

Lead Biosorption by *Salvinia Natans* Biomass: Equilibrium Study

Lívia K. S. Lima, Jean F. L. Silva, Meuris G. C. da Silva, Melissa G. A. Vieira*

School of Chemical Engineering, State University of Campinas, UNICAMP, 13083-825 Campinas-SP, Brazil
 melissagav@feq.unicamp.br

The high amount of residual metal ions released in wastewaters from process such as mining, painting, smelting, batteries manufacture, and others, becomes a problem to the environment. In view of this, the adsorption process arises as an alternative treatment to metal ion removal. The use of some biological materials as adsorbents like aquatic plants has shown high affinity by metal ions. Therefore, the aim of this study was to evaluate the performance of aquatic macrophyte *Salvinia natans* in Pb^{2+} removal. Langmuir model best fitted to equilibrium data and the maximum uptake capacity was $0.614 \text{ mmol.g}^{-1}$. In order to know the biosorption mechanism FT-IR analyses were performed for *S. natans* before and after uptake of metal ion. The results showed different functional groups on the biomass surface and the ability of these groups bind with Pb^{2+} ion in aqueous solution.

1. Introduction

Pb is commonly used in manufacture of the Lead–acid batteries and others applications as shielding from radiation. The waste of this metal is extremely hazardous for the environment. The mostly used removal process of this metal from wastewater is chemical precipitation. Although the chemical precipitation method is quite effective, the resultant heavy metal hydroxide sludge is classified as a hazardous waste, which needs further treatment before disposal (Miretzky and Munóz, 2011). Traditional technologies such as filtration, reverse osmosis and precipitation are not capable of remove adequately the metal ions from water or it is too expensive. Adsorption is one of the most economical methods on removing toxic metal ions from liquid effluents. Studies have been carried out aiming at developing more effective and selective adsorbent materials, which are abundant in nature, requiring little processing in order to decrease cost (Wang and Zhang, 2010). A wide range of biological materials as chitosan (Heidari et al., 2013), alginate (Bée et al., 2011), beech sawdust (Božić et al., 2013), alligator weed (Wang and Zhang, 2010), *Lemna minor* (Lima et al., 2011) and others has been studied. Among these materials the aquatic macrophyte *Salvinia natans* has been studied in this work. The advantages of this kind of material are the low cost associated with a high affinity of metal ions (Lima et al., 2013). Studies using *Salvinia* species has been conducted in recent years. Dhir and Kumar (2010) studied the removal of Cr^{6+} , Ni^{2+} and Cd^{2+} by one of the *Salvinia* species. Batch experiments were performed and the authors obtained a higher value of adsorption for Cr^{6+} , about $0.763 \text{ mmol.g}^{-1}$ followed by Ni^{2+} and Cd^{2+} with removal of 0.704 and $0.348 \text{ mmol.g}^{-1}$, respectively. Baral et al. (2008) evaluated thermally activated weed *Salvinia cucullata* for removal of Cr^{6+} . The experiments were conducted in continuous system where they found a maximum uptake capacity of 3 mmol.g^{-1} at a flow rate of 3.6 L.h^{-1} , biomass weight 50 g and ion concentration 100 mg.L^{-1} . The uptake of metal ion by macrophytes may be attributed to the functional groups present in cell wall of these materials such as carboxyl, hydroxyl, amino and halites (Lima et al., 2013). Thus, the aim of this research is to study the capacity of the aquatic macrophyte *Salvinia natans* to remove Pb^{2+} ion from aqueous solution. Equilibrium experiments were carried out in batch. The Langmuir, Freundlich and D-R models were applied to experimental data. The changes in morphology and functional groups were

analyzed by a scanning electron microscopy (SEM) and spectroscopy in the infrared region (FT-IR), respectively.

2. Materials and Methods

2.1 Biomass

The biomass *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. After that, the biomass was sieved and fractions measuring 0.855 mm were collected and used in experiments.

2.2 SEM/EDX analyses

The *S. Natans* surface was evaluated 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 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 which functional groups were present in the surface of the 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 Batch adsorption experiments and thermodynamics

The metal ions solutions were prepared from nitrate salts of lead, $\text{Pb}(\text{NO}_3)_2$ (Vetec). The metal ion concentrations were determined by atomic absorption spectrometry (Perkin Elmer AA Analyst 100 with air-acetylene oxidizing flame).

Equilibrium experiments were conducted by mixing 100 mL of solution with different concentrations of Pb^{2+} (0.025 to 4 $\text{mmol}\cdot\text{L}^{-1}$) with 0.2 g of biomass at pH 4. The solution in contact with the biomass was maintained under stirring for a period of 2 h, time enough to reach equilibrium. The results were fitted by Langmuir, Freundlich and D-R models that can be expressed as Eq. (1), Eq. (2) and Eq. (3) respectively:

$$q = \frac{q_{\max} b C}{1 + b C} \quad (1)$$

$$q = k_F C^{1/n} \quad (2)$$

$$\ln q_e = \ln q_m - K_{DR} \varepsilon^2 \quad (3)$$

Where: q is the metal ions uptake at equilibrium ($\text{mmol}\cdot\text{g}^{-1}$); q_{\max} is the maximum Langmuir uptake ($\text{mmol}\cdot\text{g}^{-1}$); C is the final metal ions concentration at equilibrium ($\text{mmol}\cdot\text{L}^{-1}$); b is the Langmuir affinity constant ($\text{L}\cdot\text{g}^{-1}$). k_F is the Freundlich constant and indicates the adsorption capacity of the adsorbent ($\text{mmol}\cdot\text{g}^{-1}$) and $1/n$ is the heterogeneity factor. K_{DR} is the porosity factor [$\text{mol}^2\cdot\text{J}^{-2}$], q_m is the monomolecular adsorption capacity of ion biosorption by the biomass surface [$\text{mg}\cdot\text{g}^{-1}$] and the variable ε can be related to the equilibrium concentration [C_e , $\text{g}\cdot\text{L}^{-1}$] as follows:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (4)$$

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

A plot of $\ln(q_e)$ versus ε^2 [$\text{J}^2\cdot\text{mol}^{-2}$] yields a straight line confirming the model. E is the mean free energy of adsorption per molecule of the adsorbate when it is transferred from the solution to the biomass surface [$\text{kJ}\cdot\text{mol}^{-1}$], which can be calculated by the following equation (Ergene et al., 2009):

$$E = (-2 K_{DR})^{1/2} \quad (5)$$

The thermodynamic parameters for the adsorption process ΔH [kJ.mol⁻¹], ΔS [J.K⁻¹mol⁻¹] and ΔG [kJ.mol⁻¹] were evaluated using Eq. (6) and Eq. (7):

$$\Delta G = -RT \ln(K_d) \quad (6)$$

$$\ln(K_d) = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

where K_d is the adsorbate distribution coefficient = q_{eq}/C_{eq} in L.g⁻¹.

The plot of $\ln(K_d)$ versus $1/T$ must be linear with inclination of the straight line ($-\Delta H/R$) and intercept the y axis at ($\Delta S/R$), providing the values for ΔH and ΔS . The variation in Gibbs free energy (ΔG) is the fundamental criterion of process spontaneity.

3. Results and Discussion

3.1 SEM/EDX Analysis

The morphology of biomass was observed by scanning electron microscopy (SEM) before and after biosorption Pb²⁺ (Figure 1 a-b). It is possible to observe in Figure 1 (a) the roughness of the surface which can be attributed to some alkali metals as sodium, potassium and others salts deposition (Yang and Chen, 2008). After the biosorption process there were not significant changes in biomass surface morphology, even with stirring. The mapping of lead ions onto biomass surface, showed in Figure 1 (b), indicates a homogeneous distribution of the metal ion in the *S. natans* surface.

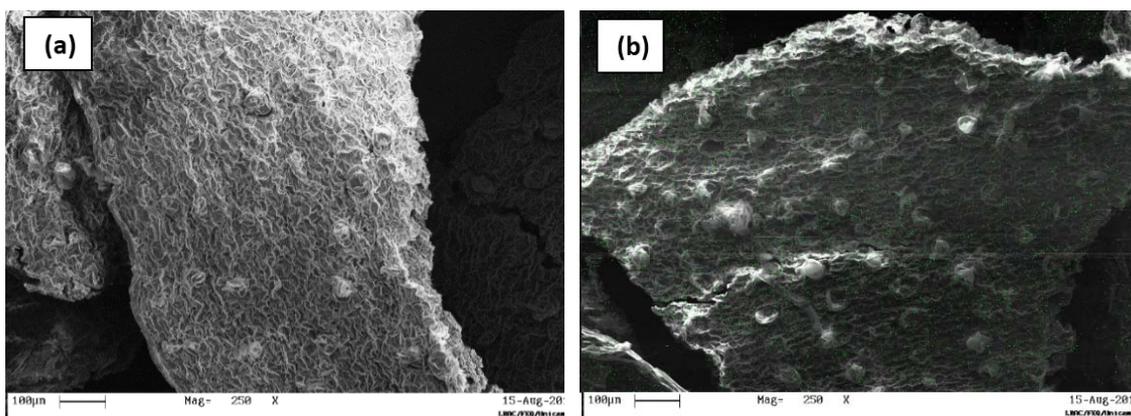


Figure 1: SEM-EDX micrographs of *S. natans* (a) raw biomass, (b) saturated with Pb²⁺.

3.2 FT-IR analysis

Through the FT-IR spectrum of the biomass before and after biosorption process was possible to determine which functional groups are present in *S. natans* cell wall. It was expected that the adsorption of Pb²⁺ showed a changing in bands and peaks which was observed how observed in Table 1. Peaks corresponding to phosphanate and C-X were not observed in the spectrum after biosorption process. The bands < 800 cm⁻¹ are finger print zone which can be attributed to phosphate and sulphur functional groups (Sharma and Goyal, 2010).

Table 1: FT-IR spectra of row biomass and saturated with lead.

Peaks and Bands		Description
Raw <i>S. natans</i>	Saturated <i>S. natans</i>	
679	679	C-Cl
914	-	C-X
1030	1040	Alcohol
1240	1240	C-O de esters e ethers
1640	1640	C=O de amide
2340	-	Phosphonate
2360	-	Phosphanate
2850	2850	C-H of aliphatic chain
2920	2920	C-H of aliphatic chain
3200-3500	3200-3500	O-H

3.3 Batch Adsorption Experiments and Thermodynamics

The biosorption data were fitted to isotherms models as shown in Figure 2 as well as the Langmuir, Freundlich and D-R models parameters are shown in Table 2. The Langmuir model fitted better to the experimental data with maximum biosorption capacity (q_{max}) of $0.614 \text{ mmol.g}^{-1}$ for a temperature of $15 \text{ }^\circ\text{C}$. Due the sensibility of the macrophyte it is possible to observe that according the temperature the biosorption process can be favored. Some studies using biological material to remove Pb^{2+} show that the results obtained in this work are in according to literature. Keskinan et al. (2007) obtained 0.224 and $0.216 \text{ mmol.g}^{-1}$ for removal of Pb^{2+} using *Myriophyllum spicatum* and *Ceratophyllum demersum* as biosorbents, respectively. Hamza et al. (2013) used sugarcane bagasse to Pb^{2+} removal and achieved a maximum uptake of $0.273 \text{ mmol.g}^{-1}$. Sekhar et al. (2004) used the bark of *Hemidesmus indicus* plant to remove Pb^{2+} and attained $0.452 \text{ mmol.g}^{-1}$ of removal in a continuous system. The D-R model shows through the free energy if the process occurs by a chemical or physical way. The results obtained for all temperatures (Table 2) exhibit $E < 8 \text{ kJ.mol}^{-1}$ which means that adsorption process is physical (Argun et al., 2007).

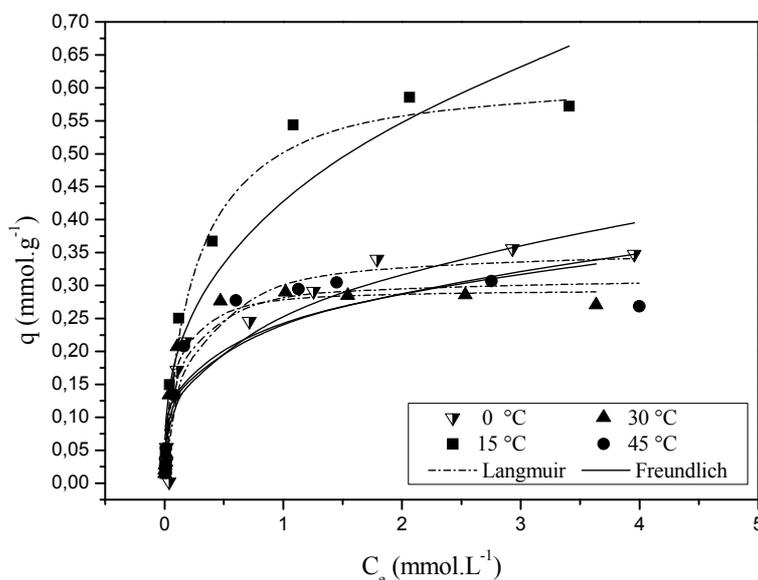


Figure 2: Langmuir and Freundlich model fitted isotherm to experimental data.

Table 2: Langmuir, Freundlich and D-R parameters for biosorption on *S. natans* biomass.

T (°C)	Langmuir			Freundlich			Dubinin-Radushkevich		
	q_L (mmol.g ⁻¹)	b^*	R^2	k_F	n	R^2	q_m (mmol.g ⁻¹)	$-k_{DR}$ (10 ⁻⁵ mol ² .J ⁻²)	E (kJ.mol ⁻¹)
0	0.355	6.117	0.949	0.256	3.154	0.890	0.269	0.028	4.218
15	0.614	5.471	0.989	0.439	2.964	0.936	0.508	0.022	4.814
30	0.295	19.251	0.990	0.245	4.204	0.832	0.301	0.015	5.814
45	0.311	10.487	0.984	0.242	3.816	0.830	0.308	0.018	5.331

*Unit of b (L.mmol⁻¹)

Table 3 shows the thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption. The negative values of ΔG° indicate the adsorption progress degree of spontaneity. In Table 3 it is clear that the reaction is spontaneous in nature since all values of ΔG° are negative at all the temperature studied. The negative values of ΔG° increase with the increase of the temperature, which means that the adsorption was more spontaneous at higher temperature. Positive ΔH value confirms that the sorption is endothermic in nature. Positive value of change in entropy (ΔS°) reflects the affinity of the adsorbents for the lead ions (Das et al., 2013).

Table 3: Thermodynamic parameters.

ΔH° (J.mol ⁻¹)	ΔS° (J.mol ⁻¹)	ΔG° (kJ.mol ⁻¹)			
		0 °C (273 K)	15 °C (288 K)	30 °C (303 K)	45 °C (318 K)
8.541	54.143	-14.797	-15.609	-16.422	-17.234

4. Conclusions

This work shows that the biosorption process achieved better results under low temperature conditions. The Langmuir model fitted better to experimental data and the maximum uptake exhibited was 0.614 mmol.g⁻¹. The morphological micrographs showed the presence of microstructures on the surface of biomass, mainly attributed to the deposition alkali metals and crystalline salts. There were no morphological changes after biosorption process. The D-R model showed that the process is physical. Also the thermodynamics showed the spontaneity of biosorption and the endothermic nature. The results indicated *Salvinia natans* constitutes a promising low-cost biosorbent for the removal of metal ions.

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