

# KINETIC MODELLING OF CADMIUM AND LEAD REMOVAL BY AQUATIC MOSSES

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**Abstract** - Because biosorption is a low cost and effective method for treating metal-bearing wastewaters, understanding the process kinetics is relevant for design purposes. In the present study, the performance of the aquatic moss *Fontinalis antipyretica* for removing cadmium and lead from simulated wastewaters has been evaluated. Five kinetic models (first-order, pseudo-first-order, Elovich, modified Ritchie second-order and pseudo-second-order) were fitted to the experimental data and compared. Previously, the effect of parameters such as the initial solution pH, contact time, and initial metal ion concentration on biosorption was investigated. The initial pH of the solution was found to have an optimum value in the range of 4.0-6.0. The equilibrium sorption capacity of cadmium and 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 of the moss, at equilibrium, is the same for both metals (4.8 mg g<sup>-1</sup>). Nevertheless, when the initial concentration increases up to 100 mg L<sup>-1</sup>, the uptake of Pb(II) was higher than 78%. The pseudo-second order biosorption kinetics provided the better correlation with the experimental data ( $R^2 \geq 0.999$ ).

**Keywords:** Biosorption; Aquatic moss; Cadmium; Lead; Kinetics; Modelling.

## INTRODUCTION

The use of metals has seriously affected the environment since the Industrial Revolution. Today, two hundred and fifty years later, in the Metal Removal Age, we are all too aware of the risks inherent to the uncontrolled dissemination of heavy metals in the environment. The metals that are of greatest concern are those that, by either their presence or their accumulation, can have a toxic or an inhibitory effect on living beings. If directly discharged into the sewage system, they may seriously damage the operation of sewage processes, as well as make the biological sludge unsuitable for application to agricultural land.

Cadmium and lead pollution have been recognized as a potential risk to air, soil and water.

Contact with excessive levels of these metals at work and at home inflict costs and suffering from adverse health effects, as well as impaired intellectual development of many millions of children and adults. According to Tackett (1987), lead has been found to be keenly toxic to human beings when present in high amount. Adults ingest between 0.3 to 0.6 mg of lead in their diet and approximately 10% is retained in the body. Lead damages the liver, kidney and reproductive system, brain functions and basic cellular processes (US EPA, 1984). Adverse health effects due to cadmium are also well documented and it has been reported to cause lung insufficiency, cancer, renal disturbances, bone lesions and hypertension in humans (Lee and White, 2007). The main sources that contribute to lead pollution include the use of leaded gasoline, lead smelting, lead mining

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and coal combustion, the use of lead-based paints and lead-containing pipes in water supply systems, and additionally ceramic glazes, batteries and cosmetics manufacturing. Cadmium is released into the environment through waste streams from smelting, manufacturing of pigments, plastics and batteries, and from electroplating, mining and refining processes (Forster *et al.*, 1997). Cd(II) and Pb(II) are included in the priority group of the metals for removal and/or recovery, as referred by Volesky (2001), regarding the association of environmental risk and reserve depletion.

Traditional methods (chemical precipitation, coagulation, complexation) of metal ions removal from aqueous effluents are insufficient to reduce concentrations to the limits accepted by national and international regulatory agencies. Moreover, methods such as ion exchange, activated carbon adsorption and electrolytic removal are prohibitively expensive. High capital and regeneration costs of activated carbon and ion-exchange resins have resulted in increasing research for low cost adsorbents (Singh *et al.*, 1993).

The use of micro-organisms such as bacteria, fungi and algae in treating wastewaters containing toxic metal ions is an attractive technique, but as yet not suitable for large scale applications (Yetis *et al.*, 2000). Various low cost adsorbents have been investigated for removing Cd, Pb and other metals from aqueous solutions: bentonite (Naseem and Tahir, 2001), expanded perlite (Torab-Mostaedi *et al.*, 2010), mud (Salim, 1986), volcanic ash soil (Cajuste *et al.*, 1996), pine bark (Al-Asheh *et al.*, 1998), waste tire rubber ash (Mousavi *et al.*, 2010), freshwater macrophytes (Schneider and Rubio, 1999), bacteria (Yilmaz *et al.*, 2010), aquatic mosses (Al-Asheh *et al.*, 1998; Martins and Boaventura, 2002), peat moss (McKay and Porter, 1997), alum sludge (Chu, 1999), soybean hulls, cottonseed hulls, rice straw and sugarcane bagasse (Marshall and Champagne, 1995), rice husk (Vieira *et al.*, 2012; Senthil Kumar *et al.*, 2010), olive stones (Calero *et al.*, 2009), activated carbon from lignocellulosic residues (Giraldo and Moreno-Piraján, 2008; Attia *et al.*, 2010). The literature shows an extensive list of biomass used in metal biosorption; the novelty of this work is exactly the use of an aquatic moss, a less studied material. Information about moss saturation capacities for a variety of metal ions based on equilibrium studies is scarce (Martins and Boaventura, 2002) and only some kinetic studies have been presented to provide kinetic parameters (Martins and Boaventura, 2001; Martins and Boaventura, 2002).

As stated by Shaw (1990), bryophytes are well known for exhibiting both sensitivity and tolerance

to a wide range of heavy metals. Toxic responses may be due to direct absorption of dissolved contaminants by the whole plant body. There is no barrier to uncontrolled metal absorption, such as that presented by the endodermis to root-absorbed metals in vascular plants. On the other hand, bryophytes also have no cuticle, which increases the direct access of soluble metals to the living cytoplasm in photosynthetic tissues. The combination of these factors, and the fact that they are available in most rivers in the north of Portugal, makes the aquatic mosses a potential biosorbent for heavy metal removal from polluted waters.

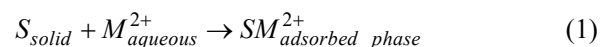
This work aims to test the aquatic moss *Fontinalis antipyretica*, abundant in non polluted rivers in the north of Portugal, for treating simulated wastewaters containing cadmium and lead, contributing to a better knowledge of biosorption processes. Five kinetic models were fitted to the experimental data and compared. The parameters that influence adsorption such as contact time, optimum initial solution pH and initial metal ion concentrations were previously studied.

## BIOSORPTION KINETIC MODELS

Metal uptake by biosorption has been modelled by a variety of sorption kinetic models. The four biosorption kinetic models used in this work are based on the Lagergren (Lagergren and Sven, 1898), Elovich (Low, 1960), Ho and McKay (Ho and McKay, 2000) and Ritchie (Ritchie, 1997) rate equations. These models were fitted to the experimental data by a non-linear regression program, software Fig.P for Windows from Biosoft, based on the Levenberg-Marquardt method.

### The Pseudo First-Order (Lagergren) Equation

Cadmium and lead biosorption kinetics can also be modelled by the pseudo first-order (Lagergren) equation (Lagergren and Sven, 1898), based on solid capacity. This model usually assumes that metal sorption onto a sorption site of the biomaterial and the initial surface coverage of sorbent is zero:



where  $S$  is a sorption site on the biomass surface and  $M^{2+}$  the metal ion. The Lagergren equation becomes:

$$\frac{dq_t}{dt} = K_L(q_e - q_t) \quad (2)$$

Integrating the Equation (1) with the boundary conditions  $t=0$ ;  $q_t=0$  and  $t=t$ ;  $q_t=q_t$ , gives:

$$q_t = q_e [1 - \exp(-K_L t)] \quad (3)$$

where  $q_e$  and  $q_t$  are the amounts of metal ion adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively, and  $K_L$  is the Lagergren rate constant ( $\text{min}^{-1}$ ).

The Lagergren kinetic equation has been used in some other metal sorption systems: sorption of Pb(II) by a composite biopolymer (Seki and Suzuki, 1996), sorption of Pb(II) by kaolinitic clay (Orumwense, 1996) and sorption of Cd(II) by the algae *Gelidium* and agar extraction algal waste (Vilar *et al.*, 2006). Additionally, Periasamy and Namasivayam (1994) reported the application of this model to the sorption of Cd(II) on peanut hull carbon.

### The Elovich Rate Equation

The Elovich equation was initially used to describe the chemisorption of gas molecules on solids (Low, 1960). Nevertheless, the Elovich equation was successfully used to describe the sorption of zinc on solids (Taylor *et al.*, 1995) and the sorption of iron, cobalt, nickel, copper and zinc on solvent-impregnated resins (Juang and Chen, 1997).

The model equation is

$$\frac{dq_t}{dt} = a \exp(-bq_t) \quad (4)$$

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

The integration of Eq. (4) with the boundary conditions  $q=0$  at  $t=0$  and  $q_t=q_t$  at  $t=t$ , gives:

$$q_t = \frac{1}{b} \ln(1 + abt) \quad (5)$$

### The Ritchie Second-Order Equation

The Ritchie rate equation assumes that a number of surface sites,  $n$ , are occupied by each metal ion (Ritchie, 1997).

$$\frac{d\theta}{dt} = k_n (1 - \theta)^n \quad (6)$$

Integrating Eq. (6) with  $n = 1$ , we get the so-called Ritchie equation:

$$\ln(1 - \theta) = \ln(1 - \theta_0) - k_1(t - t_0)$$

or

$$q_t = q_e [1 - \beta_1 \exp(-k_1(t - t_0))] \quad (7)$$

where  $\theta$  is the surface coverage at time  $t$  ( $\theta = q_t / q_e$ ),  $\theta_0$  is the value of  $\theta$  at  $t=0$  and  $\beta_1 = 1 - \theta_0$ .

The surface coverage can take a certain value,  $\theta_0 \neq 0$ , if the sorbent is assumed to have some pre-adsorbed metals on the surface. Usually, the surface coverage of the sorbent is assumed to be zero,  $\theta_0 = 0$ . In this case, Eq. (7) originates the pseudo-first order equation proposed by Lagergren and Sven (1898).

Integrating the Eq. (6) with  $n = 2, 3, \dots, k$  we get:

$$q_t = q_e \left\{ 1 - \left[ \frac{1}{\beta_n + k_n(n-1)(t - t_0)} \right]^{\alpha_n} \right\} \quad (8)$$

$$\text{where } \beta_n = \frac{1}{(1 - \theta_0)^{n-1}} \text{ and } \alpha_n = \frac{1}{n-1}.$$

For the initial condition  $t_0 = 0$ ;  $\theta_0 \neq 0$ , Eq. (8) simplifies to

$$q_t = q_e \left\{ 1 - \left[ \frac{1}{\beta_n + (k_n / \alpha_n)t} \right]^{\alpha_n} \right\} \quad (9)$$

The modified Ritchie second-order equation corresponds to  $n = 2$ :

$$q_t = q_e \left[ 1 - \left( \frac{1}{\beta_2 + k_2 t} \right) \right] \quad (10)$$

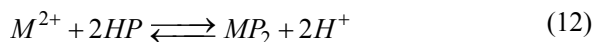
When the pre-adsorbed metal concentration is equal to zero,  $\theta_0 = 0$  and  $\beta_2 = 1$ .

### Pseudo-Second Order Equation

Assuming that the surface of the moss particles contains polar functional groups (aldehydes, acids, phenols and ketones), which can be involved in chemical bonding and are responsible for the metal cation exchange capacity, the reaction may be represented in two ways, as proposed by Coleman (1956):



or



where  $M^{2+}$  is the metal ion and  $P^-$  and  $HP$  are polar sites on the moss surface.

The rate of pseudo-second order biosorption depends on the mass of metal ions on the surface of the moss and the amount of divalent metal ions adsorbed at equilibrium. The rate law for the biosorption is then expressed by:

$$\frac{dP_t}{dt} = k[P_0 - P_t]^2 \quad (13)$$

or

$$\frac{d(HP)_t}{dt} = k[(HP)_0 - (HP)_t]^2 \quad (14)$$

where  $P_0$  and  $(HP)_0$  are the number (or concentration) of equilibrium sites available on the biosorbent,  $P_t$  and  $(HP)_t$  are the number (or concentration) of active sites occupied on the sorbent at any time  $t$ .

The kinetic rate equation becomes:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (15)$$

where  $q_t$  and  $q_e$  are the amounts of divalent metal ion adsorbed at time  $t$  and at equilibrium ( $\text{mg g}^{-1}$ ), respectively, and  $k$  is the biosorption rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

For the boundary conditions  $t=0$ ;  $q_t=0$  and  $t=t$ ;  $q_t=q_t$ , the integration of Eq. (15) gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (16)$$

This equation can be manipulated to obtain:

$$q_t = \frac{t}{\frac{1}{kq_e^2} + \frac{t}{q_e}} \quad (17)$$

In the linear form Equation (17) becomes

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (18)$$

where  $h = kq_e^2$  represents the initial sorption rate (Ho and McKay, 1998).

## MATERIALS AND METHODS

### Materials

The aquatic moss *Fontinalis antipyretica* was collected in the Selho River, at Aldão, a tributary of the Ave River in Northern Portugal. The sampling site is near the river spring, an uncontaminated site, so that the metal content in mosses was considered to be of natural origin. The samples were first rinsed with river water and then with distilled water in the laboratory, selecting only the green parts of the plants. The material was 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 seconds. The fraction with particle size between 150  $\mu\text{m}$  - 300  $\mu\text{m}$  was selected for the study.

Chemicals used were of analytical/laboratory grade, procured from Merck (Germany). Cadmium and lead solutions of the required concentrations were prepared by dissolving the exact quantities of  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  and  $\text{PbCl}_2$ , respectively, in distilled water.

A reference material (aquatic moss *Platihypnidium riparioides* from EEC - Community Bureau of Reference, Reference Material. Nr. 61) was used as a control sample for quality control of plant digestion and metal determination. The optimal conditions ( $\text{HNO}_3$  volume, microwave power, digestion time) for biomass digestion were selected from the results of zinc determination in a reference sample (566  $\mu\text{g Zn}^{2+} \text{g}^{-1}$  moss), using different experimental conditions.

### Batch Kinetic Experiments

Batch equilibrium sorption experiments were performed in duplicate in 100 mL Erlenmeyer flasks containing 50 mL of metal-containing solution of a known initial concentration into which a pre-weighted amount of dry biomass was added.

Preliminary tests were conducted to find the optimum pH value and total contact time needed to attain metal saturation of the moss.

The suspensions were mildly agitated for 300 min on a rotary shaking machine at 140 rpm. Other operating conditions were: initial metal ion concentration, 10 and 100  $\text{mg L}^{-1}$ ; moss dosage, 2  $\text{g L}^{-1}$ ; contact time, 24 h; temperature, 20 °C. Kinetic experiments were performed in duplicate at a constant

temperature of 20 °C, metal concentrations of 10 and 100 mg L<sup>-1</sup>. Taking into account the results of preliminary experiments, the initial working pH was adjusted in the range 5.0-5.2 by adding 0.1 M H<sub>2</sub>SO<sub>4</sub> or 0.1 M NaOH, as required. At fixed time intervals (3, 6, 10, 20, 30, 60, 90, 120, 180 and 300 min) one flask was taken out. Then, the solution was filtered and concentrations of metal were measured by the Atomic Absorption technique using an acetylene-air flame (AAS, VARIAN SPECTRA, model S220). Cadmium and lead standard solutions (1000 µg mL<sup>-1</sup>) were obtained from Merck. All the determinations were performed under optimization of the parameters indicated below.

| Metal | Wavelength | Slit Width | Flame             | Detection Limit |
|-------|------------|------------|-------------------|-----------------|
| Cd    | 228.8 nm   | 0.5 nm     | Air/<br>Acetylene | 0.009<br>ppm    |
| Pb    | 217.0 nm   | 1.0 nm     | Air/<br>Acetylene | 0.09<br>ppm     |

The sorption capacity,  $q_t$  (mg metal ion / g moss), at a specified time  $t$ , was calculated from the mass balance:

$$q_t = (C_0 - C_t)V / M \quad (19)$$

where  $C_0$  is the initial metal concentration in solution (mg L<sup>-1</sup>),  $C_t$  the metal concentration in solution at time  $t$  (mg L<sup>-1</sup>),  $V$  the volume of solution (mL), and  $M$  the mass of biosorbent (g dry wt.).

### Effect of the Initial Metal Concentration

For 300 min of contact time, 50 ml of metal solution with concentrations of 10, 20, 40, 60, 80 and 100 mg L<sup>-1</sup> were shaken with 100 mg of biosorbent at constant temperature (20 °C) on a rotary shaker (*Multi-stirrer, Velp Scientifica*) and pH (5.0 - 5.2).

### Parameters Estimation

The theoretical models were fitted to experimental kinetic data ( $q_t$ , mass of adsorbed metal per g of dried biomass at any time) by minimizing the sum of the squared deviations between experimental and predicted values, using a commercial software package, Fig.P for Windows from BIOSOFT (non-linear regression data analysis program).

Model goodness of fit was evaluated through the calculation of residual variances ( $S^2$ ) and regression coefficients ( $R^2$ ).

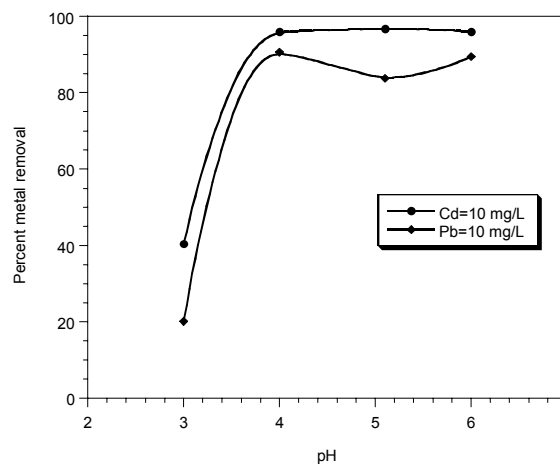
## RESULTS AND DISCUSSION

Several parameters related to the selected metal, the aqueous medium and the material characteristics could influence the metal removal by mosses. Thus, parameters such as contact time, moss dosage, initial metal concentration, temperature, pH, concentration of Ca<sup>2+</sup> and nature of the metal salt were studied for the effective removal of Cd(II) and Pb(II) by the aquatic moss *Fontinalis antipyretica*; however, some results are not shown in this paper. Batch experiments were carried out at pH < 7, because insoluble metal hydroxides start precipitating from the solution at higher pH values.

The following two sections (effect of the initial pH and selection of contact time) report the results of preliminary tests designed to define the optimum pH value and total contact time for the subsequent sorption tests.

### Effect of the Initial pH

From Cd<sup>2+</sup> and Pb<sup>2+</sup> sorption studies, Figure 1 illustrates the relationship between metal uptake and solution pH for the mosses. It is evident that pH values equal to or higher than 4.0 led to higher metal uptake for both metals. The optimum biosorption pH study was carried out only to a maximum pH of 6; above this value, insoluble cadmium and lead hydroxides were seen to precipitate out.



**Figure 1:** Effect of initial pH on the uptake of Cd(II) and Pb(II) by *Fontinalis antipyretica* ( $C_0 = 10$  mg L<sup>-1</sup>;  $X = 2$  g L<sup>-1</sup>; contact time = 24 h).

The biosorption of each metal was insignificant or nil for pH ≤ 3.0 (Figure 1). Maximum removal capacities at pH 4.0 were 91 and 96% for cadmium and lead, respectively. These values decreased to 20

and 40% upon lowering the pH to 3.0. This behaviour was also observed by Reed and Arunachalam (1994) and Kapoor *et al.* (1999), using activated carbon and the fungus *Aspergillus niger* as adsorbents, respectively. In the pH range of 4.0-6.0, the removal capacity remains approximately constant. The results obtained show that pH is an important parameter in the mechanism of heavy metal biosorption. Low *et al.* (2000) observed similar results for the sorption of cadmium and lead from aqueous solutions by spent grain. The low metal biosorption at pH 3.0 was due to the excess of hydrogen ions (positively charged) and consequent protonation of the sorbent surface. Protons apparently compete with metal ions for binding ligands on the cell wall and leads to fewer sites being available to bind metal ions. Cell wall ligands were strictly associated with these ions and limited the adsorption of metal cations as a consequence of repulsive forces. In the higher pH region the opposite occurs; there are fewer hydrogen ions in solution and, consequently, less competition for binding sites, thus freeing up more ligands and leading to enhanced biosorption. At pH 4-6 phosphate, carboxyl and amino groups on the mosses generate a negatively charged surface and electrostatic interactions between cationic species and this surface can be responsible for enhanced metal sorption (Donmez *et al.*, 1999; Aksu, 2001). However, the solution chemistry of the metal complexes involved must also be considered, as the speciation of metals in solution is pH dependant (Murphy *et al.*, 2007).

Figure 1 shows that, at pH 3.0, there is some metal uptake (20% for Cd and 40% for Pb); according to Murphy *et al.* (2007) this may be due to the presence of sulphonate groups that are dissociated around this pH value.

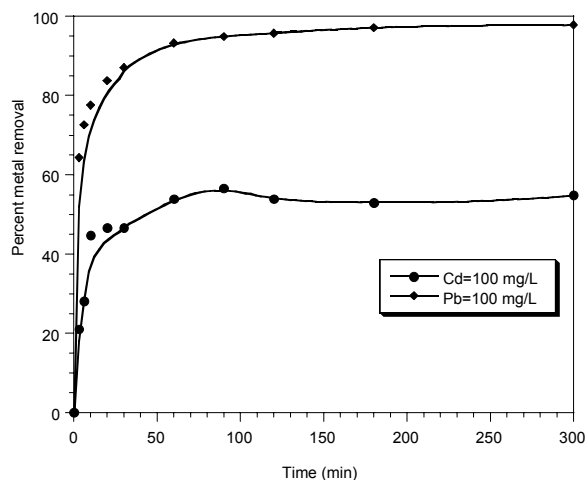
This dependence between solution pH and biosorption suggests that aquatic mosses can be developed as multi-use sorption materials. As observed, metal removal is greatly reduced at lower pH, which means that it is possible to promote an easy release of metal ions by simple pH adjustment.

Therefore, in the subsequent work, experiments were carried out at pH 5.0 - 5.2.

### Equilibrium Time for Cd(II) and Pb(II) Biosorption

Preliminary kinetic tests were carried out at pH 5.0 until maximum metal uptake was achieved and metal precipitation was avoided. The initial metal concentration in solution was 100 mg L<sup>-1</sup>, and the moss dosage 2 g L<sup>-1</sup>. Results evidencing the dependence of cadmium and lead sorption on the contact

time are plotted in Figure 2. Curves show a similar shape for both metals, characterized by a strong increase in removal capacity by mosses during the first 10 minutes and a subsequent slower phase, whose contribution to the total metal uptake is relatively small. In the initial stage a faster removal of ions was observed due to a higher driving force in which higher affinity active sites are occupied first. After that, the metal concentration decreases and the remaining active sites with lower affinities are occupied slowly. The sorption process was fast and the equilibrium attained in less than 2 h. Similar kinetic behaviour (rapid initial sorption followed by a period of much slower uptake) and equilibrium times were observed for different biosorbents: sorption of cadmium and lead by spent grain (Low *et al.*, 2000), lead by *Sphagnum* moss (Ho and McKay, 2000) and cadmium by *C. vulgaris* (Aksu, 2001). Then, to assure that equilibrium is really attained, a contact time of 5 h was adopted in subsequent experiments. The short time required to attain the equilibrium is a good indicator of the potential of the moss for a fast removal of metal ions in solution and allows using smaller reactor volumes.



**Figure 2:** Effect of contact time on Cd(II) and Pb(II) sorption by *Fontinalis antipyretica* ( $C_0 = 100 \text{ mg L}^{-1}$ ;  $X = 2 \text{ g L}^{-1}$ ; pH = 5.0).

### Effect of the Initial Metal Concentration

For 300 min of contact time, 50 mL of metal solution with a concentration in the range of 10-100 mg L<sup>-1</sup> was shaken with 100 mg biosorbent at constant temperature (20 °C) and pH (5.0-5.2). Table 1 shows the results of the sorption capacity and rate constants. The first order reaction rate constant,  $k$ , was calculated by fitting to the experimental data the

following equation:

$$C_e = C_0 \exp(-kt) ; \text{ for } t \leq 300 \text{ min} \quad (20)$$

where  $C_e$  = metal concentration at equilibrium,  $\text{mg L}^{-1}$ , and  $C_0$  = initial metal concentration,  $\text{mg L}^{-1}$ .

The initial metal concentration provides an important driving force to overcome all mass transfer resistances involving the liquid/solid interface, and leads to high metal removal. The equilibrium lead uptake values at different initial metal ion concentrations are given in Table 1 and it is clear that practically all lead ( $\approx 98\%$ ) is bound to the biosorbent, regardless of the initial concentration in solution. The affinity of the biosorbent for cadmium is lower and the uptake percentage markedly decreases (from 83.8 to 47.4%) when the initial metal concentration in solution increases from 10 to 100  $\text{mg L}^{-1}$ . At lower concentrations, the ratio of initial number of metal ions and the available sorption sites is low and subsequently the biosorption percentage becomes independent of initial concentration. For higher concentrations, however, the available sites of biosorption become fewer and consequently the removal of metallic ions depends on the initial concentration.

The cleansing yield can therefore be improved by diluting the effluent containing high metal ion concentrations.

The lead uptake rate is almost independent on the initial concentration and averages  $13.4 \times 10^{-3} \text{ min}^{-1}$ . On the other hand, the biosorption of cadmium is slower and the uptake rate decreases by about one third as the initial concentration increases from 10 to 100  $\text{mg L}^{-1}$ . The high removal capacities observed for the lower initial metal concentrations in solution (Table 1) are explained by the finite number of adsorption sites at the particle surface. However, lead uptake is insensitive to this fact due to its high electronegativity, which increases the affinity for the different functional groups.

### Biosorption Kinetic Models

#### The Pseudo First-Order Lagergren Equation

The kinetic parameters (Table 2) were obtained by fitting Equation (3) to the experimental results. The curves predicted by this model are presented in Figure 3. The correlation coefficient indicates that the least-squares fits are better for cadmium than for lead, and at lower metal concentration.

**Table 1: Effect of initial metal ion concentration on equilibrium adsorption yields and uptake rates of Cd(II) and Pb(II) (T = 20 °C; pH = 5.0 – 5.2; X = 2 g L<sup>-1</sup>).**

| $C_0$<br>$\text{mg L}^{-1}$ | Cadmium   |             |                                      | Lead  |             |                                      |
|-----------------------------|---|-------------|--------------------------------------|---|-------------|--------------------------------------|
|                             | $q_e$<br>$\text{mg g}^{-1}$ (mmol g <sup>-1</sup> ) | Uptake<br>% | $k \times 10^3$<br>$\text{min}^{-1}$ | $q_e$<br>$\text{mg g}^{-1}$ (mmol g <sup>-1</sup> ) | Uptake<br>% | $k \times 10^3$<br>$\text{min}^{-1}$ |
| 10                          | 4.2 (0.037)   | 83.8        | 6.1                                  | 4.8 (0.023)   | 96.7        | 11.4                                 |
| 20                          | 7.9 (0.070)   | 78.9        | 5.2                                  | 9.7 (0.047)   | 97.3        | 12.0                                 |
| 40                          | 14.7 (0.131)  | 73.4        | 4.4                                  | 19.8 (0.096)  | 98.9        | 14.9                                 |
| 60                          | 17.9 (0.159)  | 59.8        | 3.0                                  | 29.7 (0.143)  | 99.0        | 15.5                                 |
| 80                          | 22.7 (0.202)  | 56.7        | 2.8                                  | 39.5 (0.191)  | 98.7        | 14.5                                 |
| 100                         | 23.7 (0.211)  | 47.4        | 2.2                                  | 48.6 (0.235)  | 97.2        | 11.9                                 |

**Table 2: Pseudo first-order Lagergren rate constants for the removal of Cd(II) and Pb(II) by *Fontinalis antipyretica*.**

| Metal | $C_0$<br>$\text{mg L}^{-1}$ | $q_e$<br>$\text{mg g}^{-1}$ (mmol g <sup>-1</sup> ) | $K_L$<br>$\text{min}^{-1}$ | $S^2$  | $R^2$ |
|-------|-----------------------------|---|----------------------------|--------|-------|
| Cd    | 10                          | 4.57 (0.041)  | 0.124                      | 4.0E-2 | 0.990 |
|       | 100                         | 26.5 (0.236)  | 0.147                      | 2.58   | 0.971 |
| Pb    | 10                          | 4.67 (0.023)  | 0.399                      | 5.8E-2 | 0.975 |
|       | 100                         | 45.7 (0.221)  | 0.319                      | 10.5   | 0.953 |

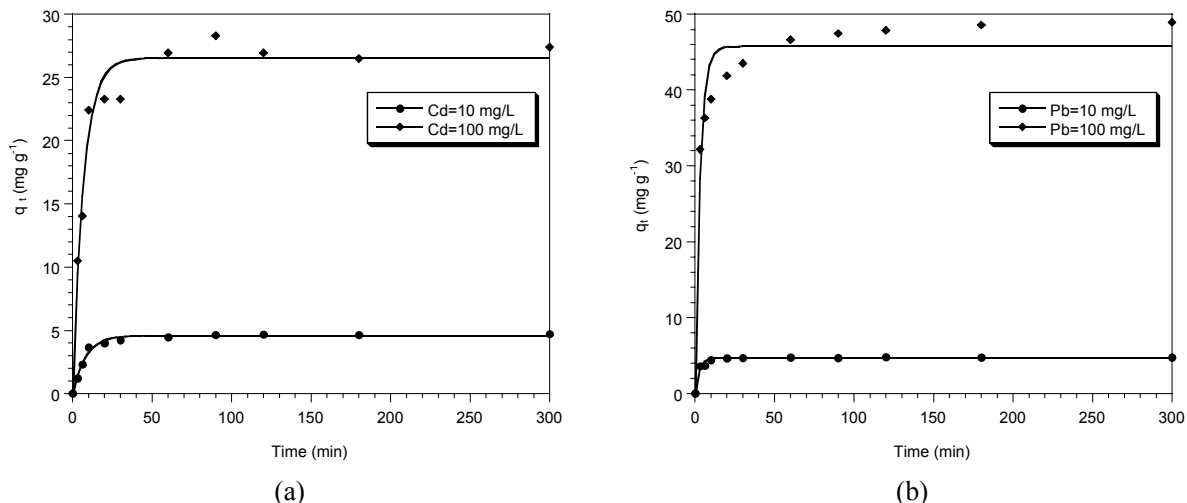


Figure 3: Pseudo first-order Lagergren sorption kinetics of (a) Cd(II) and (b) Pb(II).

### The Elovich Rate Equation

The parameters of the Elovich equation, obtained by fitting Eq. (5) to the experimental data, are presented in Table 3. Plots of  $q_t$  versus  $t$  for the Cd and Pb systems are shown in Figure 4. From the predicted curves and the values of the correlation coefficient, we conclude that the Elovich equation does not successfully describe the experimental data,

exception made for the initial lead concentration of  $100 \text{ mg L}^{-1}$ . When the initial metal concentration increased from  $10$  to  $100 \text{ mg L}^{-1}$ , the parameter  $a$  increased for cadmium, but decreased for lead, and the parameter  $b$  decreased for both metals. According to Teng and Hsieh (1999), the parameter  $a$  represents the rate of chemisorption at zero coverage and the parameter  $b$  is related to the extent of surface coverage and activation energy for chemisorption.

Table 3: Elovich equation rate constants for the removal of Cd(II) and Pb(II) by *Fontinalis antipyretica*.

| Metal | $C_0$<br>$\text{mg L}^{-1}$ | $a$<br>$\text{mg g}^{-1} \text{min}^{-1}$ | $b$<br>$\text{mg}^{-1} \text{g}$ | $S^2$   | $R^2$ |
|-------|-----------------------------|---|----------------------------------|---------|-------|
| Cd    | 10                          | 5.21                                      | 1.46                             | 2.53E-1 | 0.903 |
|       | 100                         | 66.7                                      | 0.285                            | 6.62    | 0.918 |
| Pb    | 10                          | 879                                       | 3.50                             | 9.5E-2  | 0.956 |
|       | 100                         | 206                                       | 0.170                            | 13.1    | 0.953 |

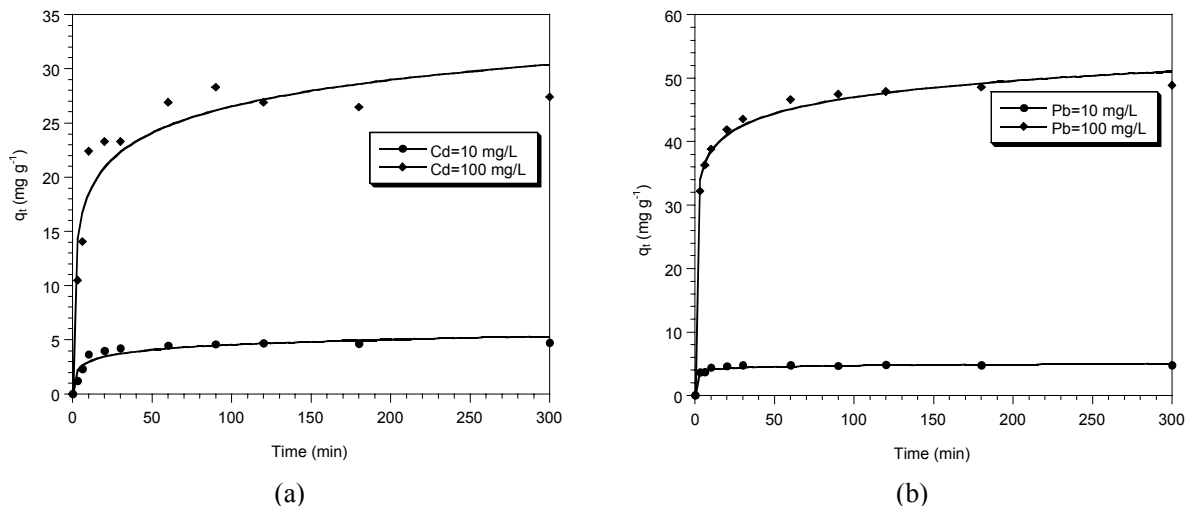


Figure 4: Elovich sorption kinetics of (a) Cd(II) and (b) Pb(II).



Thus, increasing the initial concentration should increase the rate of chemisorption, which was not in accord with the results obtained for lead. Probably, the mechanism of lead ion uptake by *Fontinalis antipyretica* is not predominantly chemisorption, and so the system cannot be described by the Elovich equation. Because the parameter  $b$  is related to the extent of surface coverage, it will decrease upon increasing the initial concentration. Biosorption of cadmium meets the conditions proposed by Teng and Hsieh (1999) but the fit is not very satisfactory ( $R^2 \approx 0.91$ ).

### The Ritchie Second-Order Equation

The parameters of the modified Ritchie second-order equation (Eq. 10) applied to the removal of Cd(II) and Pb(II) by *Fontinalis antipyretica* are presented in Table 4. The predicted curves (Figure 5) indicate that the Ritchie equation fitted better the experimental data for lead (high correlation coefficient) than for cadmium. The values of the parameter  $\beta_2$  ( $\approx 1.00$ ) suggest that the pre-adsorbed metal on the surface of mosses is close to zero, which is in accordance with the metal concentrations determined

in clean mosses ( $16.8 \mu\text{g Pb g}^{-1}$  moss;  $33.1 \mu\text{g Cd g}^{-1}$  moss).

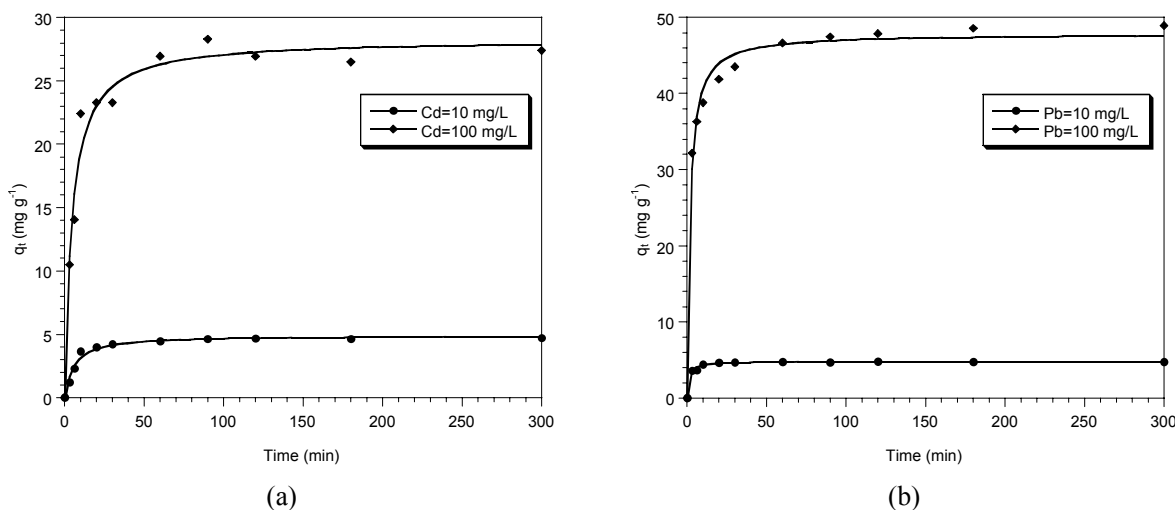
### The Pseudo-Second Order Equation

Linear plots of  $t/q_t$  versus  $t$  (Eq. 24) are shown in Figure 6 and  $k$  and  $q_e$  values, obtained from the slopes and intercepts, are presented in Table 5. The correlation coefficients (higher than 0.999) indicate a good compliance of the experimental data with the proposed pseudo-second order kinetic model.

The kinetic constant,  $k$ , decreased from  $4.20 \times 10^{-2}$  to  $1.00 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$  as the initial cadmium concentration increased from 10 to 100  $\text{mg L}^{-1}$  and a similar behaviour was observed for lead ( $k$  decreased from 0.233 to  $7.00 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ , as the initial lead concentration increased from 10 to 100  $\text{mg L}^{-1}$ ). The values of the initial sorption rates,  $h$ , were determined from the intercepts of the straight lines plotted in Figure 6. The initial sorption rate increased with the initial metal concentration for both cadmium and lead. This behaviour is opposite to that observed by Ho and McKay for the sorption of copper, nickel and lead onto *Sphagnum* moss peat (Ho and McKay, 2000).

**Table 4: Modified Ritchie rate constants for the removal of Cd(II) and Pb(II) by *Fontinalis antipyretica*.**

| Metal | $C_0$<br>$\text{mg L}^{-1}$ | $q_e$<br>$\text{mg g}^{-1}$ ( $\text{mmol g}^{-1}$ ) | $k_2$<br>$\text{min}^{-1}$ | $\beta_2$ | $S^2$  | $R^2$ |
|-------|-----------------------------|--|----------------------------|-----------|--------|-------|
| Cd    | 10                          | 4.91 (0.044)   | 0.179                      | 0.971     | 7.2E-2 | 0.978 |
|       | 100                         | 28.3 (0.252)   | 0.218                      | 0.990     | 2.35   | 0.977 |
| Pb    | 10                          | 4.82 (0.023)   | 0.863                      | 1.00      | 2.2E-2 | 0.991 |
|       | 100                         | 47.8 (0.231)   | 0.558                      | 1.01      | 2.38   | 0.991 |



**Figure 5: Modified Ritchie second-order sorption kinetics of (a) Cd(II) and (b) Pb(II).**

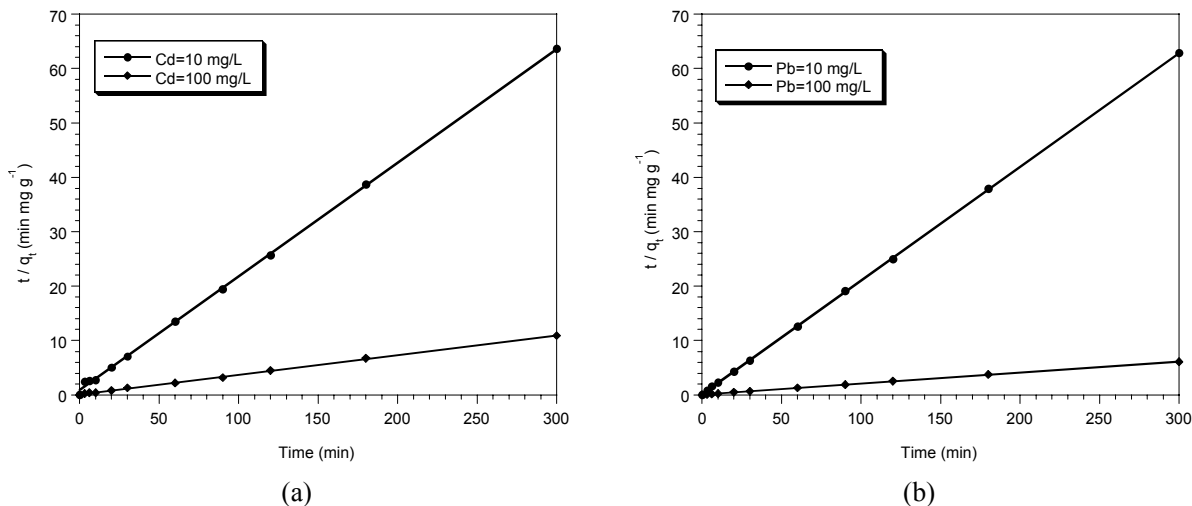


Figure 6: Pseudo second-order sorption kinetics of (a) Cd(II) and (b) Pb(II).

Table 5: Pseudo-second order rate constants for the removal of Cd(II) and Pb(II) by *Fontinalis antipyretica*.

| Metal | $C_0$<br>$mg L^{-1}$ | $q_e$<br>$mg g^{-1}$ ( $mmol g^{-1}$ ) | $k$<br>$g mg^{-1} min^{-1}$ | $h$<br>$g mg^{-1} min^{-1}$ | $S^2$   | $R^2$ |
|-------|----------------------|--|-----------------------------|-----------------------------|---------|-------|
| Cd    | 10                   | 4.80 (0.043)                           | 4.20E-2                     | 0.966                       | 1.49E-1 | 1.000 |
|       | 100                  | 27.7 (0.246)                           | 1.00E-2                     | 7.66                        | 1.1E-2  | 1.000 |
| Pb    | 10                   | 4.79 (0.023)                           | 0.233                       | 5.34                        | 1.9E-2  | 1.000 |
|       | 100                  | 49.3 (0.238)                           | 7.00E-3                     | 16.5                        | 2.6E-4  | 1.000 |

### Model Performances

A brief and simplistic analysis, comparing the regression coefficients ( $R^2$ ) for the different models of each metal (Tables 2-5), indicates that, although all values were high ( $>0.90$ ), the highest  $R^2$  corresponded to the pseudo-second order model. When the models fit the data with sensible values, the suitable procedure is to use an *F-test* to decide which model to accept. The test is based on model variances,  $F_{cal} = S^2_{model 1}/S^2_{model 2}$ . This statistical tool allows one to evaluate if one kinetic model is more accurate than another and, secondly, if this difference is statistically significant. If  $F_{cal} > F_{critic}$ , the model in the denominator (model 2) is statistically better than the other, according to the chosen level of significance.

Tables 6 and 7 show the *F* values for a level of probability of 95% and 10 degrees of freedom for the numerator and for the denominator. Considering the values of  $F_{cal}$ , for each pair and for all models analysed, the pseudo-second order model is statistically more accurate than the others models for the biosorption of Cd(II) and Pb(II) by the aquatic moss, except for cadmium at lower concentration ( $10 mg L^{-1}$ ), where the Lagergren model is better. However,

the Lagergren model is not statistically more accurate than the Ritchie model, a second order model ( $F_{cal} < 2.98$ ).

The equilibrium sorption capacities predicted by the best model, for initial cadmium concentrations of 10 and  $100 mg L^{-1}$ , are  $4.57 mg g^{-1}$  ( $0.041 mmol g^{-1}$ ) and  $27.7 mg g^{-1}$  ( $0.246 mmol g^{-1}$ ), respectively. Similarly, for the same initial concentrations of lead, the predicted sorption capacities are  $4.79 mg g^{-1}$  ( $0.023 mmol g^{-1}$ ) and  $49.3 mg g^{-1}$  ( $0.238 mmol g^{-1}$ ), respectively.

The better fit of the pseudo-second order model therefore indicates that a 1:2 binding stoichiometry applies; that is, one divalent metal ion binds to two monovalent active binding sites. It is perfectly reasonable that a divalent metal would bind to two carboxyl groups, as shown by Schiewer and Wong (1999) in experiments with brown algae. However, it is not possible to conclude that, in all the time range, the biosorption reaction is the rate-limiting step. This conclusion may not be valid because a good model fit does not necessarily indicate the real nature of the rate-limiting step. In many other biosorption cases, diffusion rather than the chemical reaction was the rate-limiting step, at least in the initial instants.

**Table 6: F-test for the biosorption of cadmium (level of probability 95%; degrees of freedom 10:10;  $F_{critic} = 2.98$ ).**

| Model                                 | Ion/C (mg L <sup>-1</sup> ) | Variance (S <sup>2</sup> ) | F calculated |      |      |
|---------------------------------------|-----------------------------|----------------------------|--------------|------|------|
| Lagergren (L)                         |                             |                            |              |      |      |
| Pseudo 2 <sup>a</sup> order (P)       | Cd 10                       | 4.0x10 <sup>-2</sup>       | P/L          |      |      |
| Ritchie 2 <sup>a</sup> ord. mod. (Rm) |                             | 1.49x10 <sup>-1</sup>      | 3.73         |      |      |
| Elovich (E)                           |                             | 7.3x10 <sup>-2</sup>       | Rm/L         | P/Rm |      |
|                                       |                             | 2.53x10 <sup>-1</sup>      | 1.83         | 2.04 |      |
|                                       |                             |                            | E/L          | E/P  | E/Rm |
|                                       |                             |                            | 6.33         | 1.70 | 3.47 |
| Lagergren (L)                         |                             |                            |              |      |      |
| Pseudo 2 <sup>a</sup> order (P)       | Cd 100                      | 2.58                       | L/P          |      |      |
| Ritchie 2 <sup>a</sup> ord. mod. (Rm) |                             | 1.1x10 <sup>-2</sup>       | 235          |      |      |
| Elovich (E)                           |                             | 2.35                       | L/Rm         | Rm/P |      |
|                                       |                             | 6.62                       | 1.10         | 214  |      |
|                                       |                             |                            | E/L          | E/P  | E/Rm |
|                                       |                             |                            | 2.57         | 602  | 2.82 |

**Table 7: F-test for the biosorption of lead (level of probability 95%; degrees of freedom 10:10;  $F_{critic} = 2.98$ ).**

| Model                                 | Ion/C (mg L <sup>-1</sup> ) | Variance (S <sup>2</sup> ) | F calculated        |                     |      |
|---------------------------------------|-----------------------------|----------------------------|---------------------|---------------------|------|
| Lagergren (L)                         |                             |                            |                     |                     |      |
| Pseudo 2 <sup>a</sup> order (P)       | Pb 10                       | 5.8x10 <sup>-2</sup>       | L/P                 |                     |      |
| Ritchie 2 <sup>a</sup> ord. mod. (Rm) |                             | 1.9x10 <sup>-2</sup>       | 3.05                |                     |      |
| Elovich (E)                           |                             | 2.2x10 <sup>-2</sup>       | L/Rm                | Rm/P                |      |
|                                       |                             | 9.5x10 <sup>-2</sup>       | 2.64                | 1.16                |      |
|                                       |                             |                            | E/L                 | E/P                 | E/Rm |
|                                       |                             |                            | 1.64                | 5.00                | 4.32 |
| Lagergren (L)                         |                             |                            |                     |                     |      |
| Pseudo 2 <sup>a</sup> order (P)       | Pb 100                      | 10.5                       | L/P                 |                     |      |
| Ritchie 2 <sup>a</sup> ord. mod. (Rm) |                             | 2.6x10 <sup>-4</sup>       | 403x10 <sup>2</sup> |                     |      |
| Elovich (E)                           |                             | 2.38                       | L/Rm                | Rm/P                |      |
|                                       |                             | 13.1                       | 4.41                | 915x10 <sup>1</sup> |      |
|                                       |                             |                            | L/E                 | E/P                 | E/Rm |
|                                       |                             |                            | 0.80                | 504x10 <sup>2</sup> | 5.50 |

The sorption capacity at equilibrium is a function of the initial metal ion concentration, as found by other researchers performing similar studies, but at different experimental conditions, such as biosorbent dose and nature of the solute (Ho and McKay, 2000; Cheung *et al.*, 2001). However, Ho and McKay (2000) obtained a similar capacity for the sorption of lead onto *Sphagnum* peat moss (47.98 mg g<sup>-1</sup>) under the same conditions (initial metal concentration = 100 mg L<sup>-1</sup>; moss dose = 2 g L<sup>-1</sup>; pH = 5; T = 20 °C) by modelling the data with the same kinetic model. The adsorption capacities of some low-cost adsorbents used in the removal of

Cd(II) and Pb(II) in aqueous solution are given in Table 8 (obtained for identical concentrations of metal in solution). It is evident that the sorption affinity of the aquatic moss *Fontinalis antipyretica* is comparable to or greater than the other available adsorbents, even with somewhat different experimental conditions.

The amount of ions adsorbed at equilibrium is greater for Pb(II) than for Cd(II) when expressed in mass of metal, which can be explained by the atomic weight values; thus, when the results are expressed in mmol of metal per gram of moss, identical values were obtained to both metals.

**Table 8: Metal adsorbed ( $q_e$ ) in equilibrium with metal concentration in solution ( $C_e$ ) for various low-cost materials.**

| Metal ion | Biosorbent                   | pH / T (°C) | $C_e$ (mg L <sup>-1</sup> ) | $q_e$ (mg g <sup>-1</sup> ) | Reference                    |
|-----------|------------------------------|-------------|-----------------------------|-----------------------------|------------------------------|
| Cd        | Algae ( <i>F. spiralis</i> ) | 5.0; 25     | 15.9                        | 42.1                        | Freitas <i>et al.</i> , 2008 |
|           | NaOH-treated spent grain     | 5.0; 28     | 13.5                        | 17.3                        | Low <i>et al.</i> , 2000     |
|           | Tree fern                    | 5.4; 25     | 84.2                        | 12.2                        | Ho, 2006                     |
|           | Waste rice polish            | 8.6; 20     | 27.8                        | 9.7                         | Singh <i>et al.</i> , 2005   |
|           | Aquatic moss                 | 5.0; 20     | 44.6                        | 27.7                        | This study                   |
| Pb        | Algae ( <i>F. spiralis</i> ) | 5.0; 25     | 16.3                        | 43.5                        | Freitas <i>et al.</i> , 2008 |
|           | NaOH-treated spent grain     | 5.0; 28     | 22.5                        | 35.5                        | Low <i>et al.</i> , 2000     |
|           | Tree fern                    | 5.4; 20     | 313                         | 41.5                        | Ho <i>et al.</i> , 2004      |
|           | Siderite (iron mine)         | 2.97; 25    | 90.0                        | 11.0                        | Erdem and Ozverdi, 2005      |
|           | Aquatic moss                 | 5.0; 20     | 1.4                         | 49.3                        | This study                   |

## CONCLUSIONS

The aquatic moss *Fontinalis antipyretica* is a low cost adsorbent that can be effectively used for removing toxic ions such as cadmium and lead from aqueous solution. The initial pH of the solution is an important parameter governing the mechanism of biosorption, and it was found that the optimum value is in the range of 4.0-6.0. The kinetics of cadmium and lead biosorption onto *Fontinalis antipyretica* were analysed by fitting four models: pseudo-first-order, Elovich, modified Ritchie second-order and pseudo-second-order equations - to the data obtained in batch experiments. In this stage of the studies it is not possible to conclude that the biosorption reaction is the rate-limiting step, because a good model fit does not necessarily indicate the real nature of the rate-limiting step. Additional work concerning diffusion is necessary to clarify definitively the rate-limiting step.

An analysis based on the *F-test* showed that pseudo-second order biosorption kinetics provided the best correlation with the experimental data, which is also corroborated by the high regression coefficients obtained ( $R^2 \geq 0.999$ ). Cadmium and lead equilibrium sorption capacity increased with the initial metal concentration. For an initial metal concentration of 10 mg L<sup>-1</sup>, the uptake capacity of the moss, at equilibrium, was the same for both metals. Nevertheless, when the initial concentration increased to 100 mg L<sup>-1</sup>, the uptake of lead was 78% higher. The results obtained suggest further investigations as to the possibility of using aquatic mosses biomass as biosorbent for metal removal from wastewaters.

## NOMENCLATURE

$a$  Elovich constant mg g<sup>-1</sup> min<sup>-1</sup>

|          |  |                                      |
|----------|--|--------------------------------------|
| $b$      | Elovich constant   | g mg <sup>-1</sup>                   |
| $C_0$    | initial metal concentration in solution                    | mg L <sup>-1</sup>                   |
| $C_e$    | metal concentration in solution at equilibrium             | mg L <sup>-1</sup>                   |
| $C_t$    | metal concentration in solution at time $t$                | mg L <sup>-1</sup>                   |
| $h$      | initial sorption rate                                      | g mg <sup>-1</sup> min <sup>-1</sup> |
| $(HP)_0$ | number of equilibrium sites available on the biosorbent    |                                      |
| $HP$     | polar sites on the moss surface                            |                                      |
| $(HP)_t$ | number of active sites occupied on the sorbent at time $t$ |                                      |
| $k$      | biosorption rate constant                                  | g mg <sup>-1</sup> min <sup>-1</sup> |
| $k_n$    | rate constant of reaction                                  | min <sup>-1</sup>                    |
| $K_L$    | Lagergren rate constant                                    | min <sup>-1</sup>                    |
| $M$      | biosorbent mass  | g                                    |
| $M^{2+}$ | metal cation   |                                      |
| $n$      | number of surface sites                                    |                                      |
| $P_0$    | number of equilibrium sites available on the biosorbent    |                                      |
| $P$      | number of polar sites on the moss surface                  |                                      |
| $P_t$    | number of active sites occupied on the sorbent at time $t$ |                                      |
| $q_e$    | amount of metal ion sorbed at equilibrium                  | mg g <sup>-1</sup>                   |
| $q_t$    | amount of metal ion sorbed at time $t$                     | mg g <sup>-1</sup>                   |
| $R^2$    | square correlation coefficient                             |                                      |
| $S$      | sorption site  |                                      |
| $S^2$    | residual variance  |                                      |
| $t$      | time   | min                                  |
| $V$      | volume of solution   | mL                                   |
| $X$      | moss concentration   | g L <sup>-1</sup>                    |

**Greek Letters**

|            |  |                          |
|------------|--|--------------------------|
| $\theta$   | surface coverage at time $t$           | $(\theta = q_t / q_e)$   |
| $\theta_0$ | surface coverage at pre-adsorbed stage | $(\theta_0 = q_0 / q_e)$ |

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