



## Removal of Pb(II) from wastewaters by *Fontinalis antipyretica* biomass: Experimental study and modelling

Ramiro J.E. Martins<sup>a,b\*</sup>, Vítor J.P. Vilar<sup>b</sup>, Rui A.R. Boaventura<sup>b</sup>

<sup>a</sup>Department of Chemical and Biological Technology, Superior School of Technology, University of Applied Sciences of Bragança, Campus de Santa Apolónia, 5301-857 Bragança, Portugal

Tel. +351 273303091; Fax +351 273313051; email: rmartins@ipb.pt

<sup>b</sup>LSRE-Laboratory of Separation and Reaction Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

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### ABSTRACT

Aquatic bryophytes are frequently used as biomonitors for trace metals in aquatic ecosystems. Nevertheless, their special characteristics also allow using them as biosorbents to clean industrial wastewaters. As biosorption is a low-cost and effective method for treating metal-bearing wastewaters, understanding the process kinetics is relevant for design purposes. In this study, the ability of the aquatic bryophyte *Fontinalis antipyretica* to remove lead from simulated wastewaters was evaluated. Previously, the effect on biosorption of parameters such as the initial solution pH, contact time and initial metal ion concentration was investigated. The biosorption process is highly pH-dependent, and the favorable pH for maximum Pb<sup>2+</sup> adsorption on the aquatic moss was found to have an optimum value in the range 4.0–6.0. The equilibrium sorption capacity of lead by *Fontinalis antipyretica* increased with the initial metal concentration. For an initial metal concentration of 10 mg L<sup>-1</sup>, the uptake capacity at equilibrium was 4.8 mg g<sup>-1</sup>. Nevertheless, when the initial concentration increased up to 100 mg L<sup>-1</sup>, the uptake of lead was 10 times higher. Maximum adsorption rates were achieved almost in the first 10–20 min of contact, and a further increase in the contact time had a negligible effect on the Pb<sup>2+</sup> sorption. Three kinetic models (pseudo-first order, pseudo-second order and Elovich) were fitted to the experimental data and compared by the F-test. The pseudo-second order biosorption kinetic model provided the better correlation with the experimental data ( $R^2 = 1.00$ ). Probably the chemisorption is the rate-limiting step and the biosorption mechanism follows a pseudo-second order reaction model. The applicability of the Langmuir and Freundlich adsorption isotherms to the present system was also assessed. The equilibrium experimental data of lead sorption was very well described by the Langmuir model with  $R^2$  values exceeding 0.993. The maximum lead sorption capacity by *Fontinalis antipyretica* attained a value of 68 mg of lead ions per gram of aquatic moss.

*Keywords:* *Fontinalis antipyretica*; Aquatic mosses; Lead; Biosorption; Removal; Kinetics

### 1. Introduction

The increasing environmental contamination by toxic

metals [1,2] is a relevant worldwide occurrence, as well as the contamination by others pollutants [3–5]. They are not biodegradable and tend to accumulate in living organisms. The consequences of their presence in aquatic ecosystems to human health, living organisms in water

\* Corresponding author.

and consumers of contaminated plants or animals are well known. Lead has been recognized as a potentially dangerous pollutant, in the same class as mercury, arsenic and vanadium [6]. Tackett [7] reports that lead was found to be markedly toxic to human beings when accumulated in high amounts. An adult ingests between 0.3–0.6 mg of lead per day in his diet and a value close to 10% is retained in the organism. As a consequence, lead can damage the kidney, liver and reproductive system, brain functions and basic cellular processes [8].

Lead is released into the environment through waste streams from lead smelting, lead mining and coal combustion, lead-based paints use and lead-containing pipes in water supply systems, and additionally, from pigments, photographic materials, ceramic glazes, automobile batteries and cosmetics manufacturing [9–11].

Thus, the removal of toxic metals and particularly lead from waters is an important environmental issue [12]. Traditional methods used for heavy metals removal from aqueous effluents (chemical oxidation or reduction, chemical precipitation, coagulation, complexation) are insufficient to achieve the limits imposed or recommended by national and international water regulatory agencies [13] or extremely expensive (ion exchange, activated carbon adsorption, electrolytic removal, reverse osmosis). The high capital investment required, as well as the high operating costs, led to increasing the search of low-cost adsorbents to be used instead of activated carbon [14]. Moreover, in these processes, chemicals are not needed and the maintenance requirements are small. Table 1 lists the cost for some commercial activated carbons and low-cost adsorbents.

In recent years several methods based on metal-sequestering properties of natural materials of biological origin have been considered for decontamination of metal-enriched waters. The principal mechanism involves the formation of complexes between the metal ion and functional groups in the surface or inside the

porous material structure, as amino, amido, carboxyl, phosphate, carbonyl and sulfonate groups. Biosorbents include a great variety of materials such as: agricultural sub-products (soybean and cottonseed hulls, rice straw and sugarcane bagasse) [23], pine bark [14,24], aquatic plants [14,24–26], peat moss [27], activated sludge [28,29], fungi and bacteria [14,30,31] and algae [9,11,14,32]. All these materials are abundant in nature and require little processing.

Since 1990 [33] aquatic bryophytes were known for exhibiting both sensitivity and tolerance to a wide range of heavy metals. Factors as the inexistence of a barrier to metal absorption and the absence of a cuticle, which increases the direct access of soluble metals to the cytoplasm, make the aquatic mosses an important support for heavy metals removal from contaminated waters.

To our knowledge, the results reported in the literature concerning lead removal by aquatic mosses are quite scarce. Therefore, the study of the biosorption equilibrium and kinetics of lead ions by the aquatic moss *Fontinalis antipyretica* seems to be a relevant research topic. Lead was the heavy metal chosen to carry out this study because (i) it is present in many industrial effluents and mine drainage waters directly discharged into rivers and lakes and (ii) it is toxic when in excess, inhibiting plant and microorganism growth. The results obtained in this work can be useful for a future application of aquatic mosses in the decontamination of metal-bearing industrial effluents.

## 2. Materials and methods

### 2.1. Lead(II) solutions

All chemicals were analytical grade and purchased from Merck (Darmstadt, Germany). The lead stock solution, 1000 mg L<sup>-1</sup>, was prepared by dissolving an accurate quantity of PbCl<sub>2</sub> in deionized water. Other lead working solutions were freshly prepared by diluting the lead stock solution with deionized water.

The solution pH was adjusted by adding diluted solutions 0.1 M of HCl and NaOH, as required.

### 2.2. The biosorbent

This type of aquatic plants was chosen because their high capacity for assimilating nutrients, toxic organics and heavy metals, which has been related in monitoring programs of rivers water quality. Another relevant reason: this material is abundant in nature, require little processing and there is not much in literature about them.

The aquatic moss *Fontinalis antipyretica* was taken from the Selho River, a tributary of the Ave River in Northern Portugal. The background metal content in mosses was considered to be of natural origin and negligible (sensibly 114 µg g<sup>-1</sup>). The samples were rinsed with river water in situ and then in the laboratory with deionized water, selecting only the green parts of the plants. The plants

Table 1  
Cost of commercial activated carbon and some low-cost adsorbents (adapted from Gupta et al. [10])

Adsorbent	Cost (US\$ kg <sup>-1</sup> )	Reference
Commercial activated carbon	1.37	[15]
Commercial activated carbon	20	[16]
Commercial activated carbon	5–6	[17]
Commercial granular activated carbon	3.30	[18]
Bagasse flyash	0.009	[19]
Bentonite	0.05	[20]
Coconut shell charcoal	0.34	[15]
Manganese oxide	0.05–0.06	[21]
Peat	0.018–0.069	[22]

were dried in an oven at 70°C for 24 h and then ground in a RETSCH ZM 100 ultra-centrifugal mill at 1400 rpm for approximately 90 s. The fraction with particle size between 150–300 µm was selected for this study.

### 2.3. Equilibrium experiments

Equal amounts of 100.0 (± 0.1) mg of the biosorbent were accurately weighted and transferred to 100 ml glass bottles and 50 mL of lead solution with concentration between 10 and 100 mg L<sup>-1</sup> was added to each bottle. The bottles were then shaken for 24 h at constant room temperature (20 ± 1°C) using a rotary shaker (P-Selecta Rotabit). Each experiment was performed in duplicate and blank solutions (metal solution without biosorbent) were shaken simultaneously. The contact time was previously determined from kinetic studies, carried out at the same temperature and stirring rate, as that required to attain equilibrium. After equilibrium was reached the liquid phase was separated from the biosorbent by vacuum filtration through 0.45 µm Gelman Sciences sterilized membranes, and the supernatant was analysed for the equilibrium lead concentration. The metal uptake was calculated by the equation:

$$q_e = (C_0 - C_e) / (m_{ads} / V) \quad (1)$$

where  $V$  (L) is the volume of lead solution,  $C_0$  (mg L<sup>-1</sup>) is the initial lead concentration,  $C_e$  (mg L<sup>-1</sup>) is the concentration of lead in solution at equilibrium, and  $m_{ads}$  (g) is the mass of biosorbent (dry weight).

### 2.4. Kinetic experiments

The influence of the initial metal concentration on biosorption rate was studied in batch mode.

Erlenmeyer flasks (11 units) with 100 ml capacity were used in this study, each one containing 50 ml of metal solution of a known initial concentration and a pre-weighed amount of dry biomass. The suspensions were mildly stirred for 300 min on a rotary shaking machine at 140 U min<sup>-1</sup>. Biosorption kinetic experiments were performed at constant temperature of 20°C, metal concentrations of 10 and 100 mg l<sup>-1</sup> and biosorbent dosage of 2 g L<sup>-1</sup>. In all cases, the initial pH was adjusted in the range 5.0–5.2 by adding 0.1 HCl or 0.1 M NaOH, as required. Samples were taken at pre-determined time intervals, one flask per sample, starting at 3 min and ending at 300 min. Then, the solution was filtered (0.45 µm Gelman Sciences sterilized membranes) and the remaining metal in aqueous solution was measured. All the experiments were conducted in duplicate.

### 2.5. Analytical methods

Lead concentrations in the filtrates were determined by acetylene-air flame atomic absorption spectrometry (AAS, Varian Spectra, model S220). The working param-

eters of AAS were 5.0 mA and 217.0 nm, respectively, for current and wavelength, giving a detection limit of 1 ppm. The instrument response was checked at predetermined times with Pb(II) solution standards. Prior to analysis the samples were acidified with concentrated nitric acid, and stored in acid-washed plastic vessels.

## 3. Theoretical background

### 3.1. Equilibrium isotherms

Two of the most commonly used isotherms were fitted to the experimental results obtained in this study, the Langmuir and Freundlich equations.

The Langmuir model assumes that the adsorbent surface is homogeneous and the biosorption energy for each biosorption site is equal. Metal ions sequestration occurs without mutual interactions between the ions adsorbed at the material surface. Langmuir equation can be represented as:

$$q_e = Q_{max} b C_e / (1 + b C_e) \quad (2)$$

where  $C_e$  (mg L<sup>-1</sup>) is the residual metal concentration in solution,  $q_e$  (mg g<sup>-1</sup>) is the amount of a metal adsorbed,  $Q_{max}$  (mg g<sup>-1</sup>) is the amount of metal at complete monolayer coverage, and  $b$  (L mg<sup>-1</sup>) is a coefficient related to the heat of biosorption. The initial sorption isotherm curve slope ( $Q_{max} b$ ) indicates the biosorbent affinity for the sorbate.

The Freundlich model is based on an exponential distribution of biosorption sites and energies and takes into consideration the possible occurrence of interactions between the sorbed ions. The Freundlich equation is:

$$q_e = K_F C_e^n \quad (3)$$

where  $K_F$  (mg<sup>1-n</sup> g<sup>-1</sup> L<sup>n</sup>) represents the biosorption capacity when metal equilibrium concentration equals to 1, and  $n$  represents the degree of biosorption dependence with equilibrium concentration.

### 3.2. Biosorption kinetic models

Kinetic models are a significant tool to identify the controlling mechanism of the biosorption process. They can be divided into two main types: reaction and diffusion-based models. Some kinetic models are only concerned with the effect of the observable parameters on the biosorption overall rate. This is the case of the pseudo-first order (Lagergren) [34], pseudo-second order [35], Elovich [36] and intraparticle diffusion [37] models presented below.

#### 3.2.1. Pseudo-first order equation

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (4)$$

where  $q_t$ ,  $q_e$ ,  $k_1$  and  $t$  are the concentration of metal ion sorbed at time  $t$  (mg g<sup>-1</sup>), concentration at equilibrium

( $\text{mg g}^{-1}$ ), Lagergren rate constant ( $\text{min}^{-1}$ ), and time of reaction (min), respectively.

### 3.2.2. Pseudo-second order equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where  $k_2$  is the pseudo-second order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

The initial sorption rate,  $r_s(i)$ , can be obtained as:

$$r_s(i) = \left. \frac{dq_t}{dt} \right|_{t=0} = k_2 q_e^2 \quad (6)$$

### 3.2.3. Elovich equation

$$q_t = \frac{1}{b} \ln(1 + abt) \quad (7)$$

where  $a$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ) and  $b$  ( $\text{g mg}^{-1}$ ) are empirical model parameters.

### 3.2.4. Intraparticle diffusion model

When the diffusion of the metal ions inside the biosorbent is the rate-limiting step, the biosorption data can be fitted by the equation

$$q_t = k_{dp} t^{1/2} \quad (8)$$

where  $k_{dp}$  is the intraparticle diffusion coefficient ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ).

## 4. Results and discussion

Langmuir and Freundlich equations were fitted to the equilibrium experimental data by nonlinear regression using the commercial software *Fig P* from BIOSOFT (minimizing the sum of the squared deviations between experimental and predicted values).

### 4.1. Effect of pH on lead removal

In the biosorption process of lead onto aquatic moss the pH value was one important environmental factor because the site dissociation and also the solution chemistry of the heavy metal, that is, hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation were all strongly influenced by pH. The results shown in Fig. 1 illustrate the effect of pH on Pb(II) removal by the aquatic bryophyte *Fontinalis antipyretica*.

At highly acidic pH values,  $\text{pH} < 3.0$ , the amount of lead removed is insignificant; this can be explained due the pH influences both metal binding sites on the cell surface and metal chemistry in water. A considerable biosorption inhibition is observed for pH 3, as cell wall ligands are closely associated with hydronium ions  $\text{H}_3\text{O}^+$  that limit

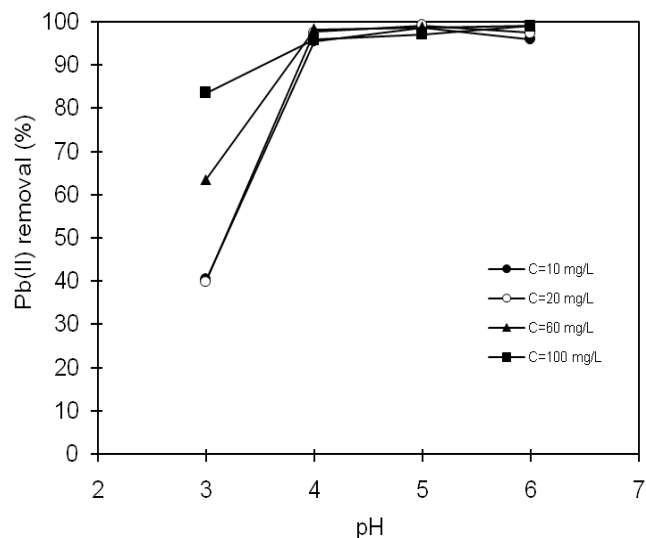


Fig. 1. Removal of Pb(II) from aqueous solutions by aquatic moss *Fontinalis antipyretica* in the pH range 3–6.

the approach of lead ions as a result of repulsive forces. On the other hand, as biosorption is proton competitive, the protons compete with metal ions for the active sites on biomass surface and so a notable metal inhibition is observed. In the pH range 4.0–6.0 the Pb(II) removal remains practically constant and around 97–99%. When the pH increases, the functional groups in the moss particles (phosphate, carboxyl, hydroxyl and amino groups) are loaded negatively, then promoting the subsequent attraction and sorption for positively charged metal onto the cell surface. The results show that the biosorption process is highly dependent on pH. The same behaviour was observed in different studies with green algae; sorption of lead from aqueous solutions by *Spirogyra* [38] and *Cladophora* [39] species. Nevertheless, at  $\text{pH} \geq 7$  insoluble metal hydroxides start precipitating from the solution. In the following work, experiments were carried out at initial  $\text{pH} 5.0 \pm 0.2$ .

### 4.2. Equilibrium studies

Biosorption equilibrium is established when the metal concentration in a bulk solution is in dynamic balance with that of the biomass interface. The degree of the moss affinity for the Pb(II) determines its distribution between the solid and liquid phases. The equilibrium data analysis is important to mathematically modelling the process, which could be used for the quantitative report of the results. The equation parameters and the underlying thermodynamic assumptions of Langmuir and Freundlich models should be able to predict metal biosorption, reflecting the mechanism of the lead uptake and the influence of variables such as pH, ionic strength, presence of competing cations, etc. Nevertheless, in



most cases, equilibrium models are used empirically as mathematical expressions which simulate favorable equilibrium uptake curves if environmental parameters, such as pH, are controlled carefully during experiments.

The biosorption capacity of aquatic mosses for Pb(II) was evaluated using the Langmuir [Eq. (1)] and Freundlich [Eq. (2)] isotherms as shown in Fig. 2.

Even though these models shed no light on the mechanistic aspect of biosorption, they provide a practical and convenient tool for comparing results using different biomass on a quantitative basis, providing information on sorption potential and reproducing the usual equilibrium uptake process behaviour with easily interpretable constants, as explained in section 3.1.

Langmuir constants ( $Q_{\max}$  and  $b$ ) and the corresponding standard error are  $68 \pm 12$  mg Pb<sup>2+</sup>/g moss and  $1.0 \pm 0.4$  L/mg Pb<sup>2+</sup>, respectively. The coefficient of correlation ( $R^2$ ) is 0.993 and the model variance ( $S^2$ ) is 3.14 (mg Pb<sup>2+</sup>/g aquatic moss)<sup>2</sup>. For  $K_F$  and  $n$ , Freundlich parameters, the average values  $\pm$  standard error obtained were in that order  $30 \pm 5$  mg<sup>1-n</sup> g<sup>-1</sup> L<sup>n</sup> and  $1.9 \pm 0.4$ , res; 0.958 and 17.2 are the coefficient of correlation and variance for this isotherm, respectively. This biosorption parameters evaluated from nonlinear regression analysis at the pre-established experimental conditions are listed in Table 2.

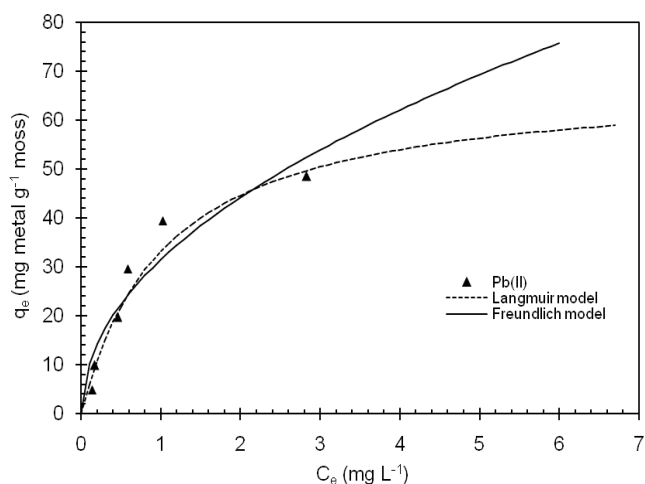


Fig. 2. Biosorption isotherms for the system Pb(II)/*Fontinalis antipyretica* (pH =  $5.0 \pm 0.2$ ;  $X_{\text{ads}} = 2$  g l<sup>-1</sup>;  $T = 20^\circ\text{C}$ ; water hardness = 101.0 mg CaCO<sub>3</sub> l<sup>-1</sup>).

Non-linear data analysis was adopted to prevent some errors in the linearization of these isotherm equations; as, modify the error structure and also violate the error variance and normality assumptions of standards least-squares [40].

Within the lead concentration range of 10–100 mg L<sup>-1</sup>, both models were suitable for describing the biosorption isotherm of Pb(II); though, the coefficients of correlation ( $R^2$ ) presented in Table 2 suggest that Langmuir isotherm describe better the biosorption of Pb(II) by *Fontinalis antipyretica* than Freundlich isotherm. For the particle diameter of 150–300  $\mu\text{m}$ , the magnitude of Freundlich constant  $n$  was greater than unity (1.9) indicating that the Pb(II) adsorption is favourable.

However, the most effective way to compare the significant improvements introduced by a correlative model against another is to use the  $F$ -test [41].  $F_{\text{cal}}$  is defined as the quotient of the variances of the two models in comparison ( $=S_{\text{Freundlich}}^2/S_{\text{Langmuir}}^2$ ), where  $S^2$  is the model variance. In the denominator is placed the variance of the model expected to produce the better fitting. From the variances presented in Table 2,  $F_{\text{cal}} = 5.48$ , value to be compared with  $F_{1-\alpha} = 5.05$  ( $\alpha = 95\%$ ; f.d.<sub>N:D</sub> = 5:5). Since  $F_{\text{cal}} > 1$  and  $F_{\text{cal}} > F_{1-\alpha}$  the Langmuir model fits the experimental data better than Freundlich model, and the improvement is statistically significant.

The calculated maximum biosorption capacity is 68 mg Pb(II) g<sup>-1</sup> (0.33 mmol g<sup>-1</sup>), which is a value of  $Q_{\max}$  that compares favourably with those obtained using other low-cost materials listed in Table 3 [9,13,38,42–46].

Such as previously mentioned in the theoretical approach, the initial curve slope ( $Q_{\max}b$ ) is one of the most important characteristics of the sorption isotherm. The initial slope calculated from the Langmuir isotherm parameters (Table 2) is 68 L g<sup>-1</sup>, which indicates a biomaterial with high affinity to lead ions in aqueous solution at low concentration. This is an important property when it is obligatory to achieve low concentrations established by water standards. This study show that the affinity of aquatic mosses to lead is greater than that obtained by a natural sorbent [13] (41.2 L g<sup>-1</sup>), an algal waste [9] (3.1 L g<sup>-1</sup>) or a waste biomass of a canned food factory [46] (3.5–9.9 L g<sup>-1</sup>, temperature range 20–50°C). Considering the high biosorption capacity showed by *Fontinalis antipyretica*, this aquatic bryophyte is promising as biosorbent for the removal and recovery of metal ions of industrial

Table 2

Langmuir and Freundlich isotherms parameters (average  $\pm$  standard error) for lead sorption onto *Fontinalis antipyretica* at optimum pH

Langmuir model				Freundlich model			
$Q_{\max}$ (mg g <sup>-1</sup> )	$b$ (L mg <sup>-1</sup> )	$R^2$	$S^2$	$K_F$ (mg <sup>1-n</sup> g <sup>-1</sup> L <sup>n</sup> )	$n$	$R^2$	$S^2$
68 $\pm$ 12	1.0 $\pm$ 0.4	0.993	3.14	30 $\pm$ 5	1.9 $\pm$ 0.4	0.958	17.2

Table 3  
Maximum adsorption capacities of Pb(II) by some low-cost adsorbents

Adsorbent	Max. adsorption capacity (mg g <sup>-1</sup> )	Reference
Aquatic mosses ( <i>Fontinalis antipyretica</i> )	68.0	Present study
Aquatic macrophyte ( <i>Ceratophyllum demersum</i> )	44.8	[42]
Green algae <i>Spirogyra</i>	140.8	[38]
Bagasse fly ash	30.0	[43]
Granulated agar extraction algal waste	20.5	[9]
Natural sorbent (quartz, aluminosilicates, etc.)	66.2	[13]
Cocoa shells	6.23	[44]
Orange peels	114	[45]
Waste biomass of <i>Phaseolus vulgaris</i> L.	42.7	[46]

effluents can also be used to recovery valuable metals from aqueous diluted solutions. Additional favorable point is that biosorption capacity was attained at ambient temperature (20°C), in contrast with other studies [46], which respect the initial premise of a low cost biosorption technology.

The favorable adjustment provided by the Langmuir isotherm and according to Weber and DiGiano [47], the moss used can probably be referred to as a heterogeneous material, and the metal adsorption occurs in homogeneous sites (uniform adsorption energy for the adsorption sites).

#### 4.3. Kinetic studies

Parameters related to the aqueous solution composition, biosorbent characteristics and the metal ion to be removed certainly influence the mechanism of metal removal by the biosorbent. On the other hand, to design a batch sorption system it is of crucial importance to know the biosorption rate. In this way, it is important to establish the time dependence of such system under various process conditions.

The biosorption rate of lead ions onto *Fontinalis antipyretica* was determined for initial metal concentrations of 10 and 100 mg L<sup>-1</sup>. Experimental kinetic data were evaluated using pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion equations [Eqs. (4)–(8)].

Figs. 3a–c show a plot of the experimental results for biosorption of Pb(II) on *Fontinalis antipyretica* as a function of time, and the curves predicted by the kinetic models (dashed and solid lines correspond, respectively, to the initial metal concentrations of 10 and 100 mg L<sup>-1</sup>).

The corresponding model parameters are presented in Table 4. These curves are characterized by a strong increase in sorption capacity by the biosorbent during the first 10 min, that gradually decreases until saturation. The sorption process is fast and the equilibrium attained in less than 2 h; so, the biosorption of lead involves purely weak intermolecular forces between the mosses and the metal in aqueous solution [48]. Similar equilibrium times were obtained for sorption of lead by industrial algal waste [48], algae *Gelidium* [48], *Sphagnum* moss [49], non-living biomass [50] and sorption of cadmium and lead by green algae [38]. When the initial lead concentration increases from 10 to 100 mg L<sup>-1</sup>, an increase

Table 4  
Kinetic models parameters (average ± standard error) for the biosorption of lead(II) by *Fontinalis antipyretica*

Pseudo-first order	$q_e$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$	$S^2$
Pb 10	4.7 ± 0.2	0.4 ± 0.1	0.974	5.8E <sup>-2</sup>
Pb 100	46 ± 3	0.3 ± 0.1	0.953	10.5
Pseudo-second order	$q_e$ (mg g <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$	$S^2$
Pb 10	4.79 ± 0.03	0.2 ± 0.1	1.00	1.9E <sup>-2</sup>
Pb 100	49.3 ± 0.3	0.007 ± 0.002	1.00	2.6E <sup>-4</sup>
Elovich	$a$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$b$ (g mg <sup>-1</sup> )	$R^2$	$S^2$
Pb 10	879 ± 481	3 ± 1	0.956	9.5E <sup>-2</sup>
Pb 100	206 ± 87	0.17 ± 0.06	0.953	13.1

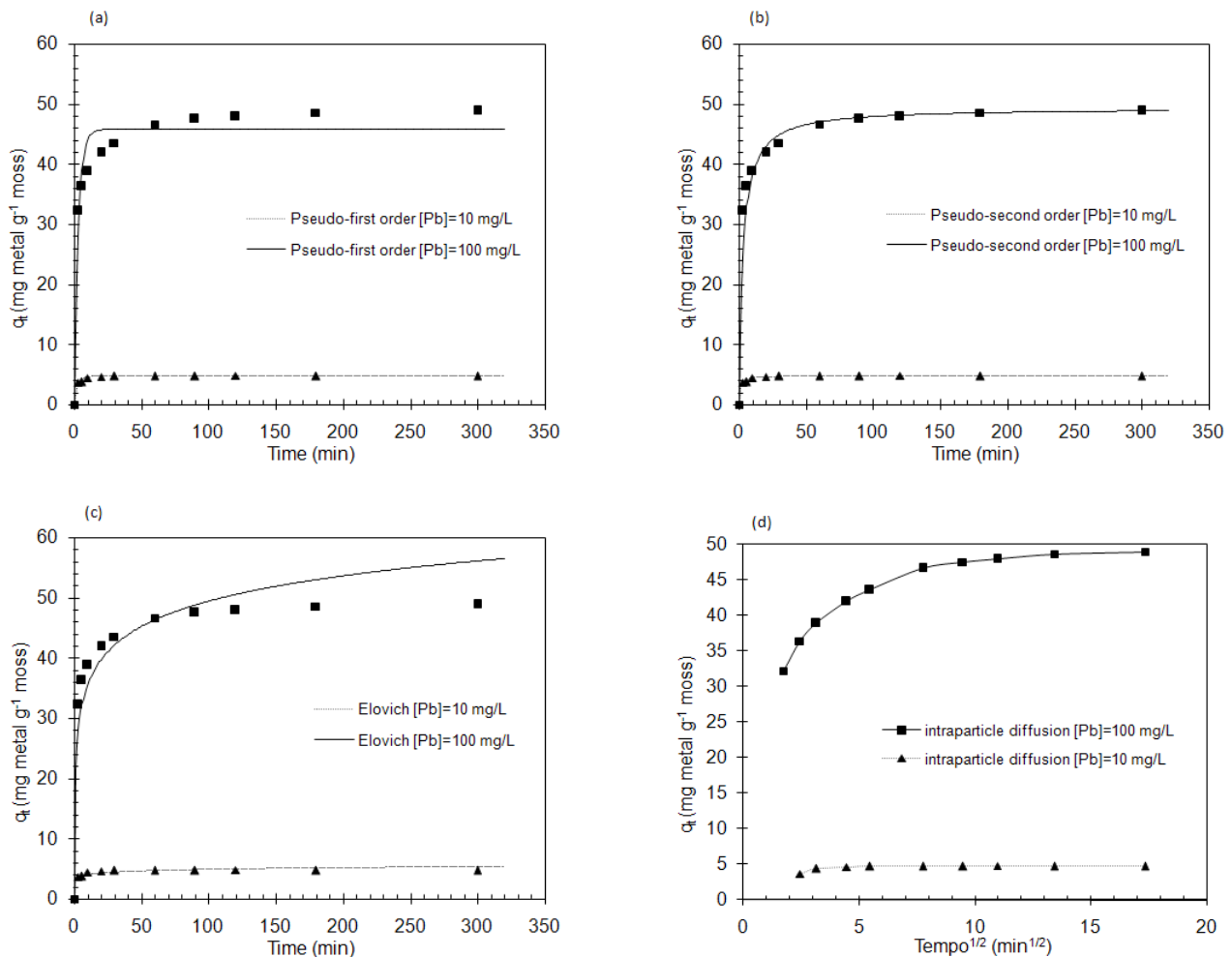


Fig. 3. Kinetic modelling of Pb(II) biosorption by *Fontinalis antipyretica*: (a) pseudo-first order model; (b) pseudo-second order model; (c) Elovich equation; (d) intraparticle diffusion equation.

of the same order on the biosorbent capacity is observed (Table 4).

From the reaction models employed in this study [Eqs. (4), (5), (7)] there is one, the pseudo-second order model, that shows a good compliance on fitting the experimental data ( $R^2 = 1.00$ ). The performances of the Lagergren, pseudo-second order and Elovich models were compared by using an *F-test* (Table 5). For the initial metal concentrations used the *F-test* also indicates that the pseudo-second order model, not only fits better ( $F_{cal} > F_{1-\alpha}$ ) the experimental data than Lagergren and Elovich models, but for 95% probability level, significant difference exists between the models within the concentration range studied. For the initial lead concentrations of 10 and 100 mg L<sup>-1</sup> the *F-test* provided values for L/P and E/P of 3.05, 5.00 and 40385, 50385, respectively ( $\alpha = 95\%$ ; f.d.<sub>N:D</sub> = 10:10,  $F_{1-\alpha} = 2.98$ ).

Application of Elovich equation in liquid phase adsorption has been significantly increased; although, in

this work was not as satisfactory as in other studies [51]. The results in Table 4 allow to infer that the chemisorptions rate (to null coverage of the adsorbent surface) is strictly related to the initial metal concentration in solution. An increase of ten times (from 10 to 100 mg L<sup>-1</sup>) in the initial Pb<sup>2+</sup> concentration resulted in a reduction of chemisorption rate in approximately four times (from 879 to 206 mg g<sup>-1</sup> min<sup>-1</sup>). Cadmium adsorption kinetics onto *P. halepensis* sawdust was studied by Semerjian [52], and also tested with the Elovich kinetic model. Recorded  $R^2$  values were very lower than in this study, indicating similar conclusions about this equation to describe metal uptake, although using different materials.

Adsorbate species are most likely transported from the bulk of the solution into the solid phase through an intra-particle diffusion process, which often may be the rate-limiting step in many biosorption processes [52]. The intra-particle diffusion can be described by the theory proposed in 1963 by Weber and Morris [37], in which

Table 5

*F*-test for the biosorption of lead (level of probability 95%; degrees of freedom 10:10;  $F_{\text{critic}} = 2.98$ )

Model	C (mg l <sup>-1</sup> )	Variance (S <sup>2</sup> )	<i>F</i> calculated	
Lagergren (L)	Pb 10	5.8×10 <sup>-2</sup>	L/P	
Pseudo-second order (P)		1.9×10 <sup>-2</sup>	3.05	
Elovich (E)		9.5×10 <sup>-2</sup>	E/L	E/P
Lagergren (L)	Pb 100	10.5	1.64	5.00
Pseudo-second order (P)		2.6×10 <sup>-4</sup>	L/P	
Elovich (E)		13.1	403×10 <sup>2</sup>	
			E/L	E/P
			1.25	504×10 <sup>2</sup>

the accumulation is proportional to the square root of contact time during the adsorption period. Plot of  $q_t$  vs.  $t^{1/2}$  is shown in Fig. 3d and linearity is not applied for the system *Fontinalis antipyretica*–Pb(II) during all the biosorption process. According Weber and Morris [37], it cannot be stated that intra-particle diffusion process is the unique rate-limiting step taking place in the sorption of Pb<sup>2+</sup> onto aquatic moss. The deviation of the linear segment of plot from the origin ( $y$ -intercept other than 0) indicates that there are others sorption steps occurring in this adsorption process.

The initial sorption rate ( $r_s(i)$ ) increased from 5.34 to 16.5 mg g<sup>-1</sup> min<sup>-1</sup> when the initial lead concentration increased from 10 to 100 mg L<sup>-1</sup>. This behaviour is concordant with the removal of copper ions from aqueous solution by tree fern [53] and lead biosorption by granulated agar extraction algal waste [5]. However, the opposite was observed by Ho and McKay when studying the sorption of copper, nickel and lead onto *Sphagnum* moss peat [45].

So, the previous facts suggest that chemisorption is the rate-limiting step and the biosorption mechanism follows a pseudo-second order reaction model.

## 5. Conclusions

The aquatic bryophyte *Fontinalis antipyretica*, a common aquatic moss in north unpolluted rivers of Portugal, has proven to be a promising material in biosorption processes. Different functional groups, at the surface or inside the porous material structure of aquatic moss are the responsible for its effectiveness as biosorbent for the removal and recovery of Pb(II) ions from contaminated waters or industrial effluents. Metal sorption and removal efficiency may be influenced by a number of factors, such as pH, contact time, and initial metal concentration. The biosorption process is highly pH-dependent, and the favorable pH for maximum Pb<sup>2+</sup> adsorption on the adsorbent under study was in the range 4.0–6.0. For the

investigated two initial lead concentrations, maximum adsorption rates were achieved almost in the first 10–20 min of contact for concentrations of 10 and 100 mg L<sup>-1</sup>. A further increase in the contact time had a negligible effect on the rate of lead ions adsorption. The equilibrium data were better fitted by the Langmuir isotherm ( $R^2 = 0.993$ ) than by the Freundlich isotherm ( $R^2 = 0.958$ ), being the improvement attained statistically significant ( $F_{\text{Freundlich/Langmuir}} = 5.48 > F_{1-\alpha} = 5.05$ ). The maximum removal capacity was determined from the Langmuir equation and found to be  $68 \pm 12$  mg g<sup>-1</sup>. The aquatic mosses exhibited a high affinity to lead ions at low concentration. This is an important achievement when it is obligatory to comply with low concentrations of lead established by water standards. The kinetics of lead adsorption was very well described by the pseudo-second-order kinetic model with  $R^2$  values exceeding 0.9999. It cannot be stated that intra-particle diffusion process is the unique rate-limiting step taking place in the sorption of Pb<sup>2+</sup> onto aquatic moss; there are others sorption steps occurring in this adsorption process. So, can be concluded that chemisorption is the rate-limiting step and that the mechanism follows a pseudo-second order reaction model.

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