

# Simultaneous heavy metal removal mechanism by dead macrophytes

Patricia Miretzky, Andrea Saralegui, Alicia Fernández Cirelli \*

Centro de Estudios Transdisciplinarios del Agua, Facultad de Ciencias Veterinarias, Universidad de Buenos Aires, Chorroarín 280, (1427) Buenos Aires, Argentina

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## Abstract

The use of dead, dried aquatic plants, for water removal of metals derived from industrial activities as a simple biosorbent material has been increasing in the last years. The mechanism of simultaneous metal removal ( $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ ) by 3 macrophytes biomass (*Spirodela intermedia*, *Lemna minor* and *Pistia stratiotes*) was investigated. *L. minor* biomass presented the highest mean removal percentage and *P. stratiotes* the lowest for all metals tested.  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  were more efficiently removed by the three of them. The simultaneous metal sorption data were analysed according to Langmuir and Freundlich isotherms. Data fitted the Langmuir model only for Ni and Cd, but Freundlich isotherm for all metals tested, as it was expected. The  $K_F$  values showed that Pb was the metal more efficiently removed from water solution. The adsorption process for the three species studied followed first order kinetics. The mechanism involved in biosorption resulted ion exchange between monovalent metals as counter ions present in the macrophytes biomass and heavy metal ions and protons taken up from water. No significant differences were observed in the metal exchange amounts while using multi-metal or individual metal solutions.

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## 1. Introduction

Water contamination with heavy metals is a very important problem in the current world. Considerable attention has been paid to methods for metal removal from industrial wastewaters because they pose serious environmental problems and are dangerous to human health. A number of methods are available to remove toxic metals from water: ion exchange, reverse osmosis, precipitation, solvent extraction, membrane technolo-

gies, electrochemical treatment, sorption, etc. The latter is by far the most versatile and widely used, and activated carbon is the most commonly used sorbent. However, the use of activated carbon is expensive, so there has been considerable interest in the use of other sorbent materials, particularly biosorbents (Ng et al., 2003). A review of literature shows that heavy metals can be removed by inexpensive biological materials as algae, fungi and bacteria (Volesky and Holan, 1995; Matheickal et al., 1999; Vasudevan et al., 2001; Ho et al., 2002; Kaewsarn, 2002).

Phytotechnologies, with an increasing development during the last two decades, involve the use of plants for metal removal. Aquatic macrophytes have been used

\* Corresponding author. Tel.: +54 11 4525 8484; fax: +54 11 4524 8490.

E-mail address: [afcirelli@fvet.uba.ar](mailto:afcirelli@fvet.uba.ar) (A. Fernández Cirelli).

during the last two decades competing with other secondary treatments, being the principal mechanism for metal uptake sorption through roots (Denny and Wilkins, 1987). The aquatic floating macrophytes *Pistia stratiotes*, and *Lemna minor* present a high growth rate and have been used for the removal of heavy metals from water column (Nasu and Kugimoto, 1981; Sridahar, 1986; Bassi et al., 1990; Jain et al., 1990; Taraldzen and Norberg-King, 1990; Wang, 1990; Wahaab et al., 1995; Maine et al., 2001; Cardwell et al., 2002; Dirilgen and Dogan, 2002; Klumpp et al., 2002; Axtell et al., 2003).

In previous studies in our laboratory, *P. stratiotes*, *Spirodela intermedia* and *L. minor*, autochthonous Pampean plain floating macrophytes (Fernández Cirelli and Miretzky, 2004) showed a high potential for removing different metals from the aquatic environment in laboratory experiences (Miretzky et al., 2004).

However, it has been demonstrated that the incorporation of heavy metals produces phytotoxic effects on plants resulting in inhibition of chlorophyll synthesis and biomass production that leads to death (Satyakala and Jamil, 1992; Delgado et al., 1993). Moreover, the use of phytotechnologies as secondary wastewater treatments implies the disposal of high volumes of contaminated plants.

The use of dead, dried aquatic plants, for metal removal as a simple biosorbent material has advantages in its high efficiency in detoxifying dilute effluents, minimization of the volume of chemical and / or biological sludge to be disposed of, no nutrient requirements, low cost, conservation, transport, handling. Also, it is possible to recover heavy metals, as once the metal binding reaches saturation, the biomass can be regenerated with acid and/or hydroxide solutions, that discharge small volumes of concentrated heavy metal (Veglio and Beolchini, 1997; Schneider and Rubio, 1999; Schneider et al., 2001; Elifantz and Tel-Or, 2002).

The aim of the present study is to investigate the mechanism of the simultaneous removal of metals derived from industrial activities (electroplating, metal finishing, textile, storage batteries, lead smelting, mining, plating, ceramic and glass industries) by dead freshwater macrophytes. These studies may be useful for low cost industrial wastewater treatment, where the simultaneous removal of several heavy metals is needed.

## 2. Materials and methods

### 2.1. Reagents

All chemicals used were of analytical-reagent grade. Milli-Q quality water (Millipore, USA) was used throughout. Cu, Pb, Cd, Ni, Zn and Mn solutions ( $10 \text{ mg l}^{-1}$ ) were prepared by dilution of  $100 \text{ mg l}^{-1}$  PE Pure Standard (Perkin–Elmer) and from Tritisol solu-

tions (Merck). Multi-elemental (Cu, Pb, Cd, Ni, Zn, Mn) solutions of different concentrations ( $0.2$ ,  $0.5$ ,  $1.0$ ,  $2.0$ ,  $4.0$ ,  $10.0$  and  $20.0 \text{ mg l}^{-1}$  on each metal) were prepared from the same stocks mentioned before. All dilutions of stock solutions were made using Milli-Q water.

Nitric acid ( $\text{HNO}_3$ ) solution ( $0.01 \text{ mol l}^{-1}$ ), prepared by dilution of concentrated acid (Mallinckrodt) was used to adjust initial pH.

All the glassware used for dilution, storage and experiments was cleaned with Extran detergent, thoroughly rinsed with tap water, soaked overnight in a 20%  $\text{HNO}_3$  solution and finally rinsed with Milli-Q water before use.

### 2.2. Biosorbents

Floating macrophytes from The Salado River lower drainage basin, Chaco-Pampa plain, Argentina ( $34^{\circ}20'$  to  $35^{\circ}40'$  S and  $57^{\circ}40'$  to  $61^{\circ}10'$ ) were collected, *P. stratiotes* from Lake Chascomús, *S. intermedia* from Vitel stream and *L. minor* from Lake Vitel. Macrophytes were washed with Milli-Q water to eliminate the remains of lake sediments and particulate matter, dried at  $60^{\circ}\text{C}$ , then pulverized in a Moulinex mill and ground to pass through a 2 mm sieve.

### 2.3. Experimental design

Sorption studies were performed in a first stage for individual metal removal. Dried and pulverized macrophytes *S. intermedia* ( $0.200 \text{ g}$ ) were suspended in  $50.0 \text{ ml}$  of  $\text{Cu}^{2+}$   $10.0 \text{ mg l}^{-1}$  solution during 1.30 h in a rotary shaker at 140 rpm. Preliminary experiments of adsorption kinetics indicated that a period of 1.30 h was sufficient to attain equilibrium. At the end of the agitation period, samples were filtered using  $0.45 \mu\text{m}$  acetate cellulose membrane (Micro Separations Inc., MSI). The experience was repeated for  $10.0 \text{ mg l}^{-1}$   $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  individual solutions. The initial and final concentration of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  in the water solution was determined and also the initial and final pH. Blanks were performed under the same conditions but in the absence of metals.

Adsorption studies were, in a second stage, performed for simultaneous metal removal. Dead macrophytes (*P. stratiotes*, *S. intermedia* and *L. minor*) ( $0.200 \text{ g}$ ) were suspended in  $50.0 \text{ ml}$  of multi-metal solution of  $10.0 \text{ mg l}^{-1}$  of each  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  during 1.30 h in a rotary shaker at 140 rpm and the experience was carried out as before. The initial and final concentration of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  in the water solution was determined and also the initial and final pH. Samples were withdrawn at the end of the experience, filtered and analysed for residual metals. The same experience was repeated for  $20.0 \text{ mg l}^{-1}$  multi-metal solution.

All the results obtained for metal adsorption experiments were corrected from blanks performed under the same conditions but in the absence of biosorbents species.

Kinetic studies were carried out by suspending dead *S. intermedia*, *L. minor* and *P. stratiotes* ( $\approx 0.200$  g) in 50.0 ml of  $0.5 \text{ mg l}^{-1}$  multi-metal solution of each  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  for 0, 0.25, 0.5, 1.0, 2.0, 5.0, 7.0, and 21.0 h. The experience was carried out as explained before. The same experience was repeated for 1.0, 2.0, 4.0, 10.0 and  $20.0 \text{ mg l}^{-1}$  initial multi-metal solution. All the results obtained for kinetics experiments were corrected from blanks performed under the same conditions but in the absence of biosorbents species.

The ionic exchange experiences were first performed with individual metal solutions. Dead macrophytes (*P. stratiotes*, *S. intermedia* and *L. minor*) (0.200 g) were suspended in 50.0 ml of  $10.0 \text{ mg l}^{-1}$   $\text{Cu}^{2+}$  solution, during 1.30 h in a rotary shaker at 140 rpm in the same way as mentioned before. The initial and final concentration of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{H}^+$  in the water solution was determined. The ions  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  were also determined because their concentration in aquatic environment was high (Lake Chascomús 0.065 and  $2.84 \text{ mg l}^{-1}$  respectively) and macrophytes had already assimilated it previous to the sampling. The same experience was carried out for  $10.0 \text{ mg l}^{-1}$   $\text{Pb}^{2+}$ ,  $10.0 \text{ mg l}^{-1}$   $\text{Cd}^{2+}$  solution,  $10.0 \text{ mg l}^{-1}$   $\text{Ni}^{2+}$  and  $10.0 \text{ mg l}^{-1}$   $\text{Zn}^{2+}$  solutions.

In a second step, ionic exchange experiences were performed with multi-metal solutions. Dead macrophytes

(*P. stratiotes*, *S. intermedia* and *L. minor*) (0.200 g) were suspended in 50.0 ml of  $10.0 \text{ mg l}^{-1}$  multi-metal solution of each  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ , during 1.30 h in a rotary shaker at 140 rpm in the same way as mentioned before. The initial and final concentration of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{H}^+$  in the water solution was determined. Blanks were carried out under the same conditions but in the absence of metals. The experience was repeated with  $20.0 \text{ mg l}^{-1}$  multi-metal solution. All the results obtained for ionic exchange experiments were corrected from blanks performed under the same conditions but in the absence of biosorbents species.

All experiments were carried out using Pyrex vessels and made in duplicate.

#### 2.4. Instrumental

Metal concentration was determined by ICP-emission (Perkin–Elmer, Optima 2000) according to norms (APHA, 1993). All determinations were performed in triplicate being the relative error  $< 1.0\%$  for all of them.

### 3. Results and discussion

The metal sorption capacity of the three different macrophytes biomass was studied. The  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  amount adsorbed by dead *S. intermedia*, *L. minor* and *P. stratiotes* in contact with 10 and  $20 \text{ mg l}^{-1}$  multi-metal solutions is shown in Table 1. In all cases, the dead macrophytes final metal concentration

Table 1  
Dead macrophytes sorption results (10 and  $20 \text{ mg l}^{-1}$  Cu, Pb, Cd, Ni and Zn solutions; nd: under detection limit)

	Initial concentration $\text{mg g}^{-1}$	Final concentration ( $10 \text{ mg l}^{-1}$ ) $\text{mg g}^{-1}$	Final concentration ( $20 \text{ mg l}^{-1}$ ) $\text{mg g}^{-1}$
<i>S. intermedia</i>			
Pb	$0.0009 \pm 0.0001$	$0.29 \pm 0.01$	$0.29 \pm 0.01$
Cd	nd	$1.89 \pm 0.09$	$2.84 \pm 0.08$
Ni	nd	$1.14 \pm 0.06$	$1.72 \pm 0.09$
Cu	$0.0073 \pm 0.0003$	$1.70 \pm 0.05$	$3.0 \pm 0.1$
Zn	$0.64 \pm 0.03$	$1.91 \pm 0.07$	$2.77 \pm 0.08$
<i>L. minor</i>			
Pb	$0.0009 \pm 0.0001$	$0.26 \pm 0.01$	$0.37 \pm 0.02$
Cd	nd	$1.87 \pm 0.09$	$2.99 \pm 0.09$
Ni	nd	$0.87 \pm 0.04$	$1.49 \pm 0.04$
Cu	$0.0076 \pm 0.0003$	$1.60 \pm 0.03$	$2.88 \pm 0.09$
Zn	$0.41 \pm 0.02$	$1.72 \pm 0.05$	$2.71 \pm 0.08$
<i>P. stratiotes</i>			
Pb	$0.0005 \pm 0.0001$	$0.31 \pm 0.02$	$0.34 \pm 0.02$
Cd	nd	$2.02 \pm 0.08$	$3.1 \pm 0.1$
Ni	nd	$0.44 \pm 0.02$	$0.82 \pm 0.03$
Cu	$0.0102 \pm 0.0004$	$0.84 \pm 0.04$	$1.52 \pm 0.07$
Zn	$0.029 \pm 0.001$	$1.13 \pm 0.05$	$1.90 \pm 0.07$

was significantly higher than the initial concentration, indicating that the biosorbents used were able to remove heavy metals from solution. All experiences were carried out at initial pH = 6.0 as it is well known that the uptakes of heavy-metal cations by most biomass types decreases from pH 6 to 2.5 (Kratochvil and Volesky, 1998).

Although the comparison of metal sorption performance based on percentage removal is only approximate, Table 2 shows the percentage metal removal from water by macrophytes biomass in experiences carried out with multi-metal solution (10 and 20 mg l<sup>-1</sup> on each metal) and with individual metal solutions (Cd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> 10 mg l<sup>-1</sup>). Data in Table 2 showed that the removal percentage is higher with the 10 mg l<sup>-1</sup> multi-metal solution than with the 20 mg l<sup>-1</sup>, suggesting saturation of the biomass exchange sites. *L. minor* biomass presented the highest mean removal percentage and *P. stratiotes* the lowest for all metals tested. Pb<sup>2+</sup> and Cd<sup>2+</sup> were the heavy metals more efficiently removed by the three macrophytes biomass. The metal sorption performance based on percentage removal was higher with individual metal solutions than with multi-metal solution.

### 3.1. Adsorption isotherms

Equilibrium isotherms are usually measured to determine the capacity of the biosorbent for metal ions. The

Table 2  
Percentage of metal removed from water

	Multi-metal 10 mg l <sup>-1</sup>	Multi-metal 20 mg l <sup>-1</sup>	Individual metal 10 mg l <sup>-1</sup>
<b>Cd</b>			
<i>S. intermedia</i>	91.29	74.16	95.66
<i>L. minor</i>	94.07	74.05	
<i>P. stratiotes</i>	83.24	66.89	
<b>Ni</b>			
<i>S. intermedia</i>	52.51	45.88	68.60
<i>L. minor</i>	69.03	55.26	
<i>P. stratiotes</i>	26.05	26.80	
<b>Cu</b>			
<i>S. intermedia</i>	76.04	68.49	78.40
<i>L. minor</i>	80.59	72.78	
<i>P. stratiotes</i>	32.77	30.24	
<b>Zn</b>			
<i>S. intermedia</i>	72.52	63.51	80.40
<i>L. minor</i>	80.39	63.42	
<i>P. stratiotes</i>	54.17	49.50	
<b>Pb</b>			
<i>S. intermedia</i>	97.65	97.73	97.00
<i>L. minor</i>	98.54	98.35	
<i>P. stratiotes</i>	94.48	94.17	

most common types are the Langmuir and Freundlich, although others are available: Redlich-Peterson, Toth, Tempkin isotherms (Ho et al., 2002). We must take in account that these models do not reflect any mechanisms of sorbate uptake, the equations are just capable of reflecting the experimental data.

#### 3.1.1. Langmuir isotherm

Langmuir is the most important model of monolayer adsorption, based in the assumption that there are a fixed number of adsorption sites, each site can hold only one adsorbate molecule (the adsorbed layer is one molecule in thickness), all sites are equivalent and there is no interaction between adsorbed molecules. The Langmuir equation can be expressed

$$C_e/Q_e = 1/K_L + a_L C_e/K_L \quad \text{or} \quad (1)$$

$$Q_e = a_L Q_{\max} C_e / (1 + a_L C_e) \quad (2)$$

where  $K_L$  (ml g<sup>-1</sup>) and  $a_L$  (ml mmol<sup>-1</sup>) are constants characteristics of the Langmuir equation.  $Q_{\max} = K_L/a_L$  (mmol g<sup>-1</sup>) is the theoretical monolayer saturation capacity or maximum adsorption;  $C_e$  is the solution ion concentration at equilibrium (mmol ml<sup>-1</sup>) and  $Q_e$  the solid phase metal ion concentration at equilibrium (mmol g<sup>-1</sup>). A plot of  $C_e/Q_e$  versus  $C_e$  gives a straight line of slope  $a_L/K_L$  and intercept  $1/K_L$ .

The simultaneous metal sorption data were analysed according to the linear form of the equation. Results are shown in Table 3. Data fitted the Langmuir model only for Ni and Cd, evidencing that in this case, sorption may be as a monolayer. As can be seen from the  $Q_{\max}$  results, at higher metal concentrations, Ni<sup>2+</sup> adsorption was higher than Cd<sup>2+</sup> adsorption for the three species studied. *P. stratiotes* showed the highest adsorption for Ni<sup>2+</sup>, presenting the three species similar behaviour with respect to Cd<sup>2+</sup>. At lower concentrations, the differences in isotherm slope ( $a_L/K_L$ ) showed that Cd<sup>2+</sup> adsorption was higher than Ni<sup>2+</sup> adsorption and the sequence was *L. minor* > *S. intermedia* > *P. stratiotes* for both, Cd<sup>2+</sup> and Ni<sup>2+</sup>.

#### 3.1.2. Freundlich isotherm

The most important multi-site adsorption isotherm for heterogeneous surfaces is the Freundlich isotherm that assumes there is an infinite supply of unreacted sorption sites.

$$Q_e = K_F C_e^{b_F} \quad (3)$$

where  $K_F$  is Freundlich constant (l g<sup>-1</sup>) and  $b_F$  the Freundlich exponent, a measure of the nonlinearity involved.

Eq. (3) can be linearized in

$$\ln Q_e = b_F \ln C_e + \ln K_F \quad (4)$$

A plot of  $\ln Q_e$  versus  $\ln C_e$  gives a straight line of slope  $b_F$  and intercept  $\ln K_F$ .

Table 3  
Langmuir isotherms fitting

Metal	Regression equation	$K_L$ ( $l\ g^{-1}$ )	$a_L$ ( $l\ mmol^{-1}$ )	$Q_{max}$ ( $mmol\ g^{-1}$ )	$r^2$	DST	$p$
<i>S. intermedia</i>							
Cd	$y = 27.981x + 0.1712$	5.85	163.43	0.036	0.999	0.0267	0.0007
Ni	$y = 16.626x + 1.9882$	0.50	8.36	0.060	0.905	0.3863	0.001
<i>L. minor</i>							
Cd	$y = 30.445x + 0.0686$	14.58	443.80	0.033	0.999	0.0129	<0.0001
Ni	$y = 17.59x + 0.7133$	1.40	24.66	0.057	0.980	0.1500	<0.0001
<i>P. stratiotes</i>							
Cd	$y = 26.982x + 0.4558$	2.19	59.19	0.037	0.996	0.0389	<0.0001
Ni	$y = 12.213x + 8.6171$	0.12	1.42	0.082	0.697	0.7830	0.02

Freundlich isotherm fitting is shown in Table 4. Examination of data suggests that the linear Freundlich isotherm is a good model for the simultaneous sorption of all metals tested, by the three macrophytes species biomass. The  $K_F$  values show that Pb is the metal more efficiently removed from water solution by *L. minor* and *S. intermedia* but not for *P. stratiotes* and both *L. minor* and *S. intermedia* show better performance than the latter. The  $b_F$  values range between the usual range (0.6–3.3) with the exception of Pb adsorption by *P. stratiotes*. The high Pb removal percentages by the three dead macrophytes (Table 2) are successfully explained by Freundlich isotherms.

### 3.2. Adsorption kinetics

The multi-metal adsorption process kinetics was tested using the first order Lagergren equation

$$\ln(Q_e - Q_t) = \ln Q_e - Kt \quad (5)$$

where  $Q_e$  is the mass adsorbed ( $mmol\ g^{-1}$ ) in the equilibrium,  $Q_t$  is the mass adsorbed at time  $t$  ( $mmol\ g^{-1}$ ) and  $K$  the first order rate constant ( $min^{-1}$ ). The results in Table 5 showed that  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  adsorption process for the three species studied followed first order kinetics.

### 3.3. Ion exchange process

The real challenge in the field of biosorption is to identify the mechanism of metal uptake by dead macrophytes. One of the mechanisms involved in biosorption is the ion exchange process between protons and / or light metals as counterions present in the biomass and heavy metal ions taken up from water (Kratovichil and Volesky, 1998; Schneider and Rubio, 1999; Elifantz and Tel-Or,

Table 4  
Freundlich isotherm fitting

Metal	Regression equation	$K_F$ ( $l\ g^{-1}$ )	$b_F$	DST	$r^2$	$p$
<i>S. intermedia</i>						
Pb	$y = 1.4142x + 2.2214$	166.49	1.41	0.1332	0.964	0.0005
Cd	$y = 0.6858x - 0.3646$	0.43	0.69	0.1583	0.954	0.0002
Ni	$y = 0.7945x - 0.7893$	0.16	0.79	0.0497	0.995	<0.0001
Cu	$y = 1.0916x + 0.0042$	1.01	1.09	0.1810	0.953	0.0002
Zn	$y = 1.1854x + 0.0117$	1.03	1.19	0.2337	0.923	0.0006
<i>L. minor</i>						
Pb	$y = 1.4847x + 2.6512$	447.92	1.48	0.1270	0.969	0.0004
Cd	$y = 0.5841x - 0.4693$	0.34	0.58	0.2192	0.912	0.0008
Ni	$y = 0.7191x - 0.6289$	0.24	0.72	0.1172	0.973	<0.0001
Cu	$y = 0.8971x - 0.1325$	0.74	0.90	0.1625	0.958	0.0001
Zn	$y = 1.1185x + 0.0242$	1.06	1.12	0.3726	0.808	0.0059
<i>P. stratiotes</i>						
Pb	$y = 0.3228x - 1.9597$	0.01	0.32	0.3331	0.717	0.0700
Cd	$y = 0.7708x - 0.4133$	0.39	0.77	0.1233	0.972	<0.0001
Ni	$y = 0.9371x - 1.0727$	0.08	0.94	0.0390	0.997	<0.0001
Cu	$y = 0.9416x - 0.9352$	0.12	0.94	0.0885	0.987	<0.0001
Zn	$y = 0.9329x - 0.6042$	0.25	0.93	0.0861	0.987	<0.0001

Table 5  
Lagergren equation fitting ( $\ln(Q_e - Qt) = \ln Q_e - Kt$ )

	$\ln Q_e$	$K$	DST	$r^2$	$p$
<i>Spirolela intermedia</i>					
Pb	-3.68724	-0.07133	0.01898	0.9965	<0.0001
Cd	-3.4221	0.10946	0.04127	0.9918	<0.0001
Ni	-3.26489	0.08555	0.01312	0.9986	<0.0001
Cu	-2.86892	-0.0806	0.0203	0.9963	<0.0001
Zn	-2.98118	-0.08867	0.02987	0.9935	<0.0001
<i>L. minor</i>					
Pb	-3.67366	-0.07194	0.02638	0.9933	0.0002
Cd	-3.41505	0.11601	0.05189	0.9886	<0.0001
Ni	-3.06526	-0.09923	0.02568	0.9961	<0.0001
Cu	-2.80885	-0.07999	0.02376	0.9949	<0.0001
Zn	-2.96799	-0.10579	0.04529	0.9895	<0.0001
<i>P. stratiotes</i>					
Pb	-3.70749	-0.07368	0.02231	0.9963	0.0019
Cd	-3.52084	0.11156	0.04789	0.9894	<0.0001
Ni	-3.80349	-0.06728	0.00598	0.9995	<0.0001
Cu	-3.70132	-0.07754	0.01336	0.9983	<0.0001
Zn	-3.24465	-0.08208	0.02285	0.9955	<0.0001

2002). Biosorbents can be viewed as natural ion-exchange materials that primarily contain weakly acidic and basic groups on the surface. In the pH range 2.5–6.0, the binding of heavy metals is determined primarily by the dissociation degree of the weakly acidic groups.

Schneider et al. (2001) suggested that heavy metals adsorb onto the dead biomass of many macrophytes through two mechanisms: specific ion exchange and simple surface precipitation, although it is not possible to differentiate between them based solely on sorption data.

To evaluate the possible presence of an ion exchange process, the chemical analysis of the solution was performed after the sorption process took place. This experience was carried out in a first step with individual

10 mg l<sup>-1</sup> metal solutions (Cd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup>). Results are shown in Table 6. The ionic balance showed that when 10 mg l<sup>-1</sup> of Pb<sup>2+</sup> solution were in contact with *S. intermedia* biomass, 1.05 meq l<sup>-1</sup> of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup> and Mn<sup>2+</sup> were released to the water solution and 1.04 meq l<sup>-1</sup> H<sup>+</sup> and Pb<sup>2+</sup> were adsorbed by *S. intermedia*. The monovalent ions represent ≈80% of the ions released to the water solution and the divalent ions 20%. H<sup>+</sup> and Pb<sup>2+</sup> were ≈98% and 2% respectively of the total ions adsorbed by *S. intermedia* biomass. In spite of Pb<sup>2+</sup> low percentage of total ions adsorbed, Pb was removed successfully from water solution (97%). Similar results were obtained for the other metals (Table 6).

Table 6  
Ionic exchange results for *S. intermedia* using individual metal solutions (meq/l)

Metal solution 10 mg l <sup>-1</sup>	Metals released to water						
	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Fe <sup>3+</sup>	Mn <sup>2+</sup>	Sum
Pb <sup>2+</sup>	0.36 ± 0.01	0.50 ± 0.02	0.057 ± 0.003	0.129 ± 0.005	0.00063 ± 0.00003	0.0069 ± 0.0003	1.05 ± 0.04
Cd <sup>2+</sup>	0.36 ± 0.01	0.48 ± 0.02	0.049 ± 0.002	0.146 ± 0.007	0.00076 ± 0.00003	0.0085 ± 0.0003	1.05 ± 0.04
Ni <sup>2+</sup>	0.31 ± 0.01	0.48 ± 0.03	0.062 ± 0.003	0.142 ± 0.007	0.0010 ± 0.0003	0.0058 ± 0.0003	1.01 ± 0.04
Cu <sup>2+</sup>	0.26 ± 0.01	0.49 ± 0.02	0.058 ± 0.002	0.153 ± 0.007	0.0010 ± 0.0004	0.0091 ± 0.0004	0.97 ± 0.04
Zn <sup>2+</sup>	0.54 ± 0.02	0.47 ± 0.02	0.061 ± 0.003	0.148 ± 0.006	0.0010 ± 0.0003	0.011 ± 0.001	1.23 ± 0.05
Metals adsorbed by biomass							
	Pb <sup>2+</sup>	Cd <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	H <sup>+</sup>	Sum
Pb <sup>2+</sup>	0.023 ± 0.001					1.02 ± 0.05	1.04 ± 0.05
Cd <sup>2+</sup>		0.042 ± 0.002				1.01 ± 0.05	1.05 ± 0.05
Ni <sup>2+</sup>			0.058 ± 0.003			0.95 ± 0.05	1.01 ± 0.05
Cu <sup>2+</sup>				0.060 ± 0.002		0.94 ± 0.05	1.00 ± 0.05
Zn <sup>2+</sup>					0.060 ± 0.003	1.14 ± 0.06	1.20 ± 0.06



Table 7  
Ionic exchange results using *multi-metal solutions* (all concentrations in meq/l)

	Metals released to water						
	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Fe <sup>3+</sup>	Mn <sup>2+</sup>	Sum
<i>S. intermedia</i>							
10 mg l <sup>-1</sup>	0.17 ± 0.01	0.65 ± 0.03	0.061 ± 0.002	0.115 ± 0.005	0.000066 ± 0.000005	0.0120 ± 0.0005	1.01 ± 0.05
20 mg l <sup>-1</sup>	0.18 ± 0.01	0.68 ± 0.03	0.149 ± 0.003	0.21 ± 0.01	0.000067 ± 0.000006	0.0293 ± 0.0008	1.24 ± 0.05
<i>L. minor</i>							
10 mg l <sup>-1</sup>	0.40 ± 0.02	0.59 ± 0.03	0.079 ± 0.004	0.25 ± 0.01	0.00074 ± 0.00004	0.0169 ± 0.0008	1.33 ± 0.06
20 mg l <sup>-1</sup>	0.40 ± 0.02	0.59 ± 0.03	0.143 ± 0.007	0.37 ± 0.02	0.00054 ± 0.00003	0.0291 ± 0.0009	1.53 ± 0.08
<i>P. stratiotes</i>							
10 mg l <sup>-1</sup>	0.81 ± 0.03	1.04 ± 0.04	0.096 ± 0.005	0.32 ± 0.01	0.0050 ± 0.00002	0.0197 ± 0.0008	2.29 ± 0.09
20 mg l <sup>-1</sup>	0.82 ± 0.03	1.09 ± 0.04	0.122 ± 0.006	0.38 ± 0.01	0.0035 ± 0.00002	0.025 ± 0.001	2.44 ± 0.09
	Metals adsorbed by biomass						
	Pb <sup>2+</sup>	Cd <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	H <sup>+</sup>	Sum
<i>S. intermedia</i>							
10 mg l <sup>-1</sup>	0.024 ± 0.001	0.042 ± 0.002	0.057 ± 0.003	0.064 ± 0.003	0.063 ± 0.003	0.78 ± 0.03	1.03 ± 0.04
20 mg l <sup>-1</sup>	0.049 ± 0.002	0.063 ± 0.003	0.091 ± 0.004	0.117 ± 0.006	0.098 ± 0.004	0.82 ± 0.04	1.24 ± 0.06
<i>L. minor</i>							
10 mg l <sup>-1</sup>	0.024 ± 0.001	0.041 ± 0.002	0.044 ± 0.002	0.060 ± 0.003	0.057 ± 0.003	1.16 ± 0.05	1.39 ± 0.06
20 mg l <sup>-1</sup>	0.048 ± 0.002	0.063 ± 0.003	0.076 ± 0.004	0.110 ± 0.006	0.098 ± 0.004	1.16 ± 0.05	1.56 ± 0.07
<i>P. stratiotes</i>							
10 mg l <sup>-1</sup>	0.023 ± 0.001	0.038 ± 0.002	0.022 ± 0.001	0.026 ± 0.001	0.043 ± 0.002	2.15 ± 0.09	2.3 ± 0.1
20 mg l <sup>-1</sup>	0.047 ± 0.002	0.057 ± 0.003	0.044 ± 0.002	0.049 ± 0.002	0.076 ± 0.003	2.18 ± 0.09	2.5 ± 0.1

In a second step, ion exchange experiences were carried out with a 10.0 mg l<sup>-1</sup> multi-metal solution of each Cu<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>. The experience was repeated with a 20 mg l<sup>-1</sup> multi-metal solution. Results are shown in Table 7. The ionic balance showed that when 10 mg l<sup>-1</sup> of heavy metal solution was added, 1.01, 1.33 and 2.29 total metal meq l<sup>-1</sup> were released to the water solution and 1.03, 1.39 and 2.3 total metal meq l<sup>-1</sup> were adsorbed by *S. intermedia*, *L. minor* and *P. stratiotes* respectively. The differences in total metal meq l<sup>-1</sup> adsorbed and released are explained by the presence of other elements in minor concentration in the biomass, not considered in the balance that were also exchanged by heavy metals. Na<sup>+</sup> and K<sup>+</sup> represent ≈74% of the total metals released to the water solution and H<sup>+</sup> and divalent metals ≈78% and 22% respectively of the total metals adsorbed by the three macrophytes.

When 20 mg l<sup>-1</sup> of heavy metal solution were added, 1.24, 1.53 and 2.44 total metal meq l<sup>-1</sup> were released to the water solution and 1.24, 1.56 and 2.5 total metal meq l<sup>-1</sup> were adsorbed. Na<sup>+</sup> and K<sup>+</sup> represent ≈74% of the total metals released to the water solution and H<sup>+</sup> and divalent metals ≈81% and 18% respectively of the total metals adsorbed by the three macrophytes.

A comparison of the results obtained (Tables 6 and 7) by using individual metal and multi-metal solutions (10 mg l<sup>-1</sup>) in the exchange experiences shows that the

amount of each metal adsorbed by macrophytes biomass is similar in both cases. We can conclude that the presence of other metals does not interfere with individual metal adsorption. Total metals amounts released to the water solution are near the same in all experiences, but the solution final pH is higher in the individual metal exchange because in the multi-metal exchange, higher number of biomass exchange sites are occupied by metals.

Our results on metal binding capacity of the three different macrophytes biomass studied are of the same order of magnitude than those for *Ascophyllum* sp. 2–2.5 meq g<sup>-1</sup>; *Eclonia radiata* 1.8–2.4 meq g<sup>-1</sup>; *Rhizopus arrhizus* 1.1 meq g<sup>-1</sup>; *Sargassum* sp. 2–2.3 meq g<sup>-1</sup>; commercial resins 0.35–5.0 meq g<sup>-1</sup>; peat moss 4.5–5.0 meq g<sup>-1</sup> (Kratochvil and Volesky, 1998).

#### 4. Conclusions

Our laboratory experiences in simultaneous metal removal by dead macrophytes biomass clearly demonstrate that the three species behave as weak cation exchange materials. The main mechanism involved in biosorption was ion exchange between monovalent metals as counterions present in the macrophytes biomass and heavy metal ions and protons taken up from water. No significant differences were observed in the metal

exchange amounts while using multi-metal or individual metal solutions.

Pb and Cd were efficiently removed by the three species, in spite of the presence of other metals in the water solution that compete for limited number of binding sites in the biomass surface. *L. minor* and *S. intermedia* biomass presented the highest mean removal percentage and *P. stratiotes* the lowest for all metals tested. As expected, metal adsorption data ( $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ ) fitted Freundlich isotherm (heterogeneous surfaces) and followed first order kinetics.

The sorption of diluted heavy metal ions, in particular, Pb and Cd by dead *S. intermedia*, *L. minor* and *P. stratiotes* appears to be an efficient and low cost alternative to be considered in industrial effluent treatment. Nevertheless, it is important to note that the effect on the biosorption of the many compounds present in industrial effluents such as other metal ions, surfactants, sequestering agents, was not taken in consideration in this study.

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