BIOSORPTION OF LEAD FROM SIMULATED INDUSTRIAL WASTEWATERS BY AQUATIC BRYOPHYTES

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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. Lead has been recognized as a potentially dangerous pollutant in the same class as mercury, arsenic and vanadium; it damages the kidney, liver and reproductive system, brain functions and basic cellular processes .

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 .

Thus, the removal of toxic metal contaminants from waters is an important environmental issue. 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 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 .

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, amide, 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), pine bark, aquatic plants, peat moss, alum and activated sludge, fungi and bacteria and algae.

The bryophytes are 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.

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

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 biosorbent

The aquatic moss *Fontinalis antipyretica* was taken from the Selho River, at Aldão, a tributary of the Ave River in Northern Portugal. The samples were rinsed in the harvest place 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 sec. It was selected the fraction with particle size [150 – 300] μm.

Biosorption isotherm experiments

A 100.0 (±0.1) g of ground moss was weighted and transfer to 100 ml glass bottles. Lead solutions of concentrations between 10 and 100 mg L^{-1} were prepared. Moss suspensions were shaken for 24 h at constant room temperature (20±1ºC) using a rotary shaker (P-Selecta Rotabit). 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 membranes, and the supernatant was analysed for the remaining Pb^{2+}.

Kinetic experiments

In batch experiments were studied the influence of pH and initial metal concentration 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: $[Pb]_0$ = 10 and 100 mg l^{-1}, $X_{moss\ dosage}$ = 2 g L^{-1} and T = 20ºC. 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 were taken out at pre-determined time intervals (3 – 300 min). Then, the solution was filtered (0.45 mm membranes) and the metal concentration in aqueous solution was measured by atomic absorption spectrophotometry.

Analytical methods

Lead concentrations 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.

3. THEORETICAL BACKGROUND

Equilibrium isotherms

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

Langmuir equation (assumes the adsorbent surface to be homogeneous and the biosorption energies for each biosorption site to be equivalent):

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

Freundlich equation (based on an exponential distribution of biosorption sites and energies; its possible the occurrence of interactions between sorbed ions):

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

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.

Pseudo-first order equation:

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

Pseudo-second order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

Elovich equation:

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

Intraparticle diffusion model:

$$q_t = k_{dp} t^{1/2} \qquad (6)$$

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.

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%.

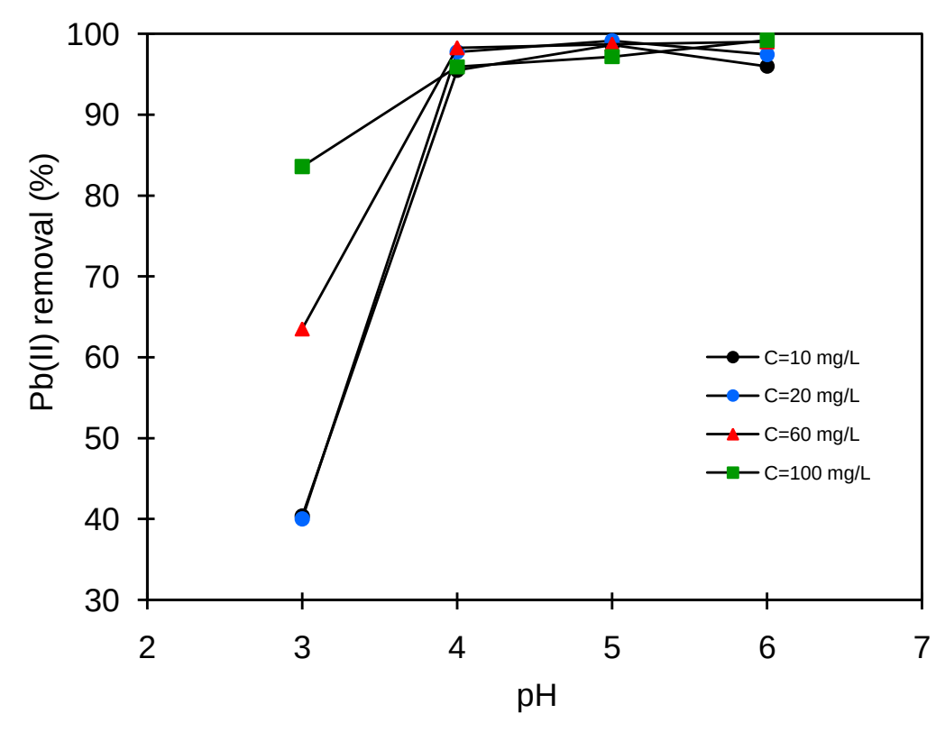

Fig. 1. Removal of Pb(II) from aqueous solutions by aquatic moss *Fontinalis antipyretica* in the pH range 3 - 6.

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.

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.

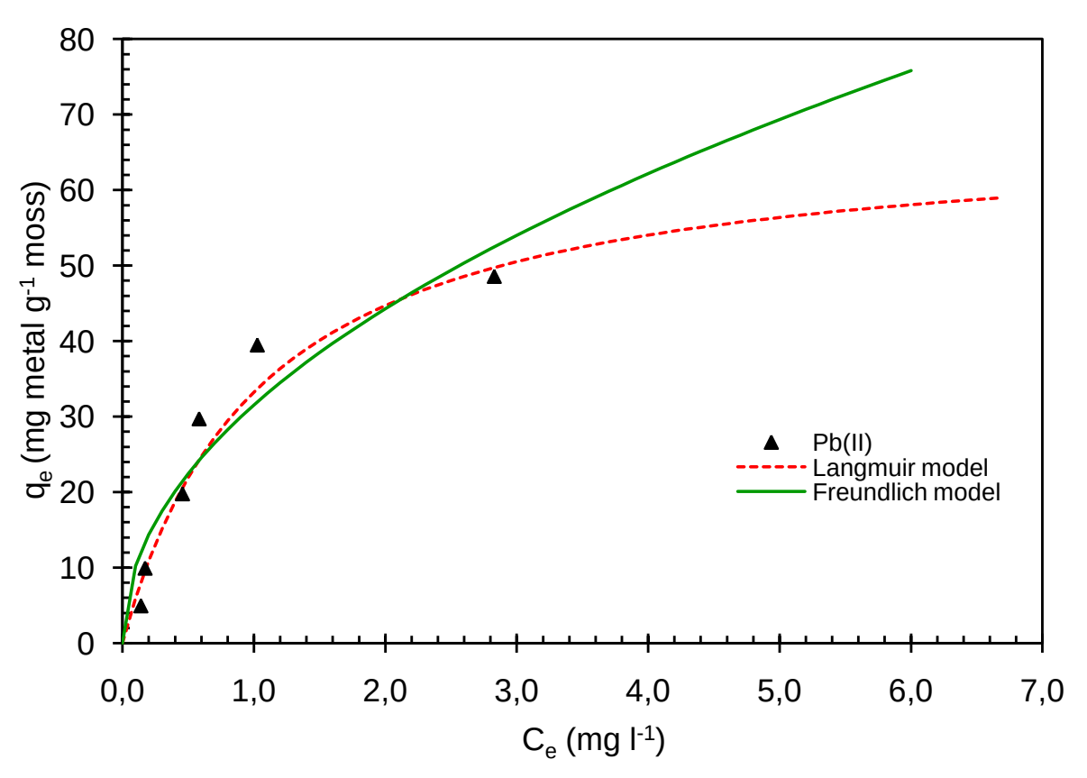

Fig. 2. Biosorption isotherms for Pb(II) by aquatic moss *Fontinalis antipyretica* (pH = 5.0±0.2; X_{ads} = 2 g L^{-1}; T = 20ºC; water hardness = 101.0 mg $CaCO_3$ L^{-1}).

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.

The most effective mean to compare the significant improvements introduced by a correlative model against another is to use a *Test-F*. From the S^2 in Table 1 was obtained F_{cal} = 5.48 (α=95%; $f.d._{N:D}$=5:5, $F_{\alpha-1}$ = 4.28). Since F_{cal} > 1.0 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}. 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

Fig. 2 shows an unexpected initial slope ($Q_{max}.b$ = 68 L g^{-1}), which indicates a biomaterial with a high affinity to lead ions at low concentration.

Kinetic studies

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.

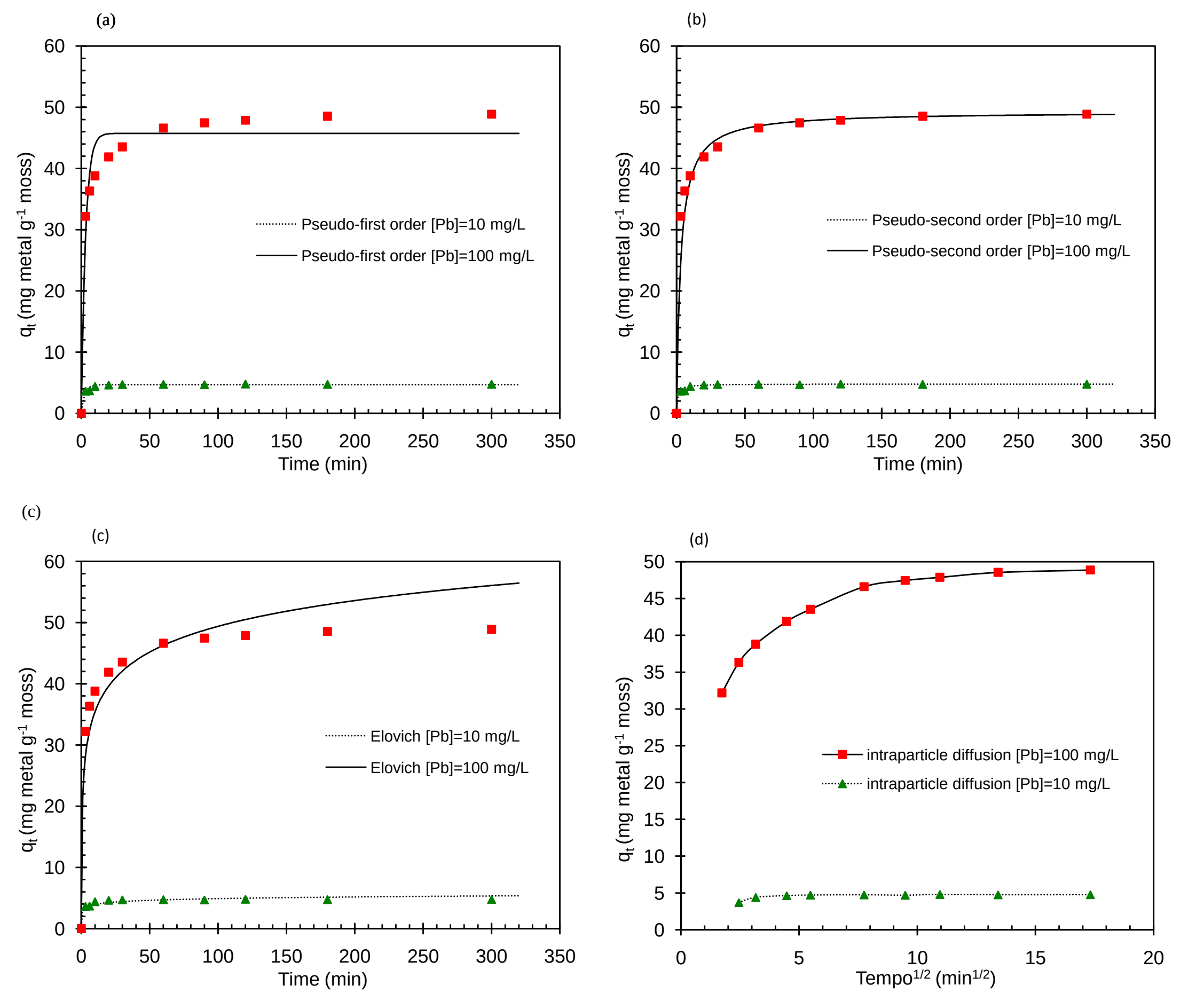

Fig. 3. Kinetic modelling of Pb(II) biosorption by aquatic mosses: (a) pseudo-first order model; (b) pseudo-second order model; (c) Elovich equation; (d) intraparticle diffusion equation.

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

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

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.

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.