BIOSORCIÓN DEL PLOMO DE AGUAS RESIDUALES INDUSTRIALES SIMULADAS POR BRIOFITAS ACUÁTICAS

BIOSORPTION OF LEAD FROM SIMULATED INDUSTRIAL WASTEWATERS BY AQUATIC BRYOPHYTES

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Resumen

Las briófitas acuáticas se utilizan con frecuencia como biomonitores para los metales en ecosistemas acuáticos. Sin embargo, sus características especiales también permiten su uso como biosorbentes para limpiar las aguas residuales industriales.Como la biosorción es un método de bajo costo y eficaz para tratar las aguas residuales contiendo metales la comprensión de la cinética del proceso es relevante en termos de proyecto.

En este estudio, la performance *da* briófita *Fontinalis antipyretica* para remover el plomo de las aguas residuales simuladas ha sido avaluado. Tres modelos cinéticos (pseudo -primera orden, pseudo-segunda orden y Elovich) fueron ayustados a los datos experimentales y comparados usando *uno teste-F*. Previamente, el efecto de parámetros como el pH inicial de la solución, tiempo de contacto y concentración inicial del ion metálico, en la biosorción fue investigado. El pH inicial de la solución tiene un valor óptimo en la gama 4.0-6.0. La capacidad de sorción del plomo no equilibrio por *la Fontinalis antipyretica* aumentó con la concentración inicial del metal. Para una concentración inicial del metal de 10 mg L^{-1}, la capacidad de acumulación del musgo, en el equilibrio, es de 4.8 mg g^{-1}.Contundo, cuando la concentración inicial aumenta hasta 100 mg L^{-1}, la acumulación del plomo es 10 veces mayor. La cinética de biosorción de pseudo-segunda orden ha fornecido la mejor correlación de los datos experimentales $(R^2 = 1.00)$.

La aplicabilidad de las los isotermas de adsorción de Langmuir y de Freundlich para el presente sistema fue testada. La capacidad de máxima de sorción de los musgos fue de 68 mg g^{-1}.

Palabras clave: musgos acuáticos, plomo, biosorción, remoción, cinética

Abstract

Aquatic bryophytes are frequently used as biomonitors for trace metals in aquatic ecosystems. Nevertheless, their special characteristics also allow using them as biosorbents to clean industrial wastewaters. As biosorption is a low cost and effective method for treating metal-bearing wastewaters, understanding the kinetics process is relevant for design purposes.

In this study, the performance of the aquatic bryophyte *Fontinalis antipyretica* for removing lead from simulated wastewaters has been evaluated. Three kinetic models (pseudo-first order, pseudo-second order and Elovich) were fitted to the experimental data and compared using a *Test-F*. 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 is in the range 4.0-6.0. The equilibrium sorption capacity of lead by *Fontinalis antipyretica* increased with the initial metal concentration. For an initial metal concentration of 10 mg L^{-1}, the uptake capacity of the moss, at equilibrium, is 4.8 mg g^{-1}. Nevertheless, when the initial concentration increases up to 100 mg L^{-1}, the uptake of lead is 10 times higher. The pseudo-second order biosorption kinetics provided the better correlation with the experimental data $(R^2 = 1.00)$.

The applicability of the Langmuir and Freundlich adsorption isotherms for the present system was tested. The maximum sorption capacity of mosses was 68 mg g^{-1}.

Key words: aquatic mosses, lead, biosorption, removal, kinetic

1. Introduction

The increasing environmental contamination by toxic metals is a relevant worldwide occurrence. They aren´t biodegradable and tend to accumulate in living organisms; its well-know the consequences due to their presence in aquatic ecosystems to human health, living organisms in water and additionally to the consumers of them [1]. Lead has been recognized as a potentially dangerous pollutant in the same class as mercury, arsenic and vanadium [2]. Tackett [3] (1987) relates that the lead has been found to be keen toxic to human beings when present in high amount. An adult ingest between 0.3 to 0.6 mg of lead in his diet and is retained in her body a value close of 10%. Lead damages the kidney, liver and reproductive system, brain functions and basic cellular processes [4].

Lead is released into the environment through waste streams from lead smelting, lead mining and coal combustion, the use of lead-based paints and lead-containing pipes in water supply systems, and additionally pigments, photographic materials, ceramic glazes, automobile batteries and cosmetics manufacturing [5, 6, 7].

Thus, the removal of toxic metal contaminants from waters is an important environmental issue [8]. Traditional methods used for heavy metals removal (chemical oxidation or reduction, chemical precipitation, coagulation, complexation) from aqueous effluents are insufficient to achieve the limits which are recommended by national and international water regulatory agencies [9] or extremely expensive (ion exchange, activated carbon adsorption, electrolytic removal, reverse osmosis). The high capital necessary, ally to the high operating costs have resulted in increasing the search of alternative adsorbents [10]. Also is true that in biosorption processes there is a minimization of the volume of chemical and contaminated sludge to be disposed in a sanitary landfill, and no maintenance requirements.

In recent years have been considered methods based on metal-sequestering properties of natural materials of biological origin. The principal mechanism involves the formation of complexes between a metal ion and functional groups in the surface or inside the porous material structure, as amino, amido, carboxyl, phosphate, carbonyl and sulfonate groups. Toxic metals removal includes a great variety of materials such as: agricultural sub-products (soybean and cottonseed hulls, rice straw and sugarcane bagasse) [11], pine bark [12], aquatic plants [12, 13, 14], peat moss [15], alum and activated sludge [16, 17], fungi and bacteria [18, 19] and algae [20, 5, 7]. These materials to be designed a low-cost biosorbents must to fulfil some criteria: are naturally abundant or an industrial process waste, and require little processing.

Already in 1990 [21] the bryophytes were know for exhibiting both sensitivity and tolerance to a wide range of heavy metals. Factors as the inexistence of a barrier to uncontrolled metal absorption and also possess no cuticle that increases the direct access for soluble metals to the cytoplasm; these make the aquatic mosses an important support for heavy metals removal from contaminated waters.

To our knowledge, there is little research results for lead removal using aquatic mosses reported in the literature. The aim of this work is to study the biosorption equilibrium and kinetic of lead ions by the aquatic moss *Fontinalis antipyretica*. Lead was the heavy metal chosen to carry out this study because (i) it is present in many industrial effluents and mine drainage waters directly discharged into rivers and lakes and (ii) it is toxic when in excess, inhibiting plant and microorganism growth.

We hope that the results obtained can support a future application of aquatic mosses to decontaminate industrial effluents.

2. Materials and methods

2.1 Lead(II) solutions

All chemicals were analytical grade and purchased from Merck-Schuchardt (Germany). The lead stock solution was prepared by dissolving an accurate quantity of $PbCl_2$ in deionized water. Other lead working solutions were freshly prepared by diluting lead stock solution with deionized water.

The solution pH was adjusted by adding 0.1 M H_2SO_4 or 0.1 M NaOH, as required.

2.2 The biosorbent

The aquatic moss *Fontinalis antipyretica* was taken from the Selho River, at Aldão, a tributary of the Ave River in Northern Portugal. The background metal content in mosses was considered to be of natural origin and negligible (sensibly 114 $\mu g\ g^{-1}$). In the harvest place the samples were rinsed with river water and plus later in laboratory with deionized water, selecting only the green parts of the plants. The plants were dried in an oven at 70ºC for 24 h and then ground in a RETSCH ZM 100 ultra-centrifugal mill at 1400 rpm for approximately 90 seconds. In this study was selected the fraction with particle size between 150 μm - 300 μm.

2.3 Biosorption isotherm experiments

A 100.0 (±0.1) gram of ground moss of particle size 150 - 300 μm was weighted and transfer to 100 ml glass bottles. Lead solutions of concentrations between 10 and 100 mg L^{-1} were prepared from a 500 mg L^{-1} metal stock solution. Moss suspensions were shaken for 24 h at constant room temperature (20±1ºC) using a rotary shaker (P-Selecta Rotabit). Blank solutions without moss were also included. The contact time was previously determined from kinetic studies, carried out at the same environmental conditions, as that allowing to attaining equilibrium. After attainment of equilibrium the liquid phase was separated from the biosorbent by vacuum filtration through 0.45 mm Gelman Sciences sterilized membranes, and the supernatant was analysed for the remaining Pb^{2+}.

2.4 Kinetic experiments

In batch experiments were studied the influence of initial metal concentration and the moss dosage on biosorption capacity of the mosses.

In this study were used contactors (Erlenmeyer flasks) with 100 ml capacity; each one containing 50 ml of metal solution of a known initial concentration into which a pre-weighted amount of dry biomass was added. The suspensions were mildly stirred for 300 min on a rotary shaking machine at 140 U min^{-1}. Other operating conditions were: initial metal ion concentration = 10 mg L^{-1}, moss dosage = 2 g L^{-1} and temperature = 20ºC. Biosorption kinetic experiments were also performed at a constant temperature of 20ºC, metal concentrations of 10 and 100 mg l^{-1}, and different amounts of biosorbent. In all cases, 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. Samples (one flask) were taken out at pre-determined time intervals (3 – 300 min). Then, the solution was filtered (0.45 mm Gelman Sciences sterilized membranes) and the metal concentration in aqueous solution was measured by atomic absorption spectrophotometry.

2.5 Analytical methods

Lead concentrations in the supernatants were determined using an atomic absorption spectrophotometry (AAS, Varian Spectra, model S220), by acetylene-air flame. The working parameters of AAS were 5.0 mA and 217.0 nm, respectively, to current and wavelength, giving a detection limit of 1 ppm. The instrument response was checked at predetermined times with Pb(II) solution standards. Prior to analysis the samples were acidified with concentrated nitric acid, and stored in acid-washed plastic vessels.

3. Theoretical background

3.1 Equilibrium isotherms

Two of the most commonly used isotherm theories were adopted in this experimental study, Langmuir and Freundlich equilibrium isotherms.

The Langmuir model assumes the adsorbent surface to be homogeneous and the biosorption energies for each biosorption site to be equivalent. Metal ions sequestration occurs without mutual interactions between the ions adsorbed at the material surface. Langmuir equation can be represented by the following Eq. (1):

$$q_e = Q_{\max} b C_e / (1 + bC_e) \qquad (1)$$

where C_e (mg L^{-1}) is the residual metal concentration in solution, q_e (mg g^{-1}) is the amount of a metal adsorbed, $Q_{\max}$ (mg g^{-1}) is the amount of metal at complete monolayer coverage, and b (L mg^{-1}) is a coefficient that relates the heat of biosorption. The initial sorption isotherm curve slope ($Q_{\max} b$) indicates the biosorbent affinity for the heavy metal ion.

Fairly to the Freundlich model, this is based on an exponential distribution of biosorption sites and energies; its possible the occurrence of interactions between sorbed ions. Eq. 2 shows the form of Freundlich equation:

$$q_e = K_F C_e^n \qquad (2)$$

where K_F (mg^{1-n} g^{-1} L^n) represents the biosorption capacity when metal equilibrium concentration equals to 1, and n represents de degree of biosorption dependence with equilibrium concentration.

3.2 Biosorption kinetic models

Kinetic models are a significant tool to know the controlling mechanism of biosorption process; these can be divided into two main types: reaction and diffusion-based models.

These equations include the pseudo-first order (Lagergren) equation [22], pseudo-second order equation [23], Elovich equation [24] and the intraparticle diffusion model [25]. The kinetic models above-mentioned are only concerned with the effect of the observable parameters on the biosorption overall rate.

Pseudo-first order equation:

$$q_t = q_e \left[1 - \exp(-k_1 t)\right] \qquad (3)$$

where q_t, q_e, k_1 and t are the concentration of metal ion sorbed at time t (mg g^{-1}), concentration at equilibrium (mg g^{-1}), Lagergren rate constant (min^{-1}), and time of reaction (min).

Pseudo-second order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

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

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

$$r_s(i) = \left.\frac{dq_t}{dt}\right|_{t=0} = k_2 q_e^2 \tag{5}$$

Elovich equation:

$$q_t = \frac{1}{b}\ln(1 + abt) \tag{6}$$

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

Intraparticle diffusion model:

When the diffusion, internal surface and pore diffusion, of metal ions inside the biosorbent is the rate-limiting step, the biosorption data can be fit by the below equation.

$$q_t = k_{dp} t^{1/2} \tag{7}$$

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

The lead uptake at each moment was calculated from the equation

$$q_t = (C_0 - C_t)/(m_{ads}/V) \tag{8}$$

where V (L) is the volume of lead solution, C_0 (mg L^{-1}) is the initial lead concentration, C_t (mg L^{-1}) is the concentration of lead in solution at a given time, and m_{ads} (g) is the mass of biosorbent (dry weight).

4. Results and discussion

The aquatic mosses biosorption capacity is described by one biosorption isotherm characterized for certain parameters; these reveal the biosorbent surface properties and the affinity to lead ions. The isotherm data analysis is important to develop a mathematical equation which suitably represents de results and could be used to design sorption systems. In order to investigate the biosorption isotherm were analysed de Langmuir and Freundlich equations. The models were fitted to the experimental data using a nonlinear regression commercial software *Fig P* of Biosoft (minimizing the sum of the squared deviations between experimental and predicted values).

4.1 Effect of pH on lead removal

The results show in Fig. 1 illustrate the pH effect on the removal of Pb(II). For pH values less than 3.0 the amount of lead removed are insignificant; this result show one possibility to regenerate the biomass using acidified water. In the pH range 4.0 to 6.0 the Pb(II) removed remains practically constant and were recorded values near of 97-99%.

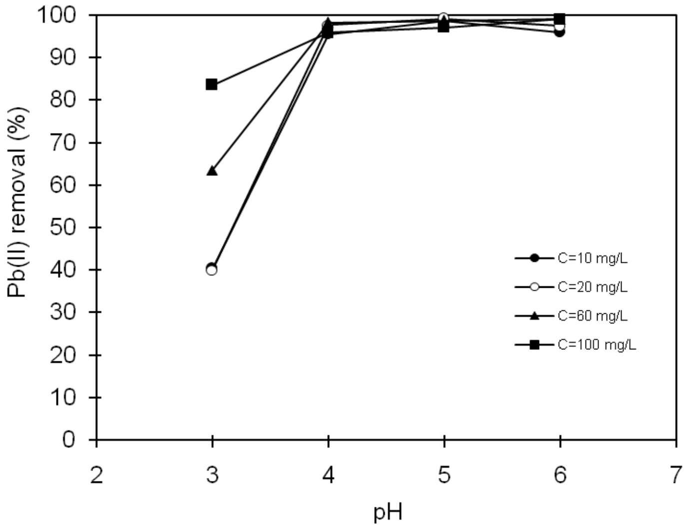

Fig. 1. Removal of Pb(II) from aqueous solutions by aquatic moss *Fontinalis antipyretica* in the pH range 3 - 6.

This trend was observed by Low *et al*. [26], in the sorption lead from aqueous solutions by spent grain. The results obtained show that pH is an important parameter in the mechanism of heavy metal biosorption. When the pH increased, the groups in the moss (phosphate, carboxyl and amino groups) were loaded negatively with subsequent attraction of cations and sorption onto the cell surface. On the other hand,at pH ≥ 7 insoluble metal hydroxides start precipitating from the solution. In this way, in the follow work, experiments were carried out with initial pH 5.0±0.2.

4.2 *Equilibrium studies*

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

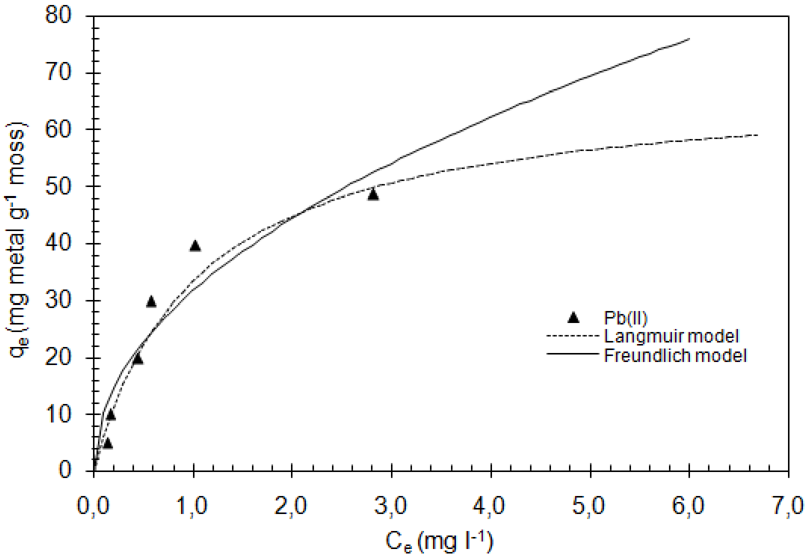

Fig. 2. Biosorption isotherms for Pb(II) by aquatic moss *Fontinalis antipyretica* (pH = 5.0±0.2; X_{ads} = 2 g l^{-1}; T = 20ºC; water hardness = 101.0 mg $CaCO_3$ l^{-1}).

The biosorption parameters obtained from the isotherms at specify experimental conditions are show in Table 1.

Table 1. Langmuir and Freundlich isotherm parameters (average ± standard error) for lead sorption onto *Fontinalis antipyretica* at pH optimum.

Langmuir model				Freundlich model			
Q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	S^2	K_F (mg^{1-n} g^{-1} L^n)	n	R^2	S^2
68 ± 12	1.0 ± 0.4	0.993	3.14	30 ± 5	1.9 ± 0,4	0.958	17.2

The regression coefficients (R^2) present in Table 1 suggest that Langmuir isotherm describe better than Freundlich isotherm the biosorption of Pb(II) by mosses. However, the most effective mean to compare the significant improvements introduced by a correlative model against another is to use a *Test-F* [27]. F_{cal} is defined as the quotient of the variances of the two models in comparison $(= S^2_{Freundlich} / S^2_{Langmuir})$, where S^2 is the model variance. In the denominator is placed the variance of the model expected to produce the better fitting. From the S^2 in Table 1 was obtained a value equal 5.48 to F_{cal} (α=95%; f.d.$_{N:D}$=5:5, $F_{\alpha-1} = 4.28$). Since $F_{cal} > 1$ and $F_{cal} > F_{\alpha-1}$ the Langmuir model fit better the experimental data than Freundlich model, and the improvement attained is statically significant.

The calculated maximum biosorption capacity gave a value of 68 mg Pb(II) g^{-1} (0.33 mmol g^{-1}). Our biosorbent exhibited a value of $Q_{\max}$ compare favourably with those obtained using others low-cost materials (Table 2).

Table 2. Maximum adsorption capacities for Pb(II) of some low-cost adsorbents.

Adsorbent	Max. adsorption capacity (mg g^{-1})	Reference
Aquatic mosses (Fontinalis antipyretica)	68.0	Present study
Aquatic macrophyte (*Ceratophyllum demersum*)	44.8	28
Sawdust of *Pinus sylvestris*	22.2	29
Granulated agar extraction algal waste	20.5	5
Natural sorbent (quartz, aluminosilicates,…)	66.2	9
Cocoa shells	6.23	30

Such as referred previously in theoretical approach, the initial sorption isotherm curve slope ($Q_{\max} b$) it's one of the most important characteristic of the sorption isotherm. Fig. 2 shows an unexpected initial slope (= 68 L g^{-1}), which indicates a biomaterial with a high affinity to lead ions at low concentration. An important property when it's obligatory to achieve the low levels established by water standards. The affinity of this material to lead it's more enhanced when compared with the initial slope obtained by a natural sorbent [9] (41.2 L g^{-1}) or an algal waste [5] (3.1 L g^{-1}). Given the high biosorption capacity showed by aquatic mosses, these can also be used in equipments to recovery valuable metals.

The removal capacity recorded is sufficiently interesting, so the use of moss is promising as biosorvent for the removal and recovery of metal ions of industrial effluents.

4.2 Kinetic studies

Parameters reported to aqueous medium, biosorbent characteristics and the metal ion chosen certainly influence the mechanism of metal removal by mosses. To design a batch sorption system is vital to know the biosorption rate. In this way, it is important to establish the time dependence of such system under various process conditions.
The rate of lead ion biosorption onto aquatic mosses was determined to initial metal concentrations 10 and 100 mg L^{-1}. Kinetic data of Pb(II) were analyzed using pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion equations (Eqs. 3-6).
Figure 3 (a-c) shows a plot of experimental results for biosorption of Pb(II) on mosses as a function of time, and the curves predicted by kinetic models. The corresponding model parameters are presented in Table 3.

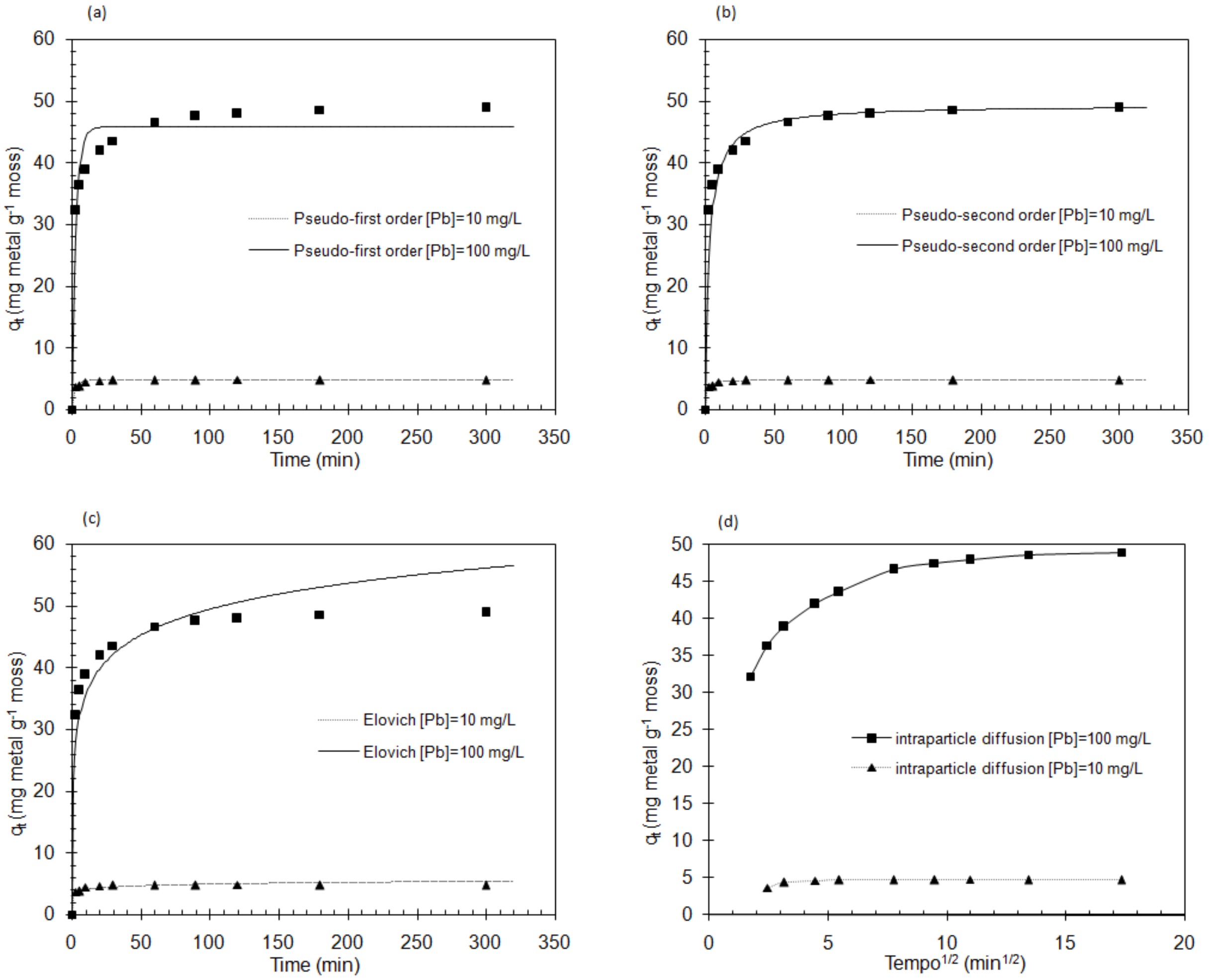

Fig. 3. Kinetic modelling of Pb(II) biosorption by aquatic mosses: (a) pseudo-first order model; (b) pseudo-second order model; (c) Elovich equation; (d) intraparticle diffusion equation.

The curves in Fig. 3 (a-c) are characterized by a strong increase in sorption capacity by biosorbent during the first 10 minutes and gradually decrease until saturation. The sorption process was fast and the equilibrium attained in less than 2 h; so, the biosorption of lead involve purely weak intermolecular forces between the mosses and the metal in aqueous solution. Similar equilibrium times were obtained for sorption of lead by *Sphagnum* moss [31] and sorption of cadmium and lead by spent grain [26].

To an increase in the initial lead concentration from 10 to 100 mg L^{-1}, returned an increase of the same order on the biosorbent capacity (Table 3).

Table 3. Kinetic models parameters for the biosorption of lead(II) by *Fontinalis antipyretica*.

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

From the models employed in this study (Eqs. 3, 4, 6) there is one, the pseudo-second order model, that shows a good compliance on fitting the experimental data (R^2=1.00). A *Test-F* allows inferring that the pseudo-second order model, not only fit better the experimental data than the Lagergren model, but for 95% average probability, significant difference exists between the two models in the concentration range studied (α=95%; f.d.$_{N:D}$=10:10, $F_{cal(P1st/P2nd)} = 3.05$, $F_{\alpha-1} = 2.98$).

The plot in Fig. 3d doesn't show a linear relation for the system mosses-Pb(II) during all the process. According Weber and Morris [25], the intraparticle diffusion is involved on the biosorption process, but it isn't the limitative stage.

The initial sorption rate ($r_s(i)$) increased for 5.34 to 16.5 mg g^{-1} min^{-1} with an increase in initial lead concentration, 10 to 100 mg L^{-1}. This behaviour is concordant with the removal of copper ions from aqueous solution by tree fern [32] and lead biosorption by granulated agar extraction algal waste [5]. However, the opposite was observed by Ho and McKay on the sorption of copper, nickel and lead onto *Sphagnum* moss peat [31].

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

5. Conclusions

The aquatic moss *Fontinalis antipyretica*, containing various functional groups in the surface or inside the porous material structure, is an effective biosorbent for the removal of Pb(II) ions of industrial effluents, and to recovery valuable metals.

The equilibrium data was fitted better for Langmuir isotherm than to Freundlich isotherm and the improvement attained are statically significant. The maximum removal capacity was determined from the Langmuir equation and found to be 68 ± 12 mg g^{-1}. The aquatic mosses exhibited a high affinity to lead ions at low concentration. An important property when it's obligatory to achieve the low levels established by water standards.

The kinetics of lead ion biosorption on aquatic mosses supporting the proposal that chemisorption is the rate-limiting step and that the mechanism follows a pseudo-second order reaction model.

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