Lead and Chromium Biosorption by
Pistia stratiotes Biomass

Lívia K. S. Lima, Bruno T. Pelosi, Meuris G. C. Silva, Melissa G. A. Vieira[*]

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

Biosorption using biological materials has been extensively studied as a promising technology to contain the environmental impacts caused by heavy metals. Among the alternative biosorbents evaluated macrophytes shows high affinity by metal ions. In addition, this kind of material are from renewable sources, biodegradable and easy to grow, supporting wide ranges of pH and temperature. Therefore, the aim of this study is to evaluate the performance of macrophyte *Pistia stratiotes* in Cr^{3+} and Pb^{2+} removal. Equilibrium isotherms data were fitted to Langmuir model and the maximum uptake capacities were 0.317 and 0.225 $mmol.g^{-1}$ for Cr^{3+} and Pb^{2+}, respectively. In order to know the biosorption mechanism FT-IR analyses were performed for *P. stratiotes* 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 Pb^{2+} ions in aqueous solution.

1. Introduction

In recent years the pollution control becomes one of prime concerns of society. The increase in untreated or partially treated wastewaters and industrial effluents into natural ecosystems pose a serious problem to the environment (Aravindhan et al., 2007). Among the several pollutants existing in industrial wastewater heavy metals has a special attention due to the toxicity and commercial value of this kind of pollutant (Araújo and Teixeira, 1997). The hazards associated with metal ions have led to the development of several wastewater reclamation technologies (Bassi et al., 2000). Traditional technologies for metal removal include complexation and precipitation, filtration, reverse osmosis, adsorption, etc. (Vieira et al., 2011) Although some of these technologies are considered of low cost the most part of them are not capable of removing trace levels of metal ions (Deans and Dixon, 1992). The use of adsorption for wastewater remediation has been gaining attention due the effective potential of removal of the metal ions by the several kinds of adsorbents existents. Activated carbon is the most popular adsorbent used for this purpose and widely used in wastewater treatment applications throughout the world (El-Shafey et al., 2002). In spite of its prolific use, activated carbon remains an expensive material since the higher the quality of the activated carbon, the greater its costs (Ngah et al., 2006). New adsorbents, for example the aquatic macrophytes, have some advantages such as low-cost and locally available material. They are easy to grow and can tolerate 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). The cell wall properties from the biosorbent are responsible for its performance during biosorption process. Functional groups such as carboxyl, methyl, hydroxyl and others have the ability of bind the metal ions onto the biomass surface enhancing high capacity of biosorption. Therefore, the main of this research is to explore the application of the aquatic macrophyte *Pistia stratiotes* in the removal of Pb^{2+} and Cr^{3+} ions from aqueous solution. Equilibrium and kinetic experiments were performed. The Langmuir and Freundlich isotherm models were applied to experimental data. The kinetics data were fitted by the pseudo-first, pseudo-second and intra-particle diffusion models. 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 aquatic macrophyte *Pistia stratiotes* 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 fractions measuring 0.855 mm were collected and used in experiments.

2.2 SEM/EDX
The surface of the *P. stratiotes* 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, Liechenstein). 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 chromium and 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 changings 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
The metal ions solutions were prepared from nitrate salts of chromium $Cr(NO_3)_3.9H_2O$ and lead $Pb(NO_3)_2$ (Vetec). The metal ions concentration were determined by atomic absorption spectrometry (Perkin Elmer AA Analyst 100 with air-acetylene oxidizing flame).
Kinetic experiments were conducted by mixing 0.5 g of biomass with 250 mL of metal ions to a fixed concentration of 2 mmol.L^{-1} and kept under constant agitation at room temperature and pH 4. Pseudo-first order, pseudo-second order and intraparticle diffusion models were fitted to kinetic data, Eq. (1), Eq. (2) and Eq. (3), respectively:

$$\frac{dq_t}{dt} = k_1(q - q_t) \tag{1}$$

$$\frac{dq_t}{dt} = k_2(q - q_t)^2 \tag{2}$$

$$q_t = k_p t^{\frac{1}{2}} \tag{3}$$

where: q represents the amount of adsorbate retained in the solid at equilibrium, q_t represents the amount of adsorbate retained at time t, k_1, k_2 e k_p are the rate constants of the reaction of pseudo-first order [min^{-1}], pseudo-second order [$g(mmol\ min^{-1})$] and intra-particle diffusion [$(mmol(g^{-1}\ min^{1/2})^{-1}$], respectively. Equilibrium experiments were conducted by mixing 100 mL of solution with different concentrations of Cr^{3+} and Pb^{2+} (0.025 to 4 mmol.L^{-1}) with 0.2 g of biomass at pH 4. The solution with the biomass was maintained under stirring for a period of 2 h. The results were fitted by Langmuir and Freundlich model that can be expressed as Eq. (4) and Eq. (5), respectively:

$$q = \frac{q_{max}bC}{1+bC} \tag{4}$$

$$q = k_F C^{1/n} \tag{5}$$

Where: q is the metal ions uptake at equilibrium (mmol.g^{-1}); q_{max} is the maximum Langmuir uptake (mmol·g^{-1}); C is the final metal ions concentration at equilibrium (mmol·L^{-1}); b is the Langmuir affinity constant (L·g^{-1}). k_F is the Freundlich constant and indicates the adsorption capacity of the adsorbent (mmol·g^{-1}) and 1/n is the heterogeneity factor.

3. Results and Discussion

3.1 SEM/EDX Analysis

The surface morphology of *P. stratiotes biomass* was observed by scanning electron microscopy (SEM) before and after biosorption with Cr^{3+} and Pb^{2+} (Figure1). We can observe trough the micrography of the raw biomass the roughness of the biomass surface which can be attributed to sodium, potassium and others salts deposition (Yang and Chen, 2008). After biosorption process with Cr^{3+} and Pb^{2+} ions there were not significant changes in biomass surface morphology. We can observe trough the EDX analysis that the ions of sodium, potassium and chloride which were initially present in the cell wall are removed during the biosorption. It is possible to say that the Cr^{3+} and Pb^{2+} ions replaced some of the ions initially present in the cell wall matrix and created stronger cross-linking (Lima et al., 2011). Figure 1 (d) and (e) shows the chromium and lead mappings, respectively, in biomass surface, which clearly indicates the homogeneity distribution of both metal ions onto adsorbent sites.
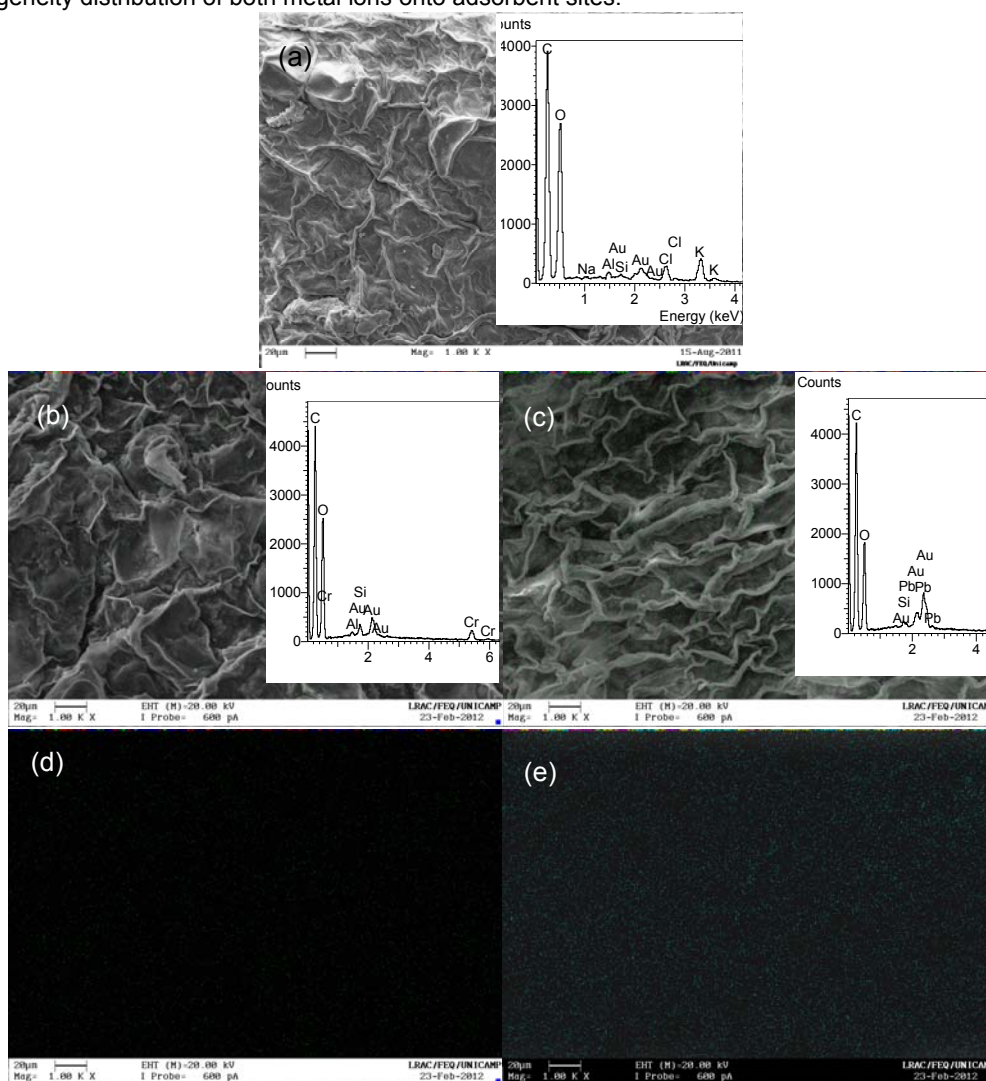

Figure 1: SEM-EDX micrographs of P. stratiotes (a) in nature, (b) saturated with Cr^{3+}, (c) saturated with Pb^{2+}, (d) Cr^{3+} and (e) Pb^{2+}

3.2 FT-IR Analysis

The FT-IR spectrum was obtained for biomass before and after chromium and lead ions biosorption process (Figure 2). The results showed us that the biomass has different functional groups such phosphate, amide, hydroxyl, as carboxyl, and inorganic ions such as Ca^{2+}, Mg^{2+}, etc. Some of these functional groups changed after biosorption process. The comparisons of the FT-IR spectra of raw biomass and after chromium and lead biosorption, gives the following bands and peaks. The bands at

$3402–3344$ cm^{-1} is the OH stretching of polymeric compounds, the band at 2924-2850 cm^{-1} is asymmetric and symmetric vibration of methylene ($C=H_2$), respectively. The bands at 1650 cm^{-1} and 1592 cm^{-1} correspond to carbonyl stretching vibration of amide considered to be due to the combined effect of double-bond stretching vibrations and NH deformation band for raw and Pb^{2+}-loaded *P. stratiotes*, respectively. The intensities of these bands on raw biomass decrease and separate the NH deformation band shifts to 1537 cm^{-1} in the Pb^{2+}-loaded biomass (Ozcan et al., 2005). The 1250-1032 cm^{-1} band is the stretching C-O of carboxylic acids. The 900 - 690 cm^{-1} peaks are aromatic compounds. The bands < 800 cm^{-1} are finger print zone which is phosphate and sulphur functional groups (Saygideger et al., 2005).
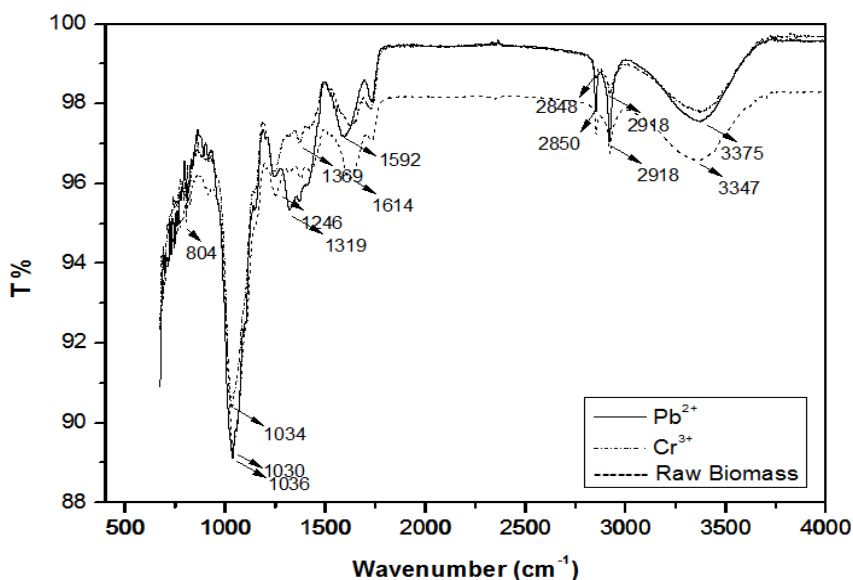

Figure 2: FT-IR spectra of alkali pre-treated biomass and alkali pre-treated saturated with chromium

3.3 Batch Adsorption experiments

The experimental isotherms data and fitted models for chromium and lead biosorption by *P. stratiotes* biomass are exhibited in Figure 3 (a) as well as the Langmuir and Freundlich models parameters are shown in Table 1. The Langmuir model fitted better to the experimental data for both ions which suggests a homogeneous uptake by *P. stratiotes* and can be confirmed by EDX analysis (Figures 1 (d) and (e)). The maximum sorption capacity (q_{max}) obtained by the model was 0.317 and 0.225 mmol·g^{-1} for Cr^{3+} and Pb^{2+}, respectively. The Cr^{3+} showed higher affinity with the biomass which can be also observed through the parameter *b* of the model which is related to the affinity of the binding sites for metal ions (Bernardo et al., 2009). In a recente study conducted by Biswajit Das et al. (2012) using *Pistia stratiotes* in Cr^{6+} removal showed that the maximum adsorption capacity of the dead macrophyte was 0,121 mmol.g^{-1}. Comparing the results obtained by the authors with the results achieved in this work for Cr^{3+}, it can be observed that the material has more affinity with the reduced specie of chromium. The living aquatic macrophyte *Pistia stratiotes*. has been extensively used in bioaccumulation processes (Suñe, 2007) and for phytoremediation (Skinner et al., 2007), which makes very important the study using the dead biomass.

Figure 3 (b) shows the chromium and lead ion kinetic curves fitted by pseudo-first-order and pseudo-second-order models. All the models parameters obtained are presented in Table 2. The best fitted model was the pseudo second order with value of correlation coefficient (R^2) of 0.984 and 0.998 for chromium and lead, respectively. The intraparticle diffusion model parameter was obtained from the plot of q_t versus $t^{0.5}$ and considering only the second stage of the process (internal diffusion). The data showed the appearance of multilinearity which represents many stages of the biosorption process. The plot also presented a straight line that does not pass through origin, in other words, the intraparticle diffusion does not control the whole process of biosorption of the metal ions by biomass (data not shown). The values of interception y-xis (Table 2) give an idea about the boundary layer thickness, i.e., the larger the intercept, the greater is the boundary layer effect.
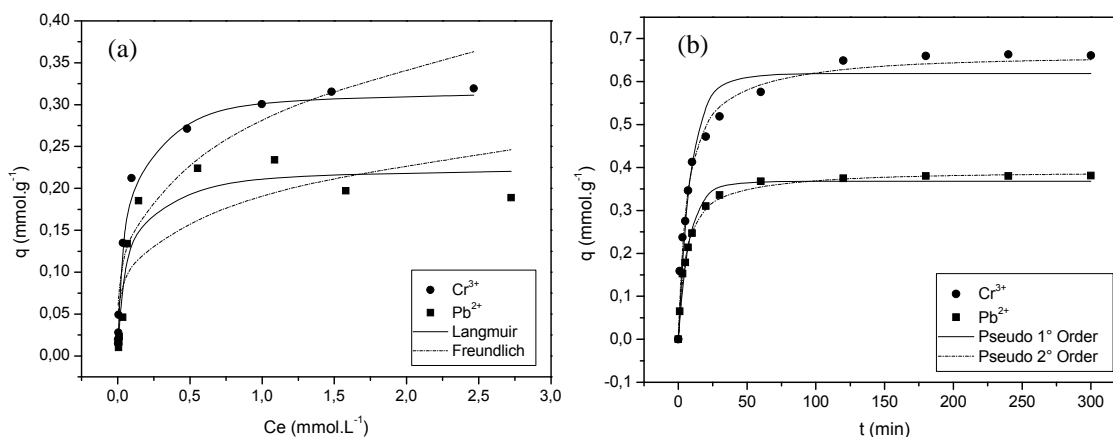
Figure 3: (a) Langmuir and Freundlich model fitted isotherm experimental data and (b) Pseudo-first-order and pseudo-second-order kinetic models for Cr^{3+} and Pb^{2+} biosorption.

Table 1: Langmuir and Freundlich parameters for biosorption on P. stratiotes biomass

Metal Ion	Langmuir			Freundlich		
	q_L (mmol.g^{-1})	b (L.mmol^{-1})	R^2	k_d	n	R^2
Cr^{3+}	0.317	20.625	0.996	0.2841	3.678	0.913
Pb^{2+}	0.225	16.628	0.939	0.1923	4.059	0.730

Table 2: Pseudo first-order, second-order and intraparticle diffusion models parameters for biosorption of Cr^{3+} and Pb^{2+} ions onto P. stratiotes biomass.

Metal Ion	Pseudo 1° Order			Pseudo 2° Order		
	q (mmol·g^{-1})	k_1 (L·mmol^{-1})	R^2	q (mmol·g^{-1})	k_2 (L·mmol^{-1})	R^2
Cr^{3+}	0.619	0.112	0.9411	0.665	0.157	0.984
Pb^{2+}	0.368	0.126	0.9801	0.392	0.184	0.998

Metal Ion	Intraparticle Diffusion		
	k_{in} (mmol·g^{-1}·min$^{-1/2}$)	c (mmol·g^{-1})	R^2
Cr^{3+}	0.029	0.339	0.9714
Pb^{2+}	0.025	0.184	0.9017

4. Conclusions

This research demonstrates the potential of the aquatic macrophyte *P. stratiotes* in Cr^{3+} and Pb^{2+} ions removal from aqueous solution. Morphological analysis showed the presence of microstructures on the surface of biomass, mainly attributed to the deposition of crystalline salts. There were no morphological changes after biosorption process. The Langmuir model fitted better to the experimental data for both ions which suggests a homogeneous uptake by *P. stratiotes* and the maximum capacity of removal were 0.317 and 0.225 mmol.g^{-1} for Cr^{3+} and Pb^{2+}, respectively. The kinetic study showed that the model of pseudo-second had a better fit to the experimental data. The kinetic data also showed that the intraparticle diffusion does not control the whole process of biosorption, and it is a determining factor only in the second process stage. All the results indicated that the *Pistia stratiotes* biomass could be used as an effective biosorbent for the treatment of chromium and lead contaminated wastewater.

References

Araújo, M. M.; Teixeira, J. A., 1997, Trivalent chromium sorption on alginate beads. Int. Biodeterior. Biodegrad. 40, 63-74.

Aravindhan, R., Rao, J.R., Nair, B.U., 2007. Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpascal pelliformis*. J. Hazard. Mater. 142, 68-76.

Bassi R., Prasher S. O., Simpson B. K., 2000, Removal of selected metal ions from aqueous solutions using chitosan flakes, Separ. Sci. Technol. 7, 232-246.

Bernardo G. R. R., Rene R. M. J., Catalina A. T .M., 2009, Chromium (III) uptake by agro-waste biosorbents: chemical characterization, sorption–desorption studies, and mechanism. J. Hazard. Mater. 170, 845-854.

Biswajit Das, Mondal N. K.,Roy P., Chattaraj S., 2013, Equilibrium, Kinetic and Thermodynamic Study on Chromium(VI) Removal from Aqueous Solution Using *Pistia Stratiotes* Biomass. Chem Sci Trans., 2**,** 85-104.

Deans R. J., Dixon B. G., 1992, Uptake of Pb^{2+} and Cu^{2+} by novel biopolymers, Water Res., 26, 469-472.

El-Shafey E., Cox M., Pichugin A. A., Appleton Q., 2002, Application of carbon sorbent for the removal of cadmium and other heavy meal ions from aqueous solution, J. Chem. Technol. Biotechnol. 7, 429-436.

Lima, L. K. S.; Kleinübing, S. J.; Silva, E. A.; Silva, M. G. C., 2011, Removal of chromium from wastewater using macrophyte Lemna as biosorbent. Chemical Engineering Transactions. 25, 303-308.

McKay G, Otterburn MS, Aja J. A., 1985, Fullter's earth and fired clay as adsorbents for dyesstuffs. Water Air Soil Pollut.;24:307.

Ngah W. S. W., Kamari A., Fatinathan S., Ng P. W., 2006, Adsorption of chromium from aqueous solution using chitosan beads. Adsorption. 12, 249-257.

Ozcan A., Ozcan A. S., Tunali S., Akar T., Kiran I, 2005, Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of *Capsicum annuum*. J. Hazard. Mater. 124, 200-208.

Saygideger S., Gulnaz O., Istifli E. S., Yucel N., 2005, Adsorption of Cd(II), Cu(II) and Ni(II) ions by *Lemna minor L.*: Effect of physicochemical environment. J. Hazard. Mater.126, 96-104.

Sharma I, Goyal, D., 2010, Adsorption kinetics: bioremoval of trivalent chromium from tannery effluent by Aspergillus sp. Biomass. Res. J. of Environ. Sci.. 4, 1-12.

Skinner, K., Wright, N., Porter-Goff, E., 2007. Mercury uptake and accumulation by four species of aquatic plants. Environ. Pollut. 145, 234–237.

Suñe N., Sánchez G., Caffaratti S., Maine M.A., 2007, Cadmium and chromium removal kinetics from solution by two aquatic macrophytes. Environ. Pollut. 145, 467–473.

Vieira, M. G. A.; Oisiovici, R.; Gimenes, M.; Silva, M. G. C., 2008, Biosorption of chromium(VI) using a Sargassum sp. packed-bed column. Bioresour. Technol.. 99, 3094 - 3099.

Yang, L.; Chen, J. P., 2008, Biosorption of hexavalent chromium onto raw and chemically modified Sargassum sp., Bioresour. Technol.. 99(2), 297-307.