

STUDY OF BINARY AND SINGLE BIOSORPTION BY THE FLOATING AQUATIC MACROPHYTE *Salvinia natans*

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Abstract - The performance of *Salvinia natans* macrophyte to recover lead and chromium from single and bicomponent solutions in batch and fixed bed systems was investigated. Equilibrium data were obtained through isotherms and fitted to Langmuir, Freundlich and D-R models for a single component system. In the fixed bed study the breakthrough curves were carried out at three different ratios of concentrations for the bicomponent study and at the concentration of 1 mmol.L⁻¹ for the single system. In order to know the biosorption mechanism, FT-IR analyses were performed for *S. natans* before and after the uptake of metal ions. The results showed different functional groups in the biomass and the ability of these groups to bind Cr⁺³ and Pb²⁺. Studies of the binary system of Cr⁺³/Pb²⁺ are not common in the literature, which makes the experimental data obtained in this work very important for providing information that could be used in adsorption processes.

Keywords: Lead; Chromium; Macrophyte; Batch; Fixed bed.

INTRODUCTION

Metal ions such as chromium and lead are chemical elements toxic to the environment and human body. They belong to the most important groups of pollutants from industrial wastewater. The harmful potential of metals associated with their power of accumulation in the environment and their toxic effects, and potential damage to health are well known and extensively studied (Axtell *et al.*, 2003; Sheng *et al.*, 2004; Saygideger *et al.*, 2005).

These kinds of pollutants are very difficult to treat due, mainly, to the inefficiency and/or the high cost related to the traditional methods. Biosorption is an alternative method of treatment which has become increasingly promising due to the large variety of existing materials and the high affinity for metal ions (Vieira *et al.*, 2008; Leyva-Ramos *et al.*, 2012).

Biosorption is a purification process which may involve complex mechanisms that depend on the chemical and morphological characteristics of the biological material used (Lima *et al.*, 2011). The term "biosorption" refers to various ways of removing pollutants using non-active biomass, where the "sequestration" of pollutants by the biomass of the cell wall may occur via mechanisms of adsorption, ion exchange, chelation, coordination, complexation, etc. (Bai and Abraham, 2001). This "sequestration" can be attributed to functional groups present in the cell wall of biomass such as carboxylates, carboxylic acids, phosphates, amines, aldehydes (Saygideger *et al.*, 2005; Bernardo *et al.*, 2009).

Among all kinds of existing biomaterials we mention aquatic macrophytes. They have some advantages, such as being a low-cost and locally available material. They are easy to grow in a wide range of

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temperature and pH. Moreover, many works have shown the high affinity of the metal ions for macrophytes in adsorption processes (Lima *et al.*, 2011).

Bunluesin *et al.* (2007) studied the removal of Cd^{2+} by the nonliving biomass of the aquatic macrophyte *Hydrilla verticillata*. They tested batch and fixed-bed systems. The Langmuir model fitted to the batch data showed a maximum removal capacity, q_{max} , of $0.133 \text{ mmol.g}^{-1}$. From fixed-bed experiments, the breakthrough curves showed that *H. verticillata* was capable of decreasing Cd^{2+} concentration from 10 mg.L^{-1} to a value below the detection limit of 0.02 mg.L^{-1} .

Miretzky and Munõz (2011) evaluated the removal of Zn^{2+} by *Eichhornia crassipes* macrophyte biomass modified by Fenton treatment. The efficiency of the Zn^{2+} sorption process under different experimental conditions was determined. Experimental data showed good fit to a Langmuir model with maximum sorption capacities of 0.114 and $0.203 \text{ mmol.g}^{-1}$ for raw and Fenton activated biomass (dose 5.0 g L^{-1} , pH 6.0), respectively.

Martins *et al.* (2014) studied the performance of the aquatic moss *Fontinalis antipyretica* for removing cadmium and lead from simulated wastewaters. The authors found that, for an initial metal concentration of 10 mg.L^{-1} , the uptake capacity of the moss, at equilibrium, was the same for both metals (4.8 mg.g^{-1}). But when the initial concentration increased up to 100 mg.L^{-1} , the uptake of Pb (II) was higher than 78%.

Seolatto *et al.* (2014) evaluated the biosorption of Cr^{3+} and Ni^{2+} by *Sargassum filipendula* pre-treated with CaCl_2 . The authors studied kinetic and equilibrium characteristics of the process. Experiments were carried out for single and bicomponent solutions in a batch reactor at pH 3.0 and temperature of $30 \text{ }^\circ\text{C}$. For single component studies the maximum adsorption capacities were 3.0 and 1.48 meq.g^{-1} for Cr^{3+} and Ni^{2+} , respectively. In the binary system a strong competitive behavior was observed. When both ions were present in solution, Ni^{2+} ions were gradually removed from the biomass and the higher the initial concentration of Cr^{3+} the higher was the Ni^{2+} desorption.

Among the several existing toxic metals, we can mention chromium and lead ions. Chromium compounds are heavily used in the tanning process due to their capacity of promoting the hardening of the skin, providing a better preservation of the final product. As a result, the effluents released are rich in Cr^{3+} ions, which represent a potential polluting source for the environment (Freitas and Melnikov, 2006).

Chromium can exist in multiple valence states, Cr^{3+} and Cr^{6+} being the most common. Cr^{3+} occurs naturally in the environment and, in low concentration, becomes an essential micronutrient for humans and

other species, while Cr^{6+} is a toxic contaminant, being produced only by human activity (Felter and Dourson, 1997; Brigatti *et al.*, 2000). In addition to pollution by tanneries, there is concern because of the ability of Cr^{6+} to be reduced to Cr^{3+} in the environment; in this case, both forms are discussed with regard to toxicity (Felter and Dourson, 1997).

Lead ions are stable in two oxidation states, Pb^{2+} and Pb^{4+} , but the environmental chemistry is dominated by the Pb^{2+} ion (Zambon, 2003). This metal is potentially toxic to animals and aquatic life. It is present in the environment as a result of a wide and extensive industrial application of chemicals, like the employment of insecticides containing lead, PbHAsO_4 , as well as the mining processes, electroplating, petroleum refining, pulp and paper and urban activity such as the use of lead in gasoline and paint (Prasad *et al.*, 2000).

Another important observation is the small number of works available in the literature using dead macrophytes for metal ion removal. Therefore, the main objective of this work is to study the application of the aquatic macrophyte *Salvinia natans* in the removal of Pb^{2+} and Cr^{3+} ions from single component and binary mixture solutions in batch and continuous fixed bed systems. Equilibrium and breakthrough curve experiments were performed. The Langmuir, Freundlich and D-R isotherm models were applied to the batch system and the Bohart-Adam model was fitted to the breakthrough curves in the single component study. Changes in functional groups present in *Salvinia natans* bioadsorbent were analyzed by spectroscopy in the infrared region (FT-IR).

MATERIALS AND METHODS

Biomass

Salvinia natans macrophyte was cultivated and collected by the CPAA (Research Center in Environmental Aquaculture) of the State University of Paraná, Brazil. After collection, the biomass was washed and dried at $55 \text{ }^\circ\text{C}$ for 24 h. After this period the biomass was sieved and fractions measuring 0.855 mm were collected and used in batch and fixed bed experiments.

Metal Ion Solutions

The chromium and lead synthetic solutions were prepared by dissolving $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ salt and $\text{Pb}(\text{NO}_3)_2$ (both from Vetec) in deionized water. The pH of the solution was adjusted to 4.0 using HNO_3 (0.5 M) and NaOH (1 M). This pH was used to avoid

precipitation of the metal ions. The presence of Cr^{3+} and Pb^{2+} ions in solution was measured using an Atomic Absorption Spectrophotometer - AA 100 - Perkin Elmer, in the Laboratory of Environmental Engineering – Unicamp.

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis was performed to identify the functional groups present in biomass and the changes in these groups after the biosorption process. The Infrared spectra were recorded in the 4000-600 cm^{-1} region using a Thermo Nicolet instrument, model IR-200. The ATR (attenuated total reflection) device allows getting information about the biomass surface.

Equilibrium Assays

Equilibrium experiments for the single component systems were conducted by mixing 100 mL of solution with different concentrations of Cr^{3+} or Pb^{2+} (0.025 to 4 mmol.L^{-1}) with 0.2 g of *S. natans* at room temperature and pH 4. The solution with the biomass was maintained under stirring for 2 h, time enough to achieve adsorption equilibrium. The samples were then centrifuged and the concentrations of the metal ion were determined by Atomic Absorption Spectrophotometry (AAS). The adsorption capacity was calculated from Eq. (1).

$$q = \frac{(C_0 - C_f) \cdot V}{m} \quad (1)$$

where q is the metal ion uptake (mmol.g^{-1}), C_0 and C_f are the initial and equilibrium concentrations of the metal ion (mmol.L^{-1}), V is the volume of solution (L), m is the weight of biosorbent (g).

Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models were used to fit the equilibrium experimental data, Eqs. (2), (3) e (4), respectively. Although the Langmuir isotherm model was developed for gas phase applications, it is widely used for liquid application and in this study it was used as a mathematical equation to fit the results.

$$q_L = \frac{q_0 b C_e}{1 + b C_e} \quad (2)$$

where q_0 represents the concentration of Cr^{3+} or Pb^{2+} in the macrophyte for a total coverage of available sites (mmol.g^{-1}), b represents the Langmuir adsorption parameter related to the biomass affinity for the ions (L.mmol^{-1}), q_e and C_e are the equilibrium

concentrations of Cr^{3+} or Pb^{2+} in the solid (mmol.g^{-1}) and fluid phases (mmol.L^{-1}), respectively. Alternatively:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F is the Freundlich constant, which indicates the adsorption capacity of the adsorbent ($\text{mmol}^{1-\frac{1}{n}} \cdot \text{L}^{\frac{1}{n}} \cdot \text{g}^{-1}$), and $1/n$ is the heterogeneity factor. In the third model:

$$\ln q_e = \ln q_m - K_{DR} \varepsilon^2 \quad (4)$$

where K_{DR} is the porosity factor ($\text{mol}^2 \cdot \text{J}^{-2}$), q_m is the monomolecular adsorption capacity of metal ion biosorption by the biomass surface (mmol.g^{-1}) and the variable ε can be related to the equilibrium concentration (Eq. (5)):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (5)$$

where ε is the Polanyi potential (J.mol^{-1}), R is the universal gas constant ($8.314 \times 10^{-3} \text{ kJ.K}^{-1} \cdot \text{mol}^{-1}$) and T is the absolute temperature.

A plot of $\ln q_{exp}$ versus ε^2 ($\text{J}^2 \cdot \text{mol}^{-2}$) must be linear, with a slope of the straight line of (K_{DR}), and intercept on the y axis at ($\ln q_m$), providing the values of K_{DR} . The parameters obtained by the linearization allow calculation of the mean free energy of adsorption E (kJ.mol^{-1}) per molecule of the adsorbate when it is transferred from the solution to the biomass surface according to Eq. (6) (Ergene *et al.* 2009).

$$E = (-2K_{DR})^{-1/2} \quad (6)$$

The equilibrium experiments for the bicomponent system were carried out by mixing 100 mL of solution containing different combinations of Cr^{3+} and Pb^{2+} concentrations (Table 1) and 0.2 g of *S. natans* at room temperature and pH 4. The mixture was maintained

Table 1: Concentrations used in the binary mixtures for equilibrium assays.

Metal ion concentration (mmol.L^{-1})	
Cr^{3+}	Pb^{2+}
0.25	0.25
0.25	0.75
0.75	0.75
1.00	2.00
2.00	1.00
2.00	2.00

under constant stirring for a period of 2 h, time enough to reach the equilibrium. The samples were then centrifuged and concentrations of the metal ions were determined.

Dynamic System Assays

The breakthrough curves were obtained using a 15 cm glass column with 1.5 cm of inner diameter. The column was packed with biomass and washed with deionized water for about 2 hours until all fine residues of the biomass had been removed. For the single system experiments, the column was fed with synthetic solution of Cr^{3+} or Pb^{2+} of 1 mmol.L^{-1} concentration, using a peristaltic pump, Masterflex brand, at a flow rate ranging from 1 to 3 mL.min^{-1} .

The breakthrough curves were fitted by the model of Bohart and Adams (1920), which has an analytical solution. This model is more appropriately used to describe adsorption breakthrough curves in a single component system. The model assumes that the rate of adsorption and the concentration of adsorbed species present in the adsorbent surface are proportional. This model was used to describe the behavior of a fixed bed in the removal of chromium and lead from the experimental data, where the equation and its solutions are shown in Table 2.

Table 2: Equation from Bohart-Adams model.

Equation	Solution	Reference
$\frac{\partial q}{\partial t} = kC(q_s - q)$	$\frac{C}{C_0} = \frac{e^\xi}{e^\xi - e^\xi - 1}$	Bohart and Adams (1920) apud Ruthven (1984)
	$\tau = kC_0 \left(t - \frac{z}{v} \right)$	
	$\xi = \frac{kq_0 z}{v} \left(1 - \frac{\varepsilon_L}{\varepsilon_L} \right)$	

z is the bed height (cm), v is the flow velocity (cm.min^{-1}), ε_L is the porosity of the bed, t is the time (min), k is the kinetic constant of adsorption ($\text{L.mmol}^{-1}.\text{min}^{-1}$) and q_s is the sorption adsorbent capacity at equilibrium with the feed concentration (mmol.g^{-1}), q is the ion concentration in the adsorbent (mmol.g^{-1}), C is the concentration of the metal ion in the solution (mmol.L^{-1}), q_0 is the maximum uptake capacity of metal per unit of mass of adsorbent (mmol.g^{-1}).

For the bicomponent system, the column was fed with a solution containing the binary mixture with the ratios of concentrations shown in Table 3. The flow rate was 1 mL.min^{-1} , determined in the single system, and the pH was 4.0. A fraction collector (FC203 Fra-

tion Collector) was used to collect aliquots at different periods of time, which were diluted and the concentration measured. The length of the mass transfer zone (MTZ) and the useful (q_u) and total (q_t) amounts removed by the column were calculated as a function of time according to the methodology described in Geankoplis (1993). A mass balance was performed on the column using the data obtained from the saturation, in which the area under the curve ($1 - C/C_0$) until the break point is proportional to q_u (Equation (7)), and the area up to the saturation of the bed is proportional to q_t (Equation (8)). The point of rupture was considered at a time (t_b), where the concentration at the column outlet was equivalent to 5% of the initial feed concentration.

$$q_u = \frac{C_0 \cdot Q}{1000 \cdot m} \int_0^{t_b} \left(1 - \frac{C|_{z=L}}{C_0} \right) dt \quad (7)$$

$$q_t = \frac{C_0 \cdot Q}{1000 \cdot m} \int_0^{t_{\text{sat}}} \left(1 - \frac{C|_{z=L}}{C_0} \right) dt \quad (8)$$

where $C|_{z=L}$ is the concentration of chromium and lead in solution at the column outlet and C_0 is the concentration of both metals in the column feed in mmol.L^{-1} .

The mass transfer zone (MTZ) was calculated using Equation (9) based on the ratio between q_u/q_t .

$$MTZ = H_L \cdot \left(1 - \frac{q_u}{q_t} \right) \quad (9)$$

where H_L is the height of the column.

Table 3: Ratio of concentrations used in the binary mixture for fixed-bed assays.

Ratio	Metal ion concentration (mmol.L^{-1})	
	Cr^{3+}	Pb^{2+}
1	1.0	1.0
2	1.0	2.0
3	2.0	1.0

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FT-IR)

In FT-IR analyses the spectrum was obtained for biomass before and after the biosorption process in the simple and competitive systems. The results presented

in Figure 1 show that the biomass has different functional groups such as carboxyl, phosphate, amide, hydroxyl and others, and some of these groups change after biosorption process. The *in natura* biomass and those saturated with metal ions for the two studied systems presented the band at 3442 cm^{-1} corresponding to the OH vibration. The bands at $3402\text{--}3344\text{ cm}^{-1}$ are assigned to the OH stretch of polymeric compounds, the band at $2924\text{--}2850\text{ cm}^{-1}$ is asymmetric and symmetric vibration of methylene (CH_2), respectively. The weak peak at 2360 cm^{-1} assigned to phosphonates is present only in the natural macrophyte, indicating the involvement of these groups in the adsorption of Pb^{2+} and Cr^{3+} ions. The peak at 1640 cm^{-1} corresponds to $\text{C}=\text{O}$ of amide. The peak at $1130\text{--}1000\text{ cm}^{-1}$ is the vibration of C-O-C and O-H of polysaccharides. The strong peaks at 1034 cm^{-1} and 1036 cm^{-1} correspond to alcohol groups. The 1250 cm^{-1} peak is the C-O stretch of carboxylic acids, the 911 cm^{-1} peak is the angular deformation of alkenes and appears only in the *in natura* biomass. The peak at 914 cm^{-1} is assigned to C-X of the halogen groups. The bands $< 800\text{ cm}^{-1}$ are the fingerprint zone which include phosphate and sulphur functional groups (Saygideger *et al.*, 2005). After the biosorption process in the single system and with the mixture of Cr^{3+} and Pb^{2+} , some functional groups of *S. natans* are lost, which implies that these groups participate in the uptake of both metal ions. In other words, the biomass has different functional groups for heavy metal binding such as phosphonates, amide, carboxyl and carboxylates and alkene groups (Saygideger *et al.*, 2005). The main groups responsible for the binding were amide, alkenes and phosphonates, carboxyl and alkenes.

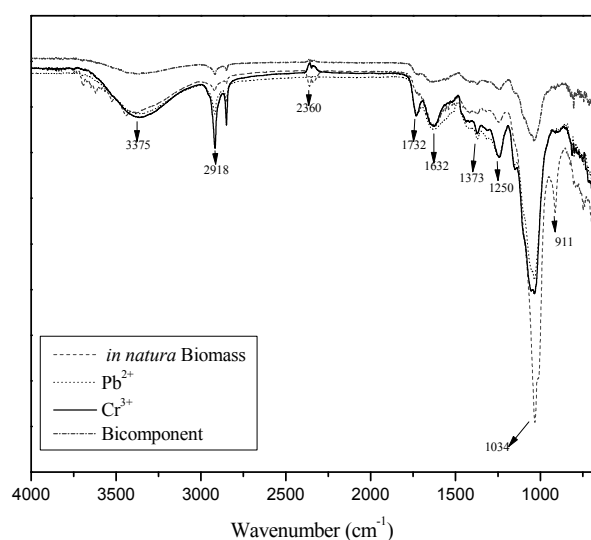


Figure 1: FT-IR spectra of raw *S. natans* and the biomass saturated with chromium and lead.

Equilibrium Assays

Figure 2 (a)-(c) shows the biosorption isotherm of Cr^{3+} and Pb^{2+} by *S. natans* for simple and binary systems. The model parameters for the single systems are shown in Table 4. The results showed that the both models, Langmuir and Freundlich, adjusted satisfactorily to the experimental data. The Langmuir model fitted better with a maximum biosorption capacity of 0.331 and 0.283 mmol.g^{-1} for Cr^{3+} and Pb^{2+} , respectively. The better results for Langmuir model fitting may be observed in the similarity of the q_L values obtained from the model and those obtained from the experiments (q_{exp}), as shown in Table 4.

Although the Langmuir isotherm model was developed for gas adsorption, it is used to fit the experimental results in this work. This model suggests homogeneity on the surface of the adsorbent. In the Langmuir model, the parameter b represents the affinity or efficiency between adsorbate and adsorbent. High values of b are reflected by the steep initial slope of a sorption isotherm and indicate a high affinity for the adsorbate (Davis *et al.*, 2003). In this work, the high values of b , especially for lead, showed the high affinity between the macrophyte and this metal. Although the maximum adsorption capacity value of chromium was slightly higher for the Langmuir model, we can observe that the values are very close for both metal ions. Another factor which describes the characteristics of a Langmuir isotherm is the dimensionless parameter R_L . The values were obtained for both metals and were found to be between 0 and 1, which indicates favourable equilibrium adsorption (Hall *et al.*, 1966). Furthermore, the corresponding Freundlich isotherm exponent n was greater than unity, also suggesting a favourable adsorption process. For chromium at pH 4 most of the ions in the ionic forms are Cr^{3+} and CrOH^{2+} , which is the product of the first hydrolysis of the trivalent species, being highly adsorbed as observed by Leyva-Ramos *et al.* (1995).

The Dubinin-Radushkevich equilibrium model provides information on the physical or chemical character of the biosorption process. When E values are between 8 and 16 kJ.mol^{-1} , the adsorption process takes place by chemical ion exchange while $E < 8\text{ kJ.mol}^{-1}$ means that the adsorption process is physical (Argun *et al.*, 2007). The E value obtained in this study was smaller than 8 kJ.mol^{-1} for both studied ions, which means that the biosorption onto the *S. natan* surface is a physical process.

The results obtained in this work are in accordance with literature studies using biological material to remove Cr^{3+} and Pb^{2+} . Keskinan *et al.* (2007) used *Myriophyllum spicatum* and *Ceratophyllum demersum*

as biosorbents, obtaining 0.224 and 0.216 mmol.g^{-1} for the removal of Pb^{2+} and Cr^{3+} , respectively. Lima *et al.* (2011) studied the removal of Cr^{3+} by the macrophyte *Lemna minor*. The tests were performed in batch, and biosorption equilibrium was reached in 6-7 hours. The authors obtained a maximum adsorption capacity of 0.129 mmol.g^{-1} .

The relative average deviation (RAD) was calcu-

lated with the aim of indicating if the fitting of the models to the experimental data was adequate. The results are shown in Table 4. It can be seen that the Langmuir and D-R models had a smaller RAD, while for the Freundlich model there was a significant increase in the distance between the experimental and calculated data, which implies a higher deviation. These results confirm the better fit of the Langmuir model.

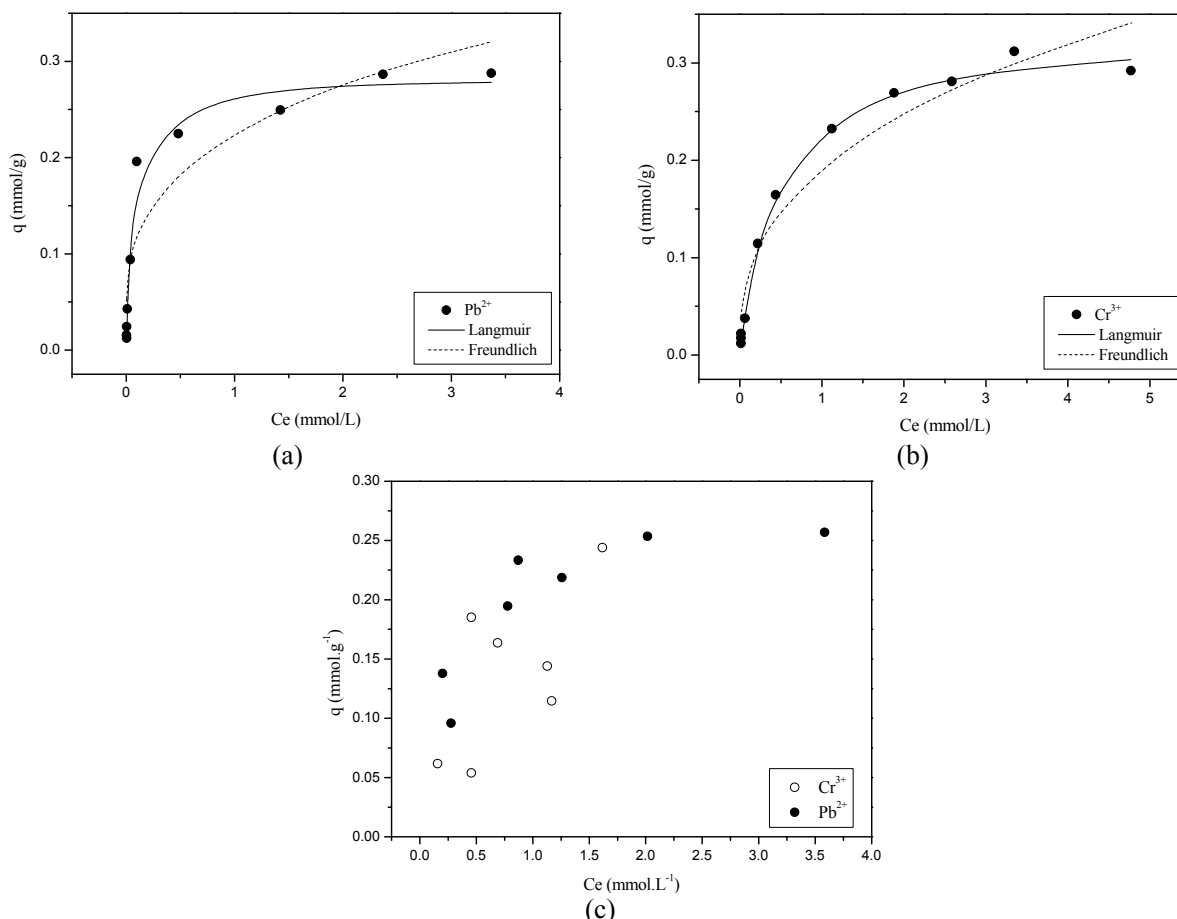


Figure 2: Equilibrium isotherms for (a) Pb^{2+} (b) Cr^{3+} and (c) the binary system of Cr^{3+} and Pb^{2+} .

Table 4: Langmuir, Freundlich and D-R isotherm model parameters.

Equilibrium	q_{exp} (mmol.g^{-1})	Langmuir						
		q_L (mmol.g^{-1})	Standard Error	b (L.mmol.g^{-1})	Standard Error	R^2	R_L	RAD (%)
Pb^{2+}	0.281	0.283	0.008	16.4	2.576	0.987	0.015	13.5
Cr^{3+}	0.286	0.331	0.007	2.326	2.326	0.995	0.074	13.99
Equilibrium	q_{exp} (mmol.g^{-1})	Freundlich						
		K_f ($\text{mmol}^{(1-1/n)}.\text{g}^{-1}.\text{L}^{1/n}$)	Standard Error	n	Standard Error	R^2	RAD (%)	
Pb^{2+}	0.281	0.231	0.016	3.730	0.618	0.905	79.7	
Cr^{3+}	0.286	0.194	0.011	2.756	0.337	0.951	53.02	
Equilibrium	q_{exp} (mmol.g^{-1})	Dubinin- Radushkevich						
		q_m (mmol.g^{-1})	Standard Error	K_{DR} ($\text{mol}^2.\text{kJ}^2$)	Standard Error	E (kJ.mol^{-1})	R^2	RAD (%)
Pb^{2+}	0.281	0.280	0.094	0.018	0.001	5.350	0.973	6.37
Cr^{3+}	0.286	0.241	0.121	0.025	0.002	4.514	0.939	13.32

It is possible to observe that, in the competitive system (Figure 2-(c)), Pb^{2+} ions have higher affinity for the active sites of the macrophyte. Thus, an experimental q_{exp} of 0.247 was obtained for Pb^{2+} , while for Cr^{3+} the q_{exp} was about 0.164. The results are in accordance with those found by Sulaymon *et al.* (2013) who studied the competitive biosorption of lead, mercury, chromium and arsenic ions onto activated sludge in batch. The authors found that Pb^{2+} was always adsorbed more favourably onto activated sludge than the other ions when present in the binary, ternary and quaternary systems. The results indicated that Pb^{2+} was the metal that experienced the least displacement in the competitive adsorption process and the presence of other metal ions had little influence on the Pb^{2+} adsorption. Figure 2-(c) also shows this behaviour of chromium ions; there is not a set baseline due the displacement of these ions.

The affinity of the metal ions for the biomaterial depends on many variables (pH, ion concentration, Pauling electronegativity, ionic radius, *softness*, etc.), making it difficult to set an absolute sequence of uptake in the adsorption process. Table 5 lists the values of Cr^{3+} and Pb^{2+} ion properties which can affect the biosorption capacity and the selective uptake.

Table 5: Physico-chemical properties of the studied metal ions.

Ion	Electronegativity ^a	Ionic radius (Å) ^b	Hydrated radius (Å) ^b	Charge/ionic radius	Softness ^c
Cr^{3+}	1.66	0.64	4.61	4.69	2.70
Pb^{2+}	2.33	1.32	4.01	1.52	3.58

^a Kinraide and Yermiyahu (2007), ^b Nightingale (1959), ^c Misono *et al.* (1967).

Analyzing each property presented in Table 5, it can be seen that, if only electrostatic interactions have an influence on the uptake of metal ions, the strongest binding is that with the highest charge/ionic radius ratio. In this particular case, Cr^{3+} should have the better adsorption capacity. This behavior is true since higher values of q_L and q_{exp} were observed in single component biosorption. However, in the competitive biosorption system, the addition of lead significantly reduced the adsorption capacity of Cr^{3+} ions, indicating that other properties may influence the ion removal.

It is known that the more electronegative the ions, the more attracted for the adsorbent surface they are, which implies that Pb^{2+} ion has preference for the biomass sites instead of Cr^{3+} . This is confirmed by the other two properties shown in Table 5, hydrated radius and softness. Small hydrated radius allows a better diffusion in the adsorbent pores. Therefore, adsorption

occurs easily with small radius. Softness, measuring the extent of binding, is called π -bonding. This means that the removal of lead is favorable due to its higher value of softness (Malamis and Katsou, 2013; Misono *et al.*, 1967). Although the most part of the properties show that lead has more affinity than chromium, this is true only in competitive biosorption. The results obtained in the single component systems showed that Cr^{3+} is more adsorbed. However, it is also true that the values of the adsorption capacities of lead and chromium are close and other variables such as surface functional groups of the macrophyte may determine the total removal capacity. Observing the physical-chemical properties, it is possible to define a sequence of affinity. According to the electronegativity, softness and the hydrated radius, ions of lead have a higher affinity, while the ratio charge/ionic radius predicts that chromium ions have more affinity.

Dynamic System Assays

In order to examine the influence of the feed flow in the removal process, assays were carried out at flow rates of 1, 2 and 3 $\text{mL}\cdot\text{min}^{-1}$. Figure 3 shows the breakthrough curves at different flow rates of operation for the removal of Cr^{3+} and Pb^{2+} . It was observed that there was an influence of the flow rate on the resistance to saturation. With increasing flow rate, from 1 $\text{mL}\cdot\text{min}^{-1}$ to 3 $\text{mL}\cdot\text{min}^{-1}$, the curve rupture becomes more marked, reducing the break point of the column. A low break point means that the residence time of the solution in the column was not sufficient to reach adsorption equilibrium due to high flow, or there was a short residence time of the column. The solution leaves the column before equilibrium of the solute/sorbent was achieved (Singh *et al.* 2012).

The calculated MTZ and adsorbed quantities are shown in Table 6. From Figure 3 it can be noted that, with the flow rate of 3 $\text{mL}\cdot\text{min}^{-1}$, a higher value of MTZ was obtained and there was a higher resistance to mass transfer for both metal ions. This means that, at higher flow rates, the removal process is not favourable. The smallest MTZ was found at the flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$, with q_u values of 0.138 and 0.078 $\text{mmol}\cdot\text{g}^{-1}$ for Pb^{2+} and Cr^{3+} , respectively. Lead showed smaller values of MTZ and higher values of q_u and q_t , which implies that this ion has more affinity by the biomass.

The difference between the single component batch experiments and fixed bed data can be observed in the ion selectivity. In the equilibrium experiments, Cr^{3+} had a higher removal from solution while in fixed bed, the Pb^{2+} ion showed better results.

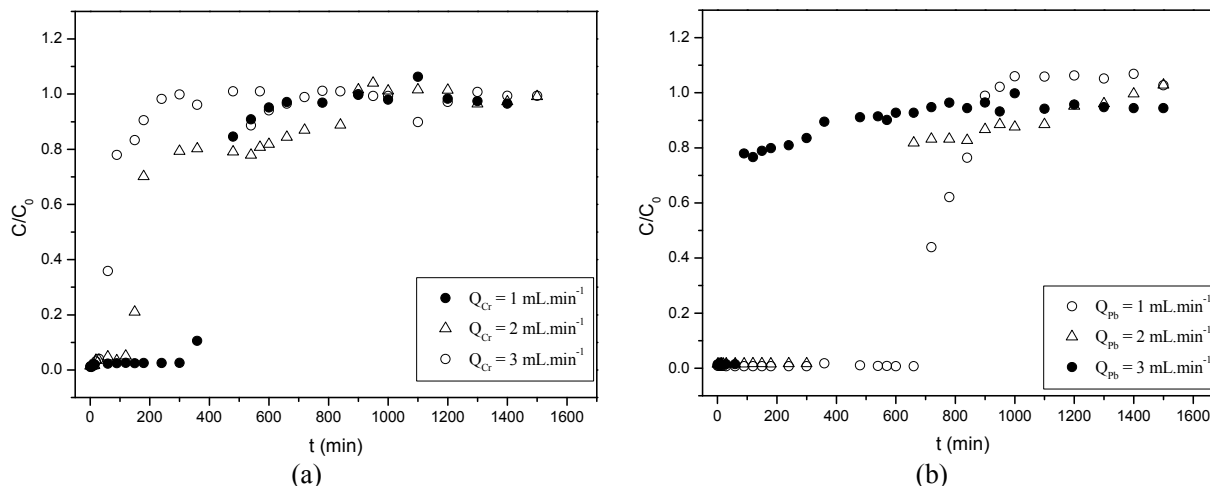


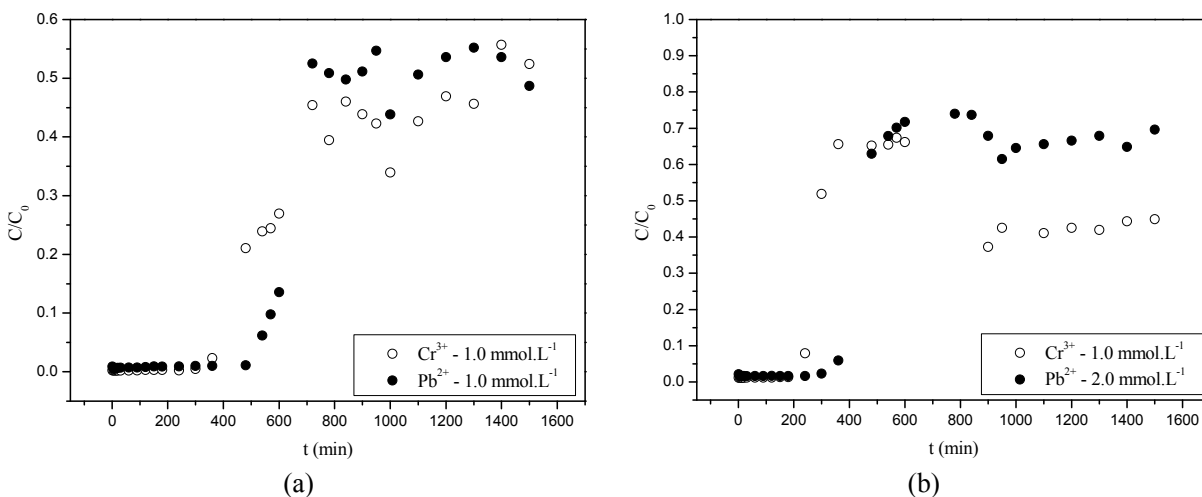
Figure 3: Breakthrough curves at different flow rates of operation for the removal of (a) Cr^{3+} and (b) Pb^{2+} .

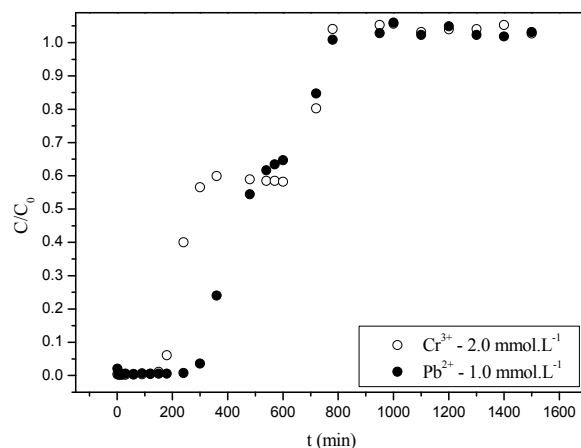
Table 6: Lead and chromium removal efficiency parameters in fixed bed.

Flow rate ($\text{mL}\cdot\text{min}^{-1}$)	Metal ions					
	Pb^{2+}			Cr^{3+}		
	MTZ (cm)	q_u ($\text{mmol}\cdot\text{g}^{-1}$)	q_t ($\text{mmol}\cdot\text{g}^{-1}$)	MTZ (cm)	q_u ($\text{mmol}\cdot\text{g}^{-1}$)	q_t ($\text{mmol}\cdot\text{g}^{-1}$)
1	1.448	0.138	0.152	3.933	0.078	0.105
2	7.030	0.144	0.272	9.017	0.054	0.135
3	10.249	0.041	0.128	10.33	0.027	0.088

In order to examine the influence of the feed concentration on the biosorption process using fixed bed for binary mixtures, experiments were performed at 3 different ratios of concentrations at a flow rate of $1 \text{ mL}\cdot\text{min}^{-1}$ and pH 4. Figure 4 shows the breakthrough curves at the experimental conditions for the removal of Cr^{3+} and Pb^{2+} . It can be observed that, for all ratios of concentrations, the time for saturation was higher for lead. When concentration of Cr^{3+} increased, the time for saturation of both metal ions in the col-

umn decreased. The same happened when the concentration of Pb^{2+} increased. Thus, when the concentration of metal ions was increased in solution, there was a greater competition for active sites of the biomass. These results are similar to those found by many researchers in single and competitive biosorption systems in columns with different metal ions and using different adsorbents (Vijayaraghavan *et al.*, 2005; Carmona *et al.*, 2012; Vilar *et al.*, 2008). The higher biosorbent affinity for Pb^{2+} can cause Cr^{3+} displacement





(c)

Figure 4: Breakthrough curves for the removal of Cr^{3+} and Pb^{2+} for (a) ratio 1, (b) ratio 2 and (c) ratio 3.

from the biosorbent surfaces. As can be observed in Figure 4, after a period of time the chromium ion concentration starts to decrease. Comparing these results with those found in fixed bed for single component experiments, lead is always adsorbed better and causes a higher displacement of chromium ions. This effect was observed in batch competitive experiments and explained by the properties of each ion studied and confirmed by the b constant of the Langmuir model that showed a higher affinity of the Pb^{2+} ion.

The maximum MTZ value corresponds to the bed height (H_L) (Equation (9)). The smaller the MTZ, the higher the efficiency of mass transfer. The parameters obtained from experimental data are shown in Table 7. From the data, it can be observed that the higher value of MTZ, or resistance to mass transfer, is for Cr^{3+} at ratio 3, where the chromium concentration is higher. This is true since the residence time of chromium in the column was lower. For the three ratios, the MTZ for chromium was higher than for lead. The higher MTZ for lead was found when the concentrations for both metals were equal (ratio 1). However, at this condition a better result of q_u (about $0.125 \text{ mmol.g}^{-1}$) for lead was obtained. This value can be explained since at this ratio the time for saturation was higher in the column. Vilar *et al.* (2008) found a

similar result for a binary system of Cu^{2+} and Pb^{2+} removal from aqueous solution by the algae *Gelidium*. The authors found that the biomass had more affinity for lead ions and also a lower MTZ than for copper.

Subsequently, the breakthrough data obtained for the single component experiments shown in Figure 3 were fitted by the Bohart-Adams model. The fitting curves obtained from the model are shown in Figures 5 and 6 for Cr^{3+} and Pb^{2+} , respectively. The parameters of the fitted model are shown in Table 8.

According to Table 8, the constant k value for lead ions was smaller when the flow was 2 mL.min^{-1} , whereas they are close with the flow rates of 1 mL.min^{-1} and 3 mL.min^{-1} . Analyzing the q parameter, it can be seen that the concentration of lead in the adsorbent was higher at the flow rate of 1 mL.min^{-1} , the concentration decreasing when the flow was increased. This fact shows that a smaller flow rate increased the lead removal rate. The opposite happens with chromium ions, where the greater the flow rate, the greater are the values of k and q . Both the experimental and the model curves shown in Figures 5 and 6 indicate that Cr^{3+} is the weakest adsorbed component and Pb^{2+} is the strongest adsorbed component since the breakpoint of chromium is the lowest value for all flow rates.

Table 7: Chromium and lead adsorption parameters in fixed bed.

Ratio	Metal Ion	MTZ (cm)	q_u (mmol.g^{-1})	q_t (mmol.g^{-1})
1	Cr^{3+}	8.169	0.108	0.237
	Pb^{2+}	6.994	0.125	0.234
2	Cr^{3+}	9.352	0.124	0.329
	Pb^{2+}	6.286	0.098	0.169
3	Cr^{3+}	9.678	0.034	0.096
	Pb^{2+}	5.643	0.074	0.119

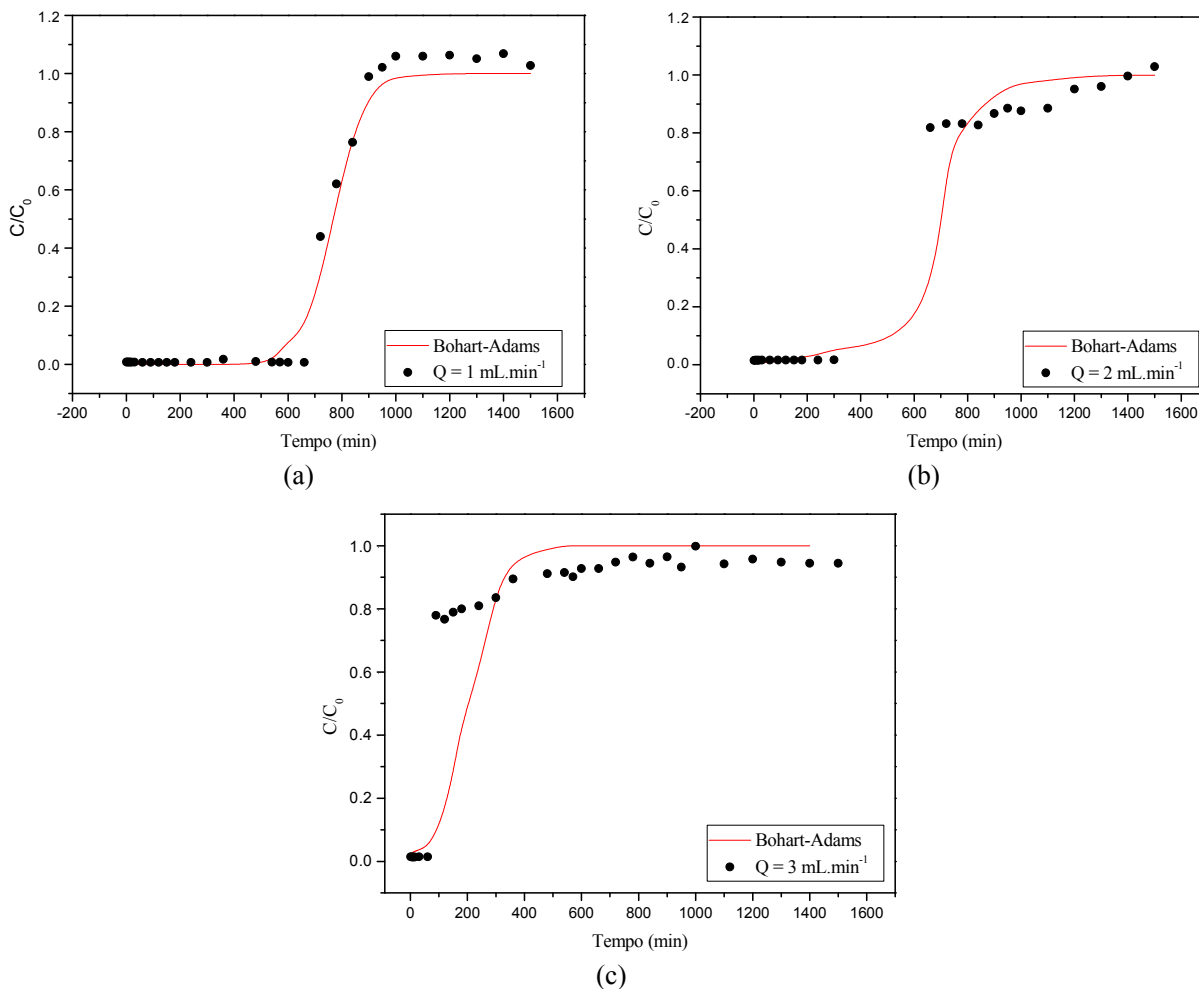
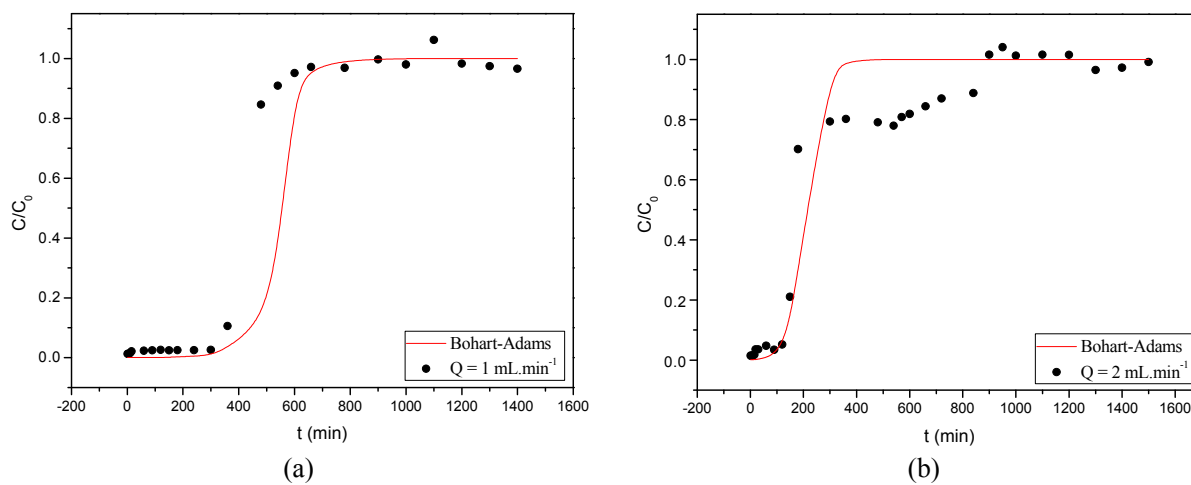


Figure 5: Fitting of the Bohart-Adams model for breakthrough curves obtained for Pb^{2+} removal by the bed at different flows: (a) $1 \text{ mL}\cdot\text{min}^{-1}$ (b) $2 \text{ mL}\cdot\text{min}^{-1}$ and (c) $3 \text{ mL}\cdot\text{min}^{-1}$.



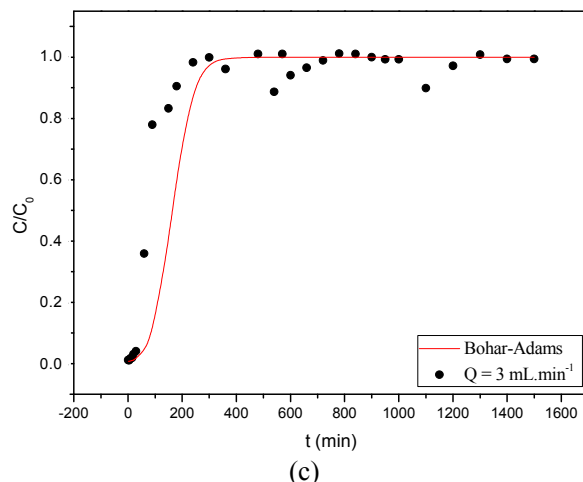


Figure 6: Fitting of the Bohart-Adams model for breakthrough curves obtained for Cr^{3+} removal by the bed at different flows: (a) $1 \text{ mL}\cdot\text{min}^{-1}$ (b) $2 \text{ mL}\cdot\text{min}^{-1}$ and (c) $3 \text{ mL}\cdot\text{min}^{-1}$.

Table 8: Bohart-Adams parameters obtained for the three flow rates studied.

	Parameters	Flow rate		
		$1 \text{ mL}\cdot\text{min}^{-1}$	$2 \text{ mL}\cdot\text{min}^{-1}$	$3 \text{ mL}\cdot\text{min}^{-1}$
Pb^{2+}	$k \text{ (L}\cdot\text{mmol}^{-1}\cdot\text{min}^{-1}\text{)}$	0.0150	0.0088	0.0165
	$q \text{ (mmol}\cdot\text{g}^{-1}\text{)}$	120	76	33
Cr^{3+}	$k \text{ (L}\cdot\text{mmol}^{-1}\cdot\text{min}^{-1}\text{)}$	0.0189	0.0291	0.0301
	$q \text{ (mmol}\cdot\text{g}^{-1}\text{)}$	20	21.5	23

CONCLUSIONS

This work evaluated the removal of single component and bicomponent mixtures of chromium and lead using the aquatic macrophyte *Salvinia natans* in batch and dynamic systems. From the FT-IR characterization, we observed that the biomass has different functional groups for heavy metal binding such as phosphonates, carboxylates, amide and hydroxide groups and these groups participate actively in the biosorption process. The single component equilibrium data showed that Cr^{3+} has a slightly higher removal capacity by the macrophyte than Pb^{2+} . The competitive isotherm showed that, during the biosorption process, there was the displacement of chromium due to the addition of lead, which implies a higher affinity of lead ions for the active sites of the biomass. The fixed-bed experiments in single component systems showed that the greater the flow rate, the lower the time of saturation of the metals in the column and the greater the MTZ. In fixed bed competitive systems, the concentration of metal ions has an influence on the adsorption process. The higher the concentration of metal ions the lower is the metal removal capacity of the column for both ions. The MTZ was higher for chromium ions for all the three ratios of concentration

studied. The experimental data showed that properties such as ion concentration, Pauling electronegativity, ionic radius, hydrated radius and *softness* have strong influence on the adsorption process, leading to higher or lower metal ions removal. Results showed the possibility of using the aquatic macrophyte *Salvinia natans* in batch and fixed-bed systems.

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