Biosorption of Cu(II), Zn(II), Cd(II) and Pb(II) by dead biomasses of green alga *Ulva lactuca* and the development of a sustainable matrix for adsorption implementation

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ABSTRACT

Many industries have high heavy metals concentrations in their effluents that should be treated before disposal in drains or natural watercourses. When adsorption process is evaluated to generate and implement an efficient, economical and sustainable method suitable for heavy metals removal from contaminated effluents, it is necessary to develop an experimental setup that contains the adsorbent.

Ulva lactuca, a marine green alga, was studied as a natural biosorbent for heavy metals at acid pH conditions. Adsorption experiments were carried out in glass columns and in batch where the alga was suspended or fixed in an agar matrix.

Langmuir and Freundlich models were applied to the experimental results. Langmuir model best describes the adsorption isotherms in all analyzed cases. The adsorption capacity increases with pH. Kinetic studies demonstrate that, in most studied cases, the adsorption follows a pseudo second order kinetics model.

Removal efficiencies of the biomaterial supported in agar or fixed in columns were: fixed in columns > suspended in batch mode > fixed in agar.

Finally, the effect of the presence of two sorbates, Cd and Pb, in the solution was measured and results demonstrate that adsorption of both metals are diminished by co/adsorption.

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1. Introduction

The increasing concentration of heavy metals in waters is manly due to effluent discharges from industries. Pollution of natural waters by metal ions has become a major issue all over the world because metal concentrations in waters often exceed the admissible values. Consequently, industries are required to diminish the contents of heavy metals in their effluents to acceptable levels. As a result, scientists are studying new and alternative technologies to remove trace metals from polluted waters [1] and industrial effluents.

Biosorption, known as the sorption of heavy metals onto biological materials, is becoming a potential alternative for toxic metals removal from waters [2,3], since is an economical, efficient and sustainable method able to replace the most widely applied industrial materials such as activated carbon and ion-exchange resins. Biosorption is a cost effective technology that uses readily available

biomass from nature [4]. In recent years the metal biosorption potential of various red, green and brown seaweeds were investigated by many scientist [5–8].

Seaweeds have a high bonding affinity with heavy metals [9,10], their cell walls have different functional groups (such as carboxyl, hydroxyl, phosphate or amine) that can bind to metal ions [11] and, depending on the pH, these groups are either protonated or deprotonated [12,13].

Many works describing metals biosorption on suspended biomass [14–20] and on fixed on different type of matrixes [21–23] among others, have been published. The advantages of using dead aquatic algae for metal removal relays on its high efficiency as biosorbents, easy handling, no nutrient requirements, low costs, and they can be easily collected along the shore tide.

The present study was focused on heavy metal biosorption equilibrium in the absence of metabolic processes. Among the diverse biomass alternatives, we have chosen *Ulva lactuca* as the biosorbent material for copper(II), cadmium(II), lead(II) and zinc(II). The aim of this work is to study this alga as a potential biosorbent of heavy metals, and its possible use for industrial wastewater treatment. Industrial application feasibility depends on the possibility
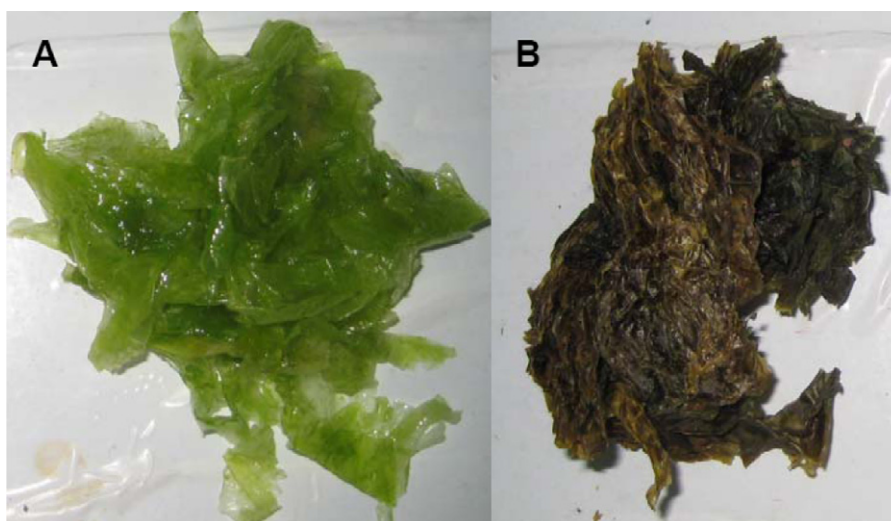

Fig. 1. *U. lactuca* fresh (A) and dried in an oven at 60 °C for 24 h (B).

to pack the biosorbent in fixed beds in order to reduce the pressure drops and the clogging probabilities. The immobilization of fine sieved material into a matrix is presented as an alternative to improve these characteristics in order to develop a cleaning technique that is effective, economic and with no secondary effects on the environment.

2. Materials and methods

2.1. Biomasses and pretreatment

U. lactuca (Fig. 1A) was collected from Mar del Plata, Argentina. The alga was carefully washed with mono distillate and Milli-Q water to remove salt, sand and microorganisms, which may overestimate the results. Then, the material was dried in an oven at 60 °C for 24 h, crushed in a mortar and sieved to obtain fine particles (<125 μm). The resulting material was stored in a dry environment at room temperature.

The specific surface area was determined by water adsorption at room temperature ($S_w = 292 \pm 6 \, m^2 \, g^{-1}$) [24,25]. Seaweeds particles were kept in a desiccators containing a saturated solution of $Ca(NO_3)_2 \cdot 6H_2O$ that ensures a relative humidity of rh = 0.56.

2.2. U. lactuca fixed in agar

A predetermined amount of pretreated algal material and 10 ml of an agar solution ($20 \, g \, l^{-1}$) previously heated, were added in a beaker. The suspension was mixed and transferred to a petri dish of known mass and dimensions. Once the alga/agar suspension solidified, the matrix obtained was cut into 0.5 cm × 0.5 cm squares, which were stored in Milli-Q water in the refrigerator for later use.

2.3. Metal solutions

All chemicals used were of analytical reagent grade and were used without further purification. All solutions and algal suspensions were prepared using Milli-Q water.

Zinc(II), copper(II), cadmium(II) and lead(II) stock solutions of $1000 \, mg \, l^{-1}$ were prepared by dissolving $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and $Pb(NO_3)_2$, respectively. All metal solution used in the experiments were obtained by stock solution dilution.

2.4. Experimental procedure

2.4.1. Batch experiments

Batch sorption experiments were performed suspending 0.1 g of biomass, or its equivalent fixed in agar, in 100 ml of Zn(II), Cu(II), Cd(II) or Pb(II) solutions. The metal concentration ranged between 0.1 and 7 mM. Suspensions were kept in constant agitation at desired and constant pH and room temperature.

After 24 h, algal biomass was filtrated with cellulose nitrate membrane filters (0.22 μm pore). Afterwards, the final metals concentrations in the remaining solution were determined and metal uptake (q) was calculated using the following mass balance equation [26]:

$$q = \frac{(C_i - C_{eq})V}{m} \tag{1}$$

where C_i is the initial metal concentration ($mg \, l^{-1}$ or mM), C_{eq} the equilibrium metal concentration ($mg \, l^{-1}$ or mM), V the solution volume (l) and m is the dry alga weight (g).

Control experiments were carried out in the absence of adsorbents in order to determine whether there is any adsorption on the container walls.

2.4.2. pH effect

The pH dependence of *U. lactuca* metal uptake was studied through batch sorption experiments in a pH range from 2 to 5.5 to avoid metals hydr(oxide) precipitation at pH values above 6 that would lead to an overestimation of the adsorption. Experiments were carried out with $1 \, g \, l^{-1}$ algal concentration and Cu(II), Zn(II), Cd(II) and Pb(II) initial concentration of 0.76, 0.89, 0.44 and 0.21 mM, respectively. pH was adjusted along the experiment using 0.1 M HCl or 0.1 M NaOH. Resulting pH was measured using a Metrohm 644 pH-meter with a combined glass microelectrode.

2.5. Column experiments

2.5.1. Biosorption in columns

The adsorption of cadmium and/or lead by *U. lactuca* packed in glass columns of 15 cm long and 0.5 cm of internal diameter were studied. At the bottom end of the column a fiberglass cap was placed to avoid seaweed particles losses. The columns were filled, and later compacted by gravity, with 0.01 g of pretreated seaweed,

as described in Section 2.1; adsorbent particles should not be too small to ensure a steady flow of liquid through the column, or too large to avoid the formation of preferential pathways and ensure a high specific surface of the material. The bottom of the column was connected to a peristaltic pump (Gilson) using a silicone tube to obtain a constant steady downward flow of 3.5 ml min^{-1}.

Solutions of 10 ml of a known concentration of lead and/or cadmium were pumped through the columns at constant pH 5.5 and room temperature. Samples of 1 ml were collected at time intervals to assess the residual concentration of metals and to determine the retained amount of metal.

The aqueous solutions containing the pollutants flowed from beginning to end of the column passing through the packed biosorbent material. Heavy metals were gradually removed from the mobile phase, decreasing their concentration in solution as they are retained on the solid phase. The graphical representation of q as a function of C_{eq} is called breakthrough curves. The metal concentration leaving the column begins to increase gradually once the adsorbent within the column is saturated with metal, and this concentration is called breakthrough point. The breakthrough curves and the breakthrough point are very important parameters to evaluate the adsorption capacity of a column and can be determined from the following equation [27–30]

$$q_R = \frac{C_{in} \times Q}{1000 \times m_s} \int_0^t \left(1 - \frac{C_{out}}{C_{in}}\right) dt \qquad (2)$$

where q_R is the mass of metal adsorbed (mmol metal g algae^{-1}) until the column is saturated; C_{in} is the solution concentration in the column inlet (mM); C_{out} the solution concentration leaving the column (mM); m_s is the amount of biomass in the column (g) and Q is the solution flow (ml min^{-1}).

The adsorption capacity of cadmium and lead was determined from Eq. (2) [28,29]. The competitive effect due to the presence of a second metal in the aqueous solution was studied using a similar procedure as described above by adding binary solutions of lead and cadmium to the columns.

2.5.2. Desorption in columns

The regeneration of the adsorbent material packed in columns was studied by successive metal adsorption/desorption cycles. Metal desorption was achieved after the column was saturated by adding 10 ml of H$_2$SO$_4$ (10^{-3} M) into the column at constant downward flow (3.5 ml min^{-1}). To quantify the amount of metal remaining in the column and to evaluate de desorption rate, aliquots of 1 ml were taken at constant time intervals.

The desorption rate may be estimated with the following equation [29]:

$$q_D = \frac{Q}{1000 \times m_s} \int_0^t C_{out} \, dt \qquad (3)$$

where q_D is the amount of desorbed metal per mass of biosorbent (mmol metal g algae^{-1}), Q, C_{out} and m_s have the same meaning as in Eq. (2).

After desorption, the columns were washed with Milli-Q water in order to eliminate the remaining acid and reuse them in other adsorption/desorption cycles.

2.6. Metal quantification

Cadmium and/or lead concentrations were determined using a selective ion electrode for each metal (Metrohm and Radiometer Analytical, respectively). Zinc concentrations were spectrophotometrically measured using zincon (2-carboxy-2′-hydroxy-5′-sulphoformacylbenzol) as a chromogenic reagent. Zinc–zincon blue complex is formed at pH values between 8.5 and 9.5 [31] and was measured at 620 nm wavelength.

Copper concentrations were spectrophotometrically measured using sodium diethyldithiocarbamate (DDTC) as reagent dissolved in ethanol–water 50% (v/v) and H$_2$SO$_4$ (10^{-3} M) [32]. DDTC forms a yellow complex with Cu at low pH. Absorbance of the corresponding solution was measured at 440 nm in a double beam UV–Vis spectrophotometer Shimadzu-Pharmaspec UV-1700.

2.7. Scanning electron microscopy (SEM)

Samples of dehydrated material with and without adsorbed metals were fixed to 10 mm metal mounts using carbon tape and spit coated with gold under vacuum in an argon atmosphere. The surface morphology of the coated samples was visualized by a file emission gun scanning electron microscope Zeiss (FEG-SEM Zeiss LEO 982 GEMINI) with combined Energy Dispersive X-ray Analyzer (EDS) at a voltage of 3.0 kV. SEM permitted the identification of interesting structural features on the seaweed surface with EDS. INCA software was used to determine the elemental composition of the surface before and after metal binding.

2.8. Reproducibility and data analysis

Unless otherwise indicated, all data shown are the mean values of three replicate experiments. Standard deviations were below 5%.

The statistical data analyses were made using SigmaPlot software package.

3. Results and discussion

3.1. Biosorption kinetics

Surface complex formation with metal ions involves the coordination of metal ions with oxygen donor atoms that constitute the biomasses cell walls, follow by the release of protons from the surface, for example:

$$\equiv SOH + Me^{2+} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \equiv SOMe^+ + H^+ \qquad (4)$$
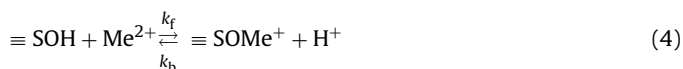
where Me^{2+} is the sorbate in solution, $\equiv$SOH is the sorbent surface site which is susceptible of coordination, $\equiv$SOMe$^+$ is the sorbate fixed on the sorbent, and k_f and k_b are the kinetic constants for the forward and back reaction steps.

Equilibrium analysis is fundamental in order to evaluate the affinity and capacity of a sorbent. However, it is important to assess how sorption rates vary with aqueous free metal concentrations, and how the kinetics rates are affected by sorption capacity or by the sorbent character [33]. The adsorption kinetics of Zn(II), Cu(II), Cd(II) and Pb(II) by *U. lactuca* as a function of time, at constant ionic strength, room temperature and pH 5.5 is shown in Fig. 2. The initial metal concentrations were 0.81, 1.00, 1.01 and 0.92 mM, respectively. The experimental coverage (q) of the metals studied was calculated using Eq. (1). The metal adsorption increased with contact time to reach maximum adsorption during the first 2 h of contact between the alga and metals. The maximum adsorption (q) for the four metals were achieved rapidly (Fig. 2), being the zinc the least adsorbed per mass of biosorbent, and the lead the most adsorbed. The q values obtained were 0.339, 0.145, 0.334 and 0.824 (mmol g^{-1}) for copper, zinc, cadmium and lead, respectively. Based on these results, the kinetic models of pseudo-first and pseudo-second order were applied for interpretation.

Table 1
Pseudo first order and pseudo second order kinetic parameters for four metals at room temperature and pH 5.5. q_e: metal uptake at equilibrium; k_1: pseudo first order constant; k_2: pseudo second order constant.

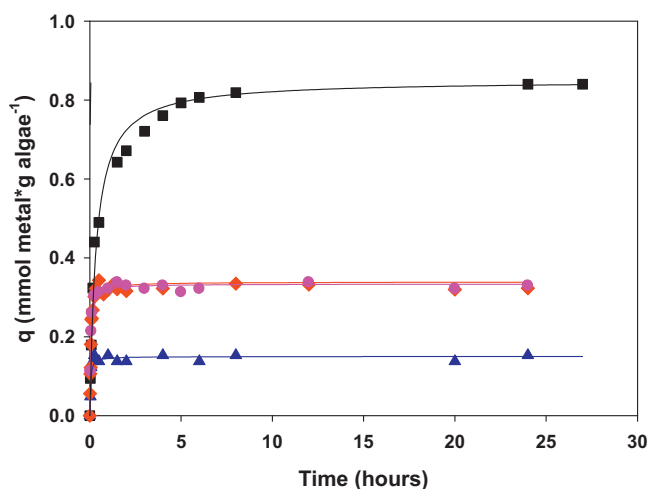| Metal		Zn(II)	Cu(II)	Pb(II)	Cd(II)
Experimental values	q_e (mmol g^{-1})	0.145	0.339	0.824	0.334
	q_{e1} (mmol g^{-1})	0.13 ± 0.03	0.29 ± 0.03	0.831 ± 0.006	0.26 ± 0.03
Pseudo-first order	k_1 (h^{-1})	13.71 ± 2.83	8.19 ± 0.85	2.89 ± 0.06	8.49 ± 0.85
	R^2	0.910	0.915	0.998	0.962
	q_{e2} (mmol g^{-1})	0.147 ± 0.002	0.324 ± 0.001	0.852 ± 0.002	0.328 ± 0.001
Pseudo-second order	k_2 (g h^{-1} mmol^{-1})	147 ± 11	266 ± 18	3.13 ± 0.18	103 ± 10
	R^2	0.996	0.999	0.999	0.999

Fig. 2. Adsorption kinetics of Zn(II) (▲); Cu(II) (◆); Cd(II) (●) and Pb(II) (■) by *U. lactuca*, at pH 5.5, constant ionic strength and room temperature.
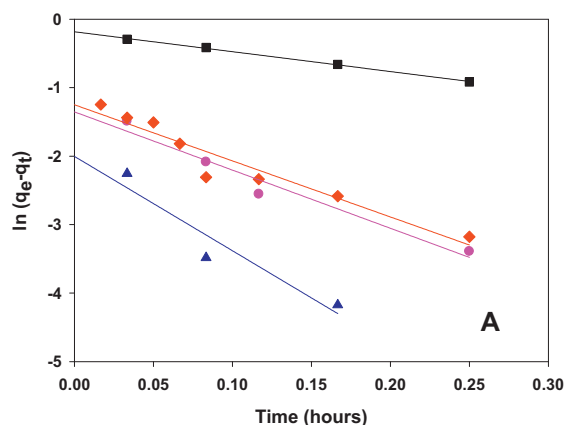
3.2. Kinetic models

3.2.1. Pseudo first order kinetic model

The pseudo first order kinetics model was applied to many systems, from organic compounds, such as dyes, to heavy metals adsorbed on biomaterials, biopolymers or solid inorganic matrices [34]. This kinetic model is based in the pseudo-first order rate expression of Lagergen:

$$\ln(q_{e1} - q_t) = \ln q_{e1} - k_1 t \qquad (5)$$

where k_1 is the pseudo first order sorption rate constant, q_{e1} is the metal uptake at equilibrium and q_t is the amount of metal ion adsorbed at any time t. The overall rate constant k_1 (h^{-1}) was calculated from the slope by plotting $\ln(q_{e1} - q_t)$ vs. t for zinc, copper, cadmium and lead (Fig. 3A).

Calculated q_{e1} values (Table 1) were lower than those obtained experimentally for zinc, copper and cadmium; whereas calculated q_{e1} for lead is similar to the experimental value.

3.2.2. Pseudo second order kinetic model

Several systems respond to a second order kinetics model for sorption reactions, and are represented by the following equation:

$$\frac{dq_t}{dt} = k_2(q_{e2} - q_t)^2 \qquad (6)$$

where k_2 is the rate of pseudo second order adsorption and q_{e2} and q_t are the amount of metal ion adsorbed at equilibrium and the amount adsorbed at any time, respectively. The sorption rate can be calculated as the initial sorption rate when t approaches zero. The pseudo-second-order equation can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{t}{q_{e2}} \qquad (7)$$

The linear plot of t/q_t against t was made in order to calculate the second order rate constant k_2 and the equilibrium adsorption capacity q_{e2} from the slope and intercept, respectively, as represented in Fig. 3B.

Calculated q_{e2} values agree with experimental values (Table 1). Pseudo second order kinetics constant, k_2, value calculated for the adsorption of cadmium by *U. lactuca* is similar to those values found in literature for the adsorption of this metal by other biosorbents, while the values for copper and zinc are considerably larger and the value for lead is smaller [6,35–37].

3.3. Sorption batch models

The relationship between the metal uptake and the sorbate equilibrium concentration at constant temperature is known as
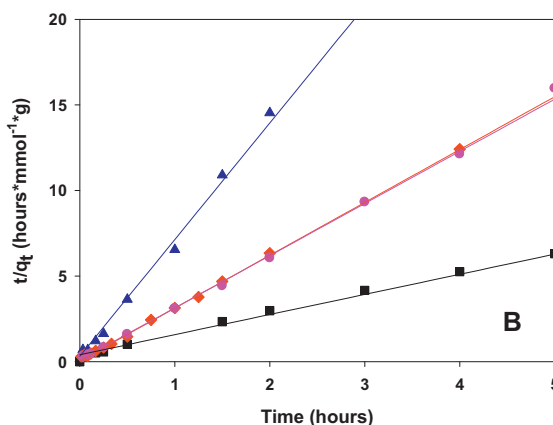

Fig. 3. Pseudo first order (A) and pseudo second order (B) kinetic models applied to the adsorption of Zn(II) (▲); Cu(II) (◆); Cd(II) (●) and Pb(II) (■) by *U. lactuca*, at pH 5.5, constant ionic strength and room temperature.
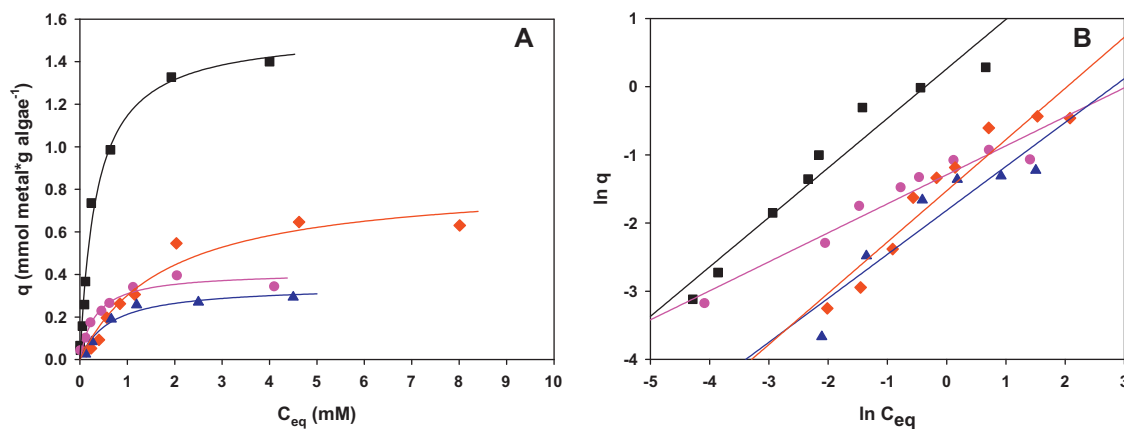
Fig. 4. Adsorption isotherms for the adsorption of Zn(II) (▲); Cu(II) (♦); Cd(II) (●) and Pb(II) (■) by *Ulva lactuca* at pH 5.5, constant ionic strength and room temperature. Plots were made using Langmuir (A) and Freundlich (B) models.

adsorption isotherm. There are a great number of expressions that describe adsorption isotherms, the most applied models are the Langmuir and Freundlich models.

3.3.1. Langmuir model

The Langmuir isotherm model indicates a reduction of the available interaction sites as the metal ion concentration increases [38]. The Langmuir isotherm assumes monolayer adsorption and is determined by the following equation:

$$q = \frac{q_{max\,L} \times K_L \times C_{eq}}{1 + K_L \times C_{eq}} \tag{8}$$

where $q_{max\,L}$ is the maximum metal uptake (mg g^{-1} or mmol g^{-1}), meaning the maximum concentration on the solid phase, C_{eq} (mmol l^{-1}) is the metal concentration at the equilibrium on the aqueous media and K_L (l mmol^{-1}) is the Langmuir equilibrium constant which is related with the free energy of the reaction.

Copper, zinc, cadmium and lead adsorption isotherms for *U. lactuca* are presented in Fig. 4A. The Langmuir isotherm, Eq. (8), was applied to estimate seaweed biosorption capacity and the corresponding parameters obtained for the four metals are indicated in Table 2. Affinity between sorbent and sorbate are represented by the constant K_L. Certainly, good biosorbents have high $q_{max\,L}$ and K_L values. The maximum coverage, $q_{max\,L}$, follow the sequence Pb > Cu > Cd > Zn. The values obtained are slightly higher than those obtained experimentally (0.66, 0.25, 0.35 and 1.40 mmol g alga^{-1}, for copper, zinc, cadmium and lead, respectively), however Langmuir model well represent the experimental data.

U. lactuca has a high saturation level for lead and copper, and average levels for zinc and cadmium compared to results found in literature for other biosorbents [6,35,36,39–41].

3.3.2. Freundlich model

Freundlich model predicts no saturation of the adsorbent by the sorbate, involving an infinite coating, indicating multilayer adsorption on the adsorbent surface. The process is represented by Eq. (9):

$$q_e = K_F \times C_{eq}^{1/n} \tag{9}$$

where K_F is the Freundlich constant indicating adsorption capacity and $1/n$ is the adsorption intensity. Linear regression analysis was used for isotherm data treatment. The linear form of the Freundlich isotherm used was:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \times \ln C_{eq} \tag{10}$$

The values of K_F and $1/n$ were calculated from the intercept and slope of the plot between $\ln q_e$ vs. $\ln C_{eq}$ (Fig. 4B). K_F, $1/n$ and the correlation coefficient (R^2) values of the Freundlich isotherm are given in Table 2.

The Langmuir model fit the experimental data better than de Freundlich model.

Metal uptake increased with contact time, the process is relatively fast and the plateau is reached in less than 5 h (Fig. 2). Metal uptakes were fast for the initial first hours and thereafter the adsorption rates were slower until final saturation. The metal uptake (q) for *U. lactuca* varies with metal concentration. When concentrations are higher than 1.15 mM, the sequence is Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} (Fig. 4A) and at concentration lower than 1.15 mM there are a castling between Cu and Cd being the biosorption sequence Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} (Fig. 4A).

3.4. Surface characterization

Scanning electron microscope (SEM) images were used for *U. lactuca* surface analysis as shown in Fig. 5. SEM images were taken by applying 5 kV voltage with different magnification times. These figures demonstrate the amorphous superficial structure of the algal biomass surface where the metal cations are adsorbed.

Table 2
Parameters obtained by plotting experimental data with Langmuir and Freundlich isotherms models for the adsorption of Zn(II), Cu(II), Cd(II) and Pb(II) by *U. lactuca*.

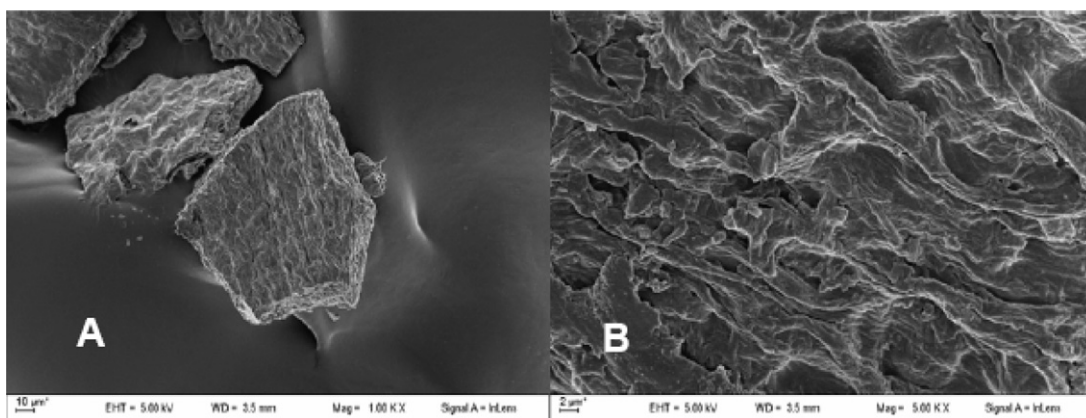| Me	Langmuir $q = \frac{q_{maxL} \times C_e}{1 + K_L \times C_e}$			Freundlich $q = K_F \times C_e^{1/n}$		
	q_{max} (mmol g^{-1})	K_L (l mmol^{-1})	R^2	K_F (l mmol^{-1})	$1/n$	R^2
Zn	0.35 ± 0.03	1.56 ± 0.46	0.959	0.16 ± 0.03	0.64 ± 0.14	0.841
Cu	0.85 ± 0.09	0.55 ± 0.14	0.954	0.22 ± 0.02	0.75 ± 0.09	0.906
Pb	1.55 ± 0.06	2.86 ± 0.32	0.989	1.30 ± 0.25	0.73 ± 0.07	0.942
Cd	0.41 ± 0.03	3.03 ± 0.64	0.959	0.27 ± 0.02	0.43 ± 0.05	0.930

Fig. 5. *U. lactuca* SEM images at two magnifications (A: 1000× and B: 5000×) and 5 kV.
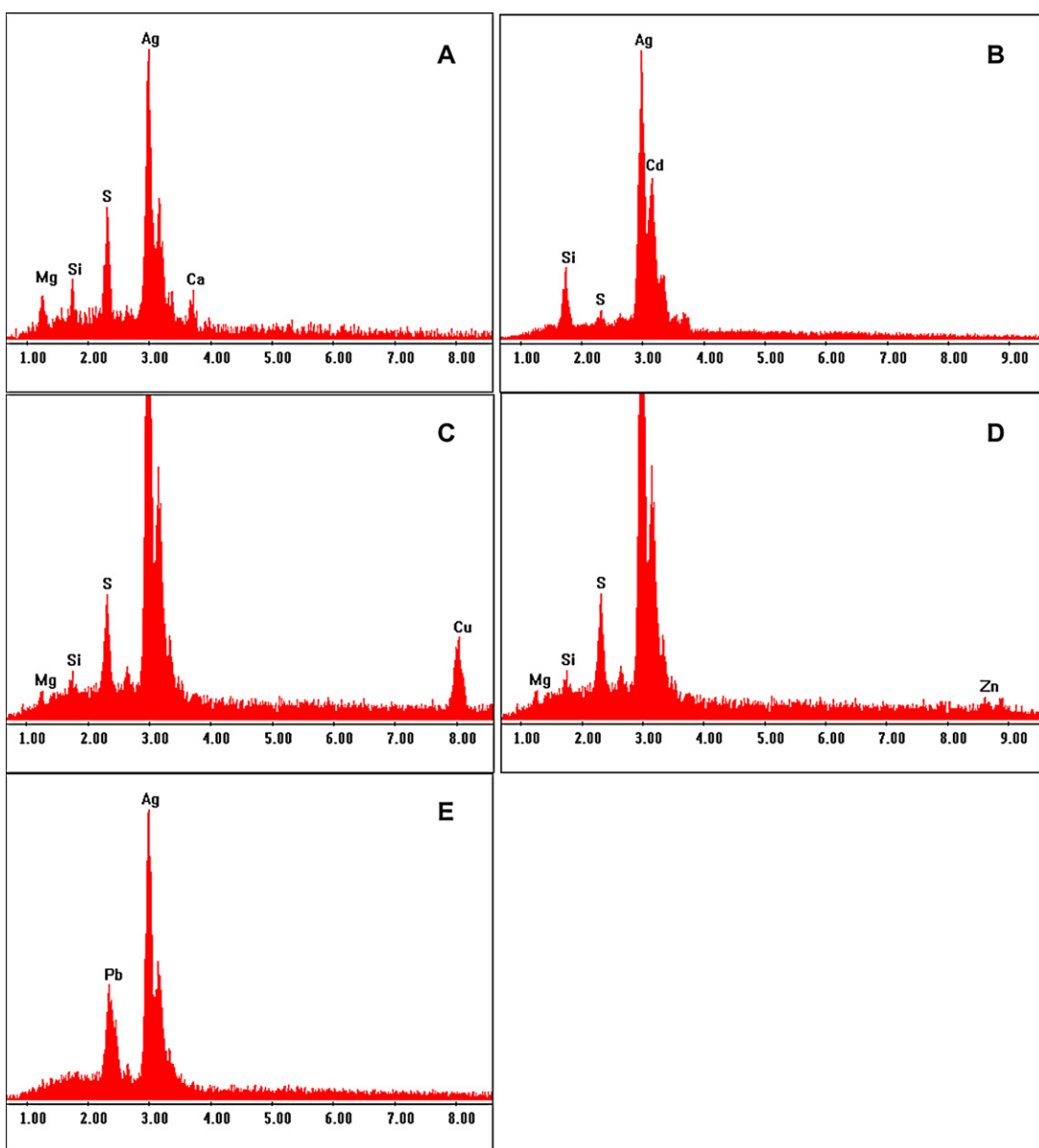

Fig. 6. EDS images of *U. lactuca*: before treatment (A); and after Cd(II), Cu(II), Zn(II) and Pb(II), desorption (B), (C), (D) and (E), respectively, at pH 5.5 and constant ionic strength.

The seaweed EDS images before and after adsorption demonstrate the presence of metal cations adsorbed on the alga surface (Fig. 6).

Biosorbent capacity has been mainly attributed to the properties of the cell wall.

The soluble fraction of *U. lactuca* cell wall is made of a polysaccharide fraction described as a high charged polyelectrolyte, named Ulvan, whose main component is a disaccharide, the β-D-glucurono-syluronic acid (1 → 4) L-rhamnose 3 sulfate [42].

Adsorptions can occur by coordination of metal with the surface functional groups, such as sulfate, carboxyl and hydroxyl. Therefore the differences in zinc(II), cadmium(II), copper(II) and lead(II) biosorption can be attributed to the different affinities of each metal for the functional groups of the polysaccharides present in the alga cellular walls. Essentially, the 2+ oxidation states complexes of the first transition series become more stable as the size of the metal ion decreases, although there are other effects arising from crystal/ligand field theory. The coordination complexes stability increase from calcium to copper and furthermore decreases with zinc, indicating that the coordination complexes of zinc are less stables than copper complexes. The tendency to form surface complexes, such as those formed between seaweeds and metals, may be compared with the tendency to form corresponding innersphere solute complexes [43]. A simultaneous growth is found when the relation between K_L and the aqueous metal sulfate complexes formation is compared. Instead, for hydroxyl groups the surface metal complexes formation constants follow an inverse behavior compared with the aqueous metal hydroxyl complexes formation constants. These results indicate that sulfated groups are the main coordination centers on cell walls.

3.5. pH influence

Solution pH influence on *U. lactuca* biosorption capacity were studied in series of batch biosorption experiments at pH values of 2, 3, 4 and 5.5 (see Appendix A – Fig. A1). The initial concentrations for copper, zinc, cadmium and lead were 0.76, 0.89, 0.44 and 0.21, respectively.

Lead biosorption exhibits a slight dependence on pH while zinc(II), cadmium(II) and copper(II) have a similar profile with a higher dependence on pH. Initial solution pH played a significant role on metal biosorption, with maximum uptake at pH values above five. In acidic conditions, the functional groups of the cell walls are protonated, which means that the majority of the binding sites are occupied by protons therefore decreasing the seaweed metal biosorbent capacity.

3.6. Adsorption onto U. lactuca immobilized in different matrices

Packed beds are arrays commonly used at industrial scale to treat wastewaters by adsorption or ion-exchange. Powdered algal materials are not feasible to be applied directly in packed beds because the small particles size produces clogging and high pressure drops hindering the operation of such kind of systems. Consequently, the biosorbent must be fixed in some matrix that permits to construct a fixed bed with material of a bigger size.

The matrix should be easy to operate, not affect the adsorptive properties of the biomass, allow a wide surface contact between the adsorbent and sorbate, and must be economically viable and sustainable. After designing a matrix that fulfills the prerequisites, it is necessary to build up an experimental system that contains it and where the effluent may flow.

3.6.1. Alga fixed in agar

The adsorption capacity of an agar-seaweed matrix was evaluated. Preliminary experiments were made to evaluated, the agar
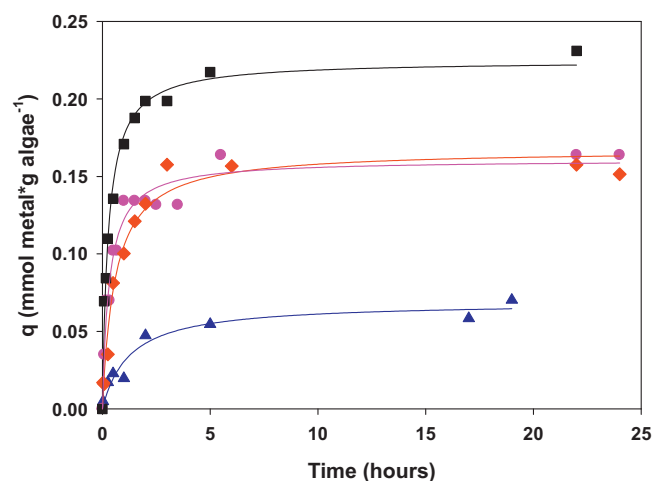

Fig. 7. Kinetic adsorption of Zn(II) (▲); Cu(II) (♦); Cd(II) (●) and Pb(II) (■) by agar–*U. lactuca* matrix, at pH 5.5, constant ionic strength and room temperature.

adsorption capacity of copper, zinc, cadmium and lead and the results demonstrate that adsorption were not significant in all the cases.

Fig. 7 shows the kinetics adsorption of Zn(II), Cu(II), Cd(II) and Pb(II) by *U. lactuca* fixed in agar, the initial concentrations were 0.79, 0.80, 0.80 and 0.45 mM, respectively.

The biosorption of heavy metals by the agar–alga matrix follows the biosorption sequence Pb > Cu ∼ Cd > Zn (Fig. 7). The lead is the most adsorbed metal even when the initial concentration was the lowest. The sequence is similar to that observed for the adsorption of these metals by the alga free in solution, but a marked decrease in the biosorption of copper and lead is observed when the biosorbent is fixed in agar.

The maximum metal uptake (q_{max}) by *U. lactuca* in suspension and fixed in agar is depicted in Table 3. The initial solution concentrations were 65 mg l^{-1} for all metals studied.

The biosorption efficiency is higher for the alga in suspension than for the biosorbent fixed in agar (Table 3). Even though the metal ions can diffuse partially through the agar matrix, the decrease on the adsorption capacity may be due to the decrease in the adsorption sites on the alga cell walls because the agar may block some of these sites.

3.6.2. Alga fixed in columns

The desorption of an adsorbed metal on a given biomass is essential to evaluate the reusable rate of the studied material and to recover the metals previously adsorbed. Desorption makes the adsorption process even more sustainable and economically feasible because it may allow to reuse the metals in a particular industrial process. Without desorption stages, once the biosorbent is saturated it should be disposed, and according to the heavy metals content on it, it must be treated as an hazardous solid waste, increasing the operative costs of the treatment system.

Many substances may be used as desorbent agents, among them are the acids. The adsorption process is pH dependant since

Table 3
Cu(II), Zn(II), Cd(II) and Pb(II) (Co = 65 mg l^{-1}) adsorption by *U. lactuca* in suspension and fixed in agar.

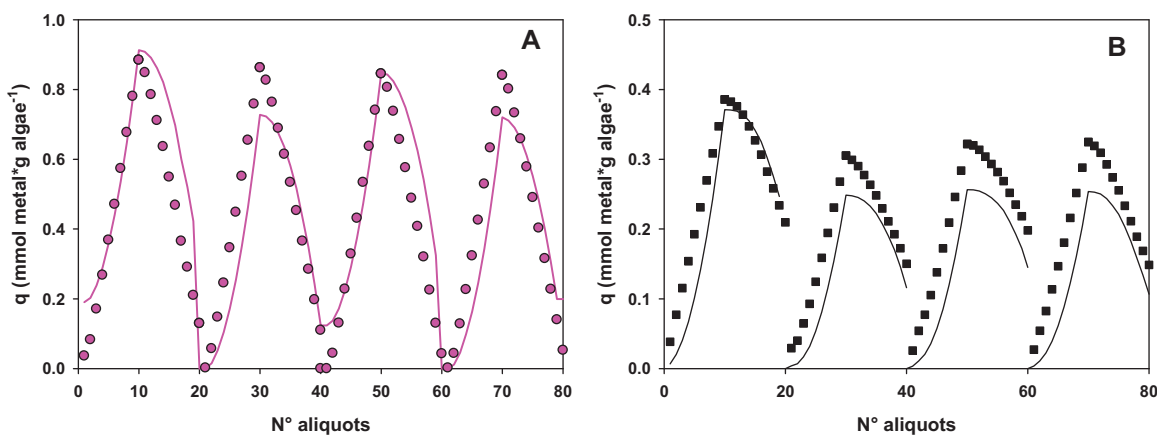| Metal	q_{max} (mg metal g alga^{-1}) Adsorbent in suspension	q_{max} (mg metal g alga^{-1}) Adsorbent fixed in agar
Cu(II)	32.80	10.01
Zn(II)	30.00	4.59
Cd(II)	49.00	9.21
Pb(II)	54.30	47.84

Fig. 8. Adsorption/desorption of (A) Cd (Co = 1 mM) and (B) Pb (Co = 0.5 mM) by *U. lactuca* fixed in columns at pH 5.5. The symbols correspond to experimental results, while solid lines were calculated using Eqs. (2) and (3), the experimental values of inner and outer concentrations and the flux of mobile phases.

protons present in solution compete with metals for the binding sites, and when proton concentration raise this may displace the metal ions that are bind to the cell walls. The desorptive agent must not degrade or damage the biomass in order to preserves its biosorption capacity.

Contaminant desorption from packed material was previously described in literature [44–46] and the results demonstrate the improve in the adsorption capacity of the adsorbent when it's fixed in columns respect to adsorption in batch mode, even when more than one sorbate is present in solution.

3.6.2.1. Adsorption–desorption in columns: mono metallic solutions. Cadmium and lead biosorption efficiency of *U. lactuca* packed in columns were measured passing monometallic solutions of each metal through the column. Later on, the biosorbed metal was easily removed by acid solution circulation.

Adsorption and desorption of cadmium by *U. lactuca* for four adsorption–desorption successive cycles are shown in Fig. 8A.

Experimental data were fitted using Eqs. (2) and (3), the experimental values of inner and outer concentrations and the flow of mobile phases. The adsorbed cadmium was desorbed from the column by adding acid, once each adsorption cycle was completed. The adsorption efficiency of the second adsorption cycle was diminished by $10 \pm 5\%$ respect to the first adsorption cycle, while the adsorption efficiency remained constant for the next adsorption cycles.

Similarly, lead adsorption by *U. lactuca* packed in bed columns and the reutilization of the packed material in successive cycles of adsorption–desorption is shown in Fig. 8B. The adsorption of the metal decreased 20% after the first adsorption–desorption cycle and remained constant for the next adsorption cycles. This decrease may be due to micro precipitation of PbSO$_4$ on the alga surface or irreversible complexation of some alga surface functional groups leading to a decrease in the alga adsorption capacity and in the desorption of lead (Fig. 8B).

3.6.2.2. Adsorption–desorption in columns: binary metals solutions. The effect of the presence of more than one sorbate in the solution was assayed by flowing binary solutions of cadmium and lead through the column. The adsorption of lead in the presence of cadmium and the adsorption of cadmium in the presence of lead were evaluated at initial cadmium and lead concentrations of 0.6 mM and 0.27 mM, respectively.

The adsorption of both metals are diminished by co/adsorption (Fig. 9), this may be due to the fact that both metals compete for the same binding sites that are present in the alga cell wall with similar
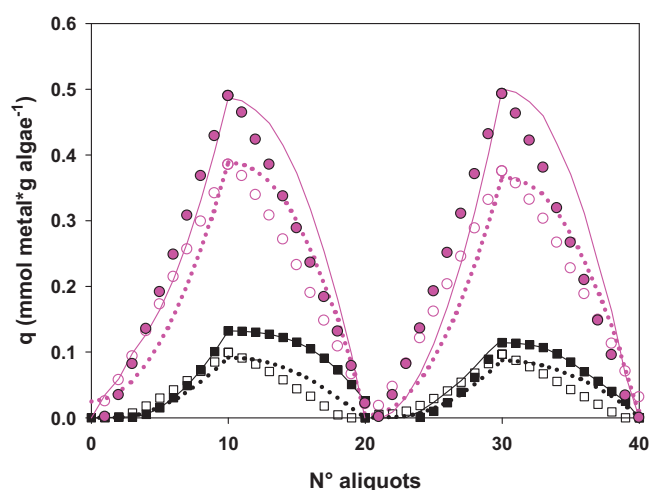

Fig. 9. Cd (○) adsorption/desorption in the presence of Pb and Pb (□) adsorption/desorption in the presence of Cd at pH 5.5 by *U. lactuca* packed in columns compared to the adsorption/desorption process of Cd (●) and Pb (■) when there is no contribution of any other ion in solution. The symbols correspond to experimental results, while lines were calculated using Eqs. (2) and (3), the experimental values of inner and outer concentrations and the flux of mobile phases.

affinity constants for the adsorptive surface ($K_{LCd} = 3.03\,\mathrm{l\,mmol^{-1}}$ and $K_{LPb} = 2.86\,\mathrm{l\,mmol^{-1}}$).

The maximum metals uptakes by *U. lactuca* packed in columns are closer to the results obtained for batch experiments, but the amount of metal added to the columns were not enough to saturate the adsorbent material.

The advantages of using columns for metal removal are the easily desorption and reutilization of the adsorbent materials and the possibility to operate the system in continuous mode, approaching the conditions required for the industrial implementation of this technology.

4. Conclusions

U. lactuca was found to be an effective biosorbent for the removal of copper, zinc, cadmium and lead from synthetic solutions. Biosorption kinetics follows a pseudo second order model and Langmuir isotherm model best reproduces the experimental data. SEM-EDS confirmed the presence of Zn(II), Cu(II), Pb(II) and Cd(II) ions on the biomass surface.
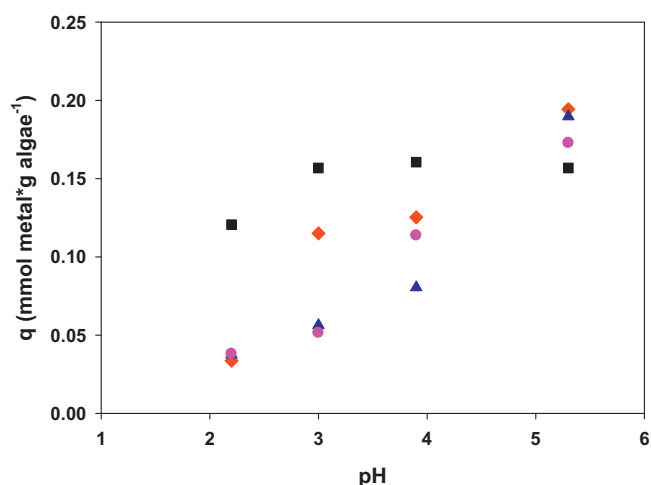
Fig. A1. *Ulva lactuca* biosorption experiments as function of pH: (♦) Cu(II); (▲) Zn(II); (■) Pb(II) and (●) Cd (II).

The results suggest that pH affects the biosorption process and that the differences in the metal adsorption behavior are due to the different metal affinities to the cell wall polysaccharides.

Removal of heavy metal ions by adsorbent fixed in agar were lower than by suspended biomass. This may be due to the decrease in the adsorption sites of the alga that may be block by agar.

The maximum metals uptakes by *U. lactuca* packed in columns were closer to the results obtained for batch experiments, but the amount of metal added to the columns were not big enough to saturate the adsorbent material. The biomass material was successfully used in successive adsorption–desorption cycles. Finally, when Cd(II) and Pb(II) binary solutions were added to the columns the adsorption rate of both metals were diminished by coadsorption.

U. lactuca seems to be an efficient and low cost alternative biosorbent to be considered for industrial wastewater treatment. Development of this technology for polluted effluents decontamination would likely increase seaweed demand and consequently increase the economies of countries that produce this good.

Acknowledgments

Appendix A.

See Fig. A1.

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