Journal of Hazardous Materials 163 (2009) 555–562

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Biosorption of cadmium, lead and copper with calcium alginate xerogels and immobilized *Fucus vesiculosus*

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ARTICLE INFO

Article history:
Received 26 March 2008
Received in revised form 27 June 2008
Accepted 1 July 2008
Available online 12 July 2008

Keywords:
Biosorption
Heavy metals
Alginate
Immobilization
Fucus vesiculosus

ABSTRACT

This paper determines the effect of immobilized brown alga *Fucus vesiculosus* in the biosorption of heavy metals with alginate xerogels. Immobilization increased the kinetic uptakes and intraparticle diffusion rates of the three metals. The Langmuir maximum biosorption capacity increased twofold for cadmium, 10 times for lead, and decreased by half for copper. According to this model, the affinity of the metals for the biomass was as follows: Cu > Pb > Cd without alga and Pb > Cu > Cd with alga. FITR confirmed that carboxyl groups were the main groups involved in the metal uptake. Calcium in the gels was displaced by heavy metals from solution according to the "egg-box" model. The restructured gel matrix became more uniform and organized as shown by scanning electron microscopy (SEM) characterization. *F. vesiculosus* immobilized in alginate xerogels constitutes an excellent biosorbent for cadmium, lead and copper, sometimes surpassing the biosorption performance of alginate alone and even the free alga.

1. Introduction

Heavy metals, such as lead, copper and specially cadmium, are a sanitary and ecological threat. They are highly toxic and recalcitrant even at very low concentrations and they can pollute drinking water resources. Research is therefore important to fully understand systems and technologies for their removal. Additionally, copper recovery can also be economically interesting because of its increasingly higher prices.

Traditional methods for removing heavy metals, including chemical precipitation and filtration, redox reactions, electrochemical treatments, reverse osmosis, ion exchange, adsorption and evaporation, are generally expensive or inadequate for treating highly diluted solutions. Biosorption is an alternative process for the treatment of this kind of effluents. It is defined as the passive binding of metals or other compounds on a biosorbent (biomass) containing chemically active sites or functional groups [1]. Dead biomass has higher metal uptakes and the process is nutrient independent [2]. Agricultural or other low-cost and readily available residual materials, such as alginate and brown algae, can be used as biosorbents.

Biomass immobilization is an essential step for an industrial scale-up of biosorption. Unlike biomass in its native state, immobilization provides biosorbent particles with the adequate size, density and mechanical strength required by continuous systems. Besides, immobilization can save the cost of separating the biomass from the treated solution which can represent up to 60% of the total cost. This process also enables biomass regeneration in various adsorption–desorption cycles. Natural polysaccharide gel matrixes such as alginate are widely used and are a cost effective alternative to synthetic polymers.

Alginate is a component of the outer cell wall of brown algae and, according to several studies [2,3], is responsible for the high metal uptakes of brown algae when compared to other algae, bacteria and fungi. *Fucus vesiculosus*, the biomass immobilized in this study, has proven to be an effective biosorbent of heavy metals [4]. Additionally, alginate in itself has biosorption capacity, favoring a possible synergic effect with the immobilized biomass [5,6].

Alginate is a linear unbranched polysaccharide of alternating blocks of β-D-mannuronic and α-L-guluronic acids. They are rich in carboxyl groups, the main functional groups involved in heavy metal biosorption [1]. Alginate gels in the presence of divalent cations according to the Rees "egg-box" model [7]. For instance, calcium atoms can crosslink and form salt bridges between the guluronic acid blocks of a pair of alginate chains. At the same time these pairs can dimerize with other pairs. The polymer gel matrix is formed by alternate free mannuronic and crosslinked guluronic blocks.

Biosorption kinetics can be adjusted to several models, such as the pseudo-first-order model proposed by Lagergren and Sven [8], the pseudo-second-order model proposed by Ho and McKay [9], and the intraparticle diffusion model proposed by Weber–Morris

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doi:10.1016/j.jhazmat.2008.07.015

[10]. If metal uptake is only controlled by diffusion through a boundary layer the kinetics generally adjusts to the pseudo-first-order model. However, biosorption involves several processes: electrostatic forces and chemical reactions between binding sites and metals; theoretically it is more correct to apply the pseudo-second-order model that fits most biosorption processes [9].

The maximum metal uptake and the affinity of the beads for a certain metal are important parameters of the biosorption process. They can be obtained from the representation of the sorption isotherms. The Langmuir isotherm is the most used in simple systems [11].

Alginate beads are most commonly used with immobilized biomass while very few studies, generally restricted to compare metal uptakes, use alginate alone [5,6,12,13]. Although brown algae are well known for their high metal uptakes and alginate is also well known as an immobilization support, there are no previous studies of a brown alga immobilized on these types of gels and on how it influences biosorption. This work describes the recovery of cadmium, lead and copper from solutions with calcium alginate xerogel beads with and without immobilized *F. vesiculosus*. Kinetic and isotherm models were used for the quantitative description and prediction of the metal uptake behavior of this polymeric material and the immobilized biomass. Data were adjusted to the pseudo-second order and intraparticle diffusion kinetic models, and the Langmuir isotherm model, obtaining the corresponding parameters. Finally, the beads were characterized with and without metal by using Fourier transformed infrared spectroscopy (FTIR) and field emission-scanning electron microscopy (FE-SEM) in order to determine possible metal binding mechanisms. This systematic approach is necessary before these beads can be applied in continuous biosorption systems.

2. Materials and methods

2.1. Alginate xerogel and immobilized biomass beads

The brown algae *F. vesiculosus* was provided by Algamar (Pontevedra, Spain). It was washed with deionized water, dried in an oven at 60 °C, ground with an agate mortar, and sieved with a mesh to a size <0.5 mm. A 2% sodium alginate solution (Fluka Chemika) with (50% (w/w) algae:alginate, 1B:1A) or without alga was dropped with the help of a syringe and under constant stirring onto a cooled 0.5 M $CaCl_2$. The resulting beads were hardened overnight in the same solution at 4 °C. Then they were filtered and the excess $CaCl_2$ was washed with deionized water. Finally, the beads were dried at room temperature to obtain the xerogels, which measured approximately 2.5 and 2 mm with and without immobilized alga, respectively.

2.2. Batch biosorption tests

The experimental procedure and conditions were based on previous studies performed with free biomass of *F. vesiculosus* [4,14]. The biosorption experiments were carried out with monometallic solutions prepared from stock solutions of 1000 mg/l of Cd^{2+}, Pb^{2+}, and Cu^{2+} prepared from chemical reagents of analytical grade: $CdSO_4{\cdot}8/3H_2O$, $Pb(NO_3)_2$ and $CuSO_4{\cdot}5H_2O$, respectively. In the case of lead, nitrate instead of sulfate was used to avoid metal precipitation, though the effect of the anion is negligible [15]. Only initial pH values of the solutions (5 for copper and lead, and 6 for cadmium), optimized from previous tests, were adjusted with diluted H_2SO_4 for Cd and Cu, HNO_3 for Pb, and NaOH as needed. Beads (1 g/l) were placed in contact with the metal solutions (75 ml) in glass 100 ml Erlenmeyers with orbital stirring at room temperature (23 ± 1 °C). Liquid samples (3 ml) were removed at different times (0, 15, 60, 120, 240, 480, and 1400 min) and the pH and metal concentration (using flame atomic absorption spectroscopy (FAAS) analysis, with an acetylene flame, PerkinElmer 1100B atomic absorption spectrometer) were measured. Metal uptake was calculated from the following expression:

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

where C_0 is the initial metal concentration (mmol/l); C_t is the metal concentration at time t (mmol/l); B is the biomass concentration (g/l).

2.2.1. Kinetic studies

Sorption data were described using different kinetic models. The pseudo-second-order kinetics equation is [9]

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

where q_2 is the maximum kinetic uptake (mmol/g of biomass); q_t is the metal uptake at time t (mmol/g of biomass); k_2 is the rate constant of the pseudo-second-order sorption (g/mmol min).

That can also be expressed as

$$\frac{1}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2}t \tag{3}$$

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

The intraparticle diffusion model proposed by Weber–Morris [10] assumes a two-step biosorption process—metal binding to the biomass surface followed by metal diffusion through its pores:

$$q_t = k_p t^{1/2} + C \tag{4}$$

where k_p is the intraparticle diffusion constant (mmol/g $min^{1/2}$).

This model applies when a linear representation of q_t vs. $t^{1/2}$ is obtained, and k_p is the slope of the curve. If this linear plot intercepts the origin, metal uptake is controlled by intraparticle diffusion [10].

2.2.2. Isotherm studies

The isotherms were obtained using a similar procedure as for the kinetic experiments [4,14]. Tests were run for 24 h, time enough to reach the equilibrium, at the initial pH values previously mentioned, with 0.5 g/l initial biomass concentration and 50 ml of different initial metal concentration solutions: 10, 25, 50, 100 and 150 mg/l. These results were adjusted to the Langmuir model that can be expressed as [11]

$$q_e = \frac{bq_{max}C_e}{1 + bC_e} \tag{5}$$

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

The Langmuir affinity constant indicates the affinity between the biomass and a certain metal, the greater its value the greater the affinity.

These sorption parameters can be calculated from the isotherm using a linear representation of the Langmuir model (C_e/q_e vs. C_e):

$$\frac{C_e}{q_e} = \frac{C_2}{q_{max}} + \frac{1}{bq_{max}} \tag{6}$$

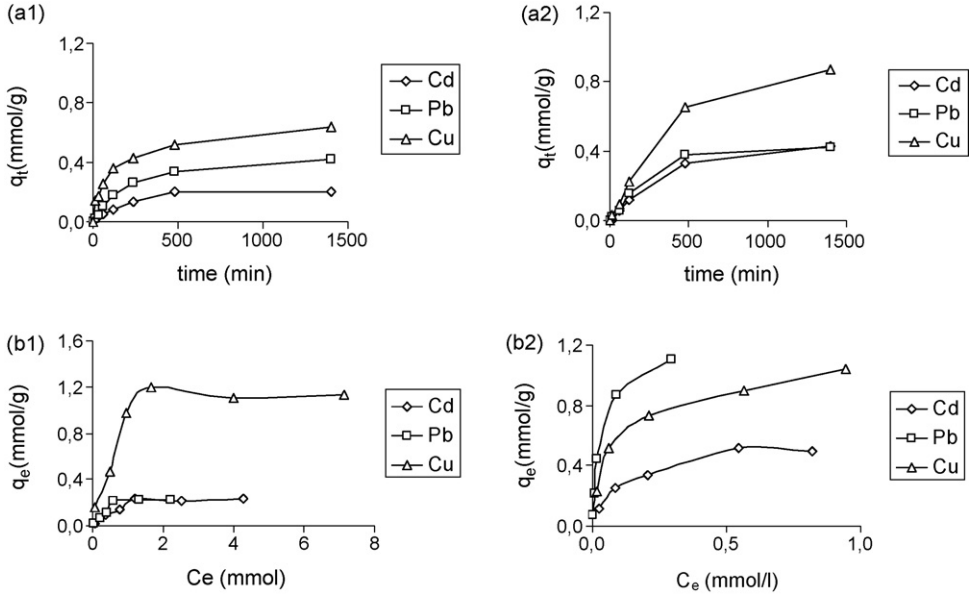

Fig. 1. Evolution of metal uptake (a) and isotherms (b) of Cd, Pb and Cu biosorption with alginate xerogels (1) and immobilized biomass (2).

2.3. Biosorbent characterization

FTIR analyses were performed on KBr discs with 2% finely ground sample were analysed in a MIDAC Prospect-IR spectrophotometer. 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}. The xerogel beads, with and without adsorbed metal, were coated with a thin layer of graphite and then gold to enhance image resolution, and examined under a FE-SEM microscope (JEOL JSM-6335F).

3. Results and discussion

3.1. Kinetic studies

Fig. 1a shows the evolution of metal concentration and metal uptake during cadmium, lead and copper biosorption with calcium alginate xerogel beads with and without immobilized alga. Equilibrium metal concentrations were attained after 8 h.

Sorption data fitted linearly to the pseudo-second-order kinetic model, indicating that the process occurred in at least two steps

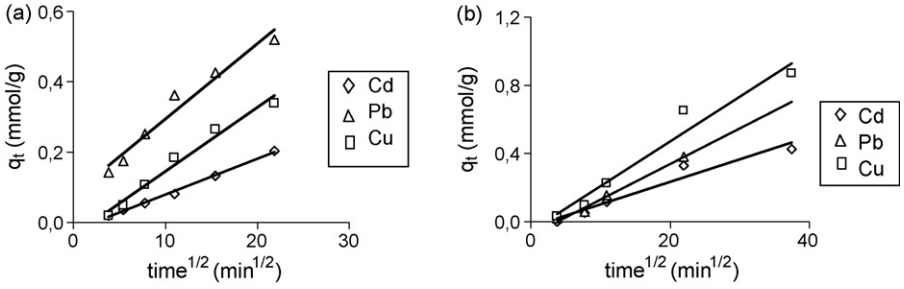

Fig. 2. Application of the intraparticle diffusion model to the biosorption of Cd, Pb and Cu with alginate xerogels (a) and immobilized biomass (b).

Table 1
Kinetic and Langmuir parameters for the biosorption of Cd, Pb and Cu with alginate xerogel beads

	Alginate			Alginate 1B:1A		
	Cd	Pb	Cu	Cd	Pb	Cu
Pseudo-second-order kinetic model						
q_2 (mmol/g)	0.235	0.503	0.675	0.595	0.548	1.27
k_2 (g/mmol min)	0.0237	7.6×10^{-3}	0.0145	4.2×10^{-4}	4.42×10^{-4}	3.41×10^{-3}
R^2	0.989	0.986	0.996	0.974	0.962	0.966
Intraparticle diffusion model						
k_p (mmol/g $min^{1/2}$)	0.0103	0.0182	0.0214	1.32×10^{-2}	2.08×10^{-2}	5.95×10^{-2}
R^2	0.996	0.977	0.960	0.948	0.988	0.956
Langmuir isotherm model						
q_{max} (mmol/g)	0.275	0.280	1.20	0.579	2.26	0.617
b (l/mmol)	1.42	2.16	2.64	8.97	31.41	12.76
R^2	0.975	0.960	0.991	0.992	0.999	0.993

(Fig. 2). According to Langmuir [16], cadmium, lead and copper are mainly found as hydrated complexes in solution rather than as dissociated cations. These complexing reactions, that are probably influenced by the pH of the solution, can inhibit or increase metal uptake and affect the diffusion properties of the ions due to their increased size [17]. Therefore, a two-step biosorption process, consisting of the dissociation of these complexes and the interaction of metals with active sites in the beads, could explain the linear fit to the pseudo-second-order kinetic model.

For alginate beads without alga, linearization of the intraparticle diffusion model was only possible up to 8 h, time at which the equilibrium metal concentration was reached (Fig. 2a). In the case of immobilized alga, this linearization was possible throughout the entire experiment, probably due to the larger size of the beads (Fig. 2b). The fitting of data indicated that diffusion was involved during biosorption, but was not the rate-controlling step since the linear plots did not intercept the origin [10]. It also confirms the participation of other processes, such as dissociation of water–metal complexes and interaction of the metals with the gels.

Table 1 shows the biosorption kinetic parameters obtained from the pseudo-second-order kinetic and intraparticle diffusion models. These values are more easily compared, along with those of the free alga, in Fig. 3. Copper had the highest intraparticle diffusion constant (k_p) and then the fastest diffusion, probably due to its smaller hydrated cation size (0.072 nm) with respect to cadmium (0.097 nm) and lead (0.120 nm). For xerogels without alga, cadmium had slower intraparticle diffusion (k_p) than lead despite its smaller cation size. Nevertheless, cadmium showed a higher kinetic rate (k_2), indicating that the interaction between this cations and alginate beads was faster than for lead. Thus, the beads probably contained a higher number of cadmium binding sites that became saturated from the outside to the inside, and that slowed its diffusion rate. It is also important to point out that the beads without alga presented a smaller uptake for cadmium than for lead and copper (Fig. 3a). Therefore, although lead diffusion was faster, its binding to biomass active sites was slower. Possible explanations include steric hindrances due to its larger cation size, and complexation reactions with active sites that are generally slower than ionic binding [18].

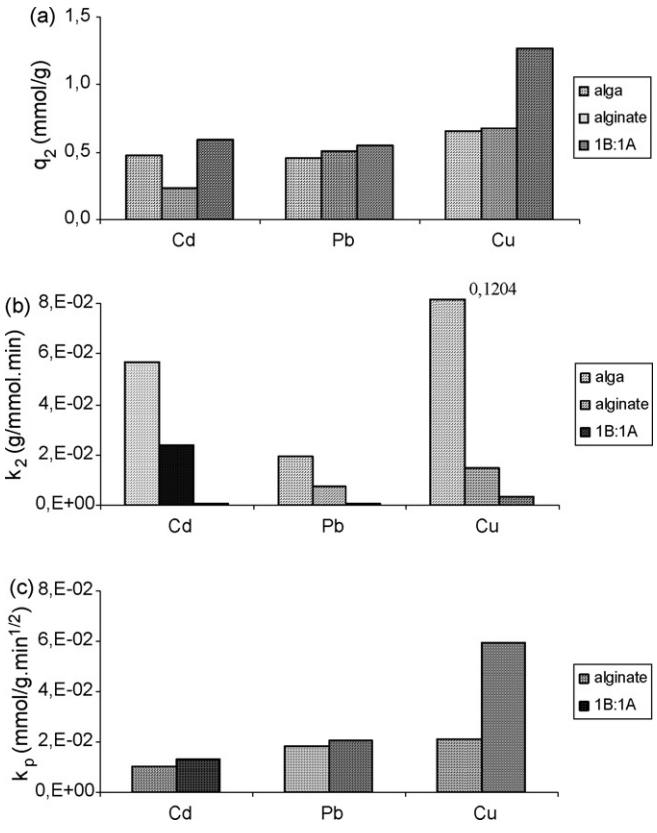

Fig. 3. (a–c) Comparison between the kinetic parameters (q_2, k_2 and k_p) of Cd, Pb and Cu biosorption with alginate, immobilized biomass, and *Fucus vesiculosus*.

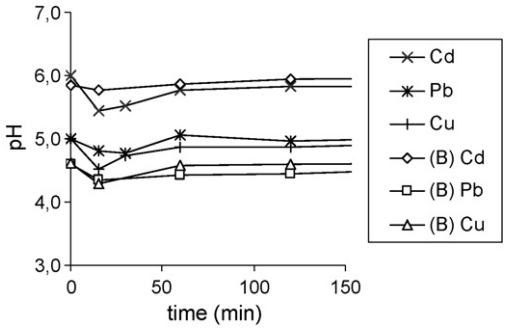

Fig. 4. Detail of the initial pH evolution during the biosorption of Cd, Pb and Cu with alginate xerogels and immobilized biomass (*B*).

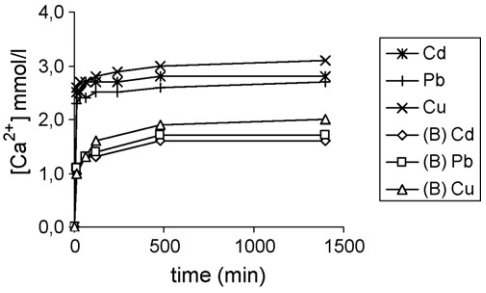

Fig. 5. Calcium release during Cd, Pb and Cu biosorption with alginate xerogels and immobilized biomass (*B*).

Xerogel beads containing immobilized alga showed the same order of kinetic uptakes (q_2) than free alga (Cu ≫ Cd ≈ Pb). This suggests that this component had a more important participation in the kinetics of the process than the alginate support itself. These values were greater than those obtained for the alginate and free alga, indicating a synergic effect between both components. Nevertheless, the kinetic sorption rates (k_2) were slower. The diffusion rate, deduced from the intraparticle diffusion constant (k_p), of immobilized alga, compared to alginate xerogels, was slightly greater for cadmium and lead but much greater for copper, the smallest ion. Therefore, alginate with immobilized alga could have presented less resistance to diffusion than xerogels without alga.

Table 2
Relationship between the amount of metal adsorbed by the xerogels and the calcium release to the solution

	Adsorbed Me (mmol)	Released Ca (mmol)
Alginate		
Cd	0.0166	0.209
Pb	0.0315	0.202
Cu	0.0498	0.232
Blank	–	0.0188
Alginate 1B:1A		
Cd	0.032	0.12
Pb	0.0315	0.128
Cu	0.0652	0.15
Blank	–	0.0116

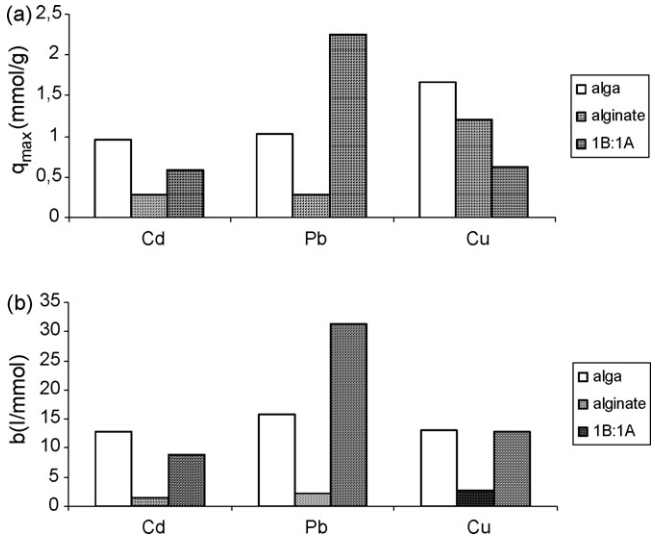

Fig. 6. (a and b) Comparison between the Langmuir parameters Cd, Pb and Cu biosorption with alginate xerogels, immobilized biomass and *F. vesiculosus*.

Although only the initial pH values of the metal solutions were adjusted before contact with the beads, pH initially dropped during biosorption, and later stabilized at values near the initial pH (Fig. 4). The final values were 5.87, 4.89, and 5.12 for alginate xerogels, and 6.1, 4.96, 5.1 for immobilized alga, with cadmium, lead and copper, respectively. These variations, albeit very small, could indicate an exchange between protons in the beads and metals in solution, specially at the beginning of the biosorption process. Such exchange has already been observed in previous studies with free alga [4,19].

Initial proton release can be related to dissociation of acidic groups, including carboxyl groups, which are the main binding sites of alginate in the biosorption of heavy metals [20]. The dissociation of these acid groups takes place at pH above the pK_a of the alginate components of the gel and the algal cell wall (3.20 for guluronic acid and 3.38 for mannuronic acid) [21]. Another source of protons is the dissociation of metal–water complexes [16]. After the initial pH decrease there was a slight increase possibly due to the exchange of protons in solution with calcium in the gels, and in the case of immobilized biomass, with other light metals present in the brown alga [22].

Calcium concentration in solution increased during metal biosorption (Fig. 5) and this release was greater than in a blank assay only with deionized water (Table 2). This suggests that calcium could be involved in the metal uptake through an

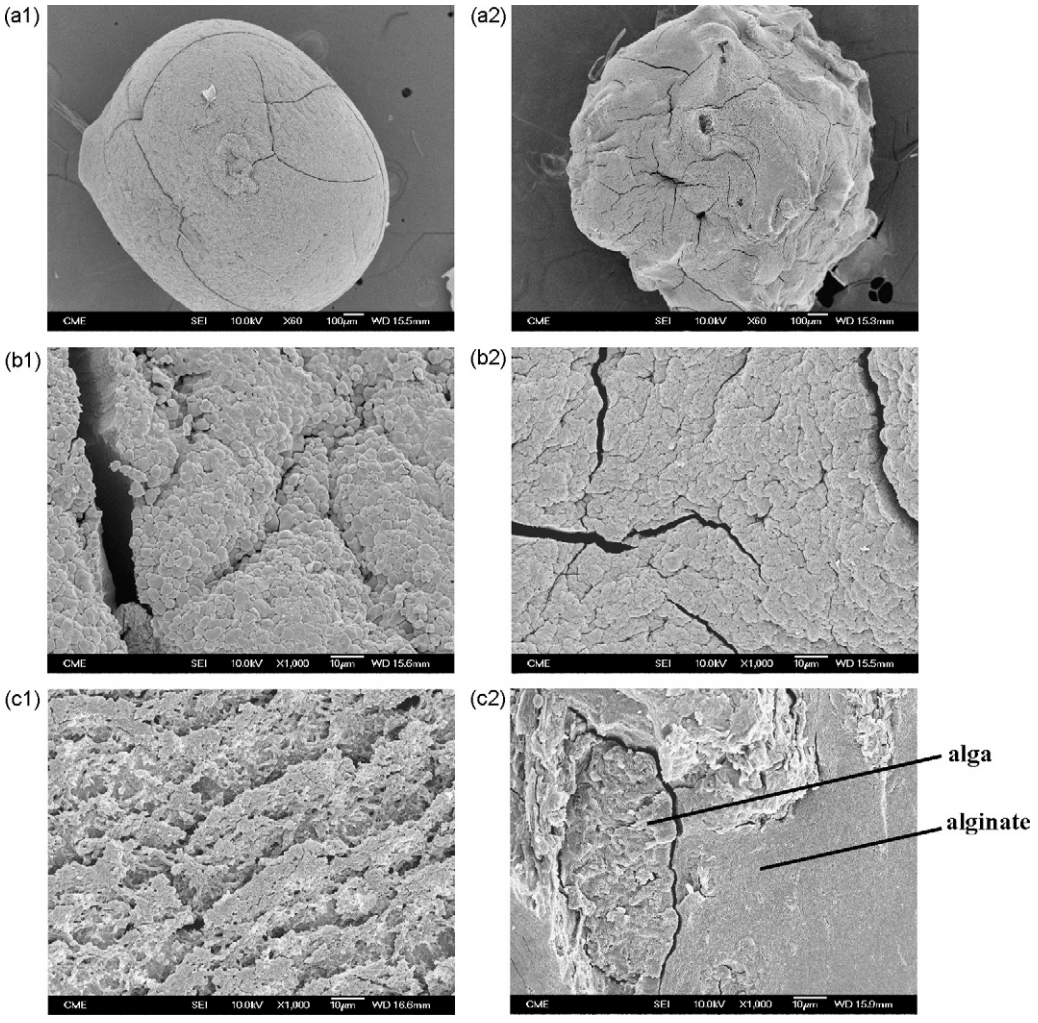

Fig. 7. FE-SEM micrographs of surface (a and b) and interior (c) of an alginate xerogel (1) and an immobilized biomass bead (2).

ion-exchange mechanism. Ion exchange between calcium from biomass and metals in solution has been observed during the biosorption of cadmium, lead and copper with brown algae and alginate [4,5,23]. Nevertheless, none direct proportional relationship was found between the amounts of metal adsorbed and calcium released. Therefore, this type of ion exchange could not be the only process participating in the biosorption.

3.2. Isotherm studies

The biosorption isotherms of cadmium, lead and copper with alginate xerogel beads with and without *F. vesiculosus* fitted the Langmuir model and the corresponding parameters that quantify this process were obtained (Table 1 and Fig. 6). Metal uptakes of xerogel beads without alga (q_{max}) showed a similar order than free alga: Cu > Pb ≈ Cd. The Langmuir affinity constants (b) followed the order: Cu > Pb > Cd. Dronnet et al. [24] obtained a similar order for the biosorption of those metals with sugar-beet pectins, polysaccharides similar to alginate. Nevertheless, the comparison has its own restrictions due to the differences in experimental conditions and the nature and preparation of the biosorbents. Equilibrium constants are related to the free energy and the enthalpy change of the biosorption. Their values increase with bond strength and affinity, providing an order of stability of the alginate–metal complexes [25]. In this case, copper formed the most stable bindings, followed by lead and cadmium the weakest.

For immobilized alga, the maximum metal uptakes and Langmuir affinity constants followed the same order: Pb ≫ Cu > Cd, but different to that obtained with free alga and alginate xerogels. That order agrees with the rule of Irving Williams concerning with the stability of complexes formed by oxygenated groups in the biomass, such as carboxyl groups, and metal cations [24]. It also agrees with the metal uptakes obtained by Sheng et al. [26] for the brown alga *Sargassum*, and Langmuir affinity constants determined by Papageorgiou et al. [6] for calcium alginate.

Immobilized alga increased the maximum cadmium and lead uptakes with respect to gels without alga, 10 times in the case of lead, with an uptake greater than the free alga itself. The presence of *F. vesiculosus* also increased the stability of the metal binding and the affinities for the three metals with respect to alginate xerogels. In the case of lead, this affinity was also higher than for free alga. Therefore, immobilized biomass has different biosorbent properties than its isolated components.

Davis et al. [23] suggested that the affinity of heavy metals by alginate is related to the amount of guluronic acid and other uronic acids. These acids contain most of the carboxyl groups in alginate

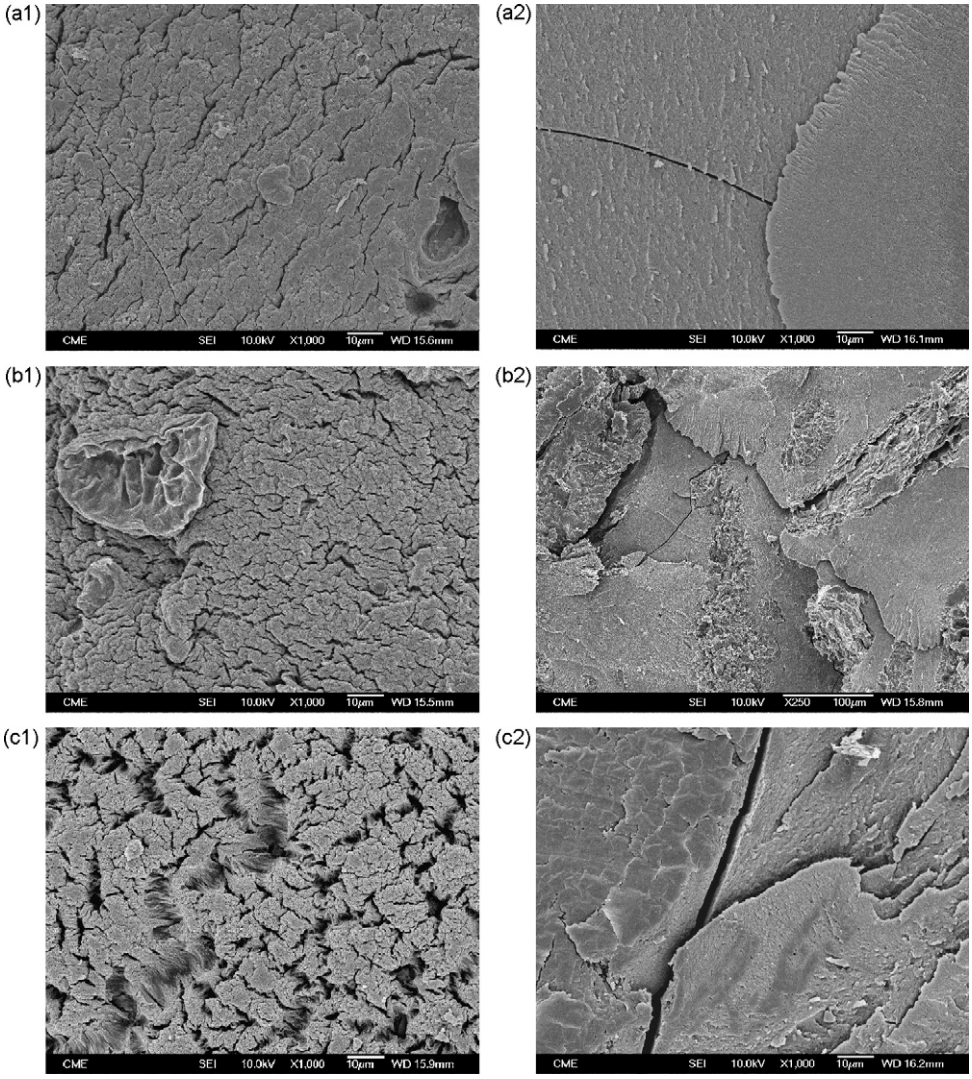

Fig. 8. FE-SEM micrographs of alginate xerogel (a) and immobilized biomass (b) after copper biosorption. (c) Alginate xerogel bead rehydrated only with water. Surface (1) and interior (2).

and would be mainly responsible for metal biosorption. These same authors have also suggested that the "egg-box" structure of the gels and the crosslinking between metal and carboxyl groups is related to the metal selectivity of alginate. The gel structure creates a specific stereochemical environment that determines this selectivity.

In a similar study, alginate was extracted from the brown alga *Laminaria digitata* and dry beads were used for the biosorption of cadmium, lead and copper [6]. These authors obtained different Langmuir parameters using different experimental procedures, with a higher biomass concentration (1 g/l), and alginate from a different source. This suggests that a standard approach is necessary to obtain these parameters in order to compare biosorption behaviors observed in different studies.

3.3. Biosorbent characterization

Fig. 7 shows the morphology of the xerogel alginate beads with and without *F. vesiculosus* before metal uptake. As shown in this figure, the immobilized alga can sometimes be clearly distinguished from the surrounding gel matrix.

SEM observation of the beads after biosorption and energy dispersive X-Ray microanalyses (EDS) confirmed the penetration of cadmium, lead and copper and a uniform distribution of these metals on the alginate surface (results not shown). After metal uptake, the gels presented a more uniform and organized structure, specially inside (Fig. 8). That change was observed after biosorption of the three metals and was significantly evident in xerogels without alga. The effect was only partially due to rehydration, since beads placed for 24 h in deionized water without metals still retained a more irregular appearance (Fig. 8).

Another explanation could be alginate regelification due to the substitution of calcium ions by cadmium, lead and copper in the "egg-box" structure of the gel, specifically in the guluronic acid blocks. This could also explain the increase in the amount of calcium released to solution with respect to metal adsorbed (Section 3.1), since less calcium would be necessary in a more organized gel structure. That greater uniformity suggests a higher stability of the substituted gels, as observed by Ouwerx et al. [27] for cadmium and copper alginate with respect to calcium.

This fact has been confirmed in other studies using different characterization techniques. For instance, Fourest and Volesky [28] deduced these type of bindings between cadmium and carboxyl groups of alginate chains in the cell wall of the brown alga *Sargassum* using FTIR. Dronnet et al. [24] also documented these type of bindings between cadmium, lead and copper and pectins using a dual wavelength spectrophotometric method (DWSM).

Non-gelated sodium alginate, the xerogel beads with and without alga, the free alga and the beads after biosorption of cadmium, lead and copper were characterized with FTIR (Fig. 9) and interpreted according to Figueira et al. [29] and Sheng et al. [30]. The main bands modified by calcium gelation, alga immobilization and heavy metal biosorption were those corresponding to hydroxyl and carboxyl stretching (symmetric and asymmetric), indicating that these were the main functional groups involved in the biosorption (Table 3). These results are similar to others obtained from alginate and brown algae with different metals [4,5,12,31]. For immobilized biomass, the displacement of the hydroxyl band after lead uptake was greater than for cadmium and copper. An increased participation of these groups would explain a more stable bond and higher equilibrium constant.

The decrease of the distance between the two carboxyl bands with respect to non-geled alginate is an indication of complexating and chelating reactions between those groups and metal cations (Table 3) [12,29]. In fact, Rendleman [18] tested the solubility of alginate and other similar polysaccharides and suggested that metal cations exert a precipitation effect on alginate. Other studies suggest the possibility of two types of bonds between carboxyl groups and divalent metal cations: bidentate complexes with one carboxyl group, and ionic binding as in the "egg-box" model with calcium [28,32].

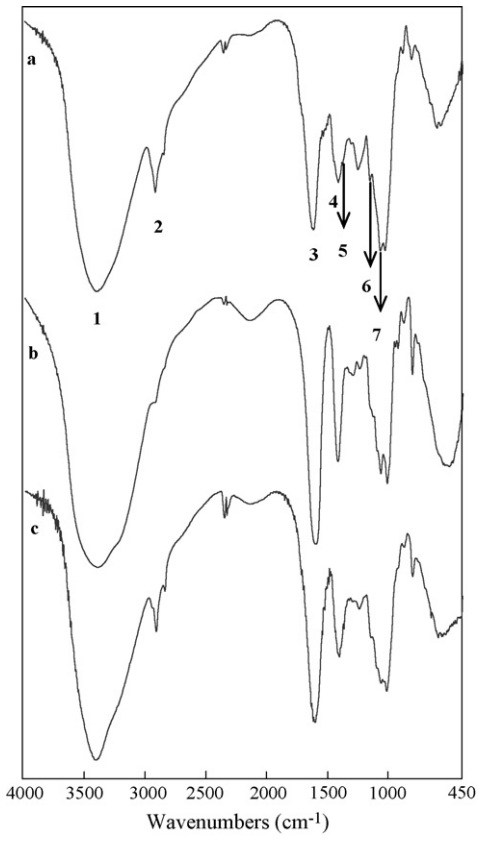

Fig. 9. FTIR spectra of the brown alga *F. vesiculosus* (a), calcium alginate xerogels (b), and the xerogels with this alga (c). The most relevant bands are numbered: (OH) stretching (1), (CH) stretching, asymmetric (3) and symmetric (4) (COOH) stretching, asymmetric (5) and symmetric (6) (SO_3) stretching, and (CO) stretching of (COH) (7).

The importance of carboxyl groups in heavy metal binding has been extensively confirmed [1]. These groups are present in uronic acids of alginate and provide negative charges to attract divalent metal cations. Carboxyl groups are also responsible for alginate

Table 3
Most relevant infrared spectral bands of different biomasses with and without adsorbed metal

Biomass	Stretching (cm^{-1})			
	(OH)	(C=O)	(C—OH)	Δ(C=O—C—OH)
Fucus vesiculosus (<0.5 mm)	3411	1625	1421	204
Alginate				
Non-geled	3416	1628	1418	210
Beads	3406	1617	1433	184
Cd	3417	1618	1421	197
Pb	3420	1618	1420	198
Cu	3420	1618	1421	197
Alginate 1B:1A				
Beads	3415	1619	1422	197
Cd	3420	1623	1420	203
Pb	3412	1617	1420	197
Cu	3409	1618	1408	210

selectivity towards metals, as explained earlier [23]. Fourest and Volesky [28] observed that cadmium, lead and copper binding was proportional to the amount of these groups in marine algae. These authors also observed that cadmium and lead uptake decreased with the partial or total sterification of carboxyl groups in the brown alga *Sargassum*. Similarly, Kapoor and Viraraghavan [33] also found a decrease in cadmium, lead and copper biosorption with fungus when these groups were blocked or sterified. Aside from carboxyl groups, other groups from the alga can participate in metal biosorption, such as sulfyhydrils and sulfonates. However, these bands were not clearly defined in the alginate xerogels with immobilized alga because of overlapping effects [29].

4. Conclusions

F. vesiculosus immobilized in alginate xerogels constitutes an excellent biosorbent for cadmium, lead and copper, sometimes with a better biosorption performance than alginate alone or even the free alga. In this way, immobilization

- improved the kinetic uptakes of the three metals but decreased the kinetic rates;
- increased the diffusion rates, specially for small cations-like copper;
- improved the cadmium and lead maximum uptakes of alginate xerogels without biomass. In the case of lead, the uptake was even higher than for free alga;
- increased the affinities towards cadmium, lead and copper, with respect to alginate gels without alga. For lead, the affinity was also higher than for free alga.

After biosorption, the metals bound mainly to carboxyl groups in the biomass. Calcium in the xerogels was displaced by heavy metals from solution according to the "egg-box" model, creating a more uniform and organized structure.

The results obtained in this study provide new insights for the characterization and quantification of biosorption with calcium alginate xerogel beads with and without immobilized alga, and constitute a preliminary approach for further applications in continuous biosorption systems. This immobilized biomass is particularly effective for lead recovery, and is readily available for dilute industrial and wastewater treatment.

Acknowledgements

The authors acknowledge the financial support received from the Ministry of Science and Technology of Spain and the European Social Fund (Project REN 2002-02196). Y.N. Mata wishes to thank these institutions for the scholarship she received through the same project.

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