

COMPETITIVE BIOSORPTION OF CHROMIUM AND LEAD INTO SALVINIA NATANS MACROPHYTE

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ABSTRACT – *Salvinia natans* macrophyte has been studied as a potential biosorbent for metal ions removal. We investigated in this work the performance of the macrophyte in recovery of lead and chromium from bicomponent synthetic solution from two different systems, batch and fixed bed. Equilibrium data were obtained by batch system through isotherms and fitted to Langmuir and Langmuir-Freundlich models. The breakthrough curves were performed at three different concentrations ratio. In order to know the biosorption mechanism FT-IR analyses were performed for *S. natans* before and after uptake of metal ions. The results showed different functional groups on the biomass surface and the ability of these groups bind with Cr⁺³ and Pb²⁺ ions in aqueous solution.

1. INTRODUCTION

Metal ions as chromium and lead are chemical elements toxic to the environment and human body and 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 is well known and extensively studied (Axtell *et al.*, 2003; Shenget *al.*, 2004; Saygidegeret *al.*, 2005).

These kind 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).

The biosorption is a purification process which may involve complex mechanisms, which depends on the chemical and morphological characteristics of the biological material used (Lima *et al.*, 2011). The term "biosorption" refers to various ways of removing the 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, phosphates, amines, aldehydes (Saygidegeret *al.*, 2005; Bernardo *et al.*, 2009).

Among all kind of biomaterials existing we can mention the aquatic macrophytes. They have some advantages such as low-cost and locally available material. They are easy to growing in a wide range of temperature and pH. Moreover, many works have shown the high affinity of the metal ions by macrophytes in adsorption process (Lima *et al.*, 2011). Wang and

Qin (2006) have tested the biomass of aquatic macrophyte *Alternantheraphiloxeroides* in removal of Ni^{2+} , Zn^{2+} and Cr^{6+} ions. The Langmuir model fitted to the experimental data showed the maximum removal capacity, q_{max} , of 0.723, 0.343 and 0.279 mmol.g^{-1} for Cr^{6+} , Zn^{2+} and Ni^{2+} , respectively.

Bunluesinet *al.*, 2007 studied the removal of Cd^{2+} by the nonliving biomass of aquatic macrophyte *Hydrillaverticillata*. They tested batch and fixed-bed systems. The Langmuir model fitted to the batch data showed the maximum removal capacity, q_{max} , of 0.133 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 *Eichhorniacrassipes* macrophyte biomass modified by Fenton treatment. The efficiency of the Zn^{2+} sorption process under different experimental conditions was determined and experimental data showed good fitting to Langmuir model with maximum sorption capacity of 0.114 and 0.203 mmol.g^{-1} for raw and Fenton activated biomass (dose 5.0 g.L^{-1} , pH 6.0), respectively.

Therefore, the main 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 binary mixture solution in batch and fixed bed system. Equilibrium and breakthrough curves experiments were performed. The Langmuir and Langmuir-Freundlich isotherm models were applied to experimental data. The changes in functional groups were analyzed by spectroscopy in the infrared region (FT-IR).

2. MATERIALS AND METHODS

2.1. Biomass

Salvinia natans macrophyte was cultivated and collected by the CPAA (Research Center in Environmental Aquaculture) of State University of Paraná, Brazil. After collected the biomass was washed and dried at 55 °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.

2.2. Metal ions solutions

The chromium and lead synthetic solutions were prepared dissolving $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ salt and $\text{Pb}(\text{NO}_3)_2$ (both trade Vetec) in deionized water. The pH of the solution was adjusted to 4 using HNO_3 (0.5 M) and NaOH (1 M).

2.2. Fourier transforms infrared spectroscopy (FT-IR)

FT-IR analysis was accomplished with the aim of observe the functional groups present in biomass and the changes in these groups after 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.

2.3. Equilibrium assays

The equilibrium experiments were carried out by mixing 100 mL of solution with different concentrations combinations of Cr^{3+} and Pb^{2+} (Table 1) with 0.2 g of *S. natans* at room temperature and pH 4. The solution with the biomass was maintained under stirring for a period of 2 h, time enough to reach the equilibrium. Then the samples were centrifuged and concentrations of the metal ions were determined by Atomic Absorption Spectrophotometry (AAS). The adsorption capacity was calculated by Eq. 1.

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

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 biomass (g).

Table 1 - Concentrations used in binary mixture 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

2.4. Dynamic System assays

The breakthrough curves were obtained using a glass column with 1.5 cm inner diameter and 15 cm high. The biomass was inserted into the column and washed with deionized water for about 2 hours until all thin residue of the biomass has been removed. The column was fed with a bicomponent synthetic solution of lead and chromium with ratio of concentrations showed in Table 2, using a peristaltic pump, Masterflex brand, at a fixed flow rate of 1 mL.min^{-1} and pH of 4. A fraction collector (FC203 Fraction Collector) was used to collect aliquots at different periods of time. After this they were diluted and measured on an Atomic Absorption Spectrophotometer (Shimadzu AA 7000). The length of the mass transfer area (MTZ) and the useful (q_u) and total (q_t) amounts removed by the column were calculated as a function of time according to Geankoplis' method (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 breaking point is proportional to q_u (Equation 1), and the area up to the saturation of bed is proportional to q_t (Equation 2). The point of rupture was considered at a time (t_b), where the concentration at the column outlet equivalent to 5% of the initial feed concentration.

$$q_u = \frac{C_0 \cdot Q}{1000 \cdot m} \int_0^{t_b} \left(1 - \frac{C|_{z=L}}{C_0} \right) dt \quad (3)$$

$$q_t = \frac{C_0 \cdot Q}{1000 \cdot m} \int_0^{t_{ro}} \left(1 - \frac{C|_{z=L}}{C_0} \right) dt \quad (4)$$

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

The mass transfer zone (MTZ) was calculated using Equation 3 based on the ratio between q_u/q_t .

$$ZTM = H_L \cdot \left(1 - \frac{q_u}{q_t} \right) \quad (5)$$

Table 2 -Ratio of concentrations used in 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

3. RESULTS AND DISCUSSION

3.1. Fourier transforms infrared spectroscopy (FT-IR)

Figure 1 shows the peaks and bands of functional groups obtained by infrared spectroscopy. The importance of this analysis is to show the functional groups present on the biomass and if they were modified with the biosorption process. The raw biomass presented the band at 3442 cm^{-1} corresponding to the vibration of OH. The weak peak at 2360 cm^{-1} assigned to phosphonates. The peak at 1640 cm^{-1} corresponding to C=O of amide. $1130\text{--}1000 \text{ cm}^{-1}$ is vibration of C-O-C and O-H of polysaccharides. The peak at 914 cm^{-1} is assigned to C-X of the groups of halogens. The bands $< 800 \text{ cm}^{-1}$ are finger print zone which are phosphate and sulphur functional groups (Saygidegeret *al.*, 2005). After the biosorption process with the mixture of Cr^{3+} and Pb^{2+} some functional groups of *S. natans* are losing, which implies that these groups participate of the uptake of both metal ions. In other words, the biomass have different functional groups for heavy metal binding such as phosphonates, halogenated, amide and hydroxide groups (Saygidegeret *al.*, 2005).

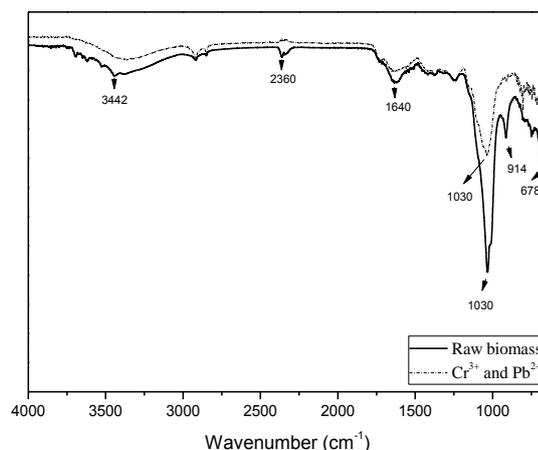


Figure 1 - FT-IR spectra of raw *S. natans* and the biomass saturated with chromium and lead.

3.2. Equilibrium assays

Figure 2 shows the adsorption equilibrium from bicomponent mixture of Cr^{3+} and Pb^{2+} . For the studied metals, we can observe that lead had a higher amount of removal from the solution than chromium. Which means that Pb^{2+} has high affinity with the active sites of the cell wall of the biomass. The results are in accordance with found in previous work (Lima *et al.*, 2012) using the *S. Natans* biomass in removal of lead present in a single component solution. We found that lead had a high removal capacity with q_{max} of $0.614 \text{ mmol.g}^{-1}$, much higher than that found in other work (Lima *et al.*, 2012) for chromium removal by the same biomass, which obtained a maximum removal capacity of $0.243 \text{ mmol.g}^{-1}$. In both papers the parameter b from Langmuir model was 13.308 and $19.251 \text{ L.mmol}^{-1}$ for chromium and lead, respectively.

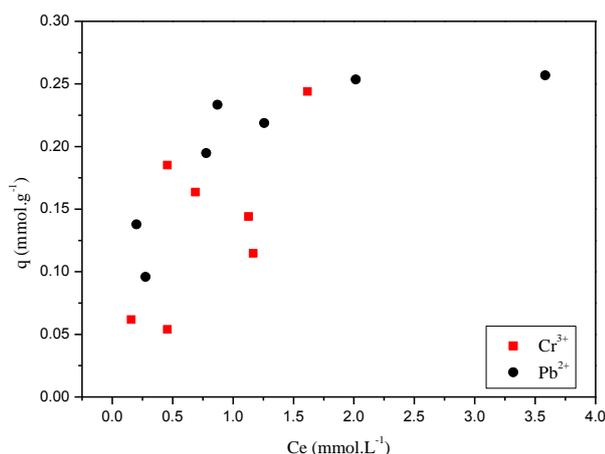


Figure 2 - Equilibrium isotherms of binary system of Cr^{3+} and Pb^{2+} .

3.3. Dynamic System assays

In order to know the influence of the feed concentration in the biosorption process, experiments were performed in 3 different ratios of concentrations at flow rate of 1 mL.min^{-1} and pH 4. Figure 3 shows the breakthrough curves at the experimental conditions

for the removal of Cr^{3+} and Pb^{2+} . We can observe that for all ratios the residence time was higher for lead. When concentration of Cr^{3+} increases, the residence time of both metal ions in column decreases. The same happens when the concentration of Pb^{2+} increases. It means that when we increased the concentration of metal ions in solution there were a greater competition for active sites of the biomass. These results are similar to those found by many researchers in a single and multicomponent systems of biosorption in columns for different metal ions and using different adsorbents (Calero *et al.*, 2009; Vijayaraghavan *et al.*, 2005; Carmona *et al.*, 2012; Vilaret *et al.*, 2008). The higher biosorbent affinities for Pb^{2+} can cause the Cr^{3+} displacement from the biosorbent surfaces.

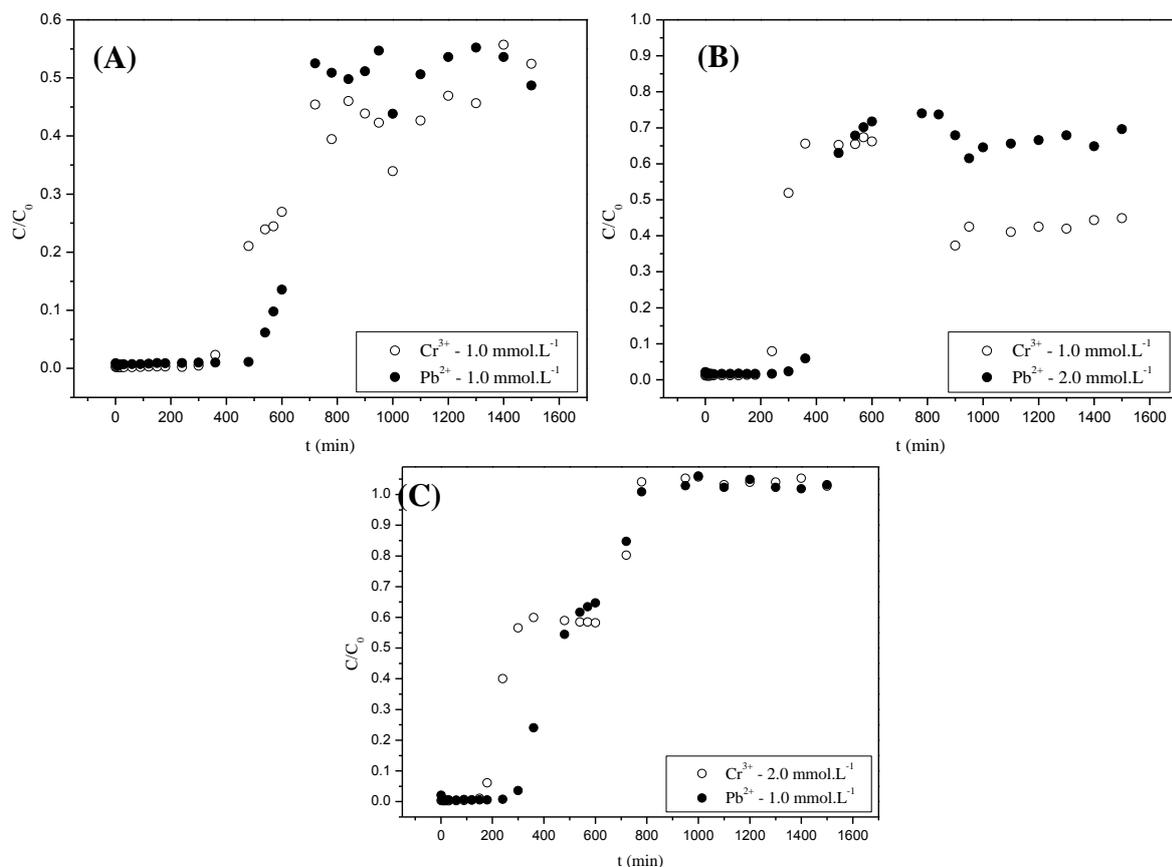


Figure 3 -Breakthrough curves for the removal of Cr^{3+} and Pb^{2+} for (a) ratio 1, (b) ratio 2 and (c) ratio 3.

The MTZ has a bed height (H_L) corresponding to the maximum value. The smaller the area (value of MTZ), the better the efficiency of mass transfer. The parameters obtained through experimental data are shown in Table 3. From the data we can observe that the higher value of MTZ, or resistance to mass transfer, is for Cr^{3+} at a ratio 3, when 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 is higher than for lead. The higher MTZ for lead was gotten when the concentration for both metals were equal (ratio 1). However, at this condition the better result of q_u (about 0.125 mmol.g⁻¹) for lead was obtained. This value can be explained since at this ratio the time of residence is higher in column. Vilaret *et al.*, (2008) found a similar result for a binary system of Cu^{2+} and Pb^{2+} removal from aqueous solution by algae *Gelidium*.

The authors found that lead had more affinity with lead ions and also a lower MTZ than copper.

Table 3–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

4. CONCLUSIONS

This work evaluated the removal of a bicomponent mixture of chromium and lead using the aquatic macrophyte *Salvinia natans* in batch and dynamic system. From the FT-IR characterization we observed that the biomass have different functional groups for heavy metal binding such as phosphonates, halogenated, amide and hydroxide groups. The equilibrium data showed that lead have more affinity for the active sites of the biomass than chromium as shown in previous work for single components study. The fixed-bed experiments showed that the concentration of metal ions have an influence in the adsorption process. The higher the concentration of metal ions the lower is the metal removal capacity of the column. The MTZ was higher to chromium ions for all the three ratios studied. Results showed the possibility of using the aquatic macrophyte *Salvinia natans* in batch and fixed-bed systems.

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