

## Removal of Cd(II), Zn(II) and Pb(II) from aqueous solutions by brown marine macro algae: Kinetic modelling

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### Abstract

Specific marine macro algae species abundant at the Portuguese coast (*Laminaria hyperborea*, *Bifurcaria bifurcata*, *Sargassum muticum* and *Fucus spiralis*) were shown to be effective for removing toxic metals (Cd(II), Zn(II) and Pb(II)) from aqueous solutions. The initial metal concentrations in solution were about 75–100 mg L<sup>-1</sup>. The observed biosorption capacities for cadmium, zinc and lead ions were in the ranges of 23.9–39.5, 18.6–32.0 and 32.3–50.4 mg g<sup>-1</sup>, respectively. Kinetic studies revealed that the metal uptake rate was rather fast, with 75% of the total amount occurring in the first 10 min for all algal species. Experimental data were well fitted by a pseudo-second order rate equation. The contribution of internal diffusion mechanism was significant only to the initial biosorption stage. Results indicate that all the studied macro algae species can provide an efficient and cost-effective technology for eliminating heavy metals from industrial effluents.

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### 1. Introduction

Heavy metals in the environment can be hazardous for the health and well being of most living species. Therefore, these pollutants should be removed from industrial wastes before discharge into water streams.

According to the ranking of metal interest priorities referred by Volesky [1], Zn(II), Pb(II) and Cd (II) are three of the most interesting heavy metals for removal and/or recovery considering the combination of environmental risk and reserve depletion.

Cadmium is used in a wide variety of industrial processes such as alloy preparation, metal plating and electronics. Lead pollution results from textile dyeing, ceramic and glass industries, petroleum refining, battery manufacture and mining

operations. Viscose rayon yarn and fiber production, metal processing industries and coal-fired power generation are sources of zinc [2]. These are just examples of the main sectors producing liquid effluents containing the mentioned metal ions as the result of their activities.

Chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, evaporation, ion exchange and reverse osmosis are some of the most commonly used procedures for removing metal ions from aqueous streams [1]. However, these processes have significant disadvantages, such as an incomplete metal removal, expensive equipment and monitoring systems, high reagent or energy requirements and/or generation of toxic sludge or other waste products that require an adequate disposal process. Those usual technologies also may be ineffective or extremely expensive when initial metal concentrations are in the range of 10–100 mg L<sup>-1</sup> [2]. For these reasons, cost-effective alternative technologies for treatment of metals contaminated waste streams are needed.

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### Nomenclature

$C_0$	initial metal concentrations in solution ( $\text{mg L}^{-1}$ )
$C_t$	metal concentrations in solution at any time $t$ ( $\text{mg L}^{-1}$ )
$C_e$	equilibrium metal concentrations in solution ( $\text{mg L}^{-1}$ )
$d$	particle size diameter (m)
$D_i$	diffusion coefficient in the solid ( $\text{m}^2 \text{min}^{-1}$ )
$D_w$	diffusion coefficient in the solid ( $\text{m}^2 \text{min}^{-1}$ )
$k_{1,\text{ads}}$	pseudo-first-order rate constant ( $\text{min}^{-1}$ )
$k_{2,\text{ads}}$	pseudo-second-order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ )
$K_w$	Weber and Morris intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-0.5}$ )
$q$	amount of metal ion adsorbed at any time $t$ ( $\text{mg g}^{-1}$ )
$q_e$	amount of metal ion adsorbed at equilibrium ( $\text{mg g}^{-1}$ )
$m$	mass of adsorbent (g)
$V$	volume (L)
$r_{1,\text{ads},\text{in}}$	initial uptake rate for the pseudo-first-order model ( $\text{mg g}^{-1} \text{min}^{-1}$ )
$r_{2,\text{ads},\text{in}}$	initial uptake rate for the pseudo-second-order model ( $\text{mg g}^{-1} \text{min}^{-1}$ )
$t$	time (min)

Biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of some industrial wastewaters. It is defined as the accumulation and concentration of pollutants from aqueous solutions onto biological materials, thus allowing the recovery and/or environmentally acceptable disposal of pollutants [3]. The major advantages of the biosorption technology are its effectiveness in quickly reducing the concentration of heavy metals ions to very low levels with high efficiency and the use of inexpensive biosorbent materials [4]. These characteristics make biosorption an ideal alternative for treating high volumes of low concentration complex wastewaters [5].

A lot of materials such as bark, chitosan, wool, cotton, clay, bacteria, fungi, alginate, dead biomass, waste fruit residues and others [4,6–8] have been reported to have an effective performance in removing heavy metals from industrial effluents.

The purpose of this study was to explore the ability of using marine macro algae species abundant at the Portuguese coast (*Laminaria hyperborea*, *Bifurcaria bifurcata*, *Sargassum muticum* and *Fucus spiralis*) for the removal of toxic metals (cadmium, lead and zinc) from aqueous solutions.

## 2. Alga selection

The brown algae (*Phaeophyta*) – *L. hyperborea*, *B. bifurcata*, *S. muticum* and *F. spiralis* – were selected for this work due to their abundance in the Portuguese coast [9]. Some relevant features concerning these species are:

- most northern shores are distinguished by the presence of large brown algae (e. g., *Laminaria* sp.);
- in some central shores the algae *B. bifurcata* can cover extensive areas in the upper sub littoral fringe;
- *F. spiralis*, although present in the north and south, is notably abundant on some shores of the central region between high water of spring tides and mean tide level;
- *S. muticum* is an invasive alga in Europe [10].

## 3. Kinetic modelling

In order to investigate the mechanism of biosorption and potential rate controlling step, reaction and diffusion controlled kinetic models have been used to fit experimental data.

### 3.1. Reaction models

The more usual kinetics reaction models are zero-order, first-order, pseudo-first-order, second-order, pseudo-second-order, reversible reaction models, third-order, Langmuir–Hinshelwood and Elovich models [11]. The pseudo-first-order Lagergren model [12] considers that the occupation rate of adsorption sites is proportional to the number of unoccupied sites [13]:

$$q = q_e(1 - e^{-k_{1,\text{ads}}t}) \quad (1)$$

where  $q$  ( $\text{mg g}^{-1}$ ) is the amount of metal ion adsorbed at any given time  $t$  (min),  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of metal ion adsorbed at equilibrium and  $k_{1,\text{ad}}$  ( $\text{min}^{-1}$ ) is the Lagergren rate constant.

According to this model, the initial uptake rate is given by:

$$r_{1,\text{ads},\text{in}} = k_{1,\text{ads}} \times q_e \quad (2)$$

Heavy metal adsorption kinetics can be also modelled by using a pseudo-second-order rate Eq. (3) [14], based on the sorption capacity of the solid phase:

$$q = \frac{t}{1/(k_{2,\text{ads}}q_e^2) + t/q_e} \quad (3)$$

where  $k_{2,\text{ad}}$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the second-order rate constant for adsorption.

This model predicts the behaviour over the whole range of adsorption and is in agreement with a mechanism where adsorption is the rate-controlling step [15]. The initial uptake rate is given by:

$$r_{2,\text{ads},\text{in}} = k_{2,\text{ads}} \times q_e^2 \quad (4)$$

### 3.2. Diffusion models

The most important mass transfer resistance for sorption from aqueous solutions has been established to be the internal (intraparticle) diffusion. The effect of external film diffusion on biosorption rate can be assumed to be not significant and ignored in any engineering analysis because when the biomass is employed as a suspension of fine particles in a perfectly mixed batch or continuous systems, all the surface binding sites are available for metal uptake [15].

The distinction between reaction and diffusion processes is often difficult to characterise. According to Ho et al. [11], a more appropriate quantitative approach to distinguishing between kinetic reaction and diffusion rate control is to perform the square root of contact time (root  $t$ -test) analysis, as proposed by Weber and Morris [16]:

$$q = K_w t^{0.5} \quad (5)$$

where  $K_w$  ( $\text{mg g}^{-1} \text{min}^{-0.5}$ ) is the Weber and Morris intraparticle diffusion rate.

A linear plot of  $q$  versus  $t^{0.5}$  indicates the prevalence of intraparticle diffusion control.

The intraparticle diffusion coefficient can be calculated using the Eq. (6) [17].

$$D_w = \frac{\pi}{8640} \left( \frac{dK_w}{q_e} \right)^2 \quad (6)$$

where  $D_w$  ( $\text{m}^2 \text{min}^{-1}$ ) is the diffusion coefficient in the solid and  $d$  (m) is the mean particle diameter.

Another kind of intraparticle diffusion model was proposed by Urano and Tachikawa [18]. The sorption kinetics rate is expressed as:

$$-\log \left[ 1 - \left( \frac{q}{q_e} \right)^2 \right] = \frac{4\pi^2 D_i t}{2.3d^2} \quad (7)$$

where  $D_i$  ( $\text{m}^2 \text{min}^{-1}$ ) is the diffusion coefficient in the solid.

## 4. Materials and methods

### 4.1. Biomass

The marine macro algae – *L. hyperborea*, *B. bifurcata*, *S. muticum* and *F. spiralis* – were collected at the coast of the Atlantic sea in the north of Portugal.

The macro alga were washed with distilled water in order to remove part of the salt coming from the seawater and dried at room temperature (about 20 °C). Then, they were powdered using a centrifugal mill (Retsch, model ZM 100) and sieved (Retsch AS 200 sieve) to get a fraction with a uniform particle size of 150–300  $\mu\text{m}$ .

Real and apparent densities, specific surface area and intraparticle porosity of the particles were measured by an ultracycrometer and a mercury intrusion porosimeter (UPY-1000, Quatachrome).

The surface functional groups on the adsorbent were studied by a Fourier transform infrared spectrometer (*Arid-Zone*<sup>TM</sup>, 1540, Bomem). The spectra were recorded from 4000 to 550  $\text{cm}^{-1}$  using KBr window.

### 4.2. Heavy metals solutions

Analytical grade salts [ $\text{Cd}(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{PbCl}_2$ ] were used to prepare solutions (concentrations about 75–100  $\text{mg L}^{-1}$ ) of Cd, Zn and Pb. The pH of each solution was adjusted at 5.0 with diluted HCl or NaOH solutions. This was the selected pH

because it was observed that, for some biomass, the highest metal uptake capacity was reached at pH around 4–5 or higher [4,15,19,20].

The metal content in solution was determined by AAS – flame method (AAS GBC 932 AB Plus spectrometer).

### 4.3. Kinetic study

In order to establish the effect of pH on the biosorption batch equilibrium, studies at three different pH values (4.0, 4.5 and 5.0) were carried out by adding 200 mg of dried marine macro algae to flasks containing 100,0 mL of 75–100  $\text{mg L}^{-1}$  metal solution. The flasks were agitated on a rotary shaker (*Multi-stirrer, Velp Scientifica*) for 1 h. Previous kinetic tests showed that 1 h contact time was sufficient to attain equilibrium at 25 °C.

Kinetic experiments were conducted in a continuously stirred vessel (1000 rpm) containing 3 L of heavy metal solution at initial pH 5.0 before adding 6.00 g of algal biomass. Samples for the determination of the residual metal ion concentrations in the solution were taken at pre-determined time intervals, during 1 h. The suspensions were centrifuged (Eppendorf centrifuge 5410) prior to metal content measurement in the filtrates. All experiments were conducted at room temperature (25 °C) and the pH of the solution was monitored continuously, but not adjusted to the initial value. Adsorption capacities were calculated from the mass balance:

$$q = \frac{(C_0 - C_t)V}{m} \quad (8)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) and  $C_t$  ( $\text{mg L}^{-1}$ ) are the metal concentrations in solution at  $t=0$  and any time  $t$ ,  $V$  (L) is the volume of the solution and  $m$  (g) is the mass of adsorbent.

In the experimental work, no special care was taken to maintain pH during the course of the experiments because, when applying this kind of biosorbents to treat large volume of industrial effluents, it may be difficult to accurately adjust the pH. However, pH dependence of metal sorption could clarify on the mechanism of metal accumulation by biomass and can help to optimize the process of metal removal [21]. Solution pH influences both cell surface metal binding sites and metal chemistry in solution [15,19–21].

The experiments were carried out in duplicate and the results are presented as mean values.

## 5. Results and discussion

### 5.1. Biomass characterization

#### 5.1.1. Textural characteristics

The values of density, specific surface area and intraparticle porosity are presented in Table 1. Real and apparent densities were about 1.7 and in the range 1.5–1.6  $\text{g cm}^{-3}$ , respectively, for all biosorbents. *S. muticum* presents the highest surface area (11.19  $\text{m}^2 \text{g}^{-1}$ ) and intraparticle porosity (8.73%).

Table 1  
Textural characteristics of the macro algae species

Macro algae	Solid density ( $\text{g cm}^{-3}$ )	Apparent density ( $\text{g cm}^{-3}$ )	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Total intraparticle porosity (%)
<i>L. hyperborea</i>	1.70	1.58	6.94	5.66
<i>S. muticum</i>	1.70	1.50	11.2	8.73
<i>F. spiralis</i>	1.65	1.50	9.05	6.85
<i>B. bifurcata</i>	1.70	1.56	5.86	5.32

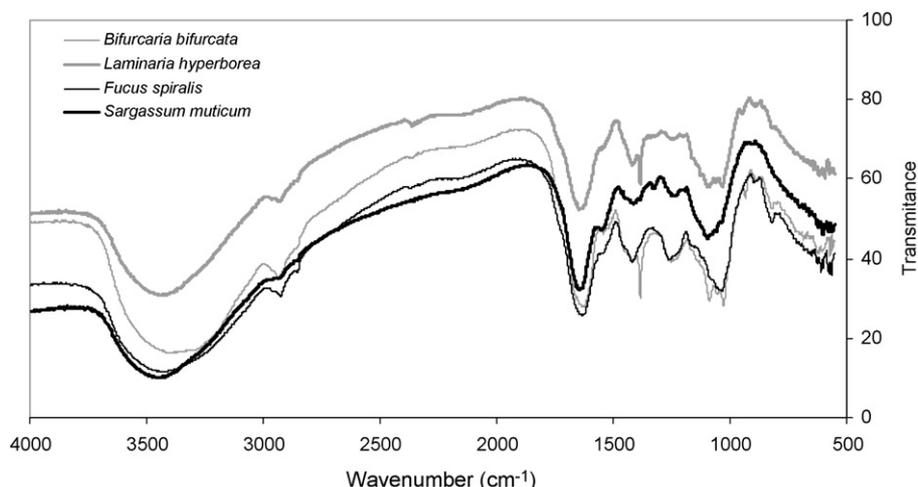


Fig. 1. FT-IR spectra of marine macro algae species.

### 5.1.2. Infrared spectroscopy

Fig. 1 presents the IR spectra of the algae. The analysis of the IR-spectra indicated broad bands at  $3420\text{--}3455 \text{ cm}^{-1}$ , representing bonded  $\text{--OH}$  and  $\text{--NH}$  groups. The bands observed at about  $2940 \text{ cm}^{-1}$  could be assigned to the  $\text{--CH}$  stretch [22]. The dominating peaks at  $1640$  correspond to the  $\text{C=O}$  stretching. The bands about  $1250 \text{ cm}^{-1}$ , represent  $\text{--SO}_3$  stretching. The double peak at  $1038$  and  $1079 \text{ cm}^{-1}$  is probably caused by  $\text{C--O}$  stretching vibrations of alcoholic groups in carbohydrates [23]. *L. hyperborea* and *B. bifurcata* behave differently from the other two species in the wavenumber range  $1600\text{--}4000 \text{ cm}^{-1}$ . For lower wavenumbers, *B. bifurcata* and *F. spiralis* show a similar pattern.

### 5.2. Sorption capacities

Metal uptake by the algal biomass after 1 h contact time increases with pH (in the range 4.0–5.0), as shown in Fig. 2, due to the competition to the binding sites between protons and metal cations.

The sorption capacity of the different algal species varies with the metal ion and follows the order  $\text{Pb(II)} > \text{Cd(II)} > \text{Zn(II)}$ . The ionic character of the binding forces decreases in the same order and can explain these results. Brady and Tobin [24] also observed that the uptake capacity of  $\text{Pb(II)}$ ,  $\text{Cd(II)}$  and  $\text{Zn(II)}$  by biomass of *Rhizopus arrhizus* followed the same order and was correlated with the covalence index of the metal ions. From biosorption studies of binary mixtures of various metal ions by biomass of *Streptoverticillium cinnamoneum*, Puranik and Paknicar [25] verified that the affinity of the biosorbent varied in the order  $\text{Pb(II)} > \text{Zn(II)} > \text{Cd(II)}$ . Chong and Volesky [26] studied the adsorption of three binary mixtures –  $\text{Cu}^{2+}/\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}/\text{Cd}^{2+}$  and  $\text{Zn}^{2+}/\text{Cd}^{2+}$  – by the algae *Ascophyllum nodosum* and concluded that the affinity of different metals increased as  $\text{Cu} > \text{Cd} > \text{Zn}$ . In the present study, *L. hyperborea* and *B. bifurcata* showed to be the most efficient biosorbents for lead (about  $50 \text{ mg g}^{-1}$  uptake capacity, at pH 5) and *S. muticum* and *F. spiralis* presented a relatively high uptake capacity for cadmium and zinc, particularly at pH 5 (Figure 2).

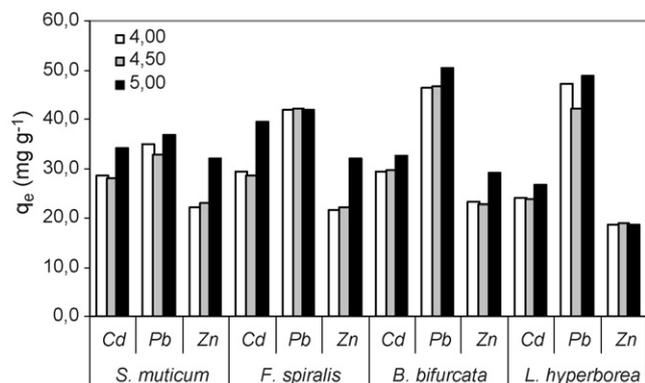


Fig. 2. Biosorption capacities of the marine macro algae species for  $\text{Zn(II)}$ ,  $\text{Pb(II)}$  and  $\text{Cd(II)}$  at different pH.

### 5.3. Kinetic modelling

Kinetic data of metal biosorption onto the marine algae were fitted to pseudo-first-order (model A) and pseudo-second-order

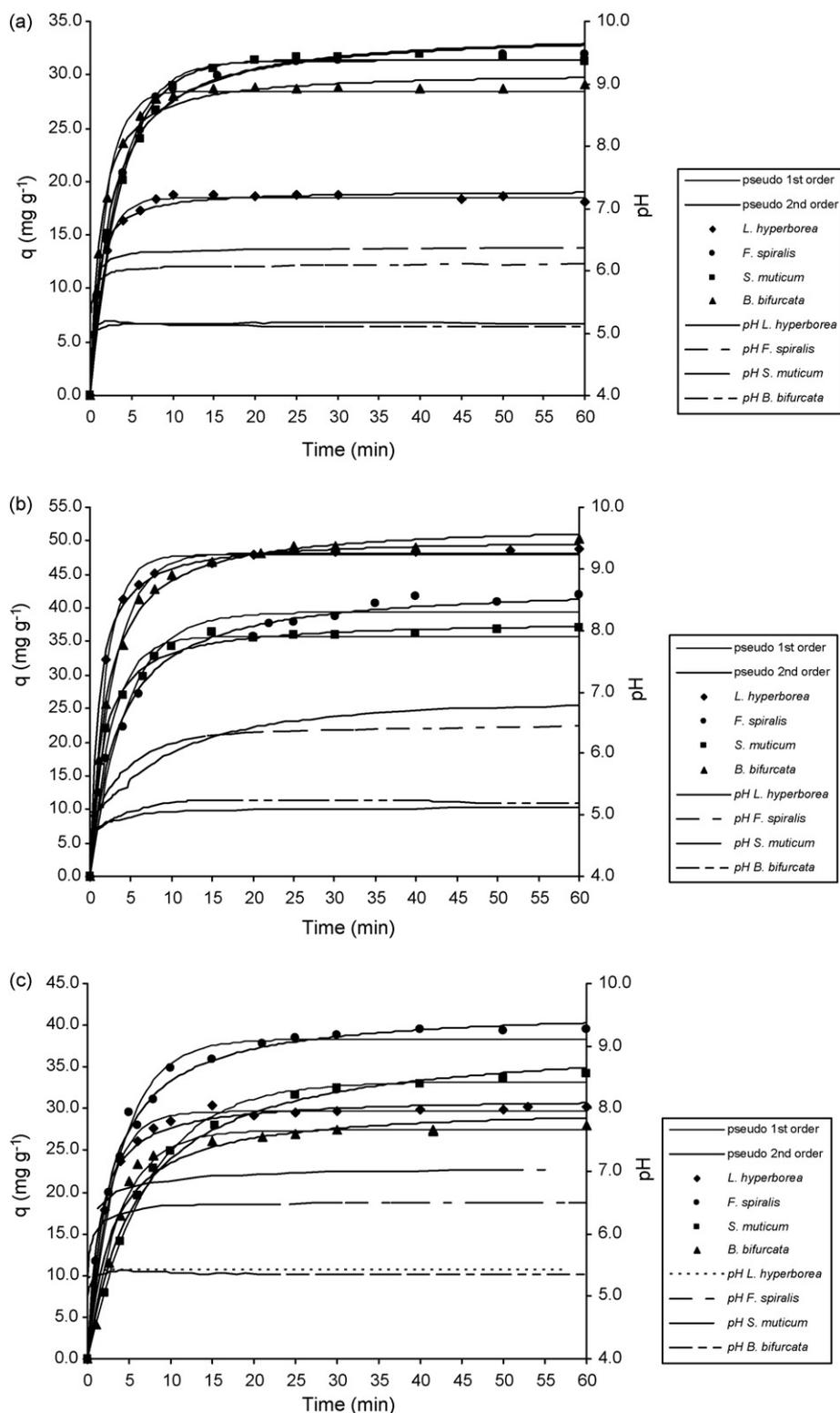


Fig. 3. Fitting of the pseudo-first and pseudo second-order kinetic models to the experimental biosorption data (Initial pH 5; no pH control), (a) Zn (II); (b) Pb (II); (c) Cd (II).

(model B) reaction models (Fig. 3) by non-linear regression analysis using the software package Fig.P for WINDOWS from BIOSOFT. Model parameters – kinetic constants, maximum uptake capacities and initial uptake rates – and the correla-

tion coefficients between experimental and predicted data are presented in Table 2.

The kinetic models adequately fit the data over the entire course of the experiment. The theoretical  $q_e$  values predicted

Table 2  
Pseudo first-order and second-order model parameters, correlation coefficients ( $R$ ) and residual variances ( $S^2$ )

Model parameters	<i>L. hyperborea</i>			<i>S. muticum</i>			<i>F. spiralis</i>			<i>B. bifurcata</i>			
	Zn	Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd	
Pseudo first-order	$q_e$ (mg g <sup>-1</sup> )	18.5	47.9	29.7	31.4	35.8	33.2	31.3	39.3	38.3	28.5	48.2	27.4
	$k_{i,ads} \times 10^2$ (min <sup>-1</sup> )	61.7	51.5	40.9	26.4	37.7	13.9	28.4	23.2	25.8	28.5	34.4	25.8
	$r_{1,ads,in}$ (mg g <sup>-1</sup> min <sup>-1</sup> )	11.4	24.6	12.2	8.28	13.9	4.61	8.89	9.11	9.88	8.12	16.6	7.06
	$R$	0.997	0.997	0.997	0.997	0.997	0.998	0.998	0.998	0.992	0.996	0.996	0.994
	$S^2$	0.15	1.61	0.44	0.658	2.16	0.48	0.605	5.93	2.58	0.583	3.09	1.18
Pseudo-second-order	$q_e$ (mg g <sup>-1</sup> )	19.2	50.3	31.3	34.1	38.2	38.4	34.3	43.5	42.1	30.3	52.7	30.3
	$k_{2,ads} \times 10^2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	7.45	2.04	2.4	1.23	1.76	0.43	1.21	0.69	0.9	2.84	0.97	1.14
	$r_{2,ads,in}$ (mg g <sup>-1</sup> min <sup>-1</sup> )	27.5	51.7	23.9	14.3	25.7	6.37	14.2	13.1	16	26.1	26.8	10.4
	$R$	0.991	0.996	0.997	0.995	0.997	0.997	0.997	0.996	0.997	0.997	0.999	0.982
	$S^2$	2.17	1.45	0.497	0.915	0.68	0.822	0.689	1.47	0.889	0.493	0.68	3.43

by the two equations are very close to the experimental  $q_e$  values (Fig. 3). The performances of both models (A and B, respectively) were compared by using an  $F$ -test, based on model variances ( $F_{cal} = S^2(B)/S^2(A)$ ) [27]. This statistical tool allows evaluating the difference in the precision of the tested models. If  $F_{cal} > F_{tab}$ , the model put at the denominator (A) is statistically better than the other, according to the chosen level of significance [28].

Table 3 reports the tabulated  $F$ -values corresponding to the chosen level of probability (95%) and the relative degrees of freedom. In the tested conditions, there was no statistical difference between the precision of the two biosorption models except for the following cases:

- The pseudo-first-order model is better for the systems Zn/*L. hyperborea* and Cd/*B. bifurcata*.
- The pseudo-second-order model is better for Pb/*S. muticum*, Pb/*F. spiralis*, Cd/*F. spiralis* and Pb/*B. bifurcata*.

The internal diffusion model fits the experimental data for the initial uptake stage. The linear plots of  $q$  versus  $t^{0.5}$  (Eq. (5)) and  $-\log[1 - (q/q_e)^2]$  versus  $t$  (Eq. (7)) indicate that the biosorption process is controlled by internal diffusion during the first 10 min.

The intraparticle mass transfer coefficients, calculated by linear regression, are summarized in Table 4. Generally, the

diffusion coefficients ( $D_i$ ) calculated according to the Urano and Tachikawa model follow the order  $Pb^{2+} > Zn^{2+} > Cd^{2+}$ . The Weber and Morris model gives lower diffusion coefficients except for the system  $Zn^{2+}/F. spiralis$ . Moreover, the values are closer than the obtained from the first model. Taking into account that the mass transfer coefficients are regulated mostly by the flow characteristics in the system [29], and as the experimental conditions were identical for all systems, it could be expected that the diffusion coefficients were in the same level. Nevertheless, differences in the diffusivities can be achieved due to the different properties of the metal ions and the interactions between the metals and the biomass [29].

The values of  $D_w$  and  $D_i$  compared with the diffusion coefficients of the metal ions in water ( $4.2 \times 10^{-8}$ ,  $5.7 \times 10^{-8}$  and  $4.3 \times 10^{-8}$  m<sup>2</sup> min<sup>-1</sup>, respectively for Zn (II), Pb(II) and Cd (II)) [30], indicate that the contribution of the intraparticle diffusion to the overall sorption kinetics is not very important.

The results of the kinetic study (Table 2) confirmed that the maximum uptake of Zn (II) and Cd (II) was achieved by *S. muticum* and *F. spiralis*, but the first species accumulates Zn (II) about twice faster than Cd (II). These findings are in accordance with the higher specific surface area and intraparticle porosity of those species. The affinity of *L. hyperborea* for Zn(II) is high, as indicated by the value of the initial uptake rate, but the accumulation capacity is relatively low. The uptake of Zn (II) and

Table 3  
 $F$ -test for residual variances of pseudo-first (A) and second-order (B) models

Macro algae	Metal	$F_{cal} = S^2(A)/S^2(B)$	$F_{cal} = S^2(B)/S^2(A)$	$F_{0.05}$	Better model
<i>L. hyperborea</i>	Zn	0.0692	14.4498	2.82	A
	Pb	1.1125	0.8989	2.82	A or B
	Cd	0.8922	1.1208	2.69	A or B
<i>S. muticum</i>	Zn	0.7191	1.3907	2.82	A or B
	Pb	3.1939	0.3131	2.82	B
	Cd	0.5797	1.7265	2.98	A or B
<i>F. spiralis</i>	Zn	0.8785	1.1393	2.69	A or B
	Pb	4.0462	0.2471	2.82	B
	Cd	2.9020	0.3446	2.58	B
<i>B. bifurcata</i>	Zn	1.1820	0.8460	2.69	A or B
	Pb	4.5325	0.2206	2.82	B
	Cd	0.3446	2.9022	2.69	A

Table 4  
Intraparticle mass transfer diffusion model parameters, correlation coefficients (R) and residual variances (S<sup>2</sup>)

	Model parameters				<i>L. hyperborea</i>			<i>S. muticum</i>			<i>F. spiralis</i>			<i>B. bifurcata</i>		
	$K_w$ (mg g <sup>-1</sup> min <sup>-0.5</sup> )	$D_w$ (m <sup>2</sup> min <sup>-1</sup> )	R	S <sup>2</sup>	Zn	Pb	Cd									
Weber and Morris	7.31	2.84 × 10 <sup>-12</sup>	0.981	6.55	9.59	12.4	7.6	10.2	11.4	12.6	11.6	16.4	8.71	11.6	16.4	8.71
		2.53 × 10 <sup>-12</sup>	0.950		1.70 × 10 <sup>-12</sup>	2.07 × 10 <sup>-12</sup>	9.21 × 10 <sup>-13</sup>	1.90 × 10 <sup>-12</sup>	1.36 × 10 <sup>-12</sup>	1.88 × 10 <sup>-12</sup>	5.29 × 10 <sup>-12</sup>	1.96 × 10 <sup>-12</sup>	1.84 × 10 <sup>-12</sup>	5.29 × 10 <sup>-12</sup>	1.96 × 10 <sup>-12</sup>	1.84 × 10 <sup>-12</sup>
			36.1		1.38	11.2	4.18	0.98	0.987	0.993	0.987	0.987	0.999	0.987	0.987	0.999
					1.09 × 10 <sup>-11</sup>	3.49 × 10 <sup>-10</sup>	7.56 × 10 <sup>-12</sup>	6.59 × 10 <sup>-12</sup>	1.06 × 10 <sup>-10</sup>	3.53 × 10 <sup>-10</sup>	1.43 × 10 <sup>-11</sup>	2.14 × 10 <sup>-10</sup>	8.61 × 10 <sup>-12</sup>	1.43 × 10 <sup>-11</sup>	2.14 × 10 <sup>-10</sup>	8.61 × 10 <sup>-12</sup>
Urano and Tachikawa	0.980	0.980	0.980	0.980	0.978	0.992	0.983	0.981	0.997	0.982	0.980	0.992	0.978	0.980	0.992	0.978
					2.39 × 10 <sup>-4</sup>	4.96 × 10 <sup>-5</sup>	2.91 × 10 <sup>-5</sup>	5.21 × 10 <sup>-5</sup>	5.27 × 10 <sup>-3</sup>	1.71 × 10 <sup>-5</sup>	6.91 × 10 <sup>-6</sup>	4.21 × 10 <sup>-5</sup>	1.19 × 10 <sup>-5</sup>	3.39 × 10 <sup>-5</sup>	8.37 × 10 <sup>-4</sup>	9.52 × 10 <sup>-6</sup>

Cd(II) by *B. bifurcata* is significant and similar, but the affinity of this species for Zn(II) is greater than for Cd(II). The best results of Pb(II) uptake were given by *L. hyperborea* and *B. bifurcata*, either in terms of equilibrium biosorption capacity or uptake rate. This probably related to the different pattern of IR spectra obtained for these species in the wavenumber range 1600–4000 cm<sup>-1</sup>. Although less efficient, the other two species were able to remove Pb(II) at the same level than Zn(II) and Cd(II).

The accumulation profiles obtained for the different macro algal species (Fig. 3) show that the metal uptake is rather fast, and more than 75% of the total uptake occurs within the first 10 min. After this initial stage, the accumulation is slower up to about 30 min contact time and then no further significant adsorption is observed. Avery et al. [31] explain this fact by considering that the accumulation of heavy metals by algae generally comprises two phases: a rapid initial phase completed within 5–10 min,

Table 5  
Metal concentration in the sorbent (q<sub>e</sub>) in equilibrium with sorbate concentration (C<sub>e</sub>)

Metal ion	Biosorbent	pH	T (°C)	C <sub>e</sub> (mg L <sup>-1</sup> )	q <sub>e</sub> (mg g <sup>-1</sup> )	Ref.
Zn(II)	<i>Padina</i> sp.	5.5	22	50	35.1	[22]
	<i>Sargassum</i> sp.	5.5	22	50	29.8	[22]
	<i>Laminaria hyperborea</i>	5.0	25	49.8	19.2	This study
	<i>Sargassum muticum</i>	5.0	25	39.0	34.1	This study
	<i>Fucus spiralis</i>	5.0	25	38.5	34.3	This study
	<i>Bifurcaria bifurcata</i>	5.0	25	44.8	30.3	This study
	Pb(II)	<i>L. hyperborea</i>	5.0	21	6.2	30.5
<i>Padina</i> sp.		5.0	22	20	122.6	[22]
<i>Sargassum</i> sp.		5.0	22	20	139.1	[22]
<i>L. hyperborea</i>		5.0	25	6.2	50.3	This study
<i>S. muticum</i>		5.0	25	31.3	38.2	This study
<i>F. spiralis</i>		5.0	25	16.3	43.5	This study
<i>B. bifurcata</i>		5.0	25	1.3	52.7	This study
Cd(II)	<i>L. hyperborea</i>	5.0	21	27.4	52.4	[4]
	<i>Padina</i> sp.	5.5	22	25	46.9	[22]
	<i>Sargassum</i> sp.	5.5	22	25	61.2	[22]
	<i>Sargassum baccularia</i>	5.0	25	25	42.4	[32]
	<i>Sargassum siliquosum</i>	5.0	25	25	49.4	[32]
	<i>Padina tetrastomatica</i>	5.0	25	25	30.2	[32]
	<i>L. hyperborea</i>	5.0	25	27.4	31.3	This study
	<i>S. muticum</i>	5.0	25	22.3	38.4	This study
	<i>F. spiralis</i>	5.0	25	15.9	42.1	This study
	<i>B. bifurcata</i>	5.0	25	18.7	30.3	This study

reversible and metabolism-independent, and a slower second phase, often irreversible, that can be due to a number of mechanisms, including covalent bonding, surface precipitation, redox reactions, crystallisation on the cell surface or, more probably, diffusion into the cell interior and binding to proteins and other intracellular sites [3]. According to Volesky [1], the rapid sorption reactions are usually not the rate-controlling factor in the biosorption process. It has been widely recognized and confirmed that the intraparticle mass transfer rate actually controls the rate of the entire sorption process. Rapid kinetics has a significant practical importance, as it will allow the use of smaller reactor volumes, ensuring efficiency and economy [15].

The results obtained in this study can be compared with some others reported in the literature [4,22,32]. Table 5 presents uptake capacities of brown marine algae obtained for metal concentrations in the liquid phase similar to those used in the present study. In spite of some differences in the experimental conditions, Cd and Zn uptake capacities are close to those obtained by other researchers. As regards Pb, we achieved an uptake capacity for *L. hyperborea* greater than that obtained by Yu et al. [4], but temperature was slightly higher. However, studies performed by Sheng et al. [22] using *Padina* sp. and *Sargassum* sp., showed higher biosorption capacities than those obtained in the present study.

## 6. Conclusions

The heavy metal uptake potential of four marine macro algae abundant at the Portuguese coast – *L. hyperborea*, *B. bifurcata*, *S. muticum* and *F. spiralis* – was evaluated. The biosorption capacities experimentally determined for Zn(II), Pb(II) and Cd(II) are in the ranges 18.6–32.0, 32.3–50.4 and 23.9–39.5 mg g<sup>-1</sup>, respectively. Lead was efficiently removed by all species by *L. hyperborea* and *B. bifurcata* exhibited the highest affinities and uptake capacities. *L. hyperborea* was less efficient to remove zinc, but all metal ions and were rapidly adsorbed by this species. *S. muticum* and *F. spiralis* showed the highest capacity for Zn(II) and Cd(II) uptake. Biosorption kinetic data were well fitted by pseudo-first-order and pseudo-second-order models. The application of diffusion-controlled models to the experimental results indicated that the contribution of the intraparticle diffusion to the overall sorption kinetics is not very important. The high uptake capacity of *L. hyperborea*, *S. muticum*, *F. spiralis* and *B. bifurcata*, for Zn(II), Pb(II) and Cd(II) suggests that these biosorbents are suitable for the removal and recovery of those metal ions from diluted wastewater streams.

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