

Research Article

Biosorption of Cr(III) and Pb(II) by *Schoenoplectus californicus* and Insights into the Binding Mechanism

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Biosorption and desorption of chromium and lead on shoots biomass of *Schoenoplectus californicus* were investigated by performing batch sorption tests in different conditions of pH, biosorbent dose, and initial concentration in simple and binary solutions. Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models were employed to describe sorption equilibrium. Filters and biomass were characterized before and after treatments by environmental scanning electron microscopy and X-ray energy-dispersive spectrometry. The optimal conditions for biosorption were found to be pH 5 for both metals. The contact time to reach pseudoequilibrium changed as a function of pH and the metal studied. The highest optimisation of biosorbent dose was 5 g L⁻¹ at pH 7 and 15 g L⁻¹ at pH 5 for both metals. The most effective extracting agents for lead and chromium proved to be HNO₃ and NaOH, respectively. The recovery of lead was greater than of chromium because the Cr(III) sorption mechanisms involve a stronger binding energy than the mechanisms for Pb(II), such as in intern sphere complexes. Both metals accounted for a high % removal (>90%) under the best sorption conditions. The use of *Schoenoplectus californicus* proved to be an efficient and economical alternative for the treatment of effluents contaminated with lead and chromium.

1. Introduction

The release of heavy metals into bodies of water occurs due to the lack of previous treatments performed on industrial wastewater; this release is a serious problem because the persistence of heavy metals in the ecosystem and the transference into the several trophic levels implies a high risk to both wildlife and humans. Therefore, it is necessary to propose alternative methods for the treatments of metal-containing effluents. The conventional metal removal technologies are chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, reverse osmosis, ion exchange, adsorption, and evaporation [1]; among these, adsorption is by far the most versatile and widely used because of its initial cost, simplicity of design,

facile operation, and insensitivity to toxic substances [2]. Considering the vast wastewater quantities, the current metal removal technologies are either not effective enough or are prohibitively expensive and inadequate. New investigations are exploring efficient and particularly cost-effective remedies [1]. Biosorption technology based on the utilisation of dead biomass offers several major advantages, such as a lack of toxicity constraints, nonrequirement of nutrient supply, high availability and low cost of biomass, and recovery-bound metal species [3]. Different types of biomass, such as algae, bacteria, fungi, and industrial and agricultural organic wastes, have been investigated for the removal of heavy metals from aqueous solutions [2–7].

Trivalent chromium is a pollutant commonly found in wastewaters, produced from leather tanning, dye, wood

preservation, electroplating industries, mining and the automotive industry [8]. It is thought to be an essential nutrient required for sugar and fat metabolism in organisms [9]. However, prolonged contact causes skin allergies and cancer. Lead has a low fusion point, which allows for easy smelting at a low cost. This led to the utilisation of lead beginning several centuries ago in the fabrication of pipes, munitions, metallic alloys, paints, and batteries and as additives in gasoline and pesticides. This metal has been implicated as the cause of health problems such as behavioural abnormalities, learning disabilities, and seizures. Both metals present strong pollution in our region, in particular, the river Matanza-Riachuelo in Buenos Aires city, due to intense industrial activity with untreated effluents since the late 19th century such as tanneries, metallurgies, chemical industry, pharmaceutical industry, electrical industry, electroplating, and foundry. Olson et al. (1998) [10] consider the Matanza River Basin as a critical area on the state of conservation within Latin American ecoregions.

Schoenoplectus californicus is an emergent aquatic plant, present in many aquatic systems, developing dense populations from south America through central America to southern USA [11]. The study on the phytoremediation and decomposition dynamics of this species demonstrated its behaviour as a sink of heavy metals [12]. Therefore, the objective of the present work is to evaluate the efficiency of Cr(III) and Pb(II) removal from aqueous solution using *S. californicus* shoots as a biosorbent. Parameters such as pH, contact time, biomass dose, and initial concentration have been studied to establish their effect on the biosorption process. According to numerous authors, the pH is one of the most important parameters affecting the biosorption process [2, 13–15]. The pH variation can affect both the configuration of the active ion-exchange sites as well as the ionic state of the sorbate in the solution [16]. Therefore, the effect of pH on the others parameters has also been studied. Sorption models were employed to understand the nature of sorption and calculate the sorption capacities. Desorption experiments have been carried out to evaluate the recovery of both metals.

2. Material and Methods

2.1. Biosorbent. The shoots biomass of *Schoenoplectus californicus* was collected from the “Durazno” stream in the high basin of the Reconquista River, located in Buenos Aires, Argentina. To remove dirt and unwanted adsorbed elements, the biomass was thoroughly washed with water, EDTA, and distilled water. It was dried at 70°C for 48 h and crushed and sieved through a 0.5 mm sieve for uniform particle size. The processed biomass sample was saved in sealed bags in a cool and dry ambience.

2.2. Characterisation of the Biosorbent. The biomass was characterised by pH and electrical conductivity (EC) in saturation paste, total carbon, total nitrogen, and structural components. The surface of sorption was characterised qualitatively by environmental scanning electron microscopy (ESEM), X-ray energy-dispersive spectroscopy

(EDX) microanalysis, and Fourier transform infrared spectroscopy (FTIR).

2.3. Biosorption Experiments. A metal stock solution (25 mmol L⁻¹) was prepared in Milli-Q water with the analytical grade salts of Pb(II) [Pb(NO₃)₂] and Cr(III) [Cr(NO₃)₃·9H₂O]. Biosorption batch studies were performed in 100 mL polyethylene tubes previously rinsed with 50% HNO₃ to remove any metal adsorbed on the walls. Preweighed biomass and a 50 mL aliquot of the dissolved metals were added to each tube and agitated on a horizontal rotator shaker at 250 rpm and constant temperature (25 ± 2°C) until the pseudoequilibrium was reached. The phases were separated by filtration using filters with 1 μm pore size. The initial pH was adjusted to the desired value with diluted NaOH and HCl. The metal concentration in the equilibrium dissolution was determined by a flame atomic absorption spectrophotometer (Perkin Elmer, A200). All experiments were conducted in triplicate.

To study the effect of pH on the biosorption of both metals, the initial pH values of 1.5 mM metal solutions were adjusted to different values (3.0–11.0) with NaOH and HCl (in suitable concentrations to minimise the change in the final volume). To obtain the contact time required to reach pseudoequilibrium, tubes were agitated during several time intervals (5–1440 minutes) with previous adjustment of the pH as indicated previously. To determine the effect of the biosorbent dose, different concentrations of the shoots biomass (5, 10, and 15 g L⁻¹) were tested. To study the effect of initial concentration and obtain the sorption isotherms, batch studies with several concentrations (0.01–2 mM) of both metal solutions (50 mL) were performed, keeping other parameters at the optimum conditions. To observe the effect of the competition between both metals, binary solutions at different concentrations (0.01–2 mM) were tested, keeping the others parameters in optimum conditions as well.

The amount of metal sorbed as a function of time, q_t (μmol g⁻¹), was calculated as follows (1):

$$q_t = \frac{(C_0 - C_t)V}{m}, \quad (1)$$

where C_0 is the initial concentration (μmol L⁻¹), C_t is the concentration at time t (μmol L⁻¹), V is the volume of the metal solution (L), and m is the mass of the biosorbent (g). When the pseudo-equilibrium is reached, q_t is the capacity of biosorption (μmol g⁻¹). The removal efficiency (%) was determined using

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100, \quad (2)$$

where C_0 and C_e are the initial and final concentrations of metal in the solution, respectively.

2.4. Equilibrium Modelling. The equilibrium sorption data can be fitted using the Langmuir and Freundlich models, which are widely used to analyse data for water and wastewater treatment applications; however, those models are

insufficient to explain the physical and chemical sorption, so the Temkin and Dubinin-Radushkevich models were also analysed. These models may indicate the heat of sorption and distinguish between physical and chemical sorption [17]. The Langmuir model ((3), linearised form) is based on the assumption that the maximum sorption occurs when a saturated monolayer of solute molecules is present on the sorption surface, and the energy of sorption is constant, with no migration of sorbate molecule in the surface plane [18, 19]

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max L}}, \quad (3)$$

where C_e ($\mu\text{mol L}^{-1}$) is the solute concentration at equilibrium, q_e ($\mu\text{mol g}^{-1}$), the amount of metal sorbed at equilibrium, $q_{\max L}$ ($\mu\text{mol g}^{-1}$), the maximum sorption capacity, and K_L (L g^{-1}) is the equilibrium constant related to the energy of sorption, which quantitatively reflects the affinity between the sorbent and sorbate [9].

The Freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between sorbed molecules [14]. The linearised form can be expressed as follows [20] (4):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (4)$$

where K_F (L g^{-1}) and n (adimensional) are approximated indicators of the capacity and intensity of sorption, respectively. Saxena et al. (2006) [17] demonstrated that, if $n > 1$, the sorption is favourable. The Temkin model assumes that adsorption is characterised by a uniform distribution of binding energies, up to some maximum binding energy [21], which results in the following isotherm equation in its linearised form (5):

$$q_e = \frac{RT}{B_T} \ln K_T + \frac{RT}{B_T} \ln C_e, \quad (5)$$

where K_T ($\text{L } \mu\text{mol}^{-1}$) is the equilibrium constant corresponding to the maximum binding energy, B_T (kJ mol^{-1}) is the heat of biosorption, and R ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ kg}^{-1}$) and T (K) are the universal gas constant and absolute temperature, respectively. Finally, the Dubinin-Radushkevich (D-R) model proposes a Gaussian distribution of energy sites and distinguishes between physical and chemical sorption as a function of biosorbent heterogeneity [17]. The linear form of the D-R isotherm equation is [22]

$$\ln q_e = \ln q_{\max \text{D-R}} - \beta \varepsilon^2, \quad (6)$$

where $q_{\max \text{D-R}}$ ($\mu\text{mol g}^{-1}$) is the maximum sorption capacity, β is the activity coefficient related to the biosorption mean free energy ($\text{mol}^2 \text{kJ}^2$), from which can be calculated the biosorption mean free energy E (kJ mol^{-1}) [$E = 1/(2\beta)^{1/2}$], and ε is the Polanyi potential [$\varepsilon = RT \ln(1 + 1/C_e)$].

2.5. Desorption Studies. For the desorption of metals, batch experiments were conducted in 100 mL polyethylene tubes

containing 50 mL of eluting solutions in contact with metal-loaded biomass for 60 min. Five different chemical agents (HNO_3 0.1 M; NaOH 0.1 M; MgCl_2 0.1 M; EDTA 0.1 M; and distilled water) were compared for their capacity to desorb test metals from the metal-loaded biomass. Previous sorption was performed by suspending the biomass in 50 mL of the 1.5 mM metal solutions at pH 5 and 7 with 15 g L^{-1} and 5 g L^{-1} biomass, respectively.

Percentage of desorption was calculated as follows (7):

$$\% \text{Desorption} = \frac{q_{fd} \times 100}{q_e}, \quad (7)$$

where q_{fd} ($\mu\text{mol g}^{-1}$) and q_e ($\mu\text{mol g}^{-1}$) are the final and initial concentrations of metals in the biomass, respectively.

Next, using the most effective agent, desorption isotherms were tested with different metal-loaded concentrations at the initial sorption pH values of 5 and 7. Finally, we estimated the recovery efficiency (%) by taking into account the initial concentration of the metals in the sorption solution as in (8), which would allow us to demonstrate the global effectiveness of the process.

Consider

$$\% \text{Recovery} = \frac{C_{fd} \times 100}{C_i}, \quad (8)$$

where C_{fd} and C_i are the final desorbed concentration in the elution solution (mmol L^{-1}) and the initial concentration of metals in the sorption solution (mmol L^{-1}), respectively.

2.6. Environmental Scanning Electron Microscopy (ESEM), X-Ray Energy-Dispersive Spectrometry (EDX). The surface of the biomass and the filters were observed before and after treatment with both metals using environmental scanning electron microscopy (ESEM) and characterised qualitatively by EDX to detect the presence of metals retained on the surface of the biomass and the filters. The analysis of characteristic X-rays emitted by a sample that is exposed to a high energy electron beam (25 kV) allows for the identification of the elements that are present in the sample by determining the energies (EDX) of the characteristic X photons emitted. The filters were analysed before and after treatment with 1.5 mM of metal at pH 5 and 7 with and without biomass, and the biomass was also analysed before and after treatment with 1.5 mM of the metal at pH 5 and 7.

2.7. Statistical Analysis. Descriptive statistics (average and standard deviation) were used to evaluate the data. Variance analysis (ANOVA) was used to determine the existence of differences between treatments. Comparisons were made using Tukey's test ($\alpha : 0.05$) following ANOVA.

3. Results and Discussion

3.1. Characterisation. According to the results presented in Table 1, the high C/N ratio and high total content of structural components (hemicellulose, cellulose, and lignin) imply that

TABLE 1: Initial characteristics of the shoots biomass of *Schoenoplectus californicus*.

Ash	(%)	14.35
C	(%)	41.7
N	(%)	1.14
Hemicellulose	(%)	37.71
Celullose	(%)	32.84
Lignin	(%)	2.14
Total fibers	(%)	72.69
C : N		37 : 1
Lignin : N		2 : 1
Paste pH		5.4
Paste CE	mS/cm	3.31
Cr	$\mu\text{g}\cdot\text{g}^{-1}$	4.00
Pb	$\mu\text{g}\cdot\text{g}^{-1}$	2.5

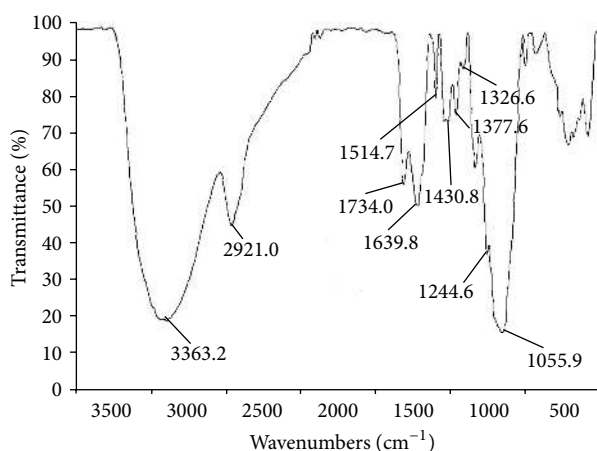


FIGURE 1: FTIR spectrum for the shoot biomass of *S. californicus*.

the substrate is less susceptible to breakdown, indicating that this material features characteristics that allow it to be employed as an effective biosorbent. The FTIR spectrum was measured within the range of 500–4000 cm^{-1} wavenumber. As shown in Figure 1, the FTIR spectrum displays a number of absorption peaks, indicating the complex nature of the biosorbent. The presence of the carboxylic hydroxyl and aromatic amines groups on the biosorbent is defined by a broad band approximately 3363 cm^{-1} , corresponding to $-\text{OH}$ and $-\text{NH}$ stretching, respectively [23]. The peak at 2921 cm^{-1} indicates the symmetric or asymmetric $-\text{CH}$ stretching vibration of aliphatic acids [24]. The band at 1639 cm^{-1} can be assigned to the $\text{C}=\text{C}$ benzene stretching ring of lignin; the band at 1514 cm^{-1} is mainly attributed to $\text{N}-\text{H}$ deformation in secondary amides due to the protein peptide bond, but can also indicate $\text{C}=\text{C}$ benzene stretching [23, 25, 26]. The carboxylate ions resulted in two bands, one at 1430 and the other at 1377 cm^{-1} , due to the COO^- symmetric stretching in the acidic group of polygalacturonic acids, the main component of pectin present in the primary plant cell wall [23–25]. The band at 1055 cm^{-1} was assigned to

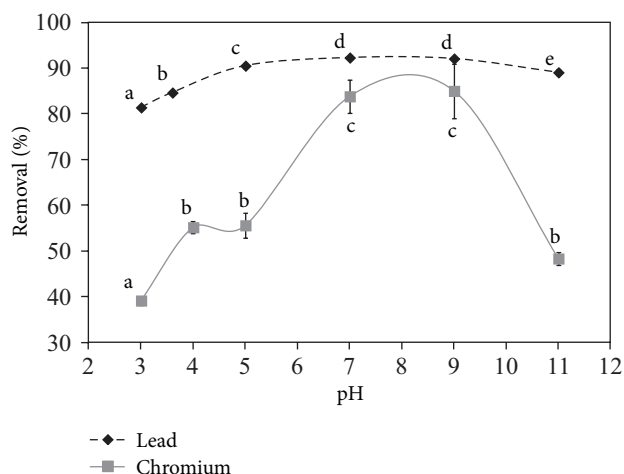


FIGURE 2: Sorption of Pb^{2+} and Cr^{3+} by the biomass of *S. californicus* (15 g L^{-1}) as a function of the solution pH (agitation time: 24 h; initial metal concentration: 1.5 mM; temperature: 25°C). Vertical bars indicate the standard deviation of three replicates, and the letters indicate the groups that correspond to the significant ($P < 0.05$) differences.

the $\text{C}-\text{O}$ stretching of polysaccharides such as cellulose and hemicellulose. Similar FTIR spectra were obtained by Yang et al. (2007) [26] with cellulose and hemicelluloses, which represent 97% of the structural fibres in *S. californicus* (see Table 1).

3.2. Effect of pH. According to numerous authors, the pH of a solution is one of the most important parameters that controls the sorption process [2, 13–16]. There are three ways in which the pH can influence metal biosorption: first, it affects the configuration of the active ion-exchange sites; second, it affects the ionic state of the sorbate in the solution; and third, extreme pH values may damage the structure of the biosorbent material [16].

Figure 2 shows the effect of the initial pH on the biosorption of $\text{Cr}(\text{III})$ and $\text{Pb}(\text{II})$ by the shoot biomass. First, the sorption of both metals is a pH-dependent phenomenon. The effect of pH on chromium is stronger compared to lead. As observed in Figure 2, the maximum removal for both metallic ions took place in the range of pH 7–9, being higher for lead. Lower pH values imply higher concentration of protons, which compete with metals for the active sites on biomass surface [5, 14, 15]. Additionally, cell wall ligands are closely associated with hydronium ions that restrict the approach of metal cations as a result of repulsive forces. As the pH increases, more ligands such as carboxyl, phosphate, phosphodiester, sulfonate, and imidazole groups carry negative charges with a subsequent attraction of metals ions, and thus biosorption onto the cell surface increases [5, 16]. The range of maximum removal can be explained because of the occurrence of two simultaneous processes: biosorption and precipitation of metallic cations. Both metals tend to hydrolysis with neutral to slightly alkaline pH values forming

TABLE 2: Percentage of removal of Cr(III) and Pb(II) with biosorbent (5 g L^{-1}) and without biosorbent at $\text{pH } 5 \pm 0.1$ and 7 ± 0.1 at different initial metal concentrations (agitation time: 24 h; temperature: 25°C ; BS: biosorbent; C_i : initial concentration).

C_i	Chromium (III)				Lead (III)			
	pH 5		pH 7		pH 5		pH 7	
	With BS	Without BS	With BS	Without BS	With BS	Without BS	With BS	Without BS
0.1 mM	$79,7 \pm 0,4$	$37,1 \pm 1,9$	$59,6 \pm 2,0$	$87,0 \pm 0,4$	$65,1 \pm 1,7$	$31,3 \pm 1,6$	$83,0 \pm 1,5$	$89,1 \pm 2,5$
0.5 mM	$79,4 \pm 0,5$	$27,7 \pm 1,4$	$82,5 \pm 2,3$	$99,7 \pm 0,3$	$86,3 \pm 2,1$	$7,7 \pm 0,4$	$66,4 \pm 4,6$	$43,5 \pm 5,0$
1.5 mM	$59,4 \pm 3,5$	$31,2 \pm 1,6$	$95,4 \pm 1,5$	$99,9 \pm 0,0$	$92,2 \pm 0,8$	$3,0 \pm 0,2$	$93,4 \pm 0,2$	$23,5 \pm 0,6$

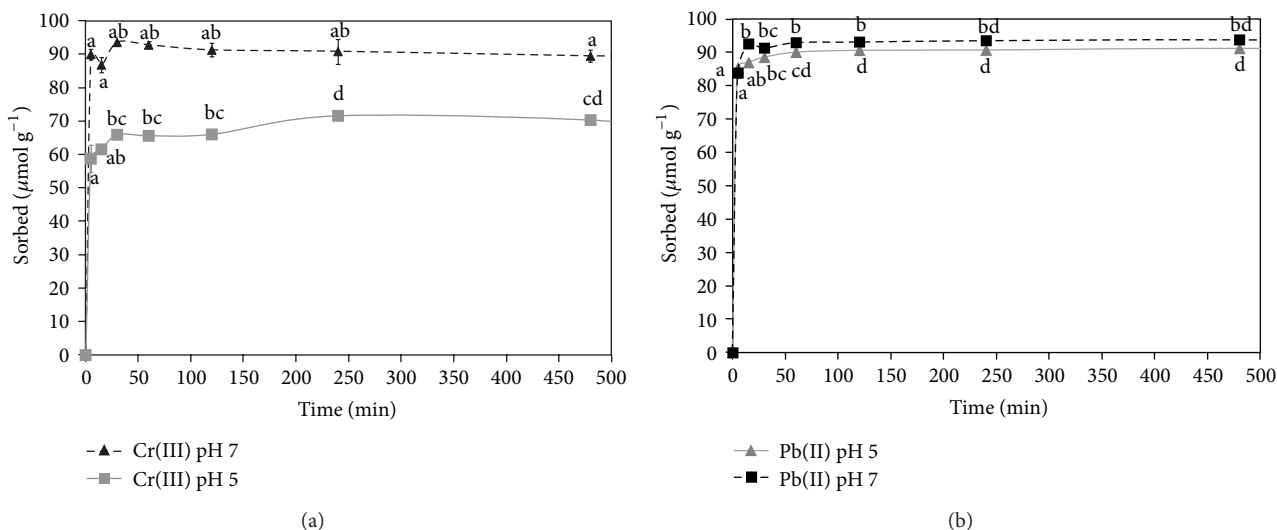


FIGURE 3: Sorption of Cr^{3+} (a) and Pb^{2+} (b) by the biomass of *S. californicus* (15 g L^{-1}) as a function of the contact time at $\text{pH } 5 \pm 0.1$ and 7 ± 0.1 (initial metal concentration: 1.5 mM ; temperature: 25°C). Vertical bars indicate the standard deviation of three replicates, and the letters indicate the groups that correspond to the significant ($P < 0.05$) differences.

insoluble species and to greater values they can dissociate into their respective anions [13, 15].

Finally, to separate both processes, experiments with and without biosorbent were conducted at different concentrations at pH 5 and 7. As observed in Table 2, removal of lead at both pH values is always greater in the presence of biosorbent with probable surface precipitation, except for the concentration of 0.1 mM at pH 7. The removal of metal in absence of biomass indicates lead precipitation in the form $\text{Pb}(\text{OH})_2$ or $\text{Pb}(\text{CO}_3)_2$. At pH 5 this process is less important because the lead is mainly dissolved in the form PbOH^+ . In the case of chromium, different trends were observed. While at pH 5, the behaviour is similar to that described for lead, at pH 7 the removal of chromium by precipitation is only greater than its removal by both the adsorption and precipitation processes combined. This can be explained because, at pH 7, the insoluble species $\text{Cr}(\text{OH})_3$ is the predominant form, and the dissolved organic matter proceeding the biosorbent could complex the metal and keep it dissolved. These results prove that the presence of biosorbent increases the removal of both metals at pH 5, and at pH 7, the removal of both lead and chromium implies two processes: precipitation and adsorption, in which the former is the predominant process.

Therefore, according to several authors [5, 6, 8, 9, 13–15, 19, 24, 27, 28], pH 5 is the optimum value to study

the biosorption process, and pH 7 is the optimum value for the removal of both metals by the shoots biomass of *S. californicus*. Expanding upon this work, all other variables were tested at pH 5 and 7.

3.3. Effect of Contact Time. An ideal biosorbent should rapidly sorb high concentrations of heavy metals from solutions [6] and reach the pseudo-equilibrium state in a relatively short time. Additionally, this information is necessary to design a sorption processing system because knowing the rate at which the metal uptake occurs will help us to evaluate the performance of biosorption [24]. Taking the previous points into consideration, the effect of contact time on the biosorption of Cr(III) and Pb(II) was studied over the time period of 5 min to 24 h. Figure 3 show the biosorption of both metals as a function of time. At pH 7, it was observed that 5 and 15 min were necessary to reach the pseudo-equilibrium state of chromium and lead, respectively, removing approximately 90% of the metal from the aqueous solution. Instead, at pH 5, Cr(III) and Pb(II) reached that state at 240 and 60 min, respectively, whereas two phases of sorption were observed: a fast, initial one from 0 to 5 min, followed by a slow, final phase to reach pseudo-equilibrium. This behaviour can be explained by the

strong forces between the metals and the sorbent [2]; fast diffusion onto the external surface was followed by slow pore diffusion into the intraparticle matrix to attain pseudo-equilibrium. Furthermore, the faster initial rate may be due to the availability of the uncovered sorption sites of the adsorbent at the beginning [24]. The differences observed in both pH values are because, at pH 7, the predominant reaction is the precipitation, which could occur at different velocities than sorption reactions. In most cases, both chemical kinetics and multiple transport processes are occurring simultaneously. In the case of the sorption reactions, these include transport processes (transport in the solution phase, transport across a liquid film at the particle/liquid interface, transport in liquid-filled macropores, diffusion of sorbate occluded in micropores, and along pore-wall surfaces) that are rate limiting [29].

Considering the previous results, a contact time of 20 min was used in all experiments at pH 7, and 60 min and 240 min were used for lead and chromium, respectively, at pH 5.

3.4. Effect of Biosorbent Dose. The removal percentage and biosorption capacity ($\mu\text{mol}\cdot\text{g}^{-1}$) for Pb(II) and Cr(III) ions as function of biomass dosage and pH were studied. Taking into account Figure 4, it can be concluded that the effect of the biosorbent dosage on both metals was similar but had different tendencies at pH 5 and 7. At pH 7 (Figure 4(b)), the metal biosorption (q_e : $\mu\text{mol}\cdot\text{g}^{-1}$) was inversely related to the biosorbent dosage in the solution. This result may occur because, at low doses, all types of sites are entirely exposed and the biosorption on the saturated surface is faster, leading to a higher biosorption capacity [3]. Although increasing removal percentages at high doses may be attributed to the availability of a larger quantity of sorption sites [2], a partial aggregation of the biosorbent, which occurs at higher biomass dosages, resulted in a decrease in the effective surface area for metal uptake. Instead, at pH 5 (Figure 4(a)), in agreement with several authors [3, 6, 24], it was observed that a decrease in the biosorption capacity and an increase in the removal percentage, with increasing biosorbent dose, were attributed to the availability of a larger quantity of sorption sites and no aggregation of the biosorbent.

In view of the obtained results, the optimum dosages selected for all other experiments were 5 g L^{-1} and 15 g L^{-1} at pH 7 and 5, respectively, for both metals.

3.5. Effect of Initial Concentration in Simple and Binary Solutions. Biosorption isotherms are important for describing how sorbate will interact with a biosorbent and are critical in optimising the use of the biosorbent [14]. In a sorption isotherm, the principal aspects to consider are the quantification of the relationship between equilibrium concentrations of the solute in the solid phase (q_e : $\mu\text{mol}\cdot\text{g}^{-1}$) and the solute dissolved in the solution (C_e : $\mu\text{mol}\cdot\text{L}^{-1}$) as well as the forms that isotherms take. Taking the previous points into consideration, we can estimate the sorption affinity and capacity.

Figure 5 illustrates the isotherms of both metals (simple and competitive) at pH 5 and 7, respectively, at low and

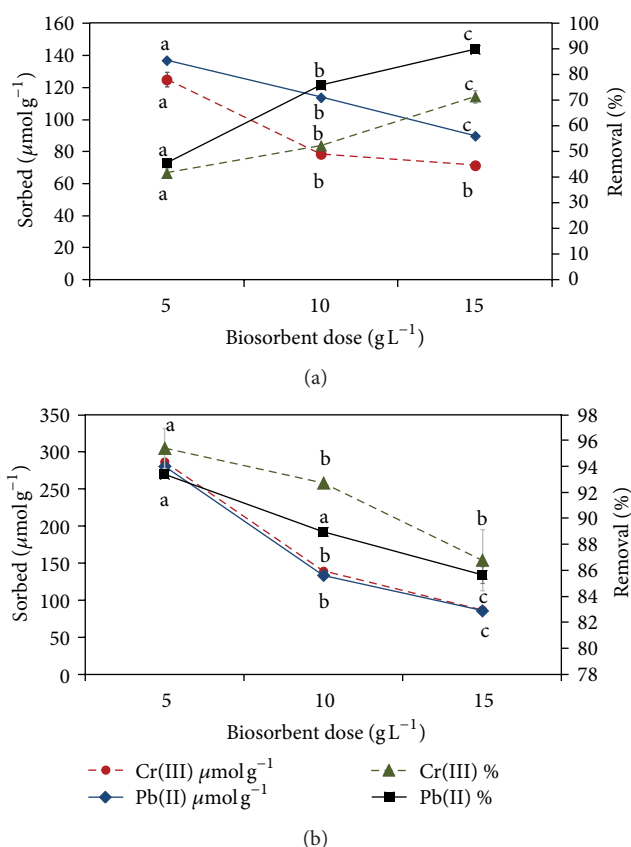


FIGURE 4: Sorption of Cr(III) and Pb(II) by the biomass of *S. californicus* as a function of the biosorbent dose at pH 5 ± 0.1 (a) and 7 ± 0.1 (b) (initial metal concentration: 1.5 mM ; temperature: 25°C). Vertical bars indicate the standard deviation of three replicates, and the letters indicate the groups that correspond to the significant ($P < 0.05$) differences.

high initial concentrations. At pH 5 (Figure 5(a)), contrary at pH 7, were observed typical sorption isotherms in the whole interval of concentrations studied (0.01 mM – 2 mM). The presence of both metals in solutions caused an effect of competence for active sites of sorption decreasing the sorption capacity (q_e) compared to simple sorption. At low concentrations, the isotherms fitted to lineal and sigmoid forms for Cr(III) and Pb(II), respectively (Figure 5(b)), and at high concentrations ($>0.5\text{ mM}$), the tendencies of the curves changed, indicating that different processes were involved at low and high concentrations, with a tendency for saturating active sites. The affinity of lead for the biosorbent was higher compared to the affinity of chromium. At pH 7 (Figures 5(c) and 5(d)), changes were observed in the isotherms shapes and sorption capacities compared to the results obtained at pH 5 for both metals. Interestingly, the interval of concentrations studied did not entirely fit to a typical profile for biosorption (Figure 5(c)). At low concentrations (Figure 5(d)), a tendency to reach saturation and a linear relationship were observed for lead and chromium, respectively; at high concentrations, precipitation became the dominant process, whereas normal isotherms of sorption were not observed. In competitive

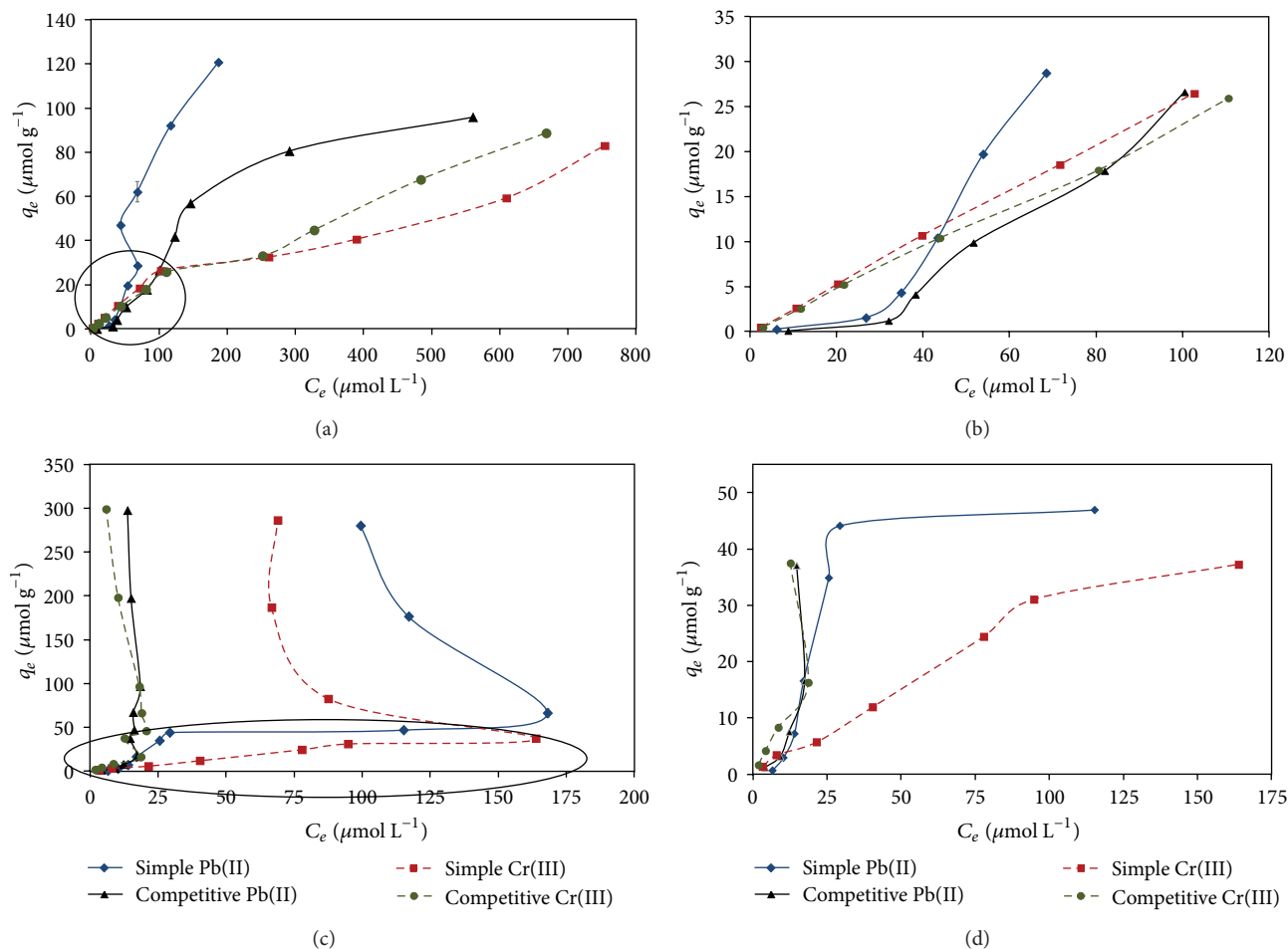


FIGURE 5: Sorption of Cr^{3+} and Pb^{2+} by the biomass of *S. californicus* (5 g L^{-1}) as a function of the biosorbent dose at pH 5 ± 0.1 at high (a) and low (b) initial concentrations and at pH 7 ± 0.1 at high (c) and low (d) initial concentrations (temperature: 25°C).

sorption, the shapes of curves changed such that normal sorption isotherms were not detected. This behaviour might be explained by a saturation of solution and precipitation of both metals. At this pH, it is probable that the precipitation process masks the sorption process.

3.6. Equilibrium Modelling. Analysis of equilibrium data is important for developing an equation that can be used for design purposes [30]. The isotherms presented before can be decrypted by models characterised by certain constants whose values express the surface properties and the affinity of the biosorbent [28]. The sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that of the interface, giving it the biosorption capacity [14]. There are several isotherm models proposed for sorption studies; we have chosen the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models because they are the most widely used in the literature, due to their simplicity, good agreement with experimental data and better analysis of the biosorption process [4, 9, 13, 15, 19, 27].

Table 3 presents the constants obtained for the four models. The experimental data fit the Langmuir isotherm

satisfactorily, with high R^2 values (>0.94), except for lead at simple sorption. This model served to estimate the maximum metal uptake ($q_{\text{max}L}$), which could not be reached in the experiments [31]. The best $q_{\text{max}L}$ for complete monolayer coverage is for chromium, having obtained the highest values at pH 5 in competence ($312.5 \mu\text{mol g}^{-1}$) and at pH 7 in simple sorption ($370.4 \mu\text{mol g}^{-1}$). In the case of the Freundlich model, the experimental data for simple and competitive sorption at pH 5 only fit well for chromium ($R^2 > 0.97$), in which the n values were higher than one, indicating that biosorption is favourable. For the Temkin model, the constant B_T , which is related to the heat of sorption and measures the variation in the energy of sorption [32], can be compared with the information deduced from the Langmuir model fit. For a higher heat of sorption, the binding energy required is major; therefore, the maximum sorption capacity may be lower. Comparing each metal individually, the condition that a higher B_T corresponding to lower $q_{\text{max}L}$ is satisfied in all cases. Additionally, the variation in the energy of sorption was positive in every treatment, indicating that the reaction is exothermic [32]. Finally, the equilibrium data were also subjected to the D-R model to determine the nature of the

TABLE 3: Isotherm model constants for simple and competitive biosorption of lead and chromium on the shoots biomass of *S. californicus* at different pH values.

		Chromium (III)				Lead (II)			
		Simple		Competitive		Simple		Competitive	
		pH 5	pH 7	pH 5	pH 7	pH 5	pH 7	pH 5	pH 7
Langmuir	$q_{\max L}$ ($\mu\text{mol g}^{-1}$)	78,74	370,37	312,50	22,73	81,30	54,05	98,04	4,99
	K_L ($\text{L}\cdot\text{g}^{-1}$)	0,0026	0,0011	0,0007	0,0347	0,0042	0,0108	0,0019	0,0462
	R^2	0,998	0,982	0,996	0,990	0,747	0,821	0,937	0,993
Freundlich	K_F ($\text{L}\cdot\text{g}^{-1}$)	0,380	0,485	0,406	0,503	0,121	0,456	0,108	0,080
	n	1,210	1,141	1,205	0,653	0,739	0,757	0,865	0,553
	R^2	0,966	0,987	0,995	0,841	0,790	0,809	0,873	0,799
Temkin	B_T (kJ mol^{-1})	0,297	0,151	0,081	0,388	0,068	0,124	0,069	0,258
	K_T ($\text{L}\cdot\mu\text{mol}^{-1}$)	0,175	0,186	0,018	0,543	0,061	0,151	0,027	0,221
	R^2	0,894	0,976	0,866	0,936	0,868	0,884	0,962	0,750
Dubinin-Radushkevich	$q_{\max D-R}$ (mmol g^{-1})	0,69	1,55	1,03	2,50	115,94	54,17	6,46	139,91
	E (kJ mol^{-1})	8,51	8,28	8,11	8,51	5,79	6,54	6,80	6,32
	R^2	0,986	0,898	0,994	0,998	0,980	0,829	0,902	0,951

biosorption process as either physical or chemical. The mean free energy (E) provides information about the biosorption mechanism. If $E < 8 \text{ kJ mol}^{-1}$, the biosorption process is of a physical nature, and if $E > 8 \text{ kJ mol}^{-1}$, the biosorption process is of a chemical nature [14, 31, 33]. In view of the obtained results, the biosorption process onto the shoots biomass of *S. californicus* may be conducted by extern and intern sphere complexes for lead ($E = 5.8\text{--}6.8 \text{ kJ mol}^{-1}$) and chromium ($E = 8.1\text{--}8.5 \text{ kJ mol}^{-1}$), respectively.

In addition, Table 4 presents comparative data on the biosorption capacity of *S. californicus* biomass for Pb(II) and Cr(III) with those of various biosorbents reported in literature obtained by other authors using the Langmuir model. Difference in metal biosorption by various biomasses may be attributed to difference in quantity and quality of functional groups of biosorbents mainly. The results indicate that *S. californicus* biomass exhibits comparable and moderately higher biosorption capacity than those of many corresponding biosorbents in the literature. Therefore, it can be noteworthy that the *S. californicus* biomass has considerable potential for removal of Pb(II) and Cr(III) ions from aqueous solution.

3.7. Desorption Studies. Desorption studies are important for estimating the reversibility of the process, biosorbent regeneration, and recovery of metals. The possibility of biosorbent regeneration is especially important for maintaining low processing costs that result in a better overall process economy [44]. Five different agents (0.1M) were tested for desorbing the metals from the metal-loaded-pH 5 and metal-loaded-pH 7 biomasses (Table 5). We chose those agents to cover the major diversity of agents such as an acid (HNO_3), a base (NaOH), a salt (MgCl_2), a chelating agent (EDTA), and finally distilled water. Nitric acid (90% desorption) and sodium hydroxide (10% desorption) were the most effective eluting agents for lead and chromium, respectively, followed by EDTA for both metallic ions (Table 5). It was

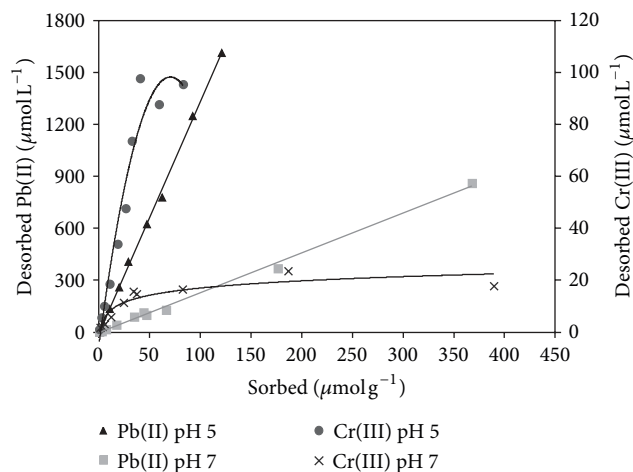


FIGURE 6: Desorption of Cr^{3+} and Pb^{2+} from metal-loaded-pH biomass of *S. californicus* as a function of concentration of metal sorbed (agitation time: 24 h; eluent agent: NaOH for Cr and HNO_3 for Pb; temperature: 25°C).

observed that the percentage of desorption was better for lead than for chromium and better at pH 5 sorption than at pH 7 sorption, indicating the different types of binding sites involved in each condition. In view of the obtained results, the chromium sorption mechanisms involve stronger forces of retention than for lead, such as in intern sphere complexes, in accordance with the results obtained with the D-R model. In the case of lead, ion exchange would be the predominant sorption mechanism using an acid-eluting agent, according to several authors [6, 45, 46]. Figure 6 illustrates the desorption capacity as a function of the concentration of metal-loaded-pH biomass using 0.1M HNO_3 and 0.1 M NaOH for Pb(II) and Cr(III), respectively. Clearly, the lead desorption profiles exhibit a linear relationship with the concentration of the metal-loaded biomass at both pH values of biosorption (R^2 0.9988 at pH 5; R^2 0.9961 at pH 7); in

TABLE 4: Comparison of biosorption capacity of *S. californicus* biomass for Pb(II) and Cr(III) ions with those of different biosorbents.

Biosorbent	Biosorption capacity (q $\mu\text{mol g}^{-1}$)		Reference
	Chromium (III)	Lead (II)	
Banana peels	—	10,5	[27]
Olive stone	78,5	28,4	[34]
<i>Zoogloea ramigera</i>	—	50,2	[35]
<i>Aspergillus flavus</i>	—	65,2	[36]
<i>Rhizopus arrhizus</i>	—	74,8	[35]
<i>Gelidium</i> algal waste	—	98,9	[5]
<i>Populus</i> spp. sawdust	106,2	101,6	[37]
Modified peanut husk	147,5	140,6	[37]
<i>Ulva lactuca</i>	—	167,5	[38]
<i>Lactarius scrobilatus</i>	—	271,2	[39]
<i>Parmelina tiliacea</i>	1002,0	365,8	[14]
Quebracho tannin resin	—	416,1	[40]
<i>Rhodococcus opacus</i>	1404,0	455,0	[28]
Tropical peats	107,7	—	[9]
<i>Colocasia esculenta</i>	116,7	—	[23]
<i>Nymphaea</i> sp.	117,5	—	[23]
<i>Rhizophora mangle</i>	125,8	—	[23]
<i>Eichornia crassipes</i>	127,1	—	[23]
<i>Cannomois virgata</i>	138,1	—	[23]
<i>Saccharomyces cerevisiae</i> waste	255,0	—	[41]
Soybean meal waste	567,0	—	[42]
<i>Moringa oleifera</i> bark	665,4	—	[43]
<i>Schoenoplectus californicus</i>	370,37	98,04	Present study
	(pH 7 simple)	(pH 5 competitive)	(Langmuir model)
<i>Schoenoplectus californicus</i>	389,07	366,96	Present study
	(pH 7 simple)	(pH 7 simple)	(Experimental data)

TABLE 5: Effects of various chemical agents (0.1 M) on the desorption of Cr(III) and Pb(II) from the metal-loaded-pH biomass of *S. californicus*.

Desorbing agent	Percentage of desorption			
	Chromium (III)		Lead (II)	
	pH 5	pH 7	pH 5	pH 7
Distilled water	0,30 \pm 0,07	0,08 \pm 0,02	0,33 \pm 0,08	0,44 \pm 0,28
HNO ₃	2,27 \pm 0,10	1,46 \pm 0,23	90,04 \pm 4,21	77,08 \pm 1,88
NaOH	10,04 \pm 0,57	1,03 \pm 0,02	8,71 \pm 0,23	14,50 \pm 0,69
MgCl ₂	0,43 \pm 0,09	0,08 \pm 0,01	5,02 \pm 2,55	9,52 \pm 0,32
EDTA	3,13 \pm 0,23	0,94 \pm 0,30	87,99 \pm 2,05	75,47 \pm 1,86

the case of chromium desorption profiles presents saturation since 40 $\mu\text{mol g}^{-1}$ sorbed. Finally, the recovery efficiency (%), which takes into account the initial concentration of the metals in the solution as in (5), would allow the global effectiveness of the process to be illustrated. The percentage of recovery of lead (~80%) is always greater than of chromium (~10%) (Figure 7), as well as the percentage of recovery in sorption-pH 5 over sorption-pH 7 for both metals. In view of the obtained results, sorption pH 5 with HNO₃ and NaOH as desorbing agents for Pb(II) and Cr(III), respectively, is the

condition that maximises the effectiveness of removal and recovery for the metal ions studied.

3.8. *Environmental Scanning Electron Microscopy (ESEM) and X-Ray Energy-Dispersive Spectrometry (EDX)*. Biomass and filters were characterised before and after treatments by observing with an environmental scanning electron microscope (ESEM) (Figure 8) and analysing by X-ray energy-dispersive spectrometry (EDX) (Figure 9). This characterisation was performed successfully in vacuum (low-vacuum) at a beam energy of 20 keV. The untreated biosorbent showed characteristics typical of the shoot biomass, with strands of plant material clearly visible, surface texture, and different levels of porosity. Figures 8(b) and 8(c) show precipitates of chromium and lead, respectively, retained in filters after being filtered through a solution at pH 7. The analysis by EDX distinguished peaks for Cr and Pb, which were identified in each figure (Figures 9(a) and 9(b)). In the case of the lead precipitates, these exhibited a rhombohedral geometry, unlike the chromium precipitates that showed an amorphous structure. Figures 8(d) and 8(e) show the biomass treated with Pb at pH 5 \pm 0.1 and 7 \pm 0.1, respectively. Clearly, particles over the biomass were observed in both figures. Figure 5(d) was generated by backscattered electrons, which

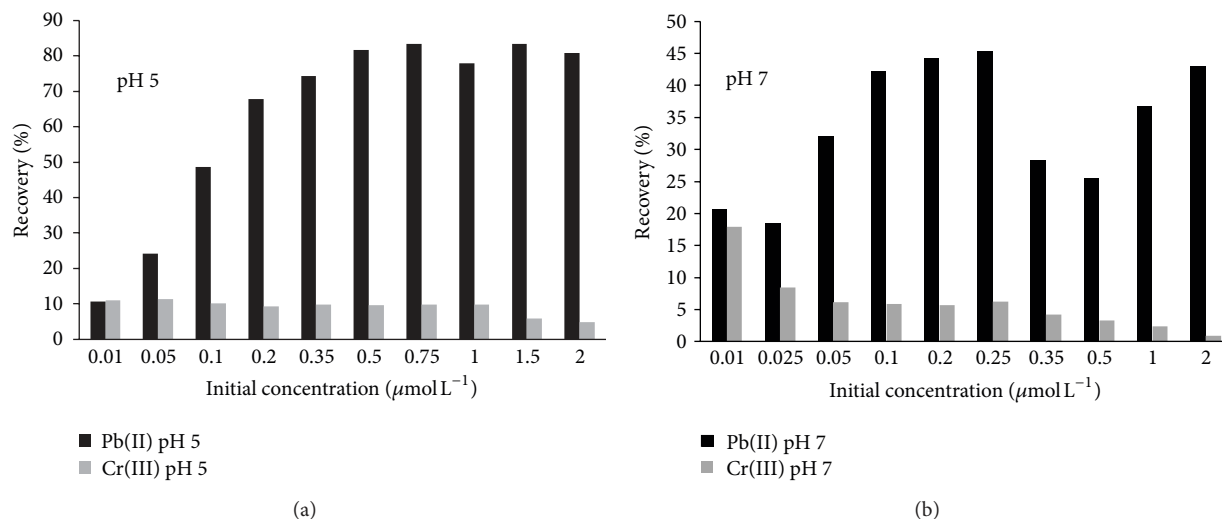


FIGURE 7: %Recovery of Cr^{3+} and Pb^{2+} by sorption-desorption on biomass of *S. californicus* as a function of initial concentration at pH 5 ± 0.1 (a) and 7 ± 0.1 (b).

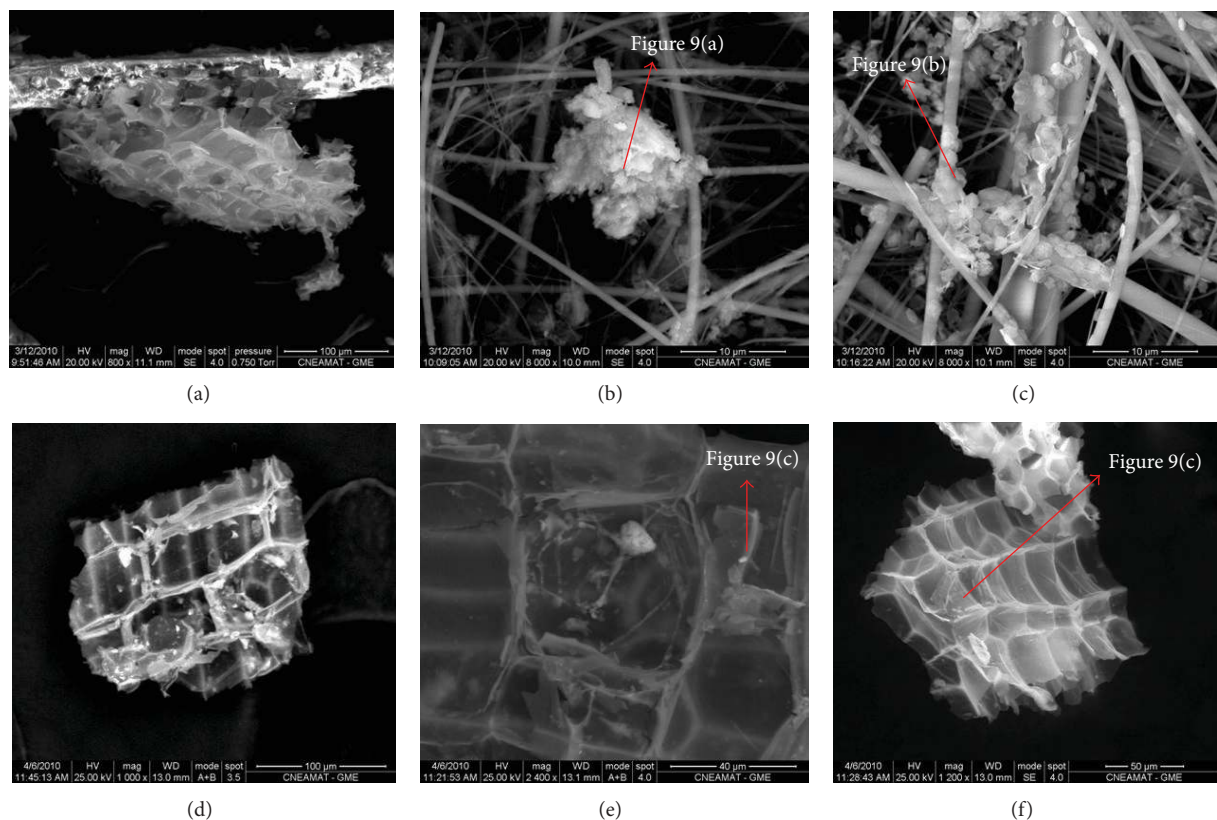


FIGURE 8: SEM micrographs of (a) untreated shoot biomass, (b) filter with Cr^{3+} precipitated at pH 7 ± 0.1 , (c) filter with Pb^{2+} precipitated at pH 7 ± 0.1 , (d) shoot biomass treated with 1.5 mmol L^{-1} Pb^{2+} at pH 5 ± 0.1 , (e) shoot biomass treated with 1.5 mmol L^{-1} Pb^{2+} at pH 7 ± 0.1 , and (f) shoot biomass treated with 1.5 mmol L^{-1} Cr^{3+} at pH 7 ± 0.1 .

would enable the identification of points with Pb on the biomass; this phenomenon is due to the high atomic number of Pb, which generates a high backscatter coefficient that is displayed as brighter points on the micrograph, safeguarding the evident topography. This shows that sorption occurs

in discrete patches onto the biomass with probable surface precipitation, in concordance with Schneider et al. (2001) [47], who have studied the adsorption/precipitation of metal oxides and hydroxides on the surface of plant materials. Figures 8(e) and 8(f), in correlation with the EDX diagrams

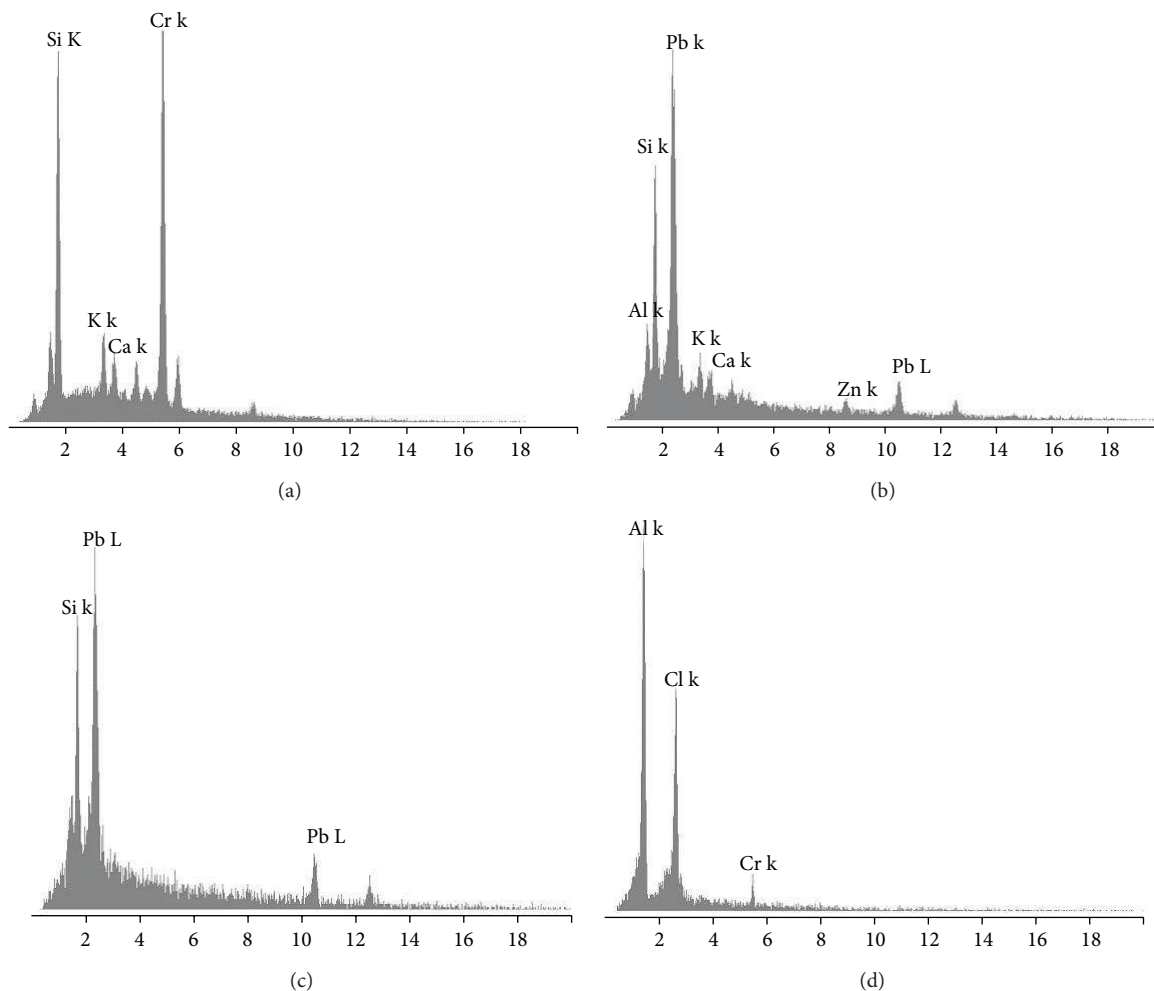


FIGURE 9: EDX analyses of (a) filter with Cr^{3+} precipitated at $\text{pH } 7 \pm 0.1$, (b) filter with Pb^{2+} precipitated at $\text{pH } 7 \pm 0.1$, (c) shoot biomass treated with $1.5 \text{ mmol L}^{-1} \text{ Pb}^{2+}$ at $\text{pH } 7 \pm 0.1$, and (d) shoot biomass treated with $1.5 \text{ mmol L}^{-1} \text{ Cr}^{3+}$ at $\text{pH } 7 \pm 0.1$.

(Figures 9(c) and 9(d), resp.), confirm the retention of Pb and Cr, respectively, by the shoots biomass of *S. californicus*.

4. Conclusions

The biosorbent studied can be used to remove Cr(III) and Pb(II) from wastewater, whereas pH is a key factor to control the removal of these metals from wastewaters. For both metals, the optimum pH for biosorption is 5, and 7–9 is the pH interval of major removal ($\sim 82\% \text{ Cr}$)/($\sim 95\% \text{ Pb}$) due to the joint process of precipitation-adsorption. The recovery of lead was greater than of chromium because the Cr(III) sorption mechanisms involve a stronger binding energy than the mechanisms for Pb(II). Biosorption pH 5 with HNO_3 and NaOH as desorbing agents for Pb(II) and Cr(III), respectively, is the condition that maximises the process effectiveness. Taking the previous points into consideration, the use of shoots biomass of *Schoenoplectus californicus* in the removal and recovery of lead (II) and chromium (III) to a lesser extent proved to be an efficient and economical alternative for the treatment of wastewaters contaminated with these metals.

Acknowledgments

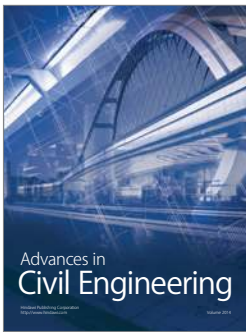
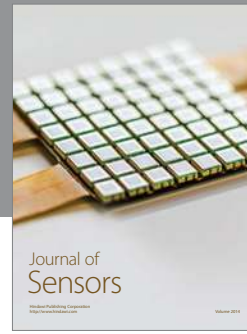
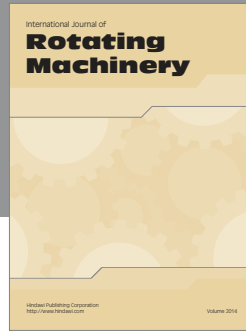
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