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Zinc and cadmium biosorption by untreated and calcium-treated *Macrocystis pyrifera* in a batch system

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ABSTRACT

Zinc and cadmium can be efficiently removed from solutions using the brown algae, *Macrocystis pyrifera*. Treatment with $CaCl_2$ allowed stabilization of the biosorbent. The maximum biosorption capacities in mono-component systems were 0.91 mmol g^{-1} and 0.89 mmol g^{-1} and the Langmuir affinity coefficients were 1.76 L $mmol^{-1}$ and 1.25 L $mmol^{-1}$ for Zn(II) and Cd(II), respectively. In two-component systems, Zn(II) and Cd(II) adsorption capacities were reduced by 50% and 40%, respectively and the biosorbent showed a preference for Cd(II) over Zn(II). HNO_3 (0.1 M) and EDTA (0.1 M) achieved 90–100% desorption of both ions from the loaded biomass. While HNO_3 preserved the biomass structure, EDTA destroyed it completely. Fourier transform infrared spectra identified the contribution of carboxylic, amine and sulfonate groups on Zn(II) and Cd(II) biosorption. These results showed that biosorption using *M. pyrifera*-treated biomass could be an affordable and simple process for cadmium and zinc removal from wastewaters.

1. Introduction

Cadmium is one of the most toxic metals (Luna et al., 2010). The major sources of cadmium released into the environment are water streams from electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining, and refining process. Cadmium tends to accumulate in living organisms causing significant threats to both, the environment and public health (Xiao et al., 2010). Zinc is an essential element for humans at low concentrations since it stimulates the activity of more than a hundred enzymes and plays an important role in the immune system. However, at high concentration it becomes toxic (Boschi et al., 2011). This metal is extensively used for galvanization and manufacturing of brass and other alloys, and in batteries and pigments (Luna et al., 2010).

The US EPA requires zinc and cadmium in drinking water not to exceed, 5 and 0.005 mg L^{-1}, respectively. Techniques used to remove/reduce the metal contents of wastewater include chemical precipitation, adsorption (on activated carbon), ion exchange, evaporation and membrane processes (Volesky, 2003). Adsorption by activated carbon is the most efficient process since it removes more than 99% of some metal ions, but the operative costs are prohibitive when treating large volumes or dilute effluents. In addition this adsorbent cannot be readily regenerated and recycled (Farooq et al., 2010). These methods mostly treat metal ions as a waste to be eliminated (landfill) with limited possibilities to recycle or valorize the materials. Some of the methods (e.g., precipitation and coagulation) produce concentrated and toxic wastes which require controlled storage and landfill disposal.

Hence, there is a need to search for an optimal technology for metal recovery. In recent years, biosorption has emerged as a cost-effective and efficient alternative for removal of heavy metals from waste waters. Microorganisms such as algae, bacteria, yeast, fungi, but also agricultural by-products (including plants leaves and root tissues) can be used as biosorbents for detoxification and recovery of toxic or valuable metals form industrial discharges. Algae are among the most promising biosorbents. Skowronski and Przytocka-Jusiak (1986) reported the sorption of cadmium onto the green micro-algae *Sitchococcus bacilliaris*. The algae most frequently studied as biosorbents are *Ascophyllum nodosum* (Carvalho et al., 1995), *Fucus vesiculosus* (Mata et al., 2008), *Laminaria japonica* (Febrianto et al., 2009), and various species of the genus *Sargassum* (Fagundes-Klen et al., 2007; Luna et al., 2010). *Macrocystis pyrifera* is a brown alga (Phaeophyta) that grows in water along the south coast of Argentina. *M. pyrifera* is frequently deposited on the beach of Bahía de Camarones causing unpleasant odors and a negative impact on local tourism and can be considered an easily available natural waste (Plaza et al., 2011, 2012). There are very few reports on the use of *M. pyrifera* as biosorbent for heavy metal removal. Seki and Suzuki employed *M. pyrifera* for the adsorption of cadmium and lead (Seki and Suzuki, 1998) and Plaza et al. (2011, 2012) used this algae for the removal of Hg(II) and Cr(III) from aqueous solutions. The presence of alginate in its cell

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wall is one of the most important characteristic for the biosorption process (Davis et al., 2003).

The sorption properties of an adsorbent, like its capacity, can be improved or changed by several pre-treatments or modifications (Oliveira et al., 2011). Pre-treatment can modify the surface characteristics/groups or contribute to exposing more metal binding sites. A number of methods have been employed to enhance the metal binding capacity of biomass and to elucidate the mechanism of biosorption. Physical treatments may consist of heating/boiling, freezing/thawing, drying and freeze-drying. Chemical treatments may proceed by washing the biomass with detergents, cross-linking with organic solvents and/or treatment with alkali or acid. Surface modification by calcium chloride, formaldehyde and glutaraldehyde treatment prevents the leaching of adsorptive components from biomass into the solution increasing the stability of the biosorbent material (Boschi et al., 2011). Besides, the pre-treatment with calcium reduced the swelling of algal biomass (Matheickal and Qiming, 1999).

In this biosorpion study, *M. pyrifera* biomass with and without calcium treatment was used in order to determine the influence of pre-treatment on metal sorption capacity. The biosorbent, was used for the uptake of zinc and cadmium ions in mono and two-component systems. The stabilization of the alginate by calcium yielded a higher metal uptake. In order to explain the mechanisms involved during the zinc and cadmium biosorption, *M. pyrifera* biomass was characterized using FT IR spectrometry and SEM EDAX (scanning electron microscopy coupled with energy disperse analysis of X-ray). Finally, the eluents, HNO_3, EDTA, $Ca(NO_3)_2$ in two concentrations were employed to evaluate the possibility of recovering the solutes and reusing the biosorbent. This fraction was called treated biosorbent.

2. Methods

2.1. Biological material: pretreatment

The brown algae, *M. pyrifera*, was collected in November and December 2009 along the coast of Bahía de Camarones and Golfo Nuevo (Patagonia Argentina).

Algae biomass was ground and sieved and the 10–16 mesh (i.e., 1.18–2 mm) particle size was retained for sorption experiments. Biomass was washed several times with distilled water until obtaining an electrical conductivity lower than 1 mS cm^{-1} and dried in an oven at 50 °C for 48 h. This biomass was called untreated biosorbent. One part of this biomass was stored for equilibrium studies. Another part of the biomass was treated for 24 h with 0.2 M $CaCl_2$ solution at pH 5.0, washed repeatedly with distilled water and dried in an oven at 50 °C for 48 h.

2.2. Sorption studies

Individual solutions of Zn(II) and Cd(II) at a concentration of 50 mg L^{-1} were prepared by dilution of stock solutions (1000 mg Zn L^{-1} and 1000 mg Cd L^{-1}, respectively). The pH was set at different initial values (i.e., 3.0, 4.0 and 5.0) by the addition of H_2SO_4.The concentration of the untreated and treated biomass was set at 0.2% w/v for kinetic studies. Flasks were maintained under agitation at 160 rpm and placed in a controlled-temperature room at 20 °C. Samples were collected and filtered through 0.45-μm membrane at different time intervals for 24 h.

The results obtained from kinetics studies in mono-component systems with untreated and treated biosorbents confirmed the necessity to treat the biomass prior to metal sorption. Thus, kinetic studies in two-component systems and equilibrium studies were performed only with treated biomass.

Zinc and cadmium sorption isotherms were obtained by mixing 0.1 g biomass with 100 mL of the metal containing solution with initial concentrations ranging between 10 and 400 mg L^{-1}; i.e., 0.15–6.11 mM (Zn) and 0.089–3.57 mM (Cd). All flasks were kept in a rotary shaker (agitation speed: 160 rpm) at 20 °C. pH values of Zn(II) and Cd(II) solutions were set at pH 4.0 and 3.0, respectively. The contact time was 2 h for both heavy metals. The optimal pH and the contact time were selected on the basis of kinetic studies.

To study the adsorption capacities for Zn(II) and Cd(II) when both metal ions were present, mixed solutions were prepared at pH 4.0. In all cases, the initial concentrations of each metal were equal and varied simultaneously from 0.05 to 2.5 mM. Treated biomass (0.1 g) was added to 100 mL of each mixed solution in 150-mL plastic bottles. The bottles were maintained under agitation at 160 rpm and 20 °C for 2 h.

2.3. Analytical methods

Experiments were carried out in duplicate and samples were filtered through a 0.45-μm membrane. Atomic absorption spectrophotometry (Shimadzu AA6650, Shimadzu Corporation Kyoto, Japan) and Inductively Couple Plasma Atomic Emission Spectroscopy (ICP-AES) using a JY 2000 spectrometer (Jobin–Yvon, Longjumeau, France) were used to measure initial and final metal concentrations after biosorption and desorption. The amount of metal adsorbed was calculated by the mass balance equation, according to the equation:

$$q = \frac{V \cdot (C_i - C_f)}{m} \quad (1)$$

where q is the solute uptake (mg g^{-1} or mmol g^{-1}); C_i and C_f the initial and final solute concentrations in solution (mg L^{-1} or mM), respectively; V solution volume (L) and m the mass of biosorbent (g, dry weight basis).

After metal sorption and desorption, biosorbents were recovered by filtration, washed three times with distilled water and dried in an oven at 50 °C for 24 h. Samples were examined using an Environmental Scanning Electron microscope (ESEM) Quanta FEG, equipped with the OXFORD Inca 350 Energy Dispersive X-ray microanalysis (EDX) system. FT-IR analyzes were performed on a FT-IR spectrometer (Perkin Elmer) using KBr pellets (the fraction of sample was about 0.1% w/w).

2.4. Mathematical models

2.4.1. Kinetic studies

The modeling and design of the adsorption processes requires establishing the kinetic characteristics of the system (Moussavi and Barikbin, 2010). The Lagergren pseudo-first and second models were used to describe the experimental data. The linear form of the pseudo first order equation (PFORE) by Lagergren is given by Joo et al. (2010):

$$\log(q_{eq} - q_t) = -\frac{k_1}{2.303}t + \log q_{eq} \quad (2)$$

where q_{eq} and q_t (mmol g^{-1}) are the sorption capacity at equilibrium and at time t, respectively and k_1 (1 min^{-1}) is the rate constant of pseudo first order. The values of k_1 and the q_{eq} were obtained from the slopes and intercepts of straight lines.

The pseudo-second order rate equation (PSORE) (Joo et al., 2010) is represented, after equation linearization, by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t \quad (3)$$

where q_{eq} (mg g^{-1}) is the sorption capacity at equilibrium (value calculated from experimental data), k_2 (g (mmol min^{-1})) is the pseudo-second order rate constant.

The prediction of the rate-limiting step is an important factor to be considered in the adsorption process. In the solid–liquid sorption process, the solute transfer is usually characterized by external mass transfer (boundary layer diffusion), or intra-particle diffusion, or both. Thus, the uptake of heavy metals can be controlled by either the mass transfer through the boundary film of liquid or by the intra-particular mass transfer. The external mass transfer coefficient, β_L (m s^{-1}) of Zn (II) and Cd(II) in the liquid film boundary can be evaluated by using the equation proposed by Gupta et al. (2001) as follows:

$$\ln\left(\frac{C_t}{C_o}-\frac{1}{1+mk_a}\right)=\ln\left(\frac{mk_a}{1+mk_a}\right)-\left(\frac{1+mk_a}{mk_a}\right)\beta_L.S_s t \tag{4}$$

where C_t and C_o (both in mg L^{-1}) are the concentrations of sorbent at time t and zero, respectively; K_a (L g^{-1}) is a constant defined as the product of the Langmuir constants ($q_m b$), m (g L^{-1}) and S_s (m^2) are the adsorbent mass and surface area, respectively. The coefficient β_L can be calculated from the slope of the regression line: $\ln[(C_t/C_o)-(1/1+mK_a)]$ vs t.

The intraparticle diffusion was explored by using the following simplified equation:

$$q_t = K_{\text{dif}} t^{1/2} + C \tag{5}$$

where C is the intercept and K_{dif} is the intraparticle diffusion rate constant. The value of q_t correlated linearly with values of $t^{1/2}$ and the rate constant K_{dif} was directly evaluated from the slope of the regression line.

2.4.2. Adsorption Isotherms: mono-component systems

The Langmuir isotherm considers sorption as a chemical phenomenon. This model suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate (Oliveira et al., 2011). The Langmuir isotherm is represented by the following equation (Volesky, 2003):

$$q_{eq}=\frac{q_m b C_{eq}}{1+bC_{eq}} \tag{6}$$

where q_{eq} is the metal uptake at the equilibrium (mmol g^{-1}); q_m is the maximum Langmuir uptake (mmol g^{-1}) at saturation of the monolayer; C_{eq} is the final concentration at the equilibrium (mmol L^{-1}); b is the Langmuir affinity constant (L mmol^{-1}). The maximum adsorption capacity (q_m) and Langmuir constant (b) were obtained after linearization of Eq. (6) (C_f/q_{eq} vs. C_f). Langmuir constant $b = 1/K$ is related to the energy of adsorption through the Arrhenius equation. The higher b (and the smaller K), the higher the affinity of the sorbent for the sorbate. The coefficient q_m can also be interpreted as the total number of binding sites that are available for biosorption, and q_{eq} as the number of binding sites that are actually occupied by the sorbate at the concentration C_{eq} (Volesky, 2003).

The Freundlich isotherm is a nonlinear sorption model which proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The general form of this model is:

$$q_{eq}=K_f C_{eq}^{1/n} \tag{7}$$

where K_f is a constant related to the biosorption capacity and $1/n$ is an empirical parameter related to the biosorption intensity, which varies with the heterogeneity of the material. The parameters were obtained by linear regression after linearization ($\ln q_{eq}$ vs $\ln C_{eq}$).

The equilibrium data were also analyzed with the Dubinin–Radushkevich (D–R) isotherm model to determine the nature of the biosorption processes (i.e., physical *vs.* chemical). The linear representation of D–R isotherm equation is given by:

$$\ln q_{eq} = \ln q_m - \beta\varepsilon^2 \tag{8}$$

where q_{eq} is the amount of metal ions sorbed per unit weight of biomass (mol g^{-1}), q_m is the maximum sorption capacity (mol g^{-1}), β is the activity coefficient related to biosorption mean free energy (mol J^{-1}) and ε is the Polanyi potential ($\varepsilon = RT\ \ln(1+1/C_{eq})$: the amount of energy required to pull a sorbed molecule from its sorption site to infinity (Malik et al., 2005). The Polanyi adsorption theory postulates fixed volumes of sorption sites close to the sorbent surface and existence of a sorption potential over these sites. The sorption potential is related to an excess of sorption energy over the condensation energy and is independent of temperature (Polanyi, 1932). The sorption energy E [kJ mol^{-1}] for Zn(II) and Cd(II) ions onto *M. pyrifera* untreated and treated biomass was calculated using:

$$E=\frac{1}{\sqrt{-2\beta}} \tag{9}$$

2.4.3. Adsorption Isotherms: two-component systems

When several components are present, there are interference and competition among the different components for adsorption sites. The isotherm models for a mono-component system are thus inapplicable (Shahzad Baig et al., 2009). The biosorption isotherms of the binary solutions were analyzed with the Langmuir multicomponent competitive models shown below (Oliveira et al., 2011):

$$q_{\text{Zn}}=\frac{q_{m\text{Zn}} b_{\text{Zn}} C_{eq\text{Zn}}}{1+b_{\text{Zn}}C_{eq\text{Zn}}+b_{\text{Cd}}C_{eq\text{Cd}}} \tag{10a}$$

$$q_{\text{Cd}}=\frac{q_{m\text{Cd}} b_{\text{Cd}} C_{eq\text{Cd}}}{1+b_{\text{Cd}}C_{eq\text{Cd}}+b_{\text{Zn}}C_{eq\text{Zn}}} \tag{10b}$$

Theoretically, qm and b parameters used in Eqs. (10a) and (10b) can be obtained applying Eq. (6) for mono-component systems. However, in two-component systems, the affinity could change for each component, so they should be calculated by the mathematical arrangement of Eq. (10), and their linear regressions, according to Eqs. (11a) and (11b):

$$C_{eq\text{Zn}}\left(\frac{q_{m\text{Zn}}}{q_{\text{Zn}}}-1\right)=\frac{1}{b_{\text{Zn}}}+\frac{b_{\text{Cd}}}{b_{\text{Zn}}}.C_{eq\text{Cd}} \tag{11a}$$

$$C_{eq\text{Cd}}\left(\frac{q_{m\text{Cd}}}{q_{\text{Cd}}}-1\right)=\frac{1}{b_{\text{Cd}}}+\frac{b_{\text{Zn}}}{b_{\text{Cd}}}.C_{eq\text{Zn}} \tag{11b}$$

where the values of $q_{m,i}$ were the same values obtained from mono-component systems; and b_{Zn} is the affinity coefficient for Zn(II) in the presence of Cd(II) and b_{Cd} is the affinity coefficient for Cd(II) in the presence of Zn(II) in bicomponent solutions. As these equations use the q_m values obtained in monocomponent systems, they are called "approximations" (Oliveira et al., 2011).

Another model for representing binary data of biosorption equilibrium is the Langmuir non-competitive model, developed by Bailey and Ollis to describe the non-competitive inhibition during enzymatic kinetic studies. This model is represented by Eq. (12) (Fagundes-Klen et al., 2007):

$$q_t=\frac{q_m b_1 C_1\left[1+\left(\frac{K}{b_1}\right)C_2\right]}{1+b_1C_1+b_2C_2+2KC_1C_2} \tag{12}$$

where q_t is the total amount for both metals (mmol g^{-1}) adsorbed at the equilibrium, b_1 and b_2 are the affinity coefficients for each metals in a binary solution, q_m is the maximum adsorption capacity for both heavy metals (mmol g^{-1}) and K is the reciprocal of the affinity coefficient (b_i^{-1}) for both metals.

Eq. (6) was used to determine q_m and b for individual and total biosorption uptakes by simple mathematical adjustment, ignoring physicochemical effects of competition. This approach was called Langmuir uncompetitive model. These results were used to compare the cumulative affinity constant of Langmuir (b_{ZnCd}) and the affinity coefficient calculated by the semi-empirical equation (Oliveira et al., 2011):

$$b_{ZnCd} = \frac{1}{1/b'_{Zn}} + \frac{1}{1/b'_{Cd}} \tag{13}$$

where b'_{Zn} and b'_{Cd} are the affinity constants of Langmuir for Zn(II) and Cd(II) respectively, obtained by the direct application of Eq. (6) for bicomponent solutions.

In the original Langmuir isotherm model (Eq. (6)), the chemical species 1 (Cd) and 2 (Zn) compete for the occupation of the same sorption sites. Jain and Snoeyink (1973) have proposed an adsorption model for binary mixtures based on the hypothesis that a part of adsorption occurs without competition (and the hypothesis that $qm_1 \neq qm_2$). The model is described by the following equations:

$$q_1 = \frac{(q_{m1} - q_{m2})b_1 C_{eq1}}{1 + b_1 C_{eq1}} + \frac{q_{m2} b_1 C_{eq1}}{1 + b_1 C_{eq1} + b_2 C_{eq2}} \tag{14}$$

$$q_2 = \frac{q_{m2} b_2 C_{eq2}}{1 + b_1 C_{eq1} + b_2 C_{eq2}} \tag{15}$$

The first term at the right-hand side of Eq. (14) is the expression of the Langmuir isotherm for the non-competitive sorption of species 1 on a limited number of non-competitive sorption sites (corresponding to $q_{m1} - q_{m2}$). The second term represents the competitive sorption of species 1 that adsorbes on the sites q_{m2} with competition with species 2. The sorption of species 2 that adsorb on the sites q_{m2} with the competition of species 1 can be calculated by Eq. (15).

The parameters of the different models applied to analysis of the experimental data were estimated using the regression function of SigmaPlot for Windows 10.0 (Systat Software Inc).

2.5. Desorption studies

Desorption studies were carried out in batch systems. Biomass (0.2 g) loaded with Zn(II) or Cd(II) from the mono-component systems was placed in contact with 50 mL of HNO_3, EDTA or $Ca(NO_3)_2$. In each case, two different concentrations were tested: 0.1 M and 0.01 M. The flasks were kept in agitation at 150 rpm and 20 °C. Samples were withdrawn at different contact times: 0.5, 1, 3, 9, 12, and 24 h, and the released metal concentration were measured by atomic absorption spectrometry. Desorption ratio (% M_{des}) was calculated from the amount of metal ions adsorbed on the biomass and the final metal ion concentration in desorption medium, as indicated in the following equation (Mata et al., 2010):

$$\%M_{des} = \frac{M_{des}}{M_{ads}} \times 100 \tag{16}$$

where M_{des} and M_{ads} are the amounts of metal in solution after desorption and the amount of metal initially present on the biosorbent (mg or mmol) respectively (for a given mass of sorbent).

3. Results and discussion

3.1. Sorption studies

The analysis of uptake kinetics is not only useful for elucidating sorption mechanisms and determining the rate-controlling steps (the resistance to film diffusion, to intraparticle diffusion and the chemical reaction rates) but also for evaluating optimum conditions (including equilibrium time) for batch adsorption experiments (Febrianto et al., 2009). Comparing the kinetic plots q vs. t, (Fig. 1), it can be seen that the initial rate of adsorption of both metals was very similar for treated and untreated biomass; however, the metal uptake at the equilibrium increased by 70% to 100% when the biosorbent was treated with calcium. The treatment with calcium prevents the leaching of some organic components from the biomass (which can be responsible of metal binding) and increases the stability of the biosorbent. In addition, the release of organic material from the biomass may contribute to complexation of the metal ions in solutions, which, in turn, limits their availability for binding on the biosorbent. The modification of the cell wall can significantly enhance metal binding capacity without affecting biosorption kinetics (Yang and Chen, 2008).

Solution pH is another important parameter in the biosorption of metal ions from aqueous solutions (Oh et al., 2009), as it affects the solubility of metal ions and surface charge of the biosorbent (protonation/deprotonation of reactive groups, ion exchange

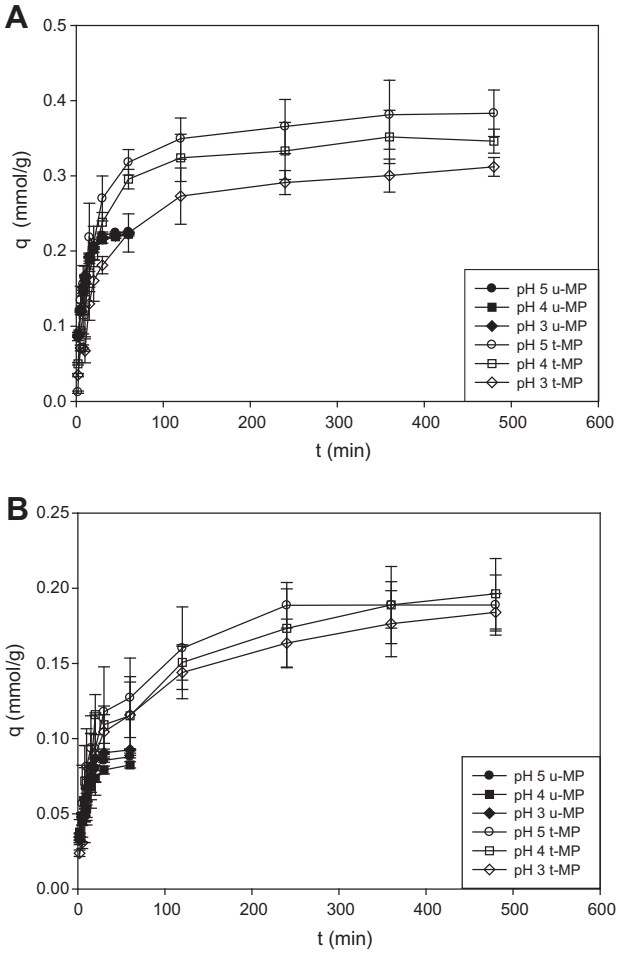

Fig. 1. Kinetic of (A) Zn(II) and (B) Cd(II) sorption onto untreated (u-MP) and calcium-treated *M. pyrifera* (t-MP) biomass. Bars represent the standard deviation of duplicate experiments.

properties, exchange of counter ions with target metal ions etc.). In most cases, the biosorption increases with pH; at low pH, the competition effect of protons and the weak acidity of reactive groups reduce the availability of reactive groups. The deprotonation of reactive groups with increasing pH favors metal uptake. The influence of pH on adsorption was only noticeable in the case of treated biomass (Fig. 1). The stabilization of biomass by calcium treatment prevents the leaching of alginate (and others carbohydrates); thus it is expected that the number of carboxylic groups with pKas in the range of 3–4.4 on the cell wall was higher on the treated than the untreated biomass. This may explain why pH has a noticeable effect on metal uptake in the case of treated biomass. During metal sorption, the pH increased from 4 to 4.6–5.3 for Zn(II) and from 3 to 3.2–3.4 for Cd(II), for treated biomass. In the case of untreated biomass the pH changes were more marked, from 4 to 5.5–6.67 for Zn(II) and from 3 to 4.1–5.3 for Cd(II). The pH change decreased when the metal concentration increased, especially when the initial pH was high (higher pH variation at pH 4 than at pH 3).

The prediction of the rate-limiting step is an important issue for the adsorption process, since it influences design and scale-up of the process. Several reaction- and diffusion-based models were employed to simulate kinetic profiles: PFORE, PSORE, intraparticle diffusion and external mass transfer. Table 1 and 2 report the values of the parameters of the different models when applied to experimental data for both metal ions. The pseudo-first order reaction equation predicts a lower value of the equilibrium adsorption capacity than the experimental value. Hence, this equation cannot provide an accurate fit of experimental data. The correlation coefficients (R^2) obtained for the PFORE model (0.91–0.95) were also statistically lower than those obtained for the PSORE model (0.99) for both metal ions with both untreated and treated biomass. This outcome means that the PSORE model provides a more accurate fit than the PFORE model. These results are in agreement with those found in the literature (Nasernejada et al., 2005; Joo et al., 2010; Uluozlu et al., 2008; Plaza et al., 2011). According to the PSORE model, the rate-limiting step is the chemical sorption process proceeding between metal cations and chemical groups in the algal biomass.

In the solid–liquid sorption process, the solute transfer is frequently controlled by resistance to external mass transfer (boundary layer diffusion), resistance to intraparticle diffusion, or even by a combination of both resistance mechanisms. The coefficient β_L can be calculated from the slope of the plot $\ln[(C_t/C_o) - (1/1 + mK_a)]$ vs. t (the slope coefficient was determined by a linear regression analysis). Experimental data followed a linear distribution, and the regression coefficients were higher (0.99) in case of Zn(II) and Cd(II) uptake by untreated than treated biomass (Table 1 and 2). The transport from the bulk of the solution to the solid

Table 1
Kinetic constants for Zn(II) onto calcium-treated and untreated *M. pyrifera* biomass.

Parameters Zn (II)	*M. pyrifera (untreated)* *pH*			*M. pyrifera (treated)* *pH*		
	3	4	5	3	4	5
Pseudo first order						
q_{exp} (mmol g^{-1})	0.22	0.22	0.23	0.29	0.34	0.37
q (mmol g^{-1})	0.17	0.16	0.17	0.23	0.24	0.24
k_1 (min^{-1})	0.11	0.10	0.11	0.018	0.018	0.018
R^2	0.95	0.95	0.95	0.92	0.92	0.91
Pseudo second order						
q (mmol g^{-1})	0.23	0.23	0.24	0.29	0.36	0.4
k_2 (g $mmol^{-1}$ min^{-1})	1.07	1.05	0.95	0.26	0.17	0.12
R^2	0.99	0.99	0.99	0.99	0.99	0.98
External mass transfer						
β_L (m s^{-1})	1.68×10^{-2}	1.13×10^{-2}	1.41×10^{-2}	3.2×10^{-6}	1.51×10^{-7}	5.5×10^{-4}
R^2	0.97	0.99	0.99	0.94	0.97	0.98
Intra-particle difussion						
K_{id} (mmol g^{-1} $min^{-1/2}$)	0.04	0.03	0.04	0.03	0.04	0.05
R^2	0.97	0.99	0.99	0.92	0.99	0.89

Table 2
Kinetic constants for Cd(II) onto calcium-treated and untreated *M. pyrifera* biomass.

Parameters Cd (II)	*M. pyrifera (untreated)* *pH*			*M. pyrifera (treated)* *pH*		
	3	4	5	3	4	5
Pseudo first order						
q_{exp} (mmol g^{-1})	0.08	0.08	0.08	0.18	0.21	0.20
q (mmol g^{-1})	0.07	0.05	0.06	0.12	0.14	0.15
k_1 (min^{-1})	0.09	0.061	0.07	2.76×10^{-03}	4.41×10^{-03}	5.9×10^{-03}
R^2	0.995	0.991	0.98	0.94	0.94	0.93
Pseudo second order						
q (mmol g^{-1})	0.1	0.08	0.09	0.18	0.21	0.2
k_2 (g $mmol^{-1}$ min^{-1})	2.05	2.62	2.1	0.20	0.15	0.23
R^2	0.999	0.999	0.999	0.999	0.999	0.997
External mass transfer						
β_L(m s^{-1})	1.72×10^{-2}	8.9×10^{-3}	1.24×10^{-2}	1.48×10^{-4}	2.4×10^{-4}	2.5×10^{-4}
R^2	0.99	0.98	0.99	0.92	0.97	0.98
Intra-particle difussion						
K_{id} (mmol g^{-1} $min^{-1/2}$)	0.02	0.01	0.01	0.02	0.02	0.01
R^2	0.99	0.99	0.99	0.97	0.90	0.94

phase by the resistance to intraparticle diffusion is frequently the rate limiting step in adsorption processes. Eq. (5) was used as a simplified model for evaluating the contribution of resistance to intraparticle diffusion on the control of uptake kinetics. Apparently the resistance to intraparticle diffusion plays a significant role in Zn(II) and Cd(II) uptake when untreated biomass was used: the determination coefficient R^2 close to 0.99 confirms that the simplified model accurately fit experimental data. However, the q_t versus $t^{0.5}$ plots did not pass through the origin in any of the cases; this means that intraparticle diffusion was not the sole rate-limiting step (Gupta et al., 2001). Both the resistance to film diffusion and intraparticle diffusion are involved in the kinetic control of Zn(II) and Cd(II) adsorption process by untreated biomass. However, it was not possible to arrive at the same conclusion in the case of treated biomass. Indeed, for both Zn(II) and Cd(II) sorption by treated biomass, the resistance to diffusion (both film and intraparticle diffusion) was not the predominant step in the control of uptake kinetics. The same conclusion was found in the case of Cr(III) uptake by *M. pyrifera* (treated biomass) (Plaza et al., 2011). The treatment of the biomass with calcium chloride improves the stability of the biosorbent (Gong et al., 2005) and reduces the swelling effects. As a consequence, the effects of resistance to film diffusion and to intraparticle diffusion were reduced.

Kinetic studies also contribute to optimize experimental parameters. According to Fig. 1, the time necessary for equilibrium was 30 min (untreated biomass) and 2 h (treated biomass) for both metals. The optimum pHs were 3.0 and 4.0 for Cd(II) and Zn(II), respectively.

3.2. Adsorption equilibrium in mono-component systems

In view of the increase in ion uptake due to calcium treatment, the equilibrium studies were done only with treated biomass. Fig. 2 represents Zn(II) and Cd(II) monocomponent isotherms for treated biomass. These data were evaluated using the Langmuir and the Freundlich models. The parameters for these models and the determination coefficient values are presented in Table 3. As expected, since the sorption isotherms showed a saturation plateau, the Langmuir model fitted the experimental data better than the Freundlich model. The maximum adsorption capacities (q_m) were 0.67 and 0.87 mmol g^{-1} and the affinity coefficients (b) were 2.40 and 1.26 L $mmol^{-1}$ for Zn(II) and Cd(II) ions sorption, respectively. Considering the values of b, the biomass presented a higher affinity for Zn(II) than for Cd(II).

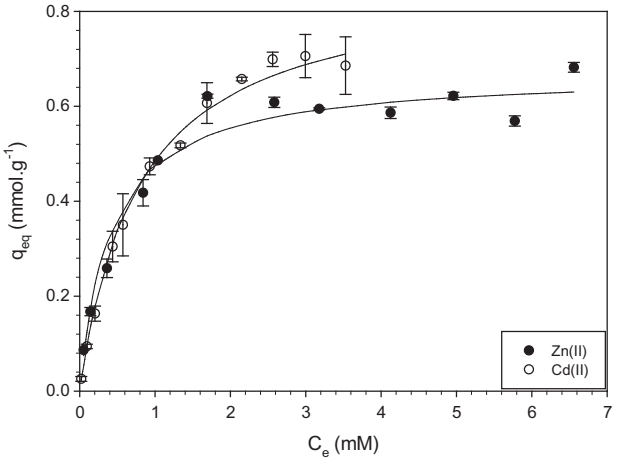

Fig. 2. Zn(II) and Cd(II) mono-component isotherm by treated *M. pyrifera* biomass. Symbols represent experimental data and continuous lines represent the adjustment with Langmuir model, bars represent the standard deviation of duplicate experiments.

The same affinity order was observed for other alga, such as *Sargassum filipendula* (Fagundes-Klen et al., 2007), *Padina* sp. and *Sargassum* sp. (Sheng et al., 2004), and *Gymnogongrus torulosus* (Areco and Dos Santos Afonso, 2010). This order of affinity is likely a function of metal ion chemical characteristics and more specifically their ionic radius (0.069 nm for Zn(II) and 0.097 nm for Cd(II)) (Hassan et al., 2009; Gabr et al., 2009). The larger ionic radius of Cd(II) reduces cadmium uptake in comparison to zinc (Ma and Tobin, 2003).

The maximum metal uptake capacities (q_m) for each heavy metal were compared with those reported in the literature (Table 4). *M. pyrifera* exhibited a good capacity for Cd(II) recovery and had a q_m lower than that reported for *F. vesiculosus* (Mata et al., 2008), *Lessonia nigrescens* (Boschi et al., 2011), *Lessonia trabeculata* (Boschi et al., 2011) but higher than that found for *Pseudomonas stutzeri KCCM 34719* (Oh et al., 2009) and *Pseudomonas stutzeri* (lyophylized cells) (Hassan et al., 2009). Regarding its Zn adsorption capacity, *M. pyrifera* exhibited a very similar maximum capacity to other algae biosorbents; however, it was less efficient than *Pseudomonas aeruginosa ASU 6a* and *Bacillus cereus AUMC B52* (Joo et al., 2010).

The equilibrium data were also fitted with the D–R isotherm model to determine the nature of the biosorption process (physical *vs* chemical). The plot of $\ln q_e$ vs ε^2 followed linearity with a high determination coefficient (i.e., 0.98 for Zn(II) and 0.99 for Cd(II)). The sorption energies (E) were in the range of 8–16 kJ mol^{-1} indicating the predominance of an ion exchange mechanism during Zn(II) and Cd(II) biosorption (Table 3).

An increase in solution pH was observed during biosorption, indicating that binding sites on the cell wall were interacting with both protons and metal ions.

3.3. Biosorption equilibrium for Zn(II)–Cd(II) two-component systems

The experimental data of simultaneous adsorption of Cd(II) and Zn(II) from equimolar solutions are presented in Fig. 3. As the metal concentrations increased, cadmium uptake exceeded that of zinc. The metal uptake values and equilibrium concentrations of both metals were employed to evaluate the parameters of the different binary isotherms: competitive (Eqs. (10a) and (10b)), Langmuir approximation (Eqs. (11a) and (11b)), uncompetitive Langmuir multicomponent (Eq. (12)), and the Jain and Snoeyink (Eqs. (14) and (15)). The parameters of the binary isotherms are presented in Table 5. The application of the Jain and Snoeyink model (Eqs. (14) and (15)) allows estimating the contribution of competition in the biosorption process (Kleinübing et al., 2011). The fraction of cadmium ion adsorbed with no competition with zinc ions is defined by the difference ($q_{mCd} - q_{mZn}$) (0.52–0.38 = 0.14 mmol g^{-1}),

Table 3
Langmuir, Freundlich and Dubinin–Radushkevich (D–R) parameters for the adsorption of Zn(II) and Cd(II) in monocomponent solutions onto treated *M. pyrifera* biomass.

Metal ion	Langmuir			Freundlich			D–R	
	q_m (mmol g^{-1})	b (L $mmol^{-1}$)	R^2	K	N	R^2	E (kJ mol^{-1})	R^2
Zn(II)	0.67	2.40	0.98	0.37	2.50	0.91	9.62	0.98
Cd(II)	0.87	1.26	0.99	0.41	1.56	0.96	8.63	0.99

Table 4
Zn(II) and Cd(II) uptake capacities of different adsorbents for monocomponent systems.

Adsorbent	q_m Zn (mmol g^{-1})	q_m Cd (mmol g^{-1})	References
Sargassum filipendula (brown algae)	0.68	1.03	Luna et al. (2010)
Sargassum filipendula (brown algae)	0.64	0.63	Fagundes-Klen et al. (2007)
Gymnogongrus torulosus (red algae)	0.68	0.66	Areco and Dos Santos Afonso (2010)
Fucus vesiculosus (brown algae)		0.96	Mata et al. (2008)
Sargassum sp.	0.5		Sheng et al. (2004)
Lessonia nigrescens	–	0.99 (pH6)	Boschi et al. (2011)
Lessonia trabeculata	–	1.47 (pH6)	Boschi et al. (2011)
Pseudomona aeruginosa ASU 6a	1.27 (pH6)		Joo et al. (2010)
Bacillus cereus AUMC B52	1.01 (pH6)		Joo et al. (2010)
Pseudomonas stutzeri KCCM 34719		0.38 (pH5)	Hassan et al. (2009)
Pseudomonas stutzeri (lyophylized cells)		0.42 (pH5)	Oh et al. (2009)
Calcium-treated *Macrocystis pyrifera* (brown algae)	0.67	0.87	This study

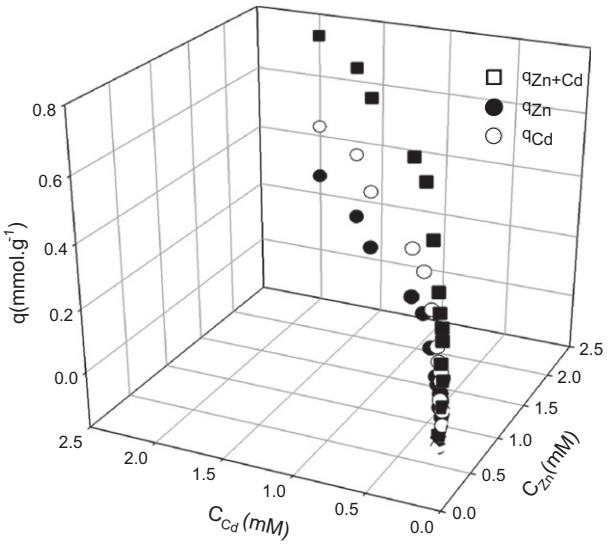

Fig. 3. Zn(II), Cd(II) and total uptake as a function of the equilibrium concentrations in Zn(II)–Cd(II) bicomponent systems using treated *M. pyrifera* biomass.

while the fraction of metal adsorbed under the control of competition effect is given by $q_{mZn} = 0.38$. According to this model, only about 27% of the biosorption of cadmium in the binary mixture occurred without competition.

The q_{Zn} and q_{Cd} calculated by the modified Langmuir competitive model gave lower values for each metal than the q_{Zn} and q_{Cd} estimated by the Langmuir model for the mono-component system. The total metal uptake value $q_{(Zn+Cd)}$ determined by the modified Langmuir uncompetitive model (Table 5) was lower than the sum of the individual q_{Zn} and q_{Cd} obtained by the Langmuir model for the mono-component system (Table 3). This finding is more evidence that the metals are competing for binding on the same sorption sites. For all models applied, b_{Cd} was higher than b_{Zn} indicating that, in binary systems, the cadmium ion has a higher affinity for the binding sites of the biosorbent, which is opposite to the behavior shown by the biosorbent in monocomponent solutions. The performance of *M. pyrifera*-treated biomass for Cd(II) and Zn(II) removal can be compared to those cited in the literature. Carvalho et al. (1995) presented data for the adsorption of these ions using the brown algae *A. nodosum*. The parameters of the competitive Langmuir isotherm were $q = 0.67$ mmol g^{-1}, $b_{Cd} = 6.67$ L $mmol^{-1}$ and $b_{Zn} = 2.27$ L $mmol^{-1}$. The maximum adsorption capacity (q) for *A. nodosum* was two times higher than that for *M. pyrifera*-treated biomass but the affinity of the heavy metals for the binding sites (b_{Zn} and b_{Cd}) were higher for *M. pyrifera* treated biomass. Fagundes-Klen et al. (2007) also investigated the simultaneous removal of Zn(II) and Cd(II) using *Sargassum filipendula* treated with 0.5 M $CaCl_2$. The application of the modified Langmuir competitive model gave: $q = 0.54$ mmol g^{-1}, $b_{Cd} = 2.28$ L $mmol^{-1}$ and $b_{Zn} = 4.78$ L $mmol^{-1}$. In this case, the biosorbent presented a higher affinity coefficient for Zn(II) than for Cd(II), contrary to the present results. Consistently with our study, Luna et al. (2010) obtained the same order of affinity for zinc and cadmium using an untreated biomass of *Sargassum filipendula* ($q = 0.67$ mmol g^{-1}, $b_{Cd} = 19.34$ L $mmol^{-1}$ and $b_{Zn} = 10.40$ L $mmol^{-1}$).

3.4. Desorption studies

Desorption is a key step in the design of a sorption process: the recycling of the sorbent contributes to reducing the volume of waste material and decreasing the cost of the process. In addition, desorption is a supplementary step in the metal concentration process. Zn(II) and Cd(II) desorption were almost complete (99–100%) when the loaded biosorbent was treated with 0.1 M HNO_3 and EDTA (Fig. 4), but when it was treated with 0.1 M $Ca(NO_3)_2$ the desorption percentages were 96.7% and 71.9% for Zn(II) and Cd(II), respectively.

Table 5
Binary adsorption constants of Zn(II) and Cd(II) on *M. pyrifera* treated biomass in bicomponent systems using different isotherms.

Model	Equation	Parameters
Langmuir multicomponent competitive	(10a)	$q_{mZn} = 0.32$ mmol g^{-1}; $q_{mCd} = 0.53$ mmol g^{-1} $b_{Zn} = 4.05$ L $mmol^{-1}$; $b_{Cd} = 5.40$ L $mmol^{-1}$ $R^2 = 0.96$; $R^2 = 0.98$
Langmuir multicomponent competitive (approximation)		$q_{mZn} = 0.67$ mmol g^{-1}; $^1b_{Zn} = 1.91$ L $mmol^{-}$ $R^2 = 0.96$ $q_{mCd} = 0.89$ mmol g^{-1}; $b_{Cd} = 4.27$ L $mmol^{-1}$ $R^2 = 0.97$
Langmuir multicomponent uncompetitive		$q_{Zn+Cd} = 0.88$ mmol g^{-1}; $b_{Zn+Cd} = 2.21$ L $mmol^{-1}$, $K = 0.45$ mmol L^{-1}; $R^2 = 0.99$
Theorical		$q_{Zn+Cd} = 1.54$ mmol g^{-1}; $b_{Zn+Cd} = 3.65$ L $mmol^{-1}$
Jain and Snoeyink		$q_{mZn} = 0.38$ mmol g^{-1}; $q_{mCd} = 0.52$ mmol.g^{-1} $b_{Zn} = 4.06$ L $mmol^{-1}$; $b_{Cd} = 5.40$ L $mmol^{-1}$ $R^2 = 0.98$

Approximately 3 h were needed to reach these desorption yields. ESEM microphotographs (Fig. SD1) showed that EDTA treatment deteriorated the structure of the cell wall, while this effect was not observed when the biomass was in contact with HNO_3. The deleterious effect of EDTA was also confirmed by the decrease of the carbon peak in the EDAX spectrum.

3.5. Biosorbent characterization

The untreated and treated biomasses were analyzed by ESEM EDX (Fig. SD1a and b). Pre-treatment with $CaCl_2$ (0.2 M) allowed the conservation of the cell structure. ESEM micrographs, showed the presence of Ca^{2+}, K^{+}, Mg^{2+}, and Na^{+} as common elements for untreated and treated biomasses. After applying the $CaCl_2$ treatment, the number of peaks decreased, indicating that several elements were replaced by calcium. Through the EDX spectrum it was possible to determine that Zn(II) and Cd(II) were distributed uniformly on the surface of the cell wall (Fig. SD2). The homogeneous distribution of the adsorbate was also observed in the case of nickel, while aggregates were formed on the *M. pyrifera* surface during Hg(II) biosorption (Plaza et al., 2011).

The FT IR analysis allowed identifying the chemicals groups involved in the sorption of heavy metals (Fig. 5). Several functional groups could be identified in the cell wall such as, carboxylic acids, amide, amine, amino and sulfonate (Fig. 5, peaks 1, 2, 3, 4, 5, 6, 7 and 8). Comparing control untreated and treated biomass with loaded biomass, a shift was observed in the location of typical peaks. The N—H stretching (from amine groups) showed a shift from 3432 cm^{-1} and 3418 cm^{-1} (control untreated and treated biomass at pH 4, respectively) to 3369 cm^{-1} (loaded Zn(II) biomass at pH 4) and from 3431 cm^{-1} and 3447 cm^{-1} (control untreated and treated biomass at pH 3, respectively) to 3396 cm^{-1} (loaded Cd(II) biomass at pH 3) (Fig. 5(1)). Although, amine groups were not the main groups present onto the cell wall of the brown alga, the FT IR results confirmed their contribution to Zn(II) and Cd(II) biosorption. The shifts, from 2936 cm^{-1} and 2918 cm^{-1} (control untreated and treated biomass at pH 4, respectively) to 2957 cm^{-1} (loaded Zn(II) biomass at pH 4) and from 2931cm^{-1} (control untreated and treated biomass at pH 3, respectively) to 2920 cm^{-1}(loaded Cd(II) biomass at pH 3) correspond to O—H stretching (Fig. 5(2)). A strong asymmetric C=O stretch band initially present at 1630 cm^{-1} (control untreated and treated biomass at pH 4 and pH 3) was also shifted to 1539 cm^{-1} (loaded Zn(II) and Cd(II) biomass) (Fig. 5(3,4)). The symmetry C=O stretch band was shifted from 1430 cm^{-1} and 1439 cm^{-1} (control untreated and treated biomass at pH 3, respectively) to 1421 cm^{-1} (loaded Cd(II) and Zn(II) biomass) (Fig. 5(5)). Also the presence of the C—O (carboxyl) was detected and it was shifted from 1260 cm^{-1} (control untreated and treated biomass at pH 4 and pH 3) to 1239 cm^{-1} and 1253 cm^{-1} (loaded Zn(II) and Cd(II) biomass) (Fig. 5(6,7)). Sulfonates were also active sites as shifts in the peaks corresponding to S=O stretching and S—O stretching were detected during Zn(II) and Cd(II) adsorption by treated biomass(Fig. 5(8)).

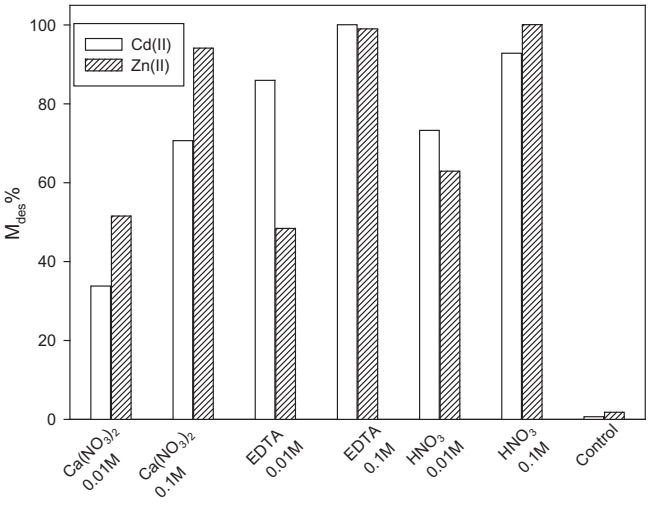

Fig. 4. Zn(II) and Cd(II) desorption performance (%M_{des}) employing different eluents.

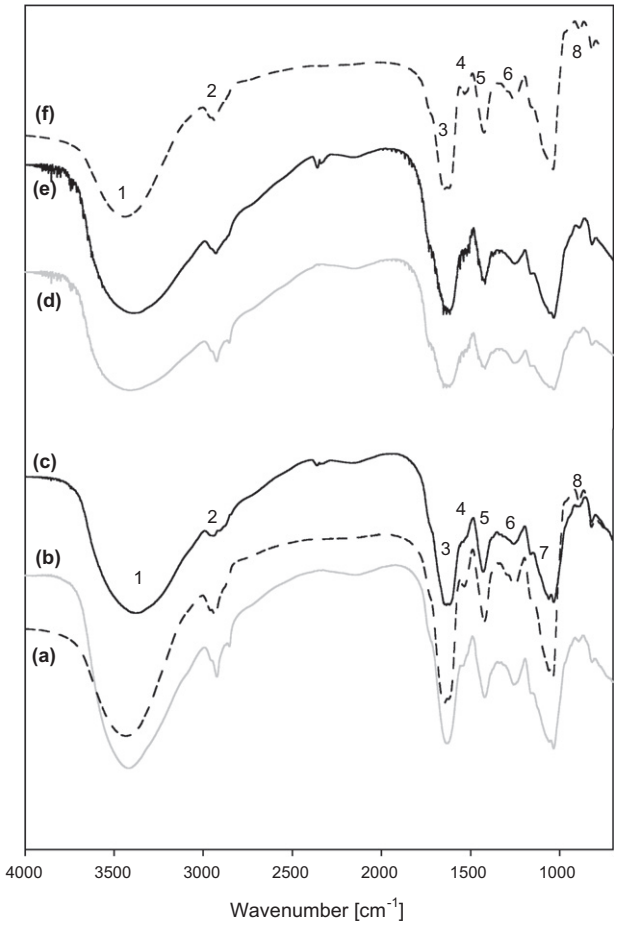

Fig. 5. FT IRspectra; (a) and (f): control *M. pyrifera* untreated biomass at pH 4 and pH 3, respectively; (b) and (d): control *M. pyrifera* treated biomass at pH 4 and 3, respectively; (c) and (e): *M. pyrifera* treated biomass loaded with Zn(II) (pH 4) and Cd(II) (pH 3), respectively. 1–8: peaks corresponding to functional groups on algal surface.

4. Conclusion

The effectiveness of $CaCl_2$ treatment was proven since calcium-treated biomass showed a higher metal uptake and greater stability than native algae. In mono-component solutions, *M. pyrifera* showed a higher affinity for Zn(II) than for Cd(II). A reciprocal trend was observed in the case of bi-component solutions where 73% of the adsorption occurred with competition. Desorption with 0.1 M HNO_3 allowed for recovery of the metals without damaging the biomass. Finally, the *M. pyrifera* treated biomass is a suitable, economic and easily available biosorbent for zinc and cadmium uptake.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2012.04.014.

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