

# IWA Conferences

## Application of aquatic mosses to decontaminate industrial effluents

--Manuscript Draft--

<b>Manuscript Number:</b>	
<b>Full Title:</b>	Application of aquatic mosses to decontaminate industrial effluents
<b>Article Type:</b>	Outline Paper for Oral Presentation
<b>Keywords:</b>	biosorption; aquatic moss; modelling; cadmium; lead.
<b>Corresponding Author:</b>	Ramiro Espinheira Martins, Ph.D. Porto, PORTUGAL
<b>Corresponding Author Secondary Information:</b>	
<b>Corresponding Author's Institution:</b>	
<b>Corresponding Author's Secondary Institution:</b>	
<b>First Author:</b>	Ramiro Espinheira Martins, Ph.D.
<b>First Author Secondary Information:</b>	
<b>All Authors:</b>	Ramiro Espinheira Martins, Ph.D. Rui Boaventura, PhD
<b>All Authors Secondary Information:</b>	
<b>Manuscript Region of Origin:</b>	PORTUGAL
<b>Abstract:</b>	<p>As 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 <i>Fontinalis antipyretica</i> for removing cadmium and lead from simulated wastewaters has been evaluated. Five kinetic models (first-order, pseudo-first-order, Elovich, 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 using a sorbent dose of 2 g l<sup>-1</sup>. 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 <i>Fontinalis antipyretica</i> 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) is higher than 78%. The pseudo-second order biosorption kinetics provided the better correlation with the experimental data .</p>

## Application of aquatic mosses to decontaminate industrial effluents

RJE Martins\*, RAR Boaventura\*\*

\* Dep. of Chemical and Biological Technology, Superior School of Technology, Polytechnic Institute of Bragança, Campus de Santa Apolónia, 5301-857 Bragança, Portugal, rmartins@ipb.pt

\*\* LSRE-Laboratory of Separation and Reaction Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, bventura@fe.up.pt

**Abstract:** As 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, 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 using a sorbent dose of 2 g l<sup>-1</sup>. 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) is higher than 78%. The pseudo-second order biosorption kinetics provided the better correlation with the experimental data ( $R^2 \geq 0.999$ ).

**Keywords:** P

### Introduction

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 to many millions of children and adults. Lead has been found to be keen toxic to human beings when present in high amount. Adverse health effects due to cadmium are too well documented and have been reported to cause lung insufficiency, cancer, renal disturbances, bone lesions and hypertension in humans (Lee and White, 2007). So, Cd(II) and Pb(II) are included in the prior group of the metals from 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 metals 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.

As stated in literature, 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 other way, bryophytes also possess no cuticle that increases the direct access of soluble metals to the living cytoplasm in photosynthetic tissues. The combination of these factors and the fact they are

available in most rivers in the north of Portugal, makes the aquatic mosses a potential biosorbent for heavy metals removal from polluted waters.

## Materials and Methods

The aquatic moss *Fontinalis antipyretica* has been picked out in the Selho River, at Aldão, a tributary of the Ave River in Northern Portugal. The samples were firstly 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 µm - 300 µm was selected for the study.

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.

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<sup>-1</sup>; moss dosage, 2 g l<sup>-1</sup>; 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 using the Atomic Absorption technique using acetylene-air flame (AAS, VARIAN SPECTRA, model S220). Cadmium and lead standard solutions (1000 µg ml<sup>-1</sup>) were obtained from Merck.

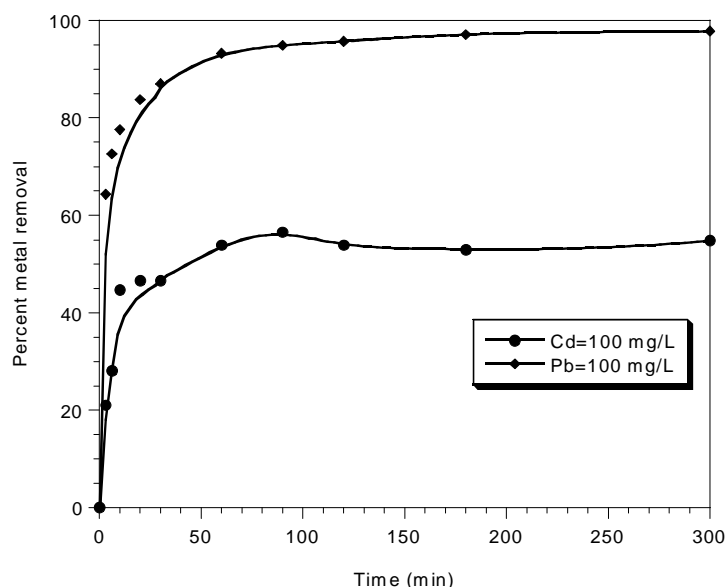
## Results and Conclusions

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 showed in this paper.

From Cd<sup>2+</sup> and Pb<sup>2+</sup> sorption studies, it was evident that pH values equal or higher 4.0 led to higher metal uptake for both metals. At pH 3.0, some metal uptake (20% for Cd and 40% for Pb); according Murphy et al. (2007) this may be due to the presence of sulphonate groups that are dissociated around this pH value. This relation of dependence between pH solution and biosorption, suggest that aquatic mosses can be developed as multi-use sorption material. As observed, metal removal is greatly reduced at lower pH, which 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.

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 cadmium and lead sorption dependence on the contact time are plotted in Fig 1. 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.



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

At the initial stage was observed a faster removal of ions due to a driving force higher and higher affinity active sites are first occupied. After that, metal concentration decreases and remaining active sites with lower affinities, which are occupied slowly. The sorption process was fast and the equilibrium attained in less than 2 h. The short time required to attain the equilibrium is a good indicator of the moss potential for a fast removal of metal ions in solution, and it will allow using smaller reactor volumes.

#### *Effect of the initial metal concentration*

For 300 min of contact time, 50 ml of metal solution with concentration in the range  $10 - 100 \text{ mg l}^{-1}$  was shaken with 100 mg biosorbent at constant temperature ( $20^\circ\text{C}$ ) and  $\text{pH}$  (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 equation  $C_e = C_0 \exp(-kt)$  for  $t \leq 300 \text{ min}$  ( $C_e =$  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 interface liquid/solid, and leads to high metal removal. The equilibrium lead uptake values at different initial metal ion concentrations are given in Table 1 and is clear that practically all lead ( $\approx 98\%$ ) is bound to the biosorbent, regardless the initial concentration in solution. The affinity of the biosorbent to 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. So, the cleansing yield can be improved by diluting the effluent containing high metal ion concentrations.

**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 <sub>0</sub> mg l <sup>-1</sup>	Cadmium			Lead		
	q <sub>e</sub> mmol g <sup>-1</sup>	Uptake %	k x 10 <sup>3</sup> min <sup>-1</sup>	q <sub>e</sub> mmol g <sup>-1</sup>	Uptake %	k x 10 <sup>3</sup> min <sup>-1</sup>
10	0.037	83.8	6.1	0.023	96.7	11.4
20	0.070	78.9	5.2	0.047	97.3	12.0
40	0.131	73.4	4.4	0.096	98.9	14.9
60	0.159	59.8	3.0	0.143	99.0	15.5
80	0.202	56.7	2.8	0.191	98.7	14.5
100	0.211	47.4	2.2	0.235	97.2	11.9

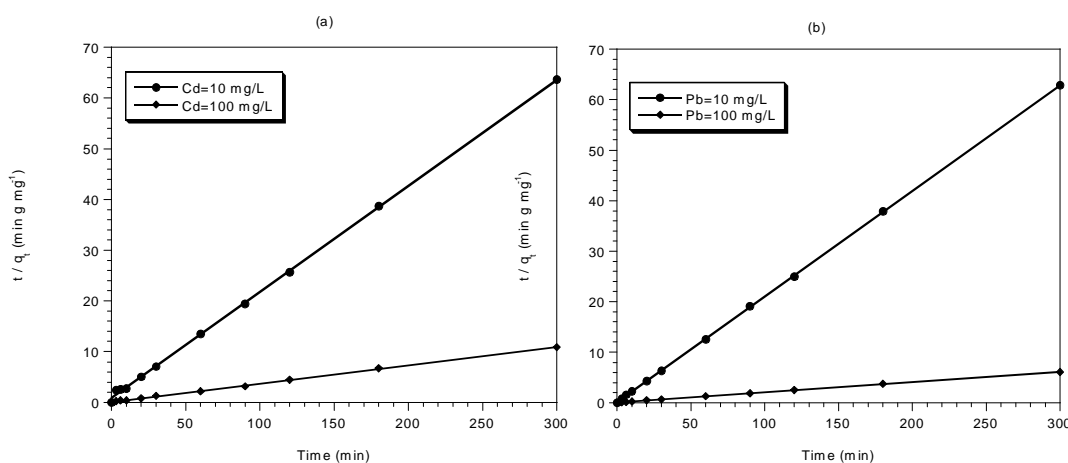
The lead uptake rate is almost independent on the initial concentration and averages 13.4x10<sup>-3</sup> min<sup>-1</sup>. On the other hand, the biosorption of cadmium is slower and the uptake rate decreases by about one third as the initial concentration increases from 10 to 100 mg l<sup>-1</sup>. 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 particles surface. However, lead uptake is insensitive to this fact due to its high electronegativity, which increases the affinity to the different functional groups.

### Biosorption kinetic models

Five kinetic models: first-order, pseudo-first-order, Elovich, Ritchie second-order and pseudo-second-order were fitted to the experimental data and compared (only show data and plot for the pseudo-second-order model).

$$\text{The pseudo-second order equation manipulated } \left( \frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \right)$$

Linear plots of  $t/q_t$  versus  $t$  are shown in Fig. 2 and  $k$  and  $q_e$  values, obtained from the slopes and intercepts, are presented in Table 2.



**Figure 2** Pseudo second-order sorption kinetics of (a) Cd(II) and (b) Pb(II).

The correlation coefficients (higher than 0.999) indicate a good compliance of the experimental data with the proposed pseudo-second order kinetic model.

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

Metal	C <sub>0</sub> mg l <sup>-1</sup>	q <sub>e</sub> mg g <sup>-1</sup> (mmol g <sup>-1</sup> )	k g mg <sup>-1</sup> min <sup>-1</sup>	h g mg <sup>-1</sup> min <sup>-1</sup>	S <sup>2</sup>	R <sup>2</sup>
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

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

*Model performances*; a brief and simplistic analysis, comparing the regression coefficients ( $R^2$ ) for the different models of each metal, allows concluded, although generically all values are high (>0.90), the higher correspond to the pseudo-second order model. So, when the models fit the data with sensible values, the suitable procedure is to use an *F-test* to decide which model to accept. For a level of probability of 95% and 10 degrees of freedom for the numerator and for the denominator, 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<sup>-1</sup>), where the Lagergren model is better. However, the Lagergren model is not statistically more accurate than Ritchie model, a second order model ( $F_{cal} < 2.98$ ). The equilibrium sorption capacities predicted by the best model, for initial cadmium/lead concentrations of 10 and 100 mg l<sup>-1</sup>, are 0.041/0.023 mmol g<sup>-1</sup> and 0.246/0.238 mmol g<sup>-1</sup>, 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 binding active sites. It is perfectly reasonable that a divalent metal would bind to two carboxyl groups as showed by Schiewer and Wong (1999), in experiments with brown algae. However, it isn't 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.

## References

- Lee, J. S. and White, K. L. (2007), A review of health effects of cd. *American J. of Industrial Medicine*, **1**, 307-317.
- Volesky, B. (2001), Detoxification of metal-bearing effluents: Biosorption for the next century. *Hydrometallurgy*, **59**(2-3), 203-216.
- Ho, Y. S. and McKay, G. (2000), The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Wat. Res.*, **34**, 735-742.
- Murphy, V., Hughes, H and McLoughlin, P. (2007), Cu (II) binding by dried biomass of red, green and brown macroalgae. *Wat. Res.*, **41**, 731-740.
- Schiewer, S. and Wong, M. H. (1999), Metal Binding Stoichiometry Isotherm Choice in Biosorption. *Environ. Sci. Technol.*, **33**, 3821-3828