KINETIC MODELLING OF CADMIUM AND LEAD REMOVAL BY AQUATIC MOSSES

R. J. E. Martins[1,2*], V. J. P. Vilar[2] and R. A. R. Boaventura[2]

[1]Department of Chemical and Biological Technology, Superior School of Technology, University of Applied
Sciences of Bragança, Campus de Santa Apolónia, 5301-857, Bragança, Portugal.
[2]LSRE-Laboratory of Separation and Reaction Engineering, Faculty of Engineering,
University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal.
Phone: (+351) 273303091, Fax: (+351) 273313051.
E-mail: rmartins@ipb.pt

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^{-1}, the uptake capacity of the moss, at equilibrium, is the same for both metals (4.8 mg g^{-1}). Nevertheless, when the initial concentration increases up to 100 mg L^{-1}, 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

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:

$$S_{solid} + M^{2+}_{aqueous} \rightarrow SM^{2+}_{adsorbed\ phase} \qquad (1)$$
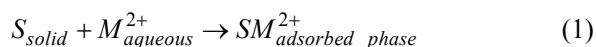
where S is a sorption site on the biomass surface and M^{2+} the metal ion. The Lagergren equation becomes:

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

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

$$q_t = q_e \left[1 - \exp(-K_L t) \right] \qquad (3)$$

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

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

where a $(mg\ g^{-1}\min^{-1})$ and b $(g\ mg^{-1})$ 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:

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

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).

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

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

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

where θ is the surface coverage at time t ($\theta = q_t / q_e$), θ_0 is the value of θ 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 $n = 2, 3, ..., k$ we get:

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

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

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

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

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

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

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):

$$M^{2+} + 2P^- \rightleftharpoons MP_2 \qquad (11)$$

or

$$M^{2+} + 2HP \rightleftharpoons MP_2 + 2H^+ \qquad (12)$$
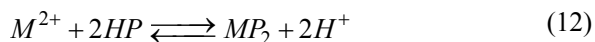
where M^{2+} is the metal ion and P^- and HP are polar sites on the moss surface.

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:

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

or

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

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:

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

where q_t and q_e are the amounts of divalent metal ion adsorbed at time t and at equilibrium (mg g⁻¹), respectively, and k is the biosorption rate constant (g mg⁻¹ min⁻¹).

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

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

This equation can be manipulated to obtain:

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

In the linear form Equation (17) becomes

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

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 ºC 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 μm - 300 μm 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 $CdCl_2.H_2O$ and $PbCl_2$, 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 (HNO_3 volume, microwave power, digestion time) for biomass digestion were selected from the results of zinc determination in a reference sample (566 μg Zn^{2+} 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 mg L⁻¹; moss dosage, 2 g L⁻¹; contact time, 24 h; temperature, 20 ºC. Kinetic experiments were performed in duplicate at a constant

temperature of 20 ºC, metal concentrations of 10 and 100 mg L^{-1}. 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_2SO_4 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^{-1}) 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/ Acetylene	0.009 ppm
Pb	217.0 nm	1.0 nm	Air/ Acetylene	0.09 ppm

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

$$q_t = (C_0 - C_t)V / M \tag{19}$$

where C_0 is the initial metal concentration in solution (mg L^{-1}), C_t the metal concentration in solution at time t (mg L^{-1}), 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^{-1} were shaken with 100 mg of biosorbent at constant temperature (20 ºC) 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^{2+} 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^{2+} and Pb^{2+} 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.
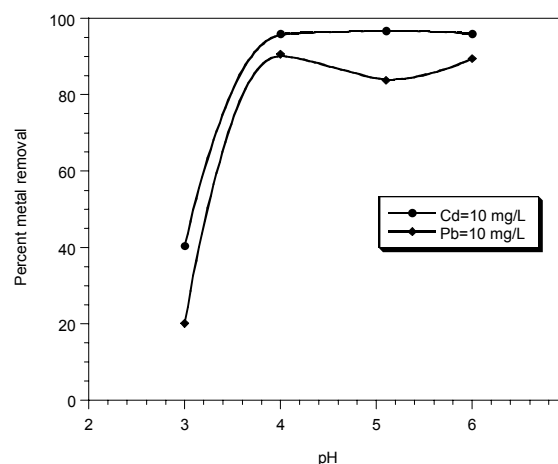
Figure 1: Effect of initial pH on the uptake of Cd(II) and Pb(II) by *Fontinalis antipyretica* (C_0 = 10 mg L^{-1}; X = 2 g L^{-1}; contact time = 24 h).

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 al 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^{-1}, and the moss dosage 2 g L^{-1}. 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 biosorvents: 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.
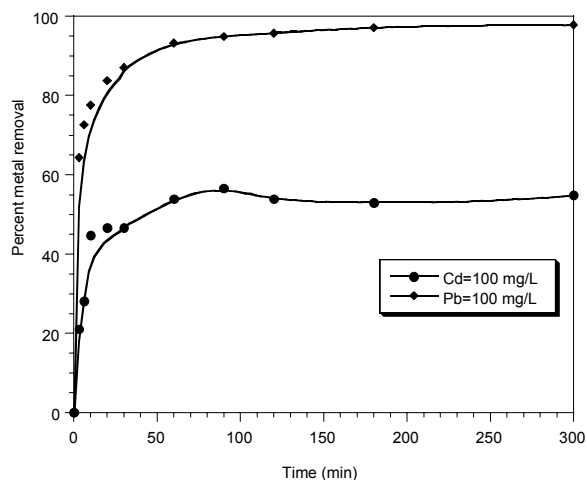
Figure 2: Effect of contact time on Cd(II) and Pb(II) sorption by *Fontinalis antipyretica* (C_0 = 100 mg L^{-1}; X = 2 g L^{-1}; pH = 5.0).

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^{-1} was shaken with 100 mg biosorbent at constant temperature (20 ℃) 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:

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

where C_e = metal concentration at equilibrium, mg L^{-1}, and C_0 = initial metal concentration, 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 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 13.4x10^{-3} 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 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 ºC; pH = 5.0 – 5.2; X = 2 g L^{-1}).

C_0 mg l^{-1}	Cadmium			Lead		
	q_e mg g^{-1} (mmol g^{-1})	Uptake %	k x10^3 min^{-1}	q_e mg g^{-1} (mmol g^{-1})	Uptake %	k x10^3 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 mg L^{-1}	q_e mg g^{-1} (mmol g^{-1})	K_L 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

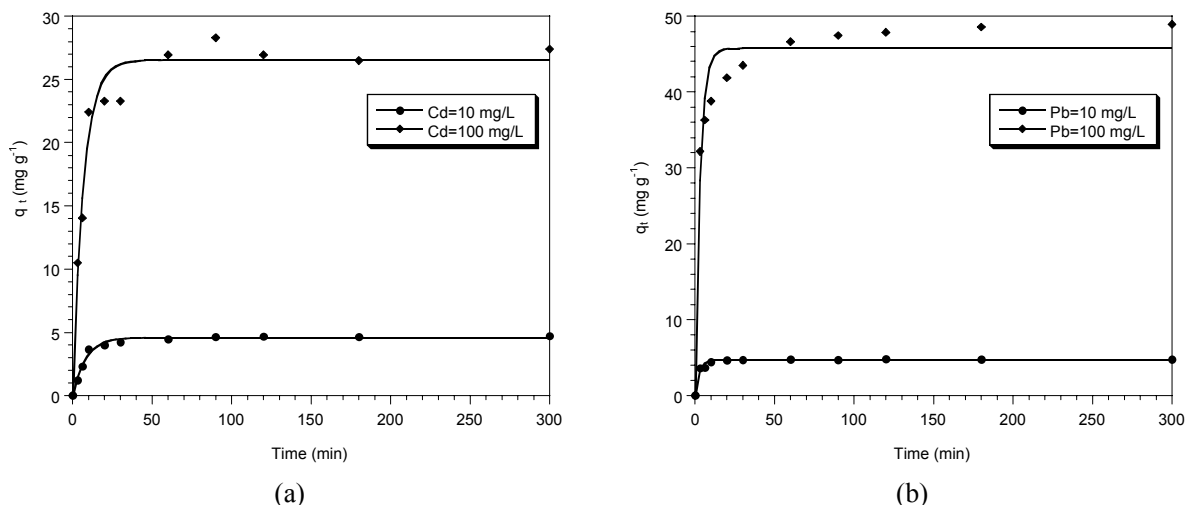(a)   (b)

Figure 3: Pseudo first-order Lagregen 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 mg L^{-1}. When the initial metal concentration increased from 10 to 100 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 mg L^{-1}	a mg g^{-1} min^{-1}	b mg^{-1} 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

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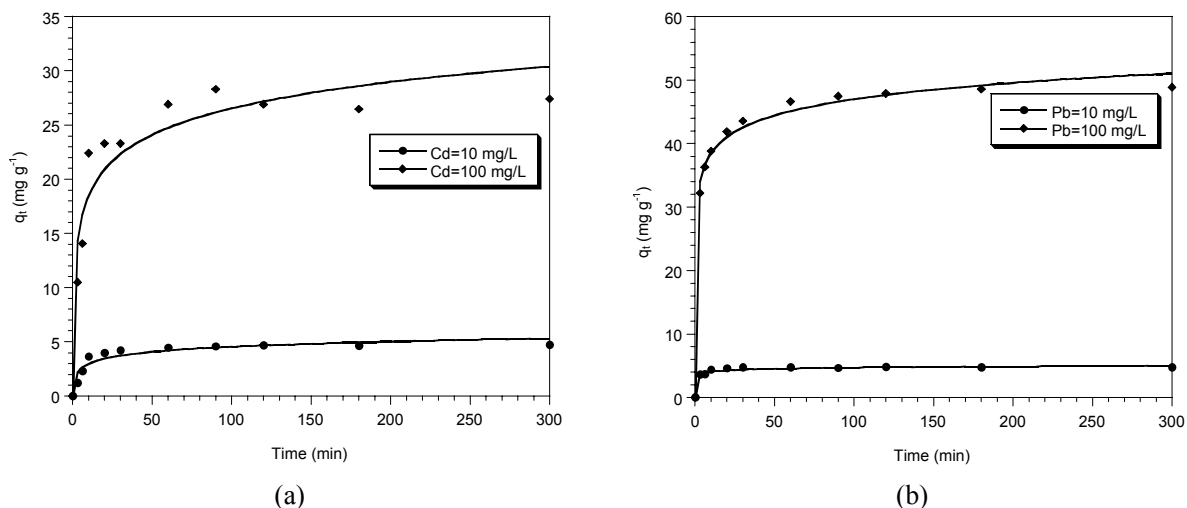
Figure 4: Elovich sorption kinetics of (a) Cd(II) and (b) Pb(II).

Thus, increasing the initial concentration should increase de 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 β_2 (≈ 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 µg Pb g^{-1} moss; 33.1 µg Cd g^{-1} moss).
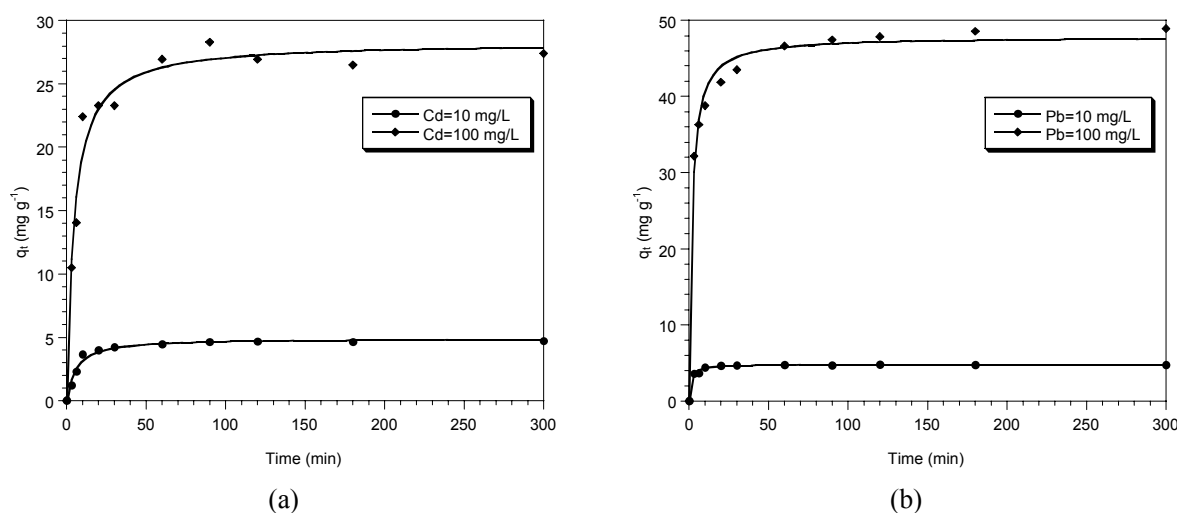
The Pseudo-Second Order Equation

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 4.20×10^{-2} to 1.00×10^{-2} g mg^{-1} min^{-1} as the initial cadmium concentration increased from 10 to 100 mg L^{-1} and a similar behaviour was observed for lead (k decreased from 0.233 to 7.00×10^{-3} g mg^{-1} min^{-1}, as the initial lead concentration increased from 10 to 100 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 mg L^{-1}	q_e mg g^{-1} (mmol g^{-1})	k_2 min^{-1}	β_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).

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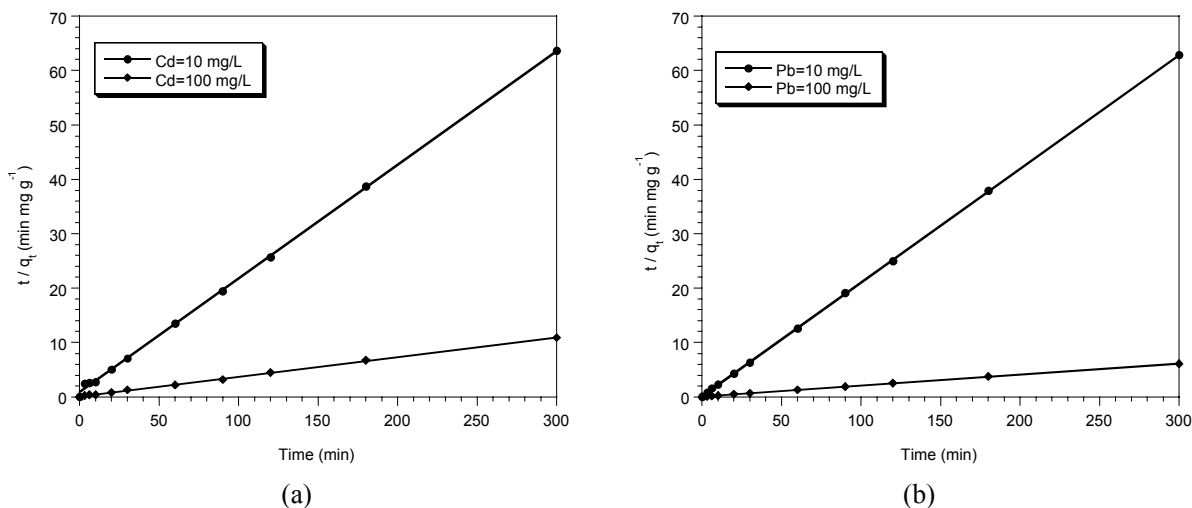
Figure 6: Pseudo second-order sorption kinetics of (a) Cd(II) and (b) Pb(II).

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

Metal	C_0 mg L^{-1}	q_e mg g^{-1} (mmol g^{-1})	k g mg^{-1} min^{-1}	h 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 significantly. 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 then 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⁻¹)	Variance (S²)	F calculated		
Lagergren (L)					
	Cd 10	4.0×10^{-2}			
Pseudo 2ª order (P)		1.49×10^{-1}	P/L 3.73		
Ritchie 2ª ord. mod. (Rm)		7.3×10^{-2}	Rm/L 1.83	P/Rm 2.04	
Elovich (E)		2.53×10^{-1}	E/L 6.33	E/P 1.70	E/Rm 3.47
Lagergren (L)					
	Cd 100	2.58			
Pseudo 2ª order (P)		1.1×10^{-2}	L/P 235		
Ritchie 2ª ord. mod. (Rm)		2.35	L/Rm 1.10	Rm/P 214	
Elovich (E)		6.62	E/L 2.57	E/P 602	E/Rm 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⁻¹)	Variance (S²)	F calculated		
Lagergren (L)					
	Pb 10	5.8×10^{-2}			
Pseudo 2ª order (P)		1.9×10^{-2}	L/P 3.05		
Ritchie 2ª ord. mod. (Rm)		2.2×10^{-2}	L/Rm 2.64	Rm/P 1.16	
Elovich (E)		9.5×10^{-2}	E/L 1.64	E/P 5.00	E/Rm 4.32
Lagergren (L)					
	Pb 100	10.5			
Pseudo 2ª order (P)		2.6×10^{-4}	L/P 403×10^{2}		
Ritchie 2ª ord. mod. (Rm)		2.38	L/Rm 4.41	Rm/P 915×10^{1}	
Elovich (E)		13.1	L/E 0.80	E/P 504×10^{2}	E/Rm 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⁻¹) under the same conditions (initial metal concentration = 100 mg L⁻¹; moss dose = 2 g L⁻¹; pH = 5; T = 20 ºC) 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^{-1})	q_e (mg g^{-1})	Reference
Cd	Algae (*F. spiralis*)	5.0; 25	15.9	42.1	Freitas *et al.*, 2008
	NaOH-treated spent grain	5.0; 28	13.5	17.3	Low *et al.*, 2000
	Tree fern	5.4; 25	84.2	12.2	Ho, 2006
	Waste rice polish	8.6; 20	27.8	9.7	Singh *et al.*, 2005
	Aquatic moss	5.0; 20	44.6	27.7	This study
Pb	Algae (*F. spiralis*)	5.0; 25	16.3	43.5	Freitas *et al.*, 2008
	NaOH-treated spent grain	5.0; 28	22.5	35.5	Low *et al.*, 2000
	Tree fern	5.4; 20	313	41.5	Ho *et al.*, 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^{-1}, the uptake capacity of the moss, at equilibrium, was the same for both metals. Nevertheless, when the initial concentration increased to 100 mg L^{-1}, 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^{-1} min^{-1}
b	Elovich constant	g mg^{-1}
C_0	initial metal concentration in solution	mg L^{-1}
C_e	metal concentration in solution at equilibrium	mg L^{-1}
C_t	metal concentration in solution at time t	mg L^{-1}
h	initial sorption rate	g mg^{-1} min^{-1}
$(HP)_0$	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^{-1} min^{-1}
k_n	rate constant of reaction	min^{-1}
K_L	Lagergren rate constant	min^{-1}
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^{-1}
q_t	amount of metal ion sorbed at time t	mg g^{-1}
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^{-1}

Greek Letters

θ	surface coverage at time t	($\theta = q_t / q_e$)
θ_0	surface coverage at pre-adsorbed stage	($\theta_0 = q_0 / q_e$)

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