

Removal of Chromium from Wastewater using Macrophyte *Lemna Minor* as Biosorbent

Livia Katia dos Santos Lima^{1*}, Sirlei Jaiana Kleinübing¹, Edson Antônio da Silva² and Meuris Gurgel Carlos da Silva¹

¹State University of Campinas, School of Chemical Engineering, Campinas, 13083-852, SP, Brazil.

iviakdsl@yahoo.com.br

²Western State University of Paraná, School of Chemical Engineering, Toledo, 85903-000, PR, Brazil.

Chromium plays an important role in the metallurgical and chemical activities. On the other hand, it may pollute aqueous streams, arising therefore several environmental problems. *Lemna minor* macrophyte was evaluated for Cu^{3+} sorption. The tests were performed in batch and biosorption equilibrium was reached in 6-7 h. The obtained maximum adsorption capacities were 12.32 mg.g^{-1} . The FT-IR results showed that biomass have different functional groups responsible for chromium ions binding, such as carboxyl, phosphate, thiol, peptidic and hydroxide.

1. Introduction

Biosorption process offers the advantages of low operating costs, possibility of metal recovery, potential biosorbent regeneration, minimization of the volume of chemical and/or biological sludge to be disposed of and high efficiency in detoxifying very dilute liquid streams. The use of dead, dried aquatic plants, for water removal of metals derived from industrial activities as a simple biosorbent material has been increasing in the last years. This technology is based on the ability of biological materials to accumulate heavy metals by the metabolic action or purely physical-chemical removal pathways (Oporto et al. 2006). Previous work has shown that *Lemna minor* macrophyte has an excellent ability in removing metals ions such as Cr^{3+} , Cr^{6+} , Pb^{2+} , Ni^{2+} e Cu from aqueous solutions (Rahmani e Sternberg, 1999; Axtel et al. 2003; Rakhshae et al. 2009, Khellaf e Zerdaoui, 2010, Shun-Xing et al. 2011). The Cr^{3+} element is present in aqueous solutions mainly in the trivalent and hexavalent oxidation states. Chromium is released into the environment by a large number of processes such as electroplating, leather tanning, wood preservation, pulp processing, steel manufacturing, photographic material, corrosive paints, etc. Due to the toxic effects of chromium, it is necessary to eliminate it from the contaminated effluents. The aim of this work is to evaluate the viability of the alkali pre-treated macrophyte *Lemna minor* to remove of Cr^{3+} from aqueous solution. Equilibrium and kinetic experiments were performed. The Langmuir isotherm model was applied to experimental data. The pseudo-first, pseudo-second-and intra-particle diffusion models were used to fit the kinetic data. The changes in functional groups were analyzed by spectroscopy in the infrared region (FT-IR).

2. Materials and Methods

2.1 Preparation of biomass

Samples of *L. minor* were cultivated and collected by the CPAA (Research Center in Environmental Aquaculture) of State University of Paraná, Brazil. The biomass was pre-treated with NaOH (1M). It has been shown that the demethylation of pectins, resulting the increasing – COOH groups, can be catalyzed by using alkali solutions (Franco et al. 2002). The biomass was ground and sieved and fractions measuring from 0.71 to 1.0 mm were collected for further experiments.

2.2 SEM/EDX

The surface morphology of *L. minor* was observed using scanning electron microscope (SEM). After drying, the samples were covered with a thin layer of gold (10 nm) using a sputter coater (SCD 0050 – Baltec, Liechtenstein) and observed using the JEOL JXA-840A scanning electron microscope (20 kV) under vacuum of 1.33×10^{-6} mBar (Jeol, Japan). To determine the chemical composition, energy dispersive X-ray spectroscopy was performed on biomass after chromium adsorption and alkaline treatment. The samples were prepared as for SEM analyses.

2.3 Metal binding batch experiments

Cr^{3+} solutions were prepared from nitrate salts of chromium $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The concentration of metal ions was determined by atomic absorption spectrometry (Perkin Elmer AA Analyst 100 with air-acetylene oxidizing flame). During the reaction process the pH was maintained constant at 4.0 by hourly addition of $0.1 \text{ mol L}^{-1} \text{ HNO}_3$.

Kinetic experiments were performed in continuously stirred beakers containing 500 mL of 20 mg L^{-1} heavy metals solution (150 rpm) and 2.0 g biosorbent, at 30°C .

The models of pseudo-first order, pseudo-second order and intra-particle diffusion were used to fit the experimental data. The equations are represented as follow, then Eq. (1), Eq. (2) and Eq. (3), respectively:

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

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

$$q_t = k_p t^{\frac{1}{2}} \quad (3)$$

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 [$\text{g}(\text{mg min}^{-1})$] and intra-particle diffusion ($\text{mg}(\text{g}^{-1} \text{min}^{1/2})$).

For equilibrium studies the concentrations of chromium solutions varied from 4 to 130 mg L^{-1} and the amount of biosorbent used was 2 g L^{-1} .

These results were adjusted to the Langmuir model that can be expressed as:

$$q_t = \frac{q_{max} bC}{1 + bC} \quad (4)$$

Where: b is the chromium uptake at equilibrium (mg g^{-1}); q_{max} is the maximum Langmuir uptake (mg g^{-1}); C is the final chromium concentration at equilibrium (mg L^{-1}); b is the Langmuir affinity constant (L g^{-1}).

2.4 Fourier transforms infrared spectroscopy (FT-IR)

FT-IR spectroscopy was used to confirm the presence of the functional groups in samples and to observe the chemical modification after chromium biosorption. Infrared spectra were recorded in the $4000\text{-}600\text{ cm}^{-1}$ region using a Thermo Nicolet instrument, model IR-200. The ATR (attenuated total reflection) device allows getting information about the surface.

3. Results and discussion

3.1 SEM/EDX analysis

The morphology of *L. minor* surface was analyzed by scanning electron microscopy (SEM) before and after the alkaline treatment and after chromium loading (Figure 1).

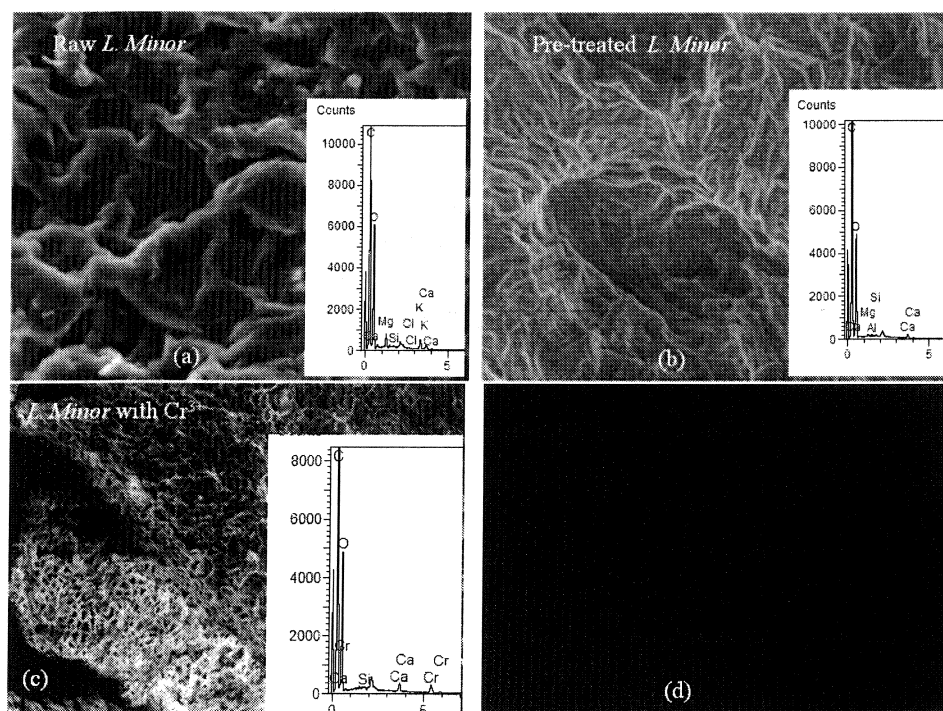


Figure 1: SEM-EDX analysis of *L. minor* in nature, alkali treated and alkali treated saturated with Cr^{3+} .

The SEM analysis of the raw biomass showed the rugosity surface with microstructures, as illustrate Figure 1 (a). This rugosity can be assigned to the naturally deposition metals in the biomass, as calcium, magnesium, potassium, etc. This rugosity is less obvious after the alkaline modification (Figure 1b). The considerable quantities of exchanger ions such as Ca^{2+} , Mg^{2+} , K^{+} and Na^{+} were lost from *L. minor* cell wall after

washing by alkali solutions. According EDX analysis, the ions initially present in the cell wall matrix, such as magnesium, calcium, aluminium etc. are removed during the chromium biosorption process (Figure 1b,c). The Cu^{3+} ions replaced some of the ions initially present in the cell wall matrix and created stronger cross-linking. Mappings chromium (Figure 1d) in the biomass surface indicated a homogeneous distribution of Cr^{3+} adsorbent sites. The main mechanism involved in biosorption was ion exchange between monovalent metals as counterions present in the macrophytes biomass and chromium ions and protons taken up from water.

3.2 FT-IR Analysis

The cell wall compositions of algal and plant biomass have containing large number of complex organic components and there are proteins, lipids, carbohydrate polymers (cellulose, xylane, mannan, etc.) and inorganic ions Ca^{2+} , Mg^{2+} , etc. The comparisons of the FT-IR spectra of alkali treated biomass, after and before chromium biosorption, were given in Figure 2. For raw *L. minor*, the band at 3432 cm^{-1} is O-H stretching of polymeric compounds, 2923 cm^{-1} is symmetric vibration of CH_2 , 1640 cm^{-1} is stretching vibration of COO , $\text{C}=\text{O}$, 1543 cm^{-1} band is stretching vibration of C-N of peptidic bond of proteins, 1416 cm^{-1} is of phenolic O-H and $\text{C}=\text{O}$ stretching of carboxylates, 1320 cm^{-1} band is vibration of phosphate groups, 1240 cm^{-1} band is vibration of carboxylic acids, 1028 cm^{-1} is vibration of C-O-C and O-H of polysaccharides, 857 cm^{-1} band is Si-H bend. The bands $< 800\text{ cm}^{-1}$ are finger print zone which is phosphate and sulphur functional groups (Saygideger et al. 2005). The FT-IR results showed that biomass have different functional groups for chromium ions binding, such as carboxyl (1644 and 1378 cm^{-1}), phosphate (1320 cm^{-1}) and thiol ($<800\text{ cm}^{-1}$), peptidic ($\sim 1543\text{ cm}^{-1}$) and hydroxide (1028 and 3445 cm^{-1}) groups.

In accordance with Sheng *et al.* (2004), the peaks at 1640 and 1416 cm^{-1} is due to the carboxylate salt COO-M , where M can be Na^+ , K^+ , Ca^{2+} , and Mg^{2+} metals, which are naturally present in the biomass. This band changes to 1644 and 1378 cm^{-1} after chromium biosorption. The species (M) naturally present in *L. minor* were replaced by chromium ions.

3.3 Batch sorption experiments by *L. minor* biomass

Langmuir isotherm was used to fit the experimental data. The results are shown in Figure 3a. Langmuir parameters obtained were q_{max} of 12.32 mg g^{-1} , b of 0.1502 L mg^{-1} and R^2 of 0.9213. The maximum amount adsorbed on a monolayer is represented by q_{max} , and b is the Langmuir association constant, which is related to the adsorption energy. The apparent Langmuir constant (b) is a measure of stability for the complex formed between metal ions and adsorptive surface layer of biosorbents under specified experimental conditions. For example, a small “ b ” value indicates that the metal ion has a high binding affinity with the biosorbent. The values of b and q_{max} indicate that *L. minor* biomass have affinity for Cr^{3+} .

Figure 3b presents Cr^{3+} ion kinetic curves adjusted with the pseudo-first-order and pseudo-second-order models. Linear correlation coefficients and pseudo-first-order (k_1) and second-order (k_2) constants, as well as the equilibrium capacity obtained, are shown in Table 1. The value of correlation coefficient R^2 is relatively high (>0.98). Therefore, it can be concluded that the models describe the biosorption kinetics of metals over *L.*

minor biomass. The intraparticle diffusion model not represented the experimental data and the results were not presented.

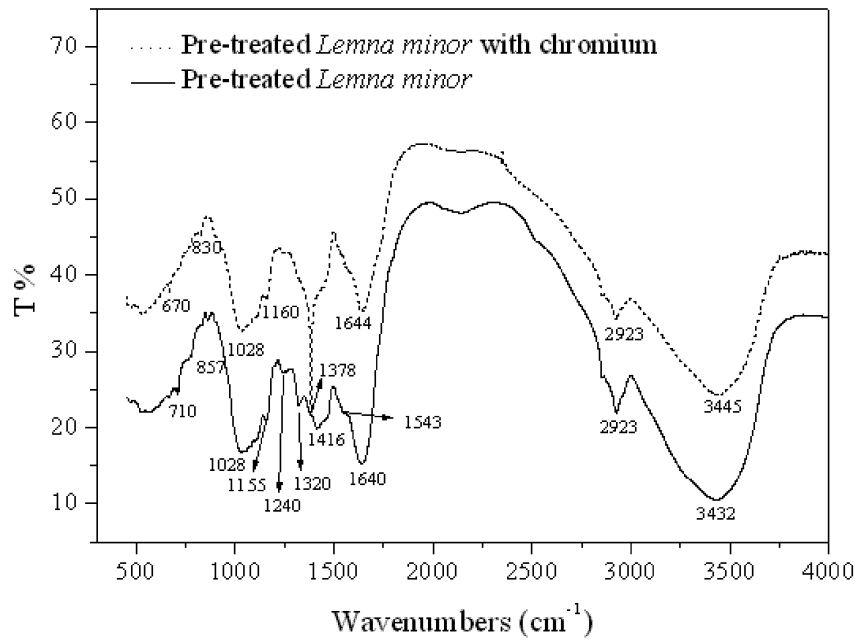


Figure 2: FT-IR spectra of alkali pre-treated biomass and alkali pre-treated saturated with chromium.

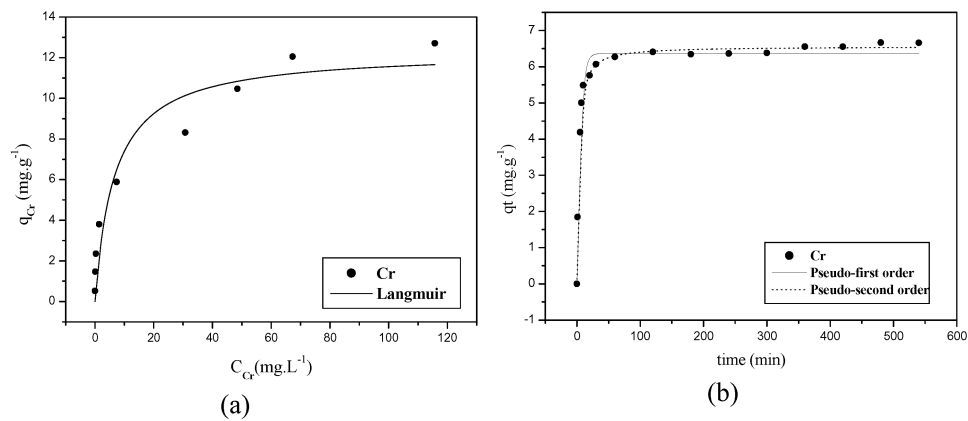


Figure 3: (a) Langmuir model fitted isotherm experimental data and (b) Pseudo-first-order and pseudo-second-order kinetic models for Cr^{3+} biosorption.

Table 1: The first-order and second-order kinetic constants for biosorption of Cr^{3+} ion on *L. minor* biomass.

First-pseudo order			Second-pseudo order		
q	k_1	R^2	q	k_2	R^2
6.366	0.221	0.9817	6.560	0.406	0.9961

4. Conclusions

This study demonstrated that the *L. minor* biomass (alkali pretreated) could be used as an effective biosorbent for the treatment of wastewater containing Cr^{3+} ions. However, *L. minor* is natural abundant environmental biomass and it may be alternative to more costly materials.

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