

FIXED BED BIOSORPTION USING AQUATIC MACROPHYTE IN LEAD REMOVAL

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ABSTRACT – Adsorption process is an efficient alternative in metal ions removal. Many materials can be used in this process; among them, we can cite biological materials such as aquatic macrophytes. The macrophytes have shown a high percentage of metal ions removal and they have an advantage of being low cost and have the possibility of growing. In view of this, the aim of this work is evaluate lead removal by *Salvinia natans* in dynamic system. Essays were carried out in a fixed bed column for different flow rates. The result showed the higher amount of lead removed from the column was $0.152 \text{ mmol.g}^{-1}$ for a flow rate of 1 mL.min^{-1} and an initial concentration of lead of 1 mmol.L^{-1} . In order to know the changes in surface morphology of *S. natans* before and after the process as well as the functional groups that participate of the removal of lead, the characterization using the SEM/EDX and FTIR techniques was performed.

1. INTRODUCTION

Metal ions is one of the many kind of pollutants released in water bodies which when in high concentration can bring serious consequences to the environment. Among the metal ions with harmful potential effects to the human body, we can highlight the lead. The toxicity of this metal can generates light or clinical effects, which can result in problems in the nervous system. The main source of this kind of pollutant are plates and pipes for plumbing, paints and pigments, coating of electrical cables, storage batteries, agricultural, etc.

In this context, the search for new technologies capable of removing metals from wastewater has become an important topic for research. Among the common methods used for this purpose, adsorption appears as an economical and efficient means for removal of metal ions when compared to techniques such as ion exchange, reverse osmosis, precipitation, electrodialysis, among others (Tarley et al., 2004; Benhima et al., 2008; Rakhshae et al., 2009).

The adsorption process using biological material offers advantages such as low operating cost, possibility of recovery of metal ions removed from the effluent, the possibility of regeneration of the bioadsorbent, minimizing the volume of chemical and/or biological sludge to be disposed and a high efficiency in detoxifying very dilute effluent (Yang and Volesky, 1999; Lima et al., 2011).

Low-cost materials such as agricultural waste, chitosan, clays, seaweed, macrophytes, industrial waste processing have been used to evaluate the removal of heavy metal ions from wastewater (Lee and Davis, 2001; Hassanein and Koumanova, 2010; Ngah *et al.*, 2002; Galindo *et al.*, 2013; Almeida Neto *et al.*, 2012; Matos *et al.*, 2009; Lima *et al.*, 2013). Among these materials, macrophytes have shown good affinity with metal ions, and are renewable in nature (Banerjee and Sarker, 1997; Saygideger *et al.*, 2005; Phetsombat *et al.*, 2006; Rahman *et al.*, 2008; Khellaf e Zerdaoui, 2010).

Maine *et al.* (2004) studied the ability of macrophytes *Pistia stratiotes* and *Salvinia herzogii* to remove Cr^{+3} in aqueous solutions. Both macrophytes were able to efficiently remove the metal ion to the initial concentrations of 1, 2, 4 and 6 mg.L^{-1} . The authors observed that at higher concentrations there was a higher rate of bioaccumulation in roots. Maximum removal of metal ion occurred in approximately 24 hours. The *Salvinia herzogii* got greater removal capacity than *Pistia stratiotes* species.

Singha *et al.* (2012) used the macrophyte *Eichhornia crassipes* for removal of Cr^{6+} ion using a fixed bed column. The authors evaluated the influence of flow rate, bed height and inlet concentration on the system performance. The authors concluded that when the flow rate increased from 1.53 to 3.07 $\text{ml min mL.min}^{-1}$ the time of rupture of the column decreased to a minimum value. The authors noted that with increasing bed height (7-35 cm) and decreasing concentration of input (10-50 ppm) in bed, the time to rupture of the column increased.

In view of this, the aim of this study was to evaluate the removal of Pb^{+2} ion using dead biomass of aquatic fern *Salvinia natans* in fixed bed column, evaluating parameters such as flow rate and inlet concentration of the solution in the bed. The biomass was characterized in terms of physical-chemical properties, before and after adsorption process, by the techniques of Scanning Electron Microscopy (SEM) with EDX mapping and Infrared Spectroscopy (FT-IR).

2. MATERIALS AND METHODS

2.1. Biomass

The aquatic macrophyte *Salvinia natans* 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. Then, the biomass was sieved and the fraction measuring 0.855 mm was used in the experiments.

2.2. SEM/EDX

The surface of the *Salvinia natans* was examined using a scanning electron microscope (SEM). The samples were dried and covered with a thin layer of gold (10 nm) using a sputter coater (SCD 0050 – Baltec, Liechtenstein). The equipment JEOL JXA-840A scanning electron microscope (20 kV) under vacuum of 1.33×10^{-6} mBar (Jeol, Japan) was used to observe the

biomaterial. The chemical composition was determined by energy dispersive X-ray spectroscopy on the biomass after lead adsorption. The samples were prepared for SEM analyses.

2.3. Fourier transforms infrared spectroscopy (FT-IR)

FT-IR spectroscopy was used to observe the functional groups present in biomass and the changing 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.

2.4. Dynamic System assays

Assays were performed using a glass column with 1.5 cm inner diameter and 15 cm high. The biomass was inserted into the column and washing with deionized water was made for about 2 hours until thin residue of the macrophyte has been removed. The column was fed with a synthetic solution of lead with 1 mmol.L^{-1} concentration, using a peristaltic pump, Masterflex brand, at a flow rate ranging of 1, 2 and 3 mL.min^{-1} .

Aliquots of the solutions were collected from the column at pre-determined time using a fraction collector (FC203 Fraction Collector) and after, they were measured on an Atomic Absorption Spectrophotometer (Shimadzu AA 7000). The length of the mass transfer area (MTZ) was calculated by Geankoplis' method (1993), as well as the useful amounts (q_u) and total (q_t) removed by the column as a function of time. The point of rupture was considered at a time (t_b), where the concentration at the column outlet is equivalent to 5% of the initial feed concentration. A mass balance on the column was performed using the data obtained from the saturation by equations 1 and 2, in which the area under the curve ($1 - C/C_0$) until the breaking point is proportional to q_u , and the area up to the saturation of bed is proportional to q_t .

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

$$q_t = \frac{C_0 \cdot Q}{1000 \cdot m} \int_0^{t_{or}} \left(1 - \frac{C|_{z=L}}{C_0} \right) dt \quad (2)$$

Where, $C|_{z=L}$ is the concentration of metal in solution at the outlet of the column and C_0 is the concentration 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 .

$$ZTM = H_L \cdot \left(1 - \frac{q_u}{q_t} \right) \quad (3)$$

The MTZ has a bed height corresponding to (H_L) as the maximum value. The smaller the MTZ is, better is the efficiency of mass transfer.

3. RESULTS AND DISCUSSION

3.2. SEM/EDX

The micrographs of *S. natans* obtained by SEM/EDX analyses can be observed in Figure 1 (a)-(c). The macrophyte has a roughness surface and the presence of microstructures, which can be attributed to the deposition of salts on the surface of the biomaterial (Yang and Chen, 2008). Figure 1 (b) shows that there are no changes in morphology of biomass surface after biosorption process. The mapping of lead in biomass surface, showed in Figure 1 (c), indicates a homogeneous distribution of the metal ion in the *S. natans* surface.

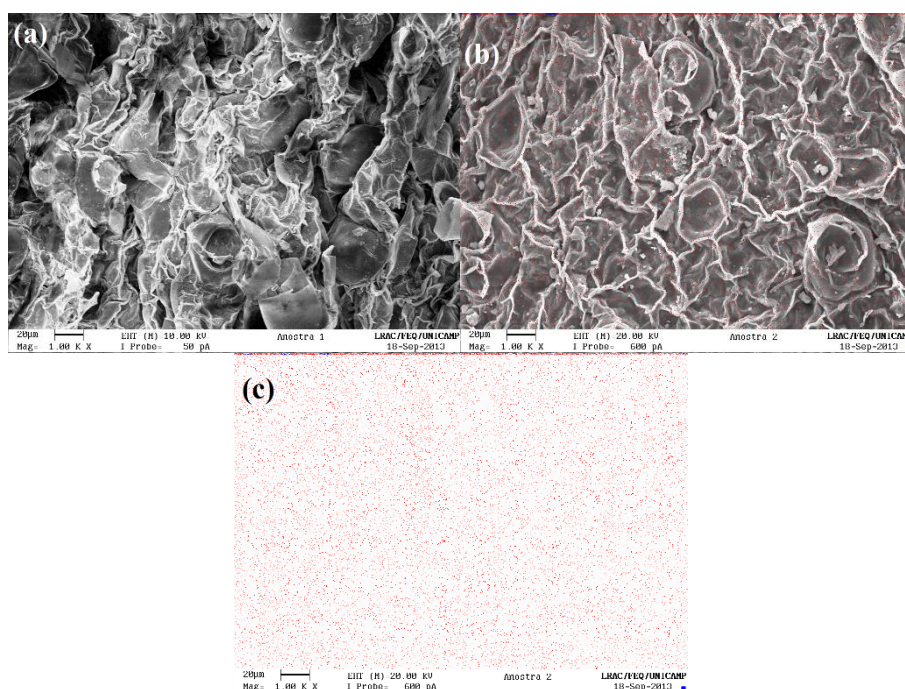


Figure 1 - SEM-EDX micrographs of *S. natans* (a) in nature, (b) saturated with Pb^{2+} , (c) Pb^{2+} mapping.

3.3. Fourier transforms infrared spectroscopy (FT-IR)

The technique of infrared spectroscopy determines which functional groups are present in biomass. The peaks and bands of Figure 2 show the changes due to adsorption

process. Analysis showed the presence of functional groups such as carboxylic phosphate, hydroxyl, amide and halogens for biomass *in natura*. The bands at 3200-3500 cm^{-1} corresponding to the vibration of OH polymer compounds, band between 2924-2850 cm^{-1} is symmetrical and the asymmetrical vibration of methylene ($\text{C}=\text{H}_2$), respectively. The peak between 1740-1722 cm^{-1} is assigned to the vibration of COO. The strong peaks at 1034 cm^{-1} and 1036 cm^{-1} present in macrophyte *in natura* and after saturation with Pb^{2+} , respectively, are corresponding to alcohols groups. The peaks at 2360 and 2340 cm^{-1} are present in nature macrophyte only and are assigned to phosphonates, indicating the involvement of these groups in the adsorption of Pb^{2+} ion.

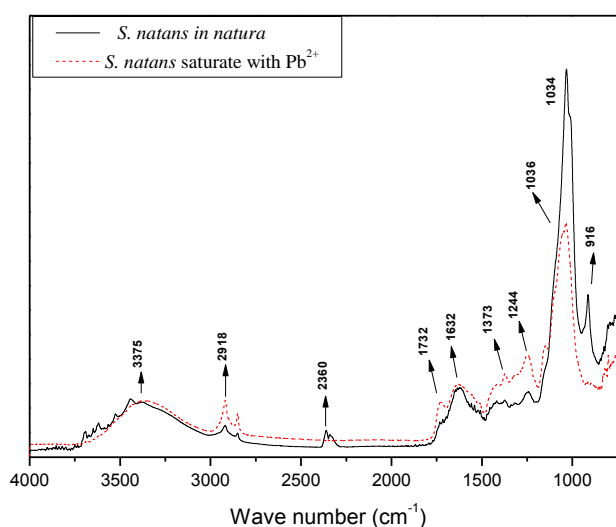


Figure 2 - FT-IR spectra of *S. natans* biomass and saturated with lead biomass.

3.4. Dynamic System assays

In order to know the influence of the feed flow in the removal process, assays were carried out in 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 Pb^{2+} . There is an influence of the flow rate in 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 time residence of the solution in the column was not sufficient to reach adsorption equilibrium due to high flow, or there is a short time for saturation of the column. The solution leaves the column before equilibrium of the solute/sorbent was achieved (Singha *et al.* 2012).

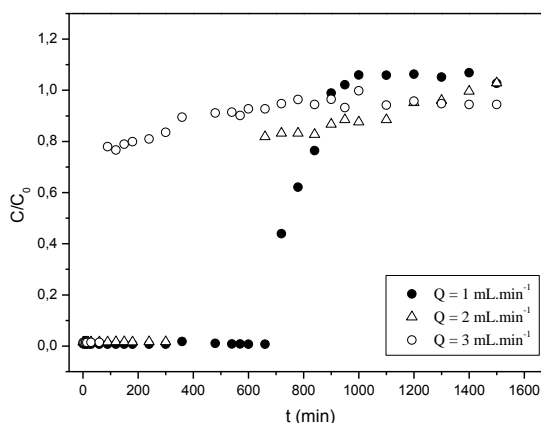


Figura 3 - Breakthrough curves at different flow rates of operation for the removal of Pb^{2+} .

Table 1 exhibits the calculated MTZ and adsorbed quantities. From Figure 3 it can be noticed that a higher value of MTZ (10.249 cm) and a higher resistance to mass transfer were gotten with flow rate of 3 mL.min⁻¹. This means that at higher flow rates the removal process is not favourable. The smaller MTZ was found to flow rate of 1 mL.min⁻¹, with values of q_u and q_t of 0.138 and 0.152 mmol.g⁻¹, respectively.

Table 1 - Lead removal efficiency parameters in fixed bed.

Flow rate (mL.min ⁻¹)	MTZ (cm)	q_u (mmol.g ⁻¹)	q_t (mmol.g ⁻¹)
1	1.448	0.138	0.152
2	7.030	0.144	0.272
3	10.249	0.041	0.128

4. CONCLUSIONS

This work evaluated the removal of lead present in a synthetic effluent by aquatic macrophyte *S. natans* using a dynamic system of fixed bed. The results obtained with SEM analyze showed the presence of microstructures in the surface of the biomass, which gives the material a rough surface and there was no change in the biomass morphology even after adsorption. The EDX technique coupled with SEM showed that the distribution of Pb^{2+} ion on the surface of macrophyte occurs homogeneously. The FT-IR results showed that are different functional groups in biomass and after process, the changes in these groups can be associated to the involvement of phosphonates in the adsorption of Pb^{2+} ion.

The dynamic assays provided a maximum and minimum MTZ value of 1.448 cm and 10.249 cm at a flow rate of 1 and 3 mL.min⁻¹, respectively. The higher the MTZ, the less efficient is the process of lead removal in the column. The study showed the feasibility of macrophyte *S. natans* in the removal of lead present in wastewater.

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