. Carboxyl groups seem to be the main functional groups involved in the biosorption process.

In general, the brown alga *F. vesiculosus* is an excellent biosorbent of cadmium, lead and copper. This biomass is economic, readily available and adequate for multiple biosorption applications, such as immobilization and column experiments.

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