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Cr(III) biosorption by forest wastes from *Araucaria angustifolia* and *Pinus elliottii*: biosorbent surface characterization and chromium quantification by spectrofluorimetry in micellar medium

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ABSTRACT

This work describes the characterization of the solid biomass, and its aqueous extracts, obtained from the cones of *Araucaria angustifolia* and *Pinus elliottii*, in order to understand the mechanism of Cr(III) biosorption in these biosorbents, as well as to characterize the residues of the process. Trivalent chromium was quantified, for the first time in a complex biomass system, by fluorescence suppression using naphthalene as probe, and the quantification could be used safely for both biosorbents *Araucaria* and *Pinus*. The results showed that Cr(III) can be effectively removed using *Araucaria* and *Pinus* wastes and their biosorption capacities are higher than those of other lignocellulosic materials under similar conditions. Carboxylic moieties present on the biosorbent surface seem to play a major role on Cr(III) binding.

Keywords: Biosorption; Forest wastes; Spectrofluorimetry micellar medium; Trivalent chromium

1. Introduction

Chromium is present in the environment in different forms, including Cr(0), Cr(II), and Cr(IV), but only hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) are important and commonly present in the natural environment and in industrial effluents [1]. For this unique metal, the two more stable species have drastically different properties: Cr(VI) is highly toxic, mutagenic, and carcinogenic to living organisms and also tends to be more mobile in the environment due to its higher solubility in water [2]. For plants and animals, Cr(III) is an essential element in the metabolism of glucose and nucleic acid synthesis. However, at large doses, it can have harmful and even fatal effects, acting as competitive inhibitor in many cellular processes [3]. The main sources of chromium pollution are mining, leather tanneries, cement industry, dyes, electroplating, steel treatment, photographic materials, and corrosive paints [1].

Removal of chromium from wastewaters is mandatory to avoid water pollution. Legislation in different

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countries demands Cr(VI) concentration in discharges be less than 0.1 mg L^{-1}, while higher concentrations (1.0 mg L^{-1}) are admissible for the less toxic Cr(III). More restrictive levels are adopted by some countries, a fact that indicates a concern regarding the presence of this toxic pollutant in surface waters.

Several treatment processes, such as chemical precipitation, membrane filtration, and adsorption (usually, using activated carbon), are used in the removal of chromium from effluents [1,4]. However, the high cost of these processes led to the development of new, cheaper, and more efficient materials. The use of biosorbents is recommended since they are abundant and easily available; relatively cheap or of no cost; and show high affinity and selectivity for heavy metals and can be recycled. The metal could also be recovered in the end of the biosorption treatment by desorption or incineration of the biomass [2] which can make the process even more attractive. Natural residues are one important category of biosorbents [5–7] and among them, lignocellulosic materials, such as forestry wastes, have been tested in the removal of chromium on the laboratory scale [8–19].

Although trees of the genus *Pinus* are native to the northern hemisphere, they grow successfully in different regions in the world. In Brazil, pine forests have been grown increasingly to meet the demand for wood and cellulose in the last decades. But, the pine forest residues, such as cones, are plentiful and are not appropriately used and disposed of. Some studies indicate the potential of *Pinus* wastes in the removal of chromium from synthetic solutions and effluents [8,18]. For instance, Ucun et al. [8] reported higher levels of removal from synthetic chromium solutions for both Cr(VI) and Cr(III) (q_{max}. 122 mg.g^{-1}), using *Pinus* cones. Park et al. [18] reported that dried leaves of *Pinus densiflora* showed that high removal rate (95%) of total Cr (Cr(VI) + Cr(III)) from aqueous solution requires a long contact time (60 h) at pH 4 and 40°C.

The use of *Araucaria* wastes as biosorbent is more recent, but studies performed with synthetic solutions indicate competitive Cr removal efficiencies ($q_{max.}$ 125 a 240 mg g^{-1}) when compared to traditional processes [10,13]. The scales from Araucaria cones were also effective in the removal of Cr(III), Cr(VI), and iron from metallurgical industry effluents [10]. *Araucaria angustifolia* is a tree native to southern Brazil and, in the last two centuries, human activities reduced the *Araucaria* forest to approximately 3% of its original area (200, 000 km^2). Its fruit is a cone that contains 10–150 seeds and the failures, where no seed is formed, are called scales. Since the seeds (nuts) represent 50% of cone weight and the other 50% is composed basically of scales, the Brazilian production of pine nuts (4,400 t y^{-1}) indicates the availability of 4,400 t y^{-1} of scales. Additionally, the effective utilization of *Araucaria* wastes can stimulate the conservation of the native subtropical Brazilian forests [20].

This work describes the characterization of the solid biomass, and their aqueous extracts, obtained from the cones of *A. angustifolia* and *Pinus elliottii*, in order to understand the mechanism of Cr(III) biosorption in these biosorbents, as well as the characterization of the residues of the process. Several characterization techniques were used and Cr(III) adsorption was tested in batch experiment using clean (washed) biosorbents in different experimental conditions. Trivalent chromium was quantified, for the first time in this kind of system, by means of fluorescence spectroscopy using naphthalene as probe [21].

2. Materials and methods

2.1. Samples preparation

Biosorbent materials used in this study come from forest residues of the species *A. angustifolia* and *P. elliottii* (referred hereafter as *Araucaria* and *Pinus*, respectively). The cones were dried in an oven (80°C, 24 h), crushed in an industrial blender (Visa LO 4.0), and sieved (<250 μm). Powdered material was conditioned in sealed plastic bottles and stored in dry, dark compartments in a temperature-controlled room (22 ± 2°C). Part of the material was subjected to sequential washing processes (10 g L^{-1}, two cycles 5 h and 2 h) under agitation (120 rpm, orbital shaker) with deionized water (MilliQPlus, Millipore) at room temperature (22 ± 2°C). The aqueous extracts of the washing process were filtered (Millipore PVDF membrane, 0.22 μm) and characterized as described below. The washed solids were dried (80°C, 24 h) and stored in the same way as the raw (unwashed) biosorbents.

2.2. Solid characterization methods

The solid biosorbents were characterized using scanning electron microscopy (SEM, PHILIPS XL 30) in secondary electrons and back scattered electrons imaging modes. The chemical composition of the material was determined by energy dispersive X-ray spectroscopy (EDS). Analyses by Fourier transform infrared spectroscopy (FT-IR) were also performed (Perkin-Elmer, Spectrum One and Varian 3100 FT-IR, Excalibur Series) in transmittance mode with samples prepared in KBr disks and spectra recorded from 4,000 to 400 cm^{-1}. The X-ray diffraction analysis was carried out using a copper tube (K α 1.5406 Å) in a Shimadzu Model 7000 diffractometer. BET analysis

was performed under N_2 using a Quantachrome Autosorb equipment. Elemental analysis (CHN) was performed in TruSpec equipment (LECO) and proximate analysis was performed following standard procedures [22].

Identification and quantification of functional groups on the biosorbent's surface were made by Boehm titration [23–24]. In the Boehm method, originally developed for activated carbon [23], a specific mass (0.5 g) of the biosorbent was placed in 50 mL solution of the different bases (0.1 mol L^{-1} KOH, 0.1 mol L^{-1}, $KHCO_3$, and 0.05 mol L^{-1} K_2CO_3) and the thermostated (22 ℃ ± 2 ℃) bottles were sealed and shaken for 24 h. After filtration, an aliquot (10 mL) of each solution containing the excess base was titrated with 0.1 mol L^{-1} HCl. The mass of surface acid functional groups (mmol g^{-1}) was calculated assuming that KOH neutralizes all acidic groups (carboxylic, lactonic, and phenolic), K_2CO_3 neutralizes carboxylic and lactonic groups, and $KHCO_3$ only neutralizes carboxylic groups [23–24].

The aqueous extracts of the biosorbents were characterized initially by analyses of color, Chemical Oxygen Demand (COD), and UV–vis absorption spectra according to APHA [25]. The determination of anions and cations was made by ion chromatography (CI) using a Dionex ion chromatograph (DX 500) and following EPA (method 300.1) and ISO (method 10304-1) standard procedures. The determination of organic and inorganic carbons was performed using a TOC analyzer (Shimadzu, equipped with an IR detector).

2.3. Batch adsorption experiments

Standard stock solutions of Cr(III) (1,000 mg L^{-1}) were prepared from $CrCl_3$ salt (Merck pa). The working solutions were prepared from the stock solution by dilution with deionized water (MilliQPlus, Millipore) and 0.1 mol L^{-1} solutions of NaOH and HCl were used to adjust the pH of the medium.

Batch experiments were performed with cleaned biosorbents (10 g L^{-1}, size <250 μm) using flasks placed on a shaker at temperature 22 ± 2 ℃, with shaking speed (150 rpm) for a period of 3 h, which is the time required to reach equilibrium, previously determined by Santos [10]. At the end of the experiment, the solutions were separated from the biomass by centrifugation and filtration (PVDF, Millipore, 0.22 μm). The influence of different experimental parameters, such as pH (1–5) and initial metal concentration (0–1×10^{-2} M), on the sorption process was evaluated. The pH >5 was not tested due to the precipitation of Cr(III) as hydroxide [2,10,18].

2.4. Determination of Cr(III) content in the solutions

Standard solutions containing 1,000 mg L^{-1} of Cr(III) (Across Organics, Geel, Belgium) were used with appropriate dilutions. All other reagents were of the best available analytical grade. Doubly deionized water with conductance < $5.6\,10^{-8}\,\Omega^{-1}\,cm^{-1}$ and pH 6.0–7.0 from a NANOpure analytical deionization system (type D-4744) was used to prepare standard and reagent solutions.

Stock solutions of naphthalene 10^{-2} mol L^{-1} (Sigma-Aldrich, Steinheim, Germany) in ethanol and sodium dodecyl sulfate (SDS) 10^{-1} mol L^{-1} (Sigma Ultra 99.0% - Sigma-Aldrich, Steinheim, Germany) in deionized water were used in the measurements. All spectroscopic measurements were made in a temperature-controlled room, 23 ± 1 ℃, in aqueous SDS 2.0×10^{-2} mol L^{-1} containing 0.024 mol L^{-1} HNO_3.

The concentration of Cr(III) in the solutions before and after the equilibrium was determined by spectrofluorimetry in micellar medium.

Fluorescence measurements were made on a Cary Eclipse Varian spectrofluorimeter, with a 450 W Xenon arc lamp and a 1.0 cm quartz cell. The excitation and emission wavelengths for naphthalene were 274 and 334 nm, respectively, with slit widths of 10 nm. In micellar spectrofluorimetry, for the quantification of Cr(III), was added 0.1% HNO_3 to suppress the fluorescence in the aqueous phase [21,26]. The results were validated by UV–vis spectroscopy using the diphenylcarbazide method [25] and by flame atomic absorption spectroscopy (FAAS).

UV–vis spectrophotometric measurements were carried out at 25.0 ± 0.1 ℃, in the water-jacketed cell compartment of a HP-8453 diode array spectrophotometer, calibrated with NIST traceable UV/Vis reference materials. FAAS measurements were carried out using a Perkin-Elmer Analyst 300 atomic absorption spectrometer (detection limit was 1.0×10^{-7} mol L^{-1}).

All vessels in contact with samples or reagents were cleaned by soaking overnight in HNO_3 (5.8 mol L^{-1}) and rinsed repeatedly with deionized water before use.

In all cases, the Cr(III) uptake was calculated by the simple concentration difference method as follows:

$$Q_e = \frac{(C_i - C_e)V}{1,000\,w} \quad (1)$$

where V is the volume of the solution in mL, w represents the mass of the sorbent in g, C_i (mmol L^{-1}) is the initial concentration, C_e (mmol L^{-1}) the equilibrium concentration, and Q_e (mmol g^{-1}) corresponds to the metal uptake capacity.

2.5. Recovery of chromium by incineration of metal-loading biosorbents

The destination of the removal Cr(III) by biosorbents was assessed by both metal desorption and metal recovery tests. The Cr desorption from biosorbents (10 g L^{-1}), and its regeneration, was tested using aqueous HCl solutions (0.8 mol L^{-1}–2.0 mol L^{-1}) at ambient temperature, under mechanic agitation (120 rpm) for different contact times (24 and 48 h). The experimental conditions were chosen from literature studies that indicate acid extraction as more efficient for chromium desorption [10,13]. The efficiency of the process was determined by measuring desorbed Cr concentration on extracts and compared with metal loading on biosorbents.

The metal recovery tests were performed by incineration of the Cr-loading biosorbents in oven (550°C) until constant weight (~4 h). The produced ashes were characterized by FT-IR, DRX, and XRF techniques.

3. Results and discussion

3.1. Biosorbent characterization

Table 1 contains the characterization parameters for the biosorbents prepared from *Araucaria* and *Pinus*.

Table 1
Basic characterization of the biosorbents produced by cones from *Araucaria* and *Pinus*

Parameter	Unit	Biosorbent	
		Araucaria	*Pinus*
pH (1%)		6.5	4.9
Specific area	$m^2 g^{-1}$	10.9	9.5
Proximate analysis			
Moisture	%w	7.3	11.6
Ash	%w (db)	4.3	5.6
Volatile matter	%w (db)	68.2	58.7
Fixed carbon	%w (db)	27.5	35.7
Elemental analysis			
C	%w (db)	41.8	53.0
H	%w (db)	5.6	5.2
N	%w (db)	0.6	0.6
Groups in surface[a]			
Carboxylic	mmol g^{-1}	0.51	0.90
Lactonic	mmol g^{-1}	0.10	0.40
Fenolic	mmol g^{-1}	0.51	0.38
Total acidic	mmol g^{-1}	1.12	1.68

[a]Quantified by Boehm titration.
db—dry basis.

The proximate analysis indicated similar composition for two biosorbents with *Pinus* presenting slightly higher levels of moisture, ash, and fixed carbon. These results are in the range reported for other biomass materials [9,10,13,15]. The ultimate analysis also indicated similar concentrations of carbon (41.8–53.0%), hydrogen (~5%), and nitrogen (~0.5%) for both biosorbents and the observed that elemental composition is typical for this kind of biomass [9,10,13].

The measured surface areas of the biosorbents were 10.9 $m^2 g^{-1}$ and 9.5 $m^2 g^{-1}$ for *Araucaria* and *Pinus*, respectively. These values are higher than those reported for other biosorbents [9,15] but, as expected, smaller than activated carbons surface areas (550–1,400 $m^2 g^{-1}$). The surface area influences the sorption process but other parameters, such as pH, are more important in determining the Cr(III) ions biosorption (see below).

The pHs obtained for a 1% aqueous solutions (10 g L^{-1}) of biosorbents are in the acid range with *Pinus* showing a higher acidity (pH 4.9) than *Araucaria* (pH 6.5). This behavior is most probably due to the influence of the chemical composition of the soluble compounds present in the biomass and will be discussed in the next item.

Metal ion binding to lignocellulosic adsorbents occurs through chemical functional groups, such as carboxyl, amino, or phenolic groups [5]. The identification and quantification of the surface groups were made by Boehm titration (Table 1) that indicated the presence of carboxylic, lactonic, and phenolic moieties in both biosorbents. The largest amount of acid sites was observed for *Pinus* (1.62 mmol g^{-1}), while the *Araucaria* has 35% less acid sites, highlighting the different surface characteristics of these biosorbents. There is a predominance of carboxylic groups in *Pinus*, whereas the phenolic groups are majority in *Araucaria* (48%). It is interesting to note a significant quantity of lactones in *Pinus* (23% of the acid groups, 0.37 mmol g^{-1}) compared to *Araucaria* (<9%). Among acid species, carboxylic groups play an important role on the adsorption process of positively charged metals such as Cr(III). For pH >4, these groups are negatively charged and it is expected that Cr(III) species bind to them [27].

Fig. 1 shows SEM images of *Araucaria* scales. A morphology characterized by heterogeneous particles (Fig. 1(A)) with a wide variety of shapes and sizes and highly irregular surface (Fig. 1(B)) was observed. In addition to the organic matrix elements (carbon and oxygen), the presence of chlorine and potassium was confirmed by the EDS spectrum (Fig. 1(C)). These elements were also observed in significant concentrations in the aqueous extracts of this biosorbent (see

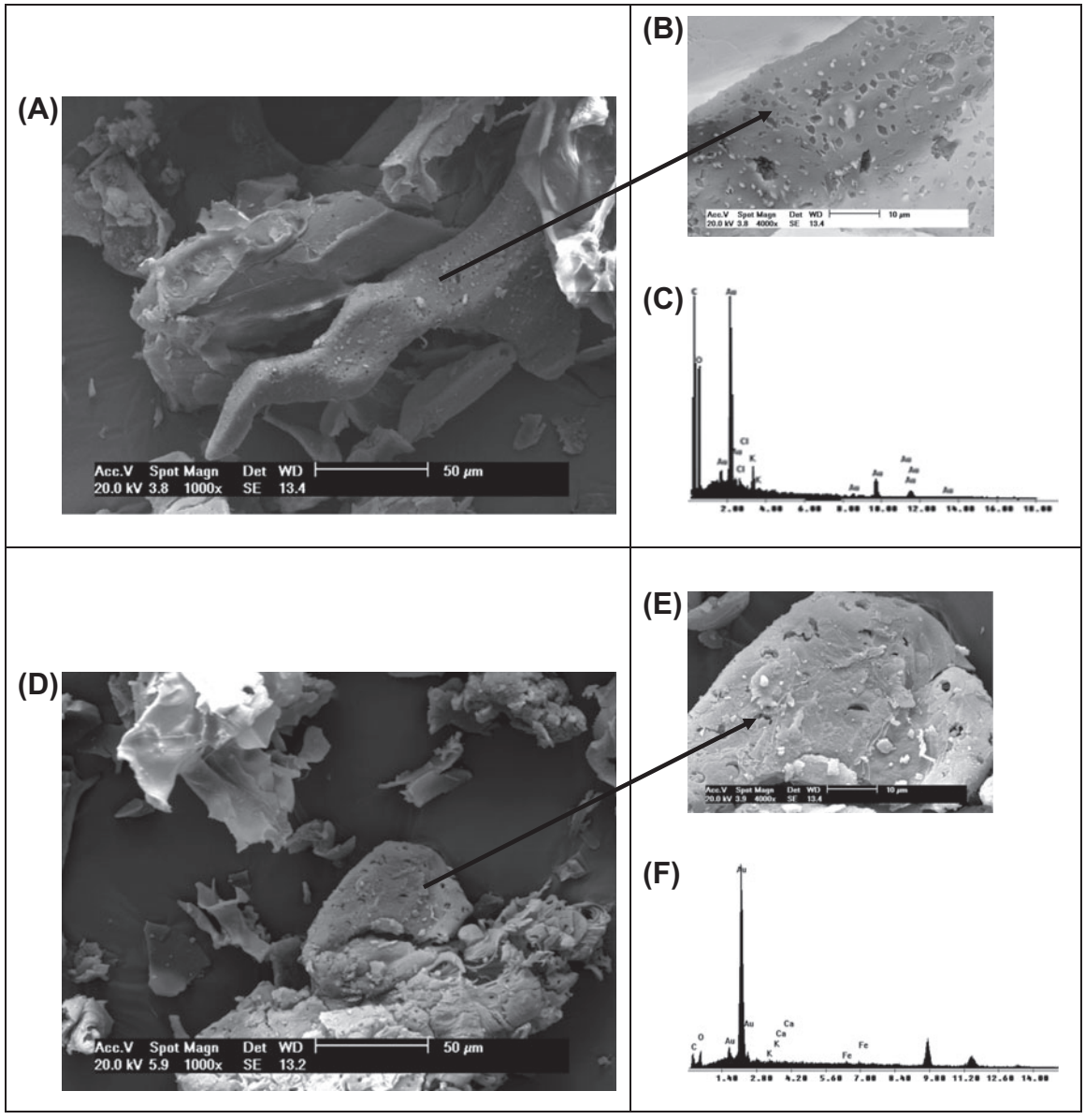

Fig. 1. SEM micrographs of the powder (<250 μm) of *Araucaria* (A) and *Pinus* (D), and detailed images (B and E) and their EDS spectra for *Araucaria* (C) and *Pinus* (F).

below). *Pinus* SEM images also presented highly heterogeneous particles (Fig. 1(D)) with few large porous structures in the surface (Fig. 1(E)). The EDS spectrum (Fig. 1(F)) of *Pinus* shows significant amounts of potassium, calcium, and irons, in agreement with the analysis of the aqueous extracts of this biosorbent (Table 2).

Fig. 2 shows the FT-IR spectra of *Araucaria* and *Pinus* biosorbents, where the complex nature of these biomaterials can be observed. The broad band around 3,500 cm^{-1} is ascribed to the stretching vibration of –OH groups, and probably, refers to the presence of cellulose, one of the main constituent of these biosorbents [5]. The absorption bands between 2,850 and 2,950 cm^{-1} are typical of the symmetric and asymmetric aliphatic C–H stretching. The strong absorption bands around 1,620 cm^{-1} are consistent with the presence of C=O stretching and/or C=C stretching in the aromatic ring. The presence of carboxylic groups is consistent with the bands around 1,730 cm^{-1}. The fingerprint region is complex due to the presence of a large variety of functional groups, as reported by Sawalha et al. [28], which is confirmed by FT-IR analyses that the carboxyl functionality is the main group responsible for binding Cr(III) on saltbush biomass.

3.2. Aqueous extracts characterization

Table 2 presents the results of characterization (pH, conductivity, color, absorption UV_{254nm}, COD, and TOC) of aqueous extracts, obtained after two successive contacts (5 h and 2 h, respectively) of biosorbent (10 g L^{-1}) with doubly deionized water. As expected, there was greater solubilization in the first wash cycle, with higher percentages of extraction of organic material for both *Pinus* (>82%) and Araucaria (>76%). These data suggest that two wash cycles were sufficient to remove the bulk of the soluble material and weakly bound solid biomass.

The extracts had higher concentration in the *Araucaria* case, especially in the first extraction cycle, when compared with the *Pinus* extracts (2–3-fold higher values for conductivity and color). The COD values for both extracts are higher than permitted levels for effluent emission charge (400 mg O_2 L^{-1}), having a negative influence on effluent quality. The COD and high UV_{254nm} absorption values are indicative of the solubilization of significant amounts of organic matter of both biosorbents. This result is consistent with the

Table 2
Characterization of aqueous extract obtained from the contact of the biosorbents with water in two cleaning cycles.

Parameter	Unit	*Araucaria*		*Pinus*	
		1° Ext.	2° Ext.	1° Ext.	2° Ext.
pH		6.54	6.60	4.94	5.30
Conductivity	mS cm^{-1}	0.27	0.04	0.08	0.01
Color	mg Pt-Co L^{-1}	1,100	250	550	200
$UV_{254\ nm}$	cm^{-1}	2.78	0.49	2.22	0.72
COD	mg O_2 L^{-1}	622	139	527	170
TOC	mg L^{-1}	227	36	191	48
Fluoride	mg L^{-1}	0.5	0.2	0.6	<LD
Chloride	mg L^{-1}	52.0	29.7	2.6	2.5
Nitrate	mg L^{-1}	5.4	5.3	5.7	5.6
Phosphate	mg L^{-1}	16.0	11.3	6.0	5.5
Sulfate	mg L^{-1}	7.0	5.3	2.2	1.9
Formate	mg L^{-1}	0.4	0.1	0.1	0.1
Acetate	mg L^{-1}	<LD	<LD	4.9	4.1
Oxalate	mg L^{-1}	<LD	<LD	1.2	1.2
Sodium	mg L^{-1}	<LD	<LD	0.7	<LD
Ammonium	mg L^{-1}	<LD	<LD	1.4	0.1
Potassium	mg L^{-1}	132	12.2	12.7	2.8
Magnesium	mg L^{-1}	0.2	<LD	0.3	<LD
Calcium	mg L^{-1}	0.8	0.4	0.5	0.1

Notes: Particle size <250 μm; temperature = 22.5°C; agitation = 120 rpm, cycles time1th 5 h/2th 2 h.

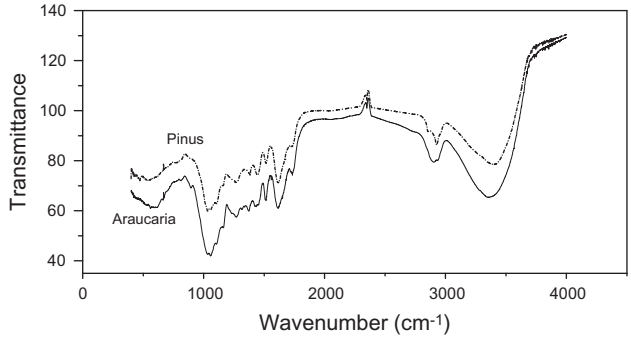

Fig. 2. FT-IR spectra of the *Araucaria* and *Pinus* powders (<250 μm).

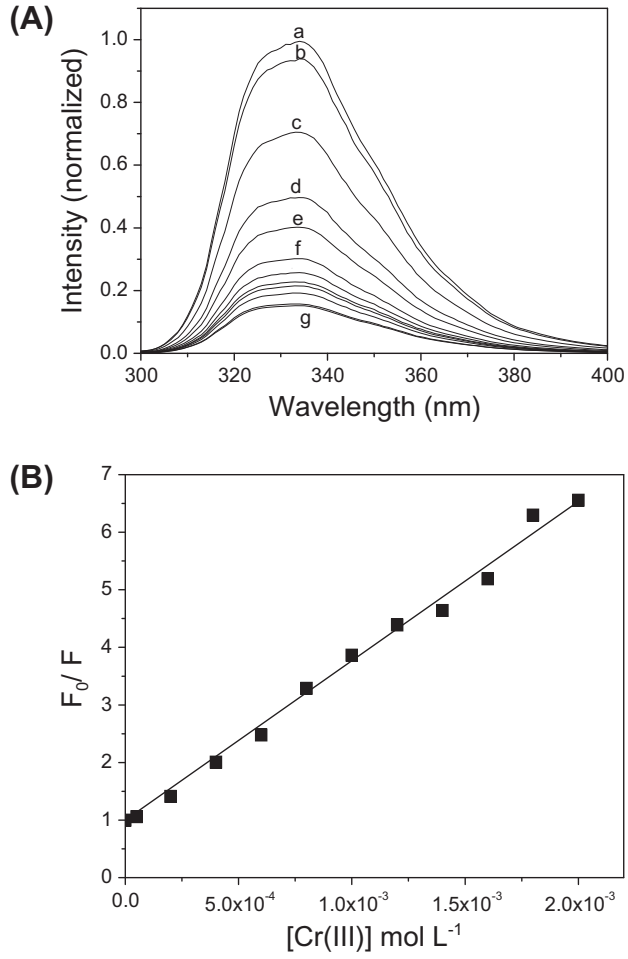

Fig. 3. (A) Emission spectra of naphthalene (1×10^{-4} mol L^{-1}) in aqueous SDS (0.02 mol L^{-1}), 0.1% HNO_3 and at $\lambda_{ex} = 274$ nm in the presence of the following Cr(III) concentrations: (a) no added Cr(III); (b) 5.0×10^{-5} mol L^{-1}; (c) 2.0×10^{-4} mol L^{-1}; (d) 4.0×10^{-4} mol L^{-1}; (e) 6.0×10^{-4} mol L^{-1}; (f) 8.0×10^{-4} mol L^{-1}; (g) 2.0×10^{-3} mol L^{-1} (B) calibration curve based on the fluorescence quenching of naphthalene (1×10^{-4} mol L^{-1}) in the presence of [SDS] = 0.02 mol L^{-1} and 0.1% HNO_3 as a function of [Cr(III)], $\lambda_{em} = 334$ nm.

relatively high total organic carbon (TOC) values obtained for these samples (Table 2). In addition, a linear correlation is observed between these parameters (Fig. 5).

It is well known that lignocellulosic wastes, such as *Pinus* and *Araucaria*, are composed mainly of hemicellulose, cellulose, and lignin [27]. Floge et al. [29] suggested that successive washing treatments of these types of lignocellulosic materials result in the solubilization of sugars, hemicellulose, and lignin fragments of low molecular weight. These compounds are probably responsible by the high organic matter levels observed in both *Pinus* and *Araucaria* aqueous extracts.

Dissolved ions are also found in higher concentrations in *Araucaria* extracts, with high levels of potassium ($132\,mg\,L^{-1}$), chloride ($52\,mg\,L^{-1}$), and phosphate ($16\,mg\,L^{-1}$) in the first extraction (expressed on mass basis to compare with discharge standards). In all cases, significant amounts of ions are found in the second extraction (up to 50% of total), indicating slower solubilization due to mass transfer processes for these compounds. The presence of potassium in the composition of the *Araucaria* pine has been reported [10,30], but little is known about other ions and their possible influence in the biosorption processes.

Similar behavior was observed in *Pinus* extractions, which showed lower concentration of anions (phosphate, nitrate, and chloride), than in *Araucaria* extracts. The presence of organic anions derived from short-chain carboxylic acids (acetate, formate, and oxalate) was observed in both the first and second extraction of the biosorbents. The organic acids may partly explain the lower pH of the extract of *Pinus* (4.94–5.30) than the extract of *Araucaria* (6.54–6.60). It is interesting to note the presence of sodium ($0.7\,mg\,L^{-1}$) and ammonium ($1.4\,mg\,L^{-1}$), in addition to potassium, calcium, and magnesium, which were also observed in extracts of *Araucaria*.

The observed values of ammonium and nitrate are much smaller than those imposed by law (effluent emission limits are $26\,mg\,L^{-1}$ for ammonia and $44\,mg\,L^{-1}$ for total nitrogen). Thus, the presence of these species in the extracts does not compromise the quality of the treated effluents.

These results complement the information on the characterization of the solid materials (Table 1) and reinforce the need for knowledge of the influence of dissolved species when biomass is used in the biosorption/reduction of effluents containing chromium [10,17]. The data presented suggests that prior washing/extraction of biosorbent is recommended, at least in the case of *Araucaria*, in order to improve the quality of the effluents. However, this step increases the cost of the washing process and generates additional wastewater to be treated/disposed adequately.

3.3. Chromium determination by spectrofluorimetry in micellar medium

Quenching of naphthalene fluorescence in SDS solution by addition of Cr(III) shows a behavior consistent with the Stern–Volmer equation:

$$\frac{F_0}{F} = 1 + K_{sv}[\mathrm{Cr(111)}] \quad (2)$$

where, (F_0) is the fluorescence in the absence and (F) in the presence of Cr (III) and K_{sv} the Stern–Volmer constant.

Fig. 3(B) shows that the plot of (F_0/F) vs. [Cr (III)] which has a linear relationship allows to calculate the Stern–Volmer constant ($K_{sv} = 2.77 \times 10^{+3}\,M$).

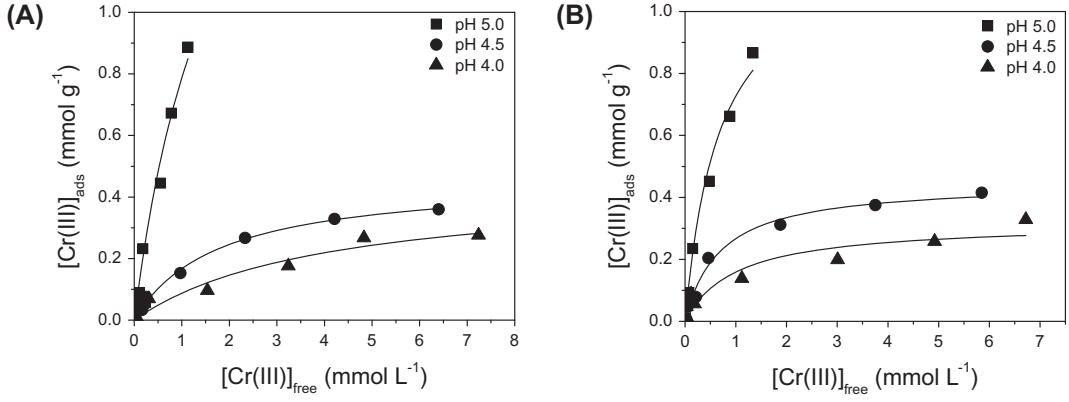

Fig. 4. Langmuir isotherms for adsorption of Cr(III) as a function of pH in (A) *Pinus* as biosorbent and (B) *Araucaria* as biosorbent.

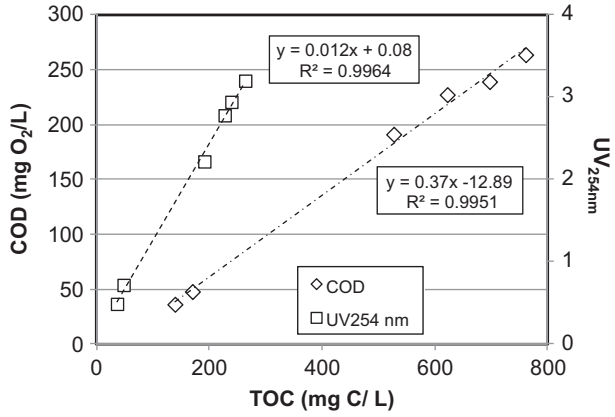

Fig. 5. Correlations between TOC and COD or UV_{254nm} absorbance of the extracts of *Araucaria* and *Pinus*.

The Stern–Volmer plot (Fig. 3(B)) can be used as calibration curve for the analytical determination of Cr(III). The results were confirmed by the diphenylcarbazide methodology and the validated method was used in the quantification of the Cr(III) species in adsorption studies using *Pinus* and Araucaria.

3.4. Adsorption tests

The isotherms were obtained using different concentrations of Cr(III) and pH values of 4.0, 4.5, and 5.0 for the two biosorbents. Figs. 4(A) and (B) show the results obtained for *Pinus* and *Araucaria*, respectively. The experimental data show that the adsorption of Cr (III) follows the Langmuir isotherm (Eq. (3)):

$$\theta = \frac{K_L[\mathrm{Cr(III)}]M}{1 + K_L[\mathrm{Cr(III)}]} \quad (3)$$

where, θ correspond to Cr(III) adsorbed per gram of biosorbent (mmol g^{-1}), K_L is the Langmuir constant, [Cr(III)] is the concentration of free chromium species, and M represents the maximum adsorption of Cr(III) (mmol g^{-1}). The solid lines in Figs. 4(A) and (B) were calculated with a nonlinear least-squares program [31], and the calculated values for the different parameters are given in Table 3. Langmuir parameters for adsorption of Cr(III) in *Araucaria* and *Pinus* (Table 3) show that there is a considerable increase in K_L and M from 4 to pH 5 for both *Araucaria* and *Pinus*.

This behavior can be explained by the role of the acid functional groups, since carboxylic and phenolic groups were confirmed by FT-IR and by Boehm titration, Table 1, in the biomaterial. At pH higher than the pK_a (~3.5), the carboxylic groups are negatively charged and Cr(III) ion (principal species at low pH) can be bound to the negatively charged groups [27]. At pH lower than pKa, the functional groups are neutral and metal uptake decreases. In addition, for pH < 3, the adsorption capacity decreases due to H^+ competition with Cr(III) ions [18,27]. These results are

Table 4
The results of the chromium desorption from biosorbents using acidic medium

Test/condition	Chromium recovery (%)	
[HCl]/reaction time	*Araucaria*	*Pinus*
A—0.8 mol L^{-1}/24 h	19	21
B—2.0 mol L^{-1}/48 h	40	42

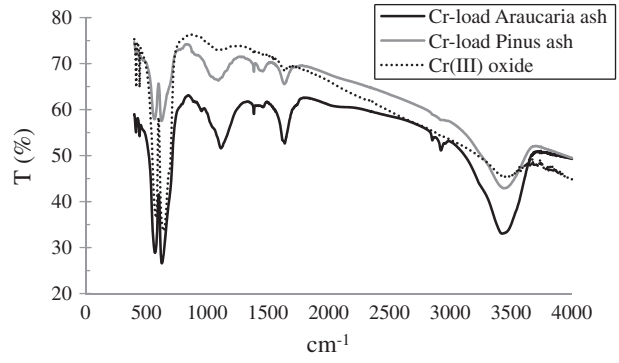

Fig. 6. FT-IR spectra of the ashes from incineration of the *Araucaria* (A) and *Pinus* (B) chromium loaded, and Cr(III) oxide standard (C).

Table 3
Langmuir parameters for adsorption of Cr(III) in biosorbents (*Araucaria* and *Pinus*, 10 g L^{-1}) at different pHs

pH	*Araucaria*		*Pinus*	
	M (mmol g^{-1})	K_L[a] (L $mmol^{-1}$)	M (mmol g^{-1})	K_L[a] (L $mmol^{-1}$)
4.0	0.32 ± 0.02	1.02	0.44 ± 0.02	0.25
4.5	0.45 ± 0.02	1.47	0.46 ± 0.01	0.57
5.0	1.22 ± 0.04	1.47	2.17 ± 0.06	0.57

[a]Standard deviation of 5% in all Langmuir constants.

Table 5
Chemical composition of *Pinus* biosorbent after Cr loading determined by X-ray fluorescence spectrometry

	Cr_2O_3	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	K_2O	Cl	LOI[a]
Biosorbent (%wt)	1.78	1.35	0.45	0.10	0.05	0.07	0.07	0.15	96.0

[a]LOI loss on ignition (ASTM D7348-08).

consistent with those previously reported by Gardea-Torresdey et al. [32] which using biosorbents to remove Cr(III), confirmed that metal was bound through carboxyl ligands. This kind of binding is in most cases reversible and biosorbed metal could be wash-released. The regenerated solution could be suitable for conventional metal recovery. In addition, the refreshed biosorbent materials can be used for other metal uptake cycles.

The maximum loading values obtained at pH 5.0 for the *Pinus* (2.17 mmol g^{-1}; 113 mg g^{-1}) and *Araucaria* (1.22 mmol g^{-1}; 63 mg g^{-1}) are above the range (6–12 mg g^{-1}) indicated in the literature for lignocellulosic biosorbents such as *Agave lechuguilla*, *Agave bagasse*, Sorghum and Oats straw, olive stones, and different sawdust [5,27].

3.5. Chromium recovery from metal-load biosorbents

The results of desorption acidic tests (Table 4) indicated low efficiency for both biosorbents. Even at stronger condition (2 mol L^{-1} HCl, 48 h), small recovery (~40%) was observed. These preliminary tests indicated strong binding of Cr with liginocelulosis surfaces groups. Reuse of metal desorbend biosorbents was not tested due to high residual Cr on biomass.

The incineration of Cr-load biosorbent produced similar green solid for Araucaria and Pinus. These solids were characterized by DRX analysis (not shown) that indicated Cr(III) oxide as a major phase. FT-IR spectra (Fig. 6) of obtained ashes match the Cr_2O_3 spectrum, corroborates for proposed assignment.

Besides ashes analysis, the efficiency of the process was shown by measuring desorbed Cr concentration on extracts and compared with metal loading on the Pinus biosorbents (Table 5) performed by X-ray fluorescence spectrometry which shows that the Cr-loaded biosorbent becomes the most important component.

4. Concluding remarks

The results of this study showed that Cr(III) can be effectively removed using Araucaria and Pinus wastes and their biosorption capacities are higher than other lignocellulosic materials under similar conditions. Carboxylic moieties, present on the biosorbent surface, seem to play a major role on Cr(III) binding. The quantification of Cr(III) using fluorescent suppression of organic probes could be used safely for both biosorbents *Araucaria* and *Pinus*.

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References

[1] J.A. Jacobs, J. Guertin, C. Avakian, Chromium(VI) Handbook, CRC Press, Boca Raton, FL, 2005.
[2] G.M. Naja, B. Volesky, Toxicity and sources, in: L.W. Wang, J.P. Chen, Y-T. Hung, N.K. Shammas (Eds.), Heavy Metal in the Environment, CRC Press, Boca Raton, FL, 2009, pp. 13–61.
[3] World Health Organization (WHO), Inorganic Chromium(III) Compounds, Concise International Chemical Assessment Document 76, Geneva, Switzerland, 2009.
[4] J.W. Patterson, Industrial Wastewater Treatment Technology, second ed, Butterorth, Stoneham, MA, 1985.
[5] V.O. Arief, K. Trilestari, J. Sunarso, N. Indraswati, S. Ismadji, Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: Characterization, biosorption parameters and mechanism studies, Clean 36 (2008) 937–962.
[6] D. Park, Y.-S. Yun, D.S. Lee, J.M. Park, The past, present, and future trends of biosorption, Biotechnol. Bioprocess Eng. 15 (2010) 86–102.
[7] J. Kumar, C. Balomajumder, P. Mondal, Application of agro-based biomasses for zinc removal from wastewater—a review, Clean 39 (2011) 641–652.
[8] H.Y. Ucun, Y.K. Bayhan, Y. Kaya, A. Cakici, O.F. Algur, Biosorption of chromium(VI) from aqueous solution by cone biomass of *Pinus sylvestris*, Bioresour. Technol. 85 (2002) 155–158.
[9] V. Sarin, K.K. Pant, Removal of chromium from industrial waste by using eucalyptus bark, Bioresour. Technol. 97 (2006) 15–20.
[10] F.A. Santos, Using the scales of the cones of *Araucaria angustifolia* for biosorption of heavy metals from electroplating effluent. Pos-Graduation Program in Materials Engineering and Technology, Pontifical Catholic University of Rio Grande do Sul, Porto Alegre, Brazil, 2007.
[11] F. Hernáinz, M. Calero, G. Blázquez, M.A. Martín-Lara, G. Tenorio, Comparative study of the biosorption of cadmium (II), chromium(III), and lead(II) by olive Stone, Environ. Progress 27 (2008) 469–478.
[12] P. Das Saha, A. Dey, P. Marik, Batch removal of chromium (VI) from aqueous solutions using wheat shell as adsorbent: Process optimization using response surface methodology, Desalin. Water Treat. 39 (2012) 95–102.

[13] J.C.P. Vanghetti, E.C. Lima, B. Royer, J.L. Brasil, B.M. Cunha, N.M. Simon, N.F. Cardoso, C.P.Z. Norena, Application of Brazilian-pine fruit coat as a biosorbent to removal of Cr(VI) from aqueous solutions—kinetics and equilibrium study, Biochem. Eng. J. 42 (2008) 67–76.
[14] M. Fabbricino, R. Gallo, Chromium removal from tannery wastewater using ground shrimp shells, Desalin. Water Treat. 23 (2010) 194–198.
[15] E. Malkoc, Y. Nuhoglu, Potential of tea factory waste for chromium(VI) removal from aqueous solutions: Thermodynamic and kinetic studies, Sep. Purif. Technol. 54 (2007) 291–298.
[16] A. Witek-Krowiak, R.G. Szafran, S. Modelski, Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent, Desal. 265 (2011) 126–134.
[17] L.C. Hsu, S.L. Wang, Y.C. Lin, M.K. Wang, P.N. Chiang, J.C. Liu, W.H. Kuan, C.C. Chen, Y.M. Tzou, Cr(VI) removal on fungal biomass of *Neurospora crassa*: The importance of dissolved organic carbons derived from the biomass to Cr(VI) reduction, Environ. Sci. Technol. 44 (2010) 6202–6209.
[18] D. Park, Y.-S. Yun, D.S. Lee, J.M. Park, Optimum condition for the removal of Cr(VI) or total Cr using dried leaves of *Pinus densiflora*, Desal. 271 (2011) 309–314.
[19] N. Balkaya, N. Bektas, Chromium(VI) sorption from dilute aqueous solutions using wool, Desalin. Water Treat. 43 (2009) 43–49.
[20] J.V.M. Bittencourt, A.R. Higa, M.C. Mazza, P.M. Ruas, C.F. Ruas, M. Caccavari, H. Fassola, Conservation, management and sustainable use of *Araucaria angustifolia* genetic resources in Brazil, in: B. Vincent, W. Amaral, B. Meilleur (Eds.), Managing forest genetic resources for livelihoods: Examples from Argentina and Brazil, International Plant Genetic Resources Institute, Rome, 2004, pp. 133–148.
[21] A.F. Silva, H.D. Fiedler, F. Nome, Ionic quenching of naphthalene fluorescence in sodium dodecyl sulfate micelles, J. Phys. Chem. A 115 (2011) 2509–2514.
[22] Association of official analytical chemists (AOAC). Official Methods of Analysis, fifteenth ed, AOAC, Washington, DC, 1990.
[23] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, Carbon 32 (1994) 759–769.
[24] A.M. Oickle, S.L. Goertzen, K.R. Hopper, Y.O. Abdalla, H.A. Andreas, Standardization of the Boehm titration: Part II. Method of agitation, effect of filtering and dilute titrant, Carbon 48 (2010) 3313–3322.
[25] A.E. Greenberg, L.S. Clasceri, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association and Water Pollution Control Federation, Washington, DC, 1992.
[26] L.V. Vargas, J. Sand, T.A.S. Brandão, H.D. Fiedler, F.H. Quina, F. Nome, Determination of environmentally important metal ions by fluorescence quenching in anionic micellar solutions, Analyst 130 (2005) 242–246.
[27] P. Miretzky, A.F. Cirelli, Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review, J. Hazard. Mater. 180 (2010) 1–19.
[28] M.F. Sawalha, J.R. Peralta-Videa, S. Geoffrey, K.M. Dokken, J. L. Gardea-Torresdey, Using FTIR to corroborate the identity of functional groups involved in the binding of Cd and Cr to saltbush (*Atriplex canescens*) biomass, Chemosphere 66 (2007) 1424–1430.
[29] K. Floge, E. Guillon, E. Marceau, M. Aplincourt, Speciation of chromium on a straw lignin: Adsorption isotherm, EPR, and XAS studies, New J. Chem. 27 (2003) 714–720.
[30] B.R. Cordenunsi, E.W. Menezes, M.I.S. Genovese, C. Colli, A. G.A. Souza, F.M. Lajolo, Chemical composition and glycemic index of Brasilian pine (*Araucaria angustifolia*) seeds, J. Agric. Food Chem. 52 (2004) 3412–3416.
[31] M.B. Fritzen, A.J. Souza, T.A.G. Silva, L. Souza, R.A. Nome, H.D. Fiedler, F. Nome, Distribution of hexavalent Cr species across the clay mineral surface-water interface, J. Colloid Interf. Sci. 296 (2006) 465–471.
[32] J.L. Gardea-Torresdey, K. Dokken, K.J. Tiemann, J.G. Parsons, J. Ramos, N.E. Pingitore, G. Gamez, Infrared and X-ray absorption spectroscopic studies on the mechanism of chromium(III) binding to alfalfa biomass, Microchem. J. 71 (2002) 157–166.