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Characterization and use of biosorbents prepared from forestry waste and their washed extracts to reduce/remove chromium

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Abstract This study aimed to characterize forestry waste of araucaria, eucalyptus and pine and their aqueous extracts to evaluate their performance in the reduction/removal biosorption of chromium. The biosorbents present a complex and rich composition of both organic and inorganic solubilizable compounds. These results confirmed the need of biomass pretreatment for its adequate use as biosorbent. The extracts obtained in the washing cycles at different pHs presented high organic loads. The pine is distinguished as the best biosorbent, and its performance is increased by prior washing in natural medium. Eucalyptus extract produces fastest Cr(VI) reduction due to the presence of high concentration of dissolved organic matter. The washing process of the biosorbents, besides improving the efficiency of overall chromium biosorption, prevents mobilization of the solubilizable compounds in the treated effluent. The biosorbents tested have potential for application in the treatment of wastewater containing chromium, at least in similar levels to those studied.

Keywords Forestry waste · Biosorption · Low-cost biosorbents · Chromium

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Introduction

The use of biosorbent material to treat wastewater containing metals has been widely studied (Volesky 2003; Mohan and Pittman 2006; Garg et al. 2007; Xiao and Huang 2009; Park et al. 2010; Elwakeel 2010; Sen et al. 2014). Several biological materials including microorganisms, algae and lignocellulosic biomasses are described in the literature as capable of removing metals from aqueous media (Sud et al. 2008; Santos et al. 2013; Pagnanelli et al. 2013; Sidiras et al. 2013; Ferraz et al. 2014; Mishra 2014; Gebrehawaria et al. 2014).

Despite the vast literature devoted to this subject, an important aspect rarely addressed is the solubilization biomass during wastewater treatment with biosorbents. However, the dissolved compounds could play a variety of roles in the biosorption process. According to Altundogan (2005), some adsorbents may partially solubilize during wastewater treatment, and cause negative impacts such as increasing the organic load of the effluent. Hsu et al. (2010), studying aqueous extracts obtained from the biomass of the *Neurospora crassa* fungus, observed high organic matter contents that might affect the quality of treated effluents. However, extractable material may present reactive properties and be useful in other processes. Díaz et al. (2012) reported that in acid medium extracts rich in organic matter are capable of reducing hexavalent chromium to trivalent chromium, an alternative to metal removal in addition to surface reactions with biomass.

The organic soluble load of the biosorbents may be related to the presence of tannins, which belong to a group of phenolic compounds from the secondary metabolism of plants (Battestin et al. 2004). Vázquez et al. (2008) studied the antioxidant activity and phenolic content of the plant extracts of eucalyptus bark and gumnuts. The phenolic compounds also present chelating properties that open possibilities of alternative uses for polyphenol-rich extracts (Vázquez et al. 2008). Despite the abovementioned research, few studies have assessed solubilizable compound and its influence on the biosorption process of metals in aqueous solutions. To the best of our knowledge, there are no data about organic compound solubilization from pine and araucaria forestry waste and information on eucalyptus is incomplete. Furthermore, in most studies biomass is washed prior to testing its biosorption performance. Thus, the study of biosorbents washing and the characterization of their rising extracts are justified.

Lignocellulosic materials such as forestry wastes have been widely tested in the removal of chromium. The main advantages of using forestry waste are: (1) its low commercial value, given its ready availability in nature and the fact that it is generated by production processes; (2) its typically regional origins, meaning that it can be used by industries located in the same area, thereby minimizing transport costs; (3) the fact that it comes from renewable sources, meaning that there is no risk of depletion, thus ensuring replenishment; (4) its high efficiency in treating wastewater containing metallic ions and (5) after biosorption metal adsorbed can be converted and reusable (Volesky 2001; Park et al. 2008; Vaghetti et al. 2008; Santos 2013).

The effective use of forestry waste may help increase profitability through better use of the by-products of native and planted forests and contribute to maintaining a sustainable cycle. In Brazil, the use of biosorbents made from wood waste is also justified by the need to dispose of this waste, produced in large quantities in planted forests, mainly eucalyptus and pine (Santos 2013). Eucalyptus trees pose a problem, in that bark falling from the trunks must be collected and disposed of, while pine cones can be used as a source of raw material. The araucaria, tree native to southern Brazil, produces a fruit that contains edible seeds (pine nuts), which are highly nutritious and a food source for birds, wild animals and people (Lorenzi 2002). Pine nuts are collected, sold and consumed throughout southern Brazil; however, little is known about using pine nut waste (Santos et al. 2011).

In this context, the present study aims to characterize araucaria, pine and eucalyptus forestry waste and their washing extracts, obtained while preparing and adapting them for use as biosorbents. The raw biomasses and the treated biosorbents by natural, acid and basic media washings, as well as their extracts, were tested for the reduction/removal of chromium in aqueous solutions. The role of solubilized compounds and the influence of the characteristics of biomass and its changes in the process are also discussed.

Materials and methods

Sample preparation

The biosorbent materials used in this study are from araucaria (*Araucaria angustifolia*), pine (*Pinus elliottii*) and eucalyptus (*Eucalyptus* spp.) forest wastes. Pine cones from araucaria and pine trees were used, as well as eucalyptus bark. Pine tree cones were used whole, whereas only cone scales of araucaria cones were used. All the biosorbent materials were dried at 80 °C for 24 h in an oven (De Leo, MDH model), ground in an industrial blender (LO 4.0 Visa) and sieved to obtain a powder with known particle size (<250 µm). After preparation, the material was placed in sealed plastic vials and stored in the dark, at controlled temperature (23 ± 3 °C) and humidity (50 ± 10 %).

The biosorbents were tested in the form of unwashed powder and powder washed with deionized water (pH 6), 0.1 mol L^{-1} potassium hydroxide solution (pH 12) or 0.05 mol L^{-1} sulfuric acid solution (pH 2). Washing is a pretreatment widely applied in the preparation of biosorbents, but the rinse extracts generated are not taken in account.

The extracts were obtained through contact between 2 g of each biosorbent and 200 mL of the wash extract (10 g L^{-1}). Washed was carried out in 5-h cycles under orbital shaking (120 rpm). The material was filtered using 8-µm quantitative filter paper and then replenished with 200 mL of extractor to obtain the extracts of the second, third and fourth washes. The conditions applied to wash the biosorbents were based on studies by Santos et al. (2013).

Biosorbent characterization methods

Solid biosorbents were characterized via surface area and pore size by BET isotherms, moisture and ash content by gravimetry (105 and 550 °C), respectively, in accordance with NBR 10664. The point of zero charge (pH_{pzc}) was measured using the 11-point technique (Mimura et al. 2010). Water retention was achieved by measuring the variation in biosorbent mass after contact with deionized water under agitation (Joseph 2009).

Surface functional groups were identified according to the Boehm method (1994) and by Fourier transform infrared spectroscopy (FTIR), conducted in a Spectrum One PerkinElmer spectrometer, with a transmittance range of 4000–400 cm^{-1}, and samples prepared on KBr disks. Mineral and chemical compositions of biosorbent ashes were determinate by X-ray diffraction (XRD, Bruker diffractometer D8 Advance) and X-ray fluorescence analyses (XRF, PANalytical Ominian).

In addition, X-ray photoelectron spectroscopy (XPS, Omicron) analysis was performed for Araucaria unwashed samples (<250 μm), before and after contact with the synthetic solution containing 1000 mg L^{-1} of chromium(VI). Potassium dichromate and chromium oxide(III) p.a. solid reagents were used for pattern identification of chromium(VI) and chromium(III), respectively.

All washed extracts (cycles 1–4) obtained in the natural, acid and basic media were characterized by pH (Gehaka PG1800, NBR 9251) and conductivity measurements (Quimis Q485 M, NBR 10223). Dissolved organic matter (DOM) was estimated by UV_{254nm} (Biospectro spectrophotometer, SP220, $b = 1$, APHA 3910B method), DOC (dissolved organic carbon, Shimadzu carbonic analyzer) and COD (chemical oxygen demand, NBR 10357). Polyphenol content was obtained using the Folin–Ciocalteu method (Vázquez et al. 2008) using a Micronal B442 spectrophotometer.

Total chromium removal experiments using solid biosorbents

The experiments conditions used were previously optimized in our laboratory (Santos et al. 2011, 2013) and consisted in a two-stage biosorption at two different pHs maintained constants. In the first stage, the biosorbents (10 g L^{-1}, <250 μm) were first added to the Cr(VI) solutions ($\sim$20 mg L^{-1} prepared from $K_2Cr_2O_7$ and adjusted for pH 2) and stirred for 15 min, when Cr(VI) is reduced to Cr(III). In the second stage of biosorption, the pH was adjusted to 5 and Cr(III) concentration monitored for up to 24 h.

Tests were conducted with unwashed biomass and after washing in natural, acid and basic media for araucaria, pine and eucalyptus biosorbents. Cr(VI) and Cr(III) contents were determined at different reactions times. Total chromium content was determined by atomic absorption spectroscopy (AAS) in a Varian AAS 55 spectrometer with an air/acetylene flame (99.99 % Air Products) and Cr(VI) concentration using the diphenylcarbizide method (NBR 13738) in a Micronal B442 spectrophotometer. Cr(III) content was calculated using the difference between total chromium and chromium(VI).

Hexavalent chromium reduction experiments using extracts

The extracts obtained from first washing cycle (first cycle), in natural medium for the three biosorbents, were tested as reducers of chromium(VI) and chromium(III). Equals volume of extract and chromium(VI) solution were mixed under agitation ($[Cr(VI)]_0 = 15$ mg L^{-1}), and pH was adjusted to 2 (Santos et al. 2011). Total chromium and Cr(VI) concentrations were determined throughout the reaction time (up to 24 h). An extracts blend (first up to fourth cycle) consisting of equal volumes of the rinse washes from four cycles was also tested under the same conditions described above. For comparison purposes, an aqueous extract of an activated charcoal (Synth, steam activated, <250 μm) was also tested.

Results and discussion

Characterization of solid biosorbents

Table 1 shows the characterization results for biosorbents prepared using araucaria, eucalyptus and pine wood waste. All biosorbents have low surface area values and pore size and similar moisture contents (around 11 %), while water retention, which assesses the surface area in aqueous medium, varies from 4.20 to 5.87 g H_2O g $biomass^{-1}$. These moisture and water retention values are compatible with those found in the literature (Sarin and Pant 2006; Derbal 2012) for similar biomasses.

The studied biosorbents present a wide ash content range from 3.11 % for pine to 17.31 % for eucalyptus. This ash variability is also reported by Schneider et al. (1999) for aquatic plants (10.2 and 20.3 %) and Vassilev et al. (2013) for a large biomass types (0.66–28.2 %).

The most interesting aspect concerning ashes is its decrease after washing, especially for eucalyptus that becomes virtually ash-free (0.37 %, decreases of −98 %). Reductions less significant for the Araucaria (−62 %) and mainly for pine (−13 %) were observed. The solubilization of inorganic compounds probably is the main cause of ash content decrease. Low ash content is an important advantage for a biomass when used as fuel. In the case of the biosorbent could be a determining factor in the feasibility of metal recovering by incineration (Santos et al. 2011).

Table 1 Characterization results for biosorbents prepared using araucaria, eucalyptus and pine wood waste

Parameters	Araucaria	Eucalyptus	Pine
Surface area (m^2 g^{-1})	3.76	0.81	0.22
Pore size (Å)	22.62	26.35	3.94
Moisture: unwashed (%)	11.37	11.06	11.55
Water retention (g H_2O g biomass^{-1})	5.87	5.34	4.20
Ash: unwashed (%) db	3.85	17.31	3.11
Ash: washed in natural medium (%) db	1.46	0.37	2.72
pH_{PZC}: unwashed	7.0	3.0	5.0
pH_{PZC}: washed in natural medium	3.0	5.0	3.0
Surface groups*			
Carboxylic groups (mmol g^{-1})	0.45	0.78	0.77
Lactonic groups (mmol g^{-1})	0.10	0.09	0.37
Phenolic groups (mmol g^{-1})	0.51	0.51	0.48
Total acid (mmol g^{-1})	1.06	1.38	1.62

* Quantified by Boehm titration

db dry basis

Determination of pH at the point of zero charge (pH_{pzc}) can be used as a preliminary study of the acid–basic behavior of biosorbents. This parameter also characterizes the buffering effect of these surfaces. The pH_{pzc} of the unwashed biosorbents varied from 3.0 for eucalyptus to 7.0 for araucaria, with pine displaying an intermediate value (5.0). These values changed after washing, with a decrease to 3.0 for araucaria and pine and an increase to 5.0 for eucalyptus. These different behaviors may be important for performance of biosorbents in relation to chromium species. In solutions with pH below pH_{pzc}, biosorbents show a predominantly positive surface charge, while at pH above pH_{pzc} the surface charge is negative. The adsorption of positively charged metallic species present in the solution is favored at a pH in which negative species predominate on the biosorbent surface. This is not the only parameter to be taken into account; the change in pH can also cause precipitation of metal species.

The presence of the acidic groups on biosorbents surface is also presented in Table 1. Carboxylic, phenolic and lactonic groups are present in all samples at different levels. A larger quantity of acid sites were recorded for pine (1.62 mmol g^{-1}), followed by eucalyptus (1.38 mmol g^{-1}) and araucaria (1.06 mmol g^{-1}). These results corroborate with pH_{pzc} data, indicating different surface characteristics for these biosorbents.

A predominance of carboxylic groups was observed in eucalyptus and pine, while phenolic groups were prevalent in araucaria. Furthermore, a larger amount of lactones was observed in pine compared with the other two biosorbents. According to Namasivayam and Sureshkumar (2008), metals bind to lignocellulosic adsorbents, such as those studied here, via specific functional groups including carboxylic, phenolic and amino groups.

Figure 1a, b and c shows the FTIR spectra of unwashed araucaria, eucalyptus and pine, after washed in natural, acid and basic media, in addition to their ashes. Figure 1a shows a substantial number of absorption bands, demonstrating the complex nature of these biomasses. The broad band at around 3500 cm^{-1}, representing stretching of the OH group, shows a strong presence. This is justified because cellulose, the natural polymer and main component of this material, in addition to being hydrophilic, exhibits this grouping three times in every mere. There is also a strong absorption band at about 1050 cm^{-1}, reflecting –CO(O–CH) or –CN stretching. The absorption bands at approximately 2900 and 600 cm^{-1} depict –CH stretching. Another major absorption band appears at about 1620 cm^{-1}, indicating the presence of C=O or C=C stretching of an aromatic ring, and at 1730 cm^{-1} signaling C=O of carboxylic groups or lactones. According to Blázquez et al. (2009), carboxylic groups are the main groups involved in chromium binding by biomasses.

Spectral comparison showed similar absorption peaks in the araucaria and pine samples and differences for eucalyptus. This result corroborates other parameters already presented. The eucalyptus bark singularities, when compared with araucaria and pine cones, are likely due to the different physiological functions of these structures in the plant (bark and fruit). These data justify

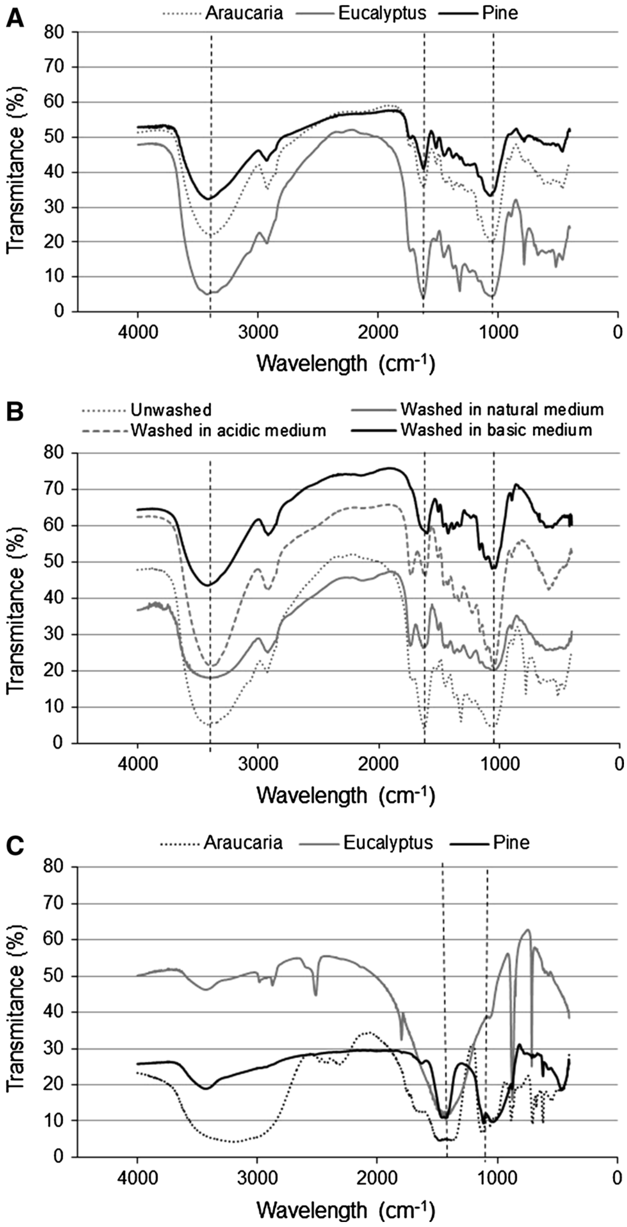

Fig. 1 FTIR spectra of the **a** unwashed araucaria, eucalyptus and pine; **b** eucalyptus before and after washing in different media and **c** ashes of the unwashed araucaria, eucalyptus and pine

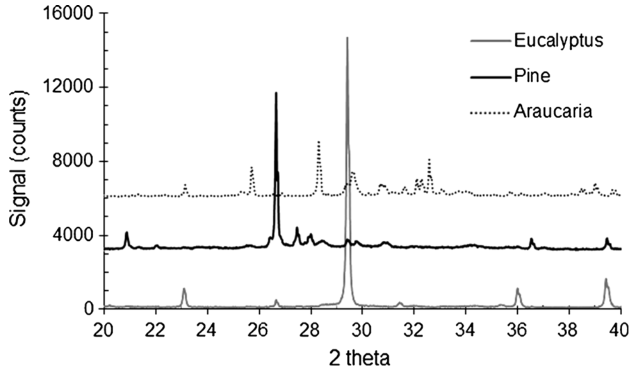

Fig. 2 X-rays diffractograms of the araucaria, eucalyptus and pine ashes

Table 2 Perceptual concentration (%) for the elements detected by X-ray fluorescence (XRF) in the ashes of the biosorbents

Element	Araucaria	Eucalyptus	Pine
K	92	5	33
Ca	nd	78	21
Si	nd	2	21
S	3	1	3
P	2	1	3
Fe	nd	2	9
Mn	1	4	nd
Remaining	2	7	10

nd not detected

the relevance of specific characterization studies for these materials in order to identify and quantify the clusters observed in IR spectra.

FTIR analysis also enables the comparison of spectra obtained after different washing treatments (Figs. 1b, S1 and S2) to identify possible solubilized and non-solubilized clusters. After rinsing in natural, acid and basic media, some changes were observed. Most important absorption reduction was observed for basic medium, indicating a most significant solubilization in this system. Again the IR eucalyptus spectra showed the greatest variations. Unfortunately, a precise assignment of functional groups is difficult due to overlapping bands.

FTIR analysis of ashes (Fig. 1c) showed different spectra for the respective biosorbents, and, as expected, significant changes occurs after incineration. According to Besler and Rodrigues (2008) mineral materials, such as ashes, although less studied than organic compounds, also generate relatively rich IR spectra. For instance, carbonate minerals present intense peaks at 1420, 876 and 710 cm^{-1}. The eucalyptus ash spectrum presents bands and peaks characteristics for calcite, indicating that this mineral is probably the main crystalline phase present (Besler and Rodrigues 2008).

Figure 2 shows the XRD diffractograms of eucalyptus, pine and araucaria ashes. The most prominent peaks for araucaria are those typical of feldspar ($KAlSi_3O_8$), sylvite

Table 3 Characterization of the extracts obtained in the first and fourth washing cycles in natural (deionized water), acidic (0.05 mol L^{-1} H_2SO_4) and basic (0.1 mol L^{-1} KOH) media

Extractor/biosorbent	Cycle	pH	Conductivity (mS cm^{-1})	UV_{254nm} (cm^{-1})	DOC (mg L^{-1})	COD (mg L^{-1})
Medium Deionized water		6.00	0.02	0.00	0	0
Araucaria	First	5.64	0.41	3.01	255	535
	Fourth	6.40	0.01	0.12	21	19
Pine	First	4.92	0.06	1.43	75	189
	Fourth	5.32	0.00	0.18	–	–
Eucalyptus	First	4.44	0.07	7.23	166	409
	Fourth	5.14	0.00	0.43	–	–
Medium Sulfuric acid (0.05 mol L^{-1})		1.57	25.14	0.00	0	–
Araucaria	First	1.62	24.90	1.58	227	545
	Fourth	1.60	23.84	0.08	–	–
Pine	First	1.71	22.30	0.99	74	180
	Fourth	1.49	25.58	0.14	–	–
Eucalyptus	First	1.44	28.80	3.18	142	295
	Fourth	1.41	28.96	0.47	–	–
Medium Potassium hydroxide (0.1 mol L^{-1})		12.67	11.68	0.007	–	–
Araucaria	First	11.83	4.81	18.06	–	–
	Fourth	12.69	8.74	1.91	–	–
Pine	First	11.33	3.16	17.2	–	–
	Fourth	12.62	8.42	1.34	–	–
Eucalyptus	First	11.67	4.36	20.96	–	–
	Fourth	12.64	8.73	1.32	–	–

(KCl) and arcanite (K_2SO_4) (Teixeira et al. 2012; Vassilev et al. 2013). Noteworthy peaks in the pine sample were quartz (SiO_2) and whitlockite ($Ca_3(PO_4)_2$), with a major calcite ($CaCO_3$) peak evident for eucalyptus (Santos 2013 and Vassilev et al. 2013). XRD diffractograms confirmed the complexity of the samples and suggested that the incinerated materials are rich in mineral phases. Furthermore, these results corroborate with calcite as a main phase of eucalyptus ash.

Table 2 presents chemical composition of the biosorbent ashes obtained by XRF analysis. Potassium, calcium and silicon are the majoritary elements in araucaria, eucalyptus and pine ashes, respectively. Besides, Si (33 %) pine ash contains significant level (21 %) of Si and Ca. These results corroborate XRD analysis, which indicated the main mineral phases that contained these elements. Other elements, including sulfur, phosphorous, iron and manganese, are present in smaller concentrations. X-ray fluorescence characterization indicates the possible reuse of these ashes as a precursory source of metals. Della et al. (2005) suggested that residual oxides can be used to manufacture several materials, including ceramic pigments, with technological, economic and ecological justifications for this application.

Characterization of aqueous extracts

Table 3 shows the characterization results for the extracts obtained in washes using deionized water (natural pH 6.00), sulfuric acid (acid pH 1.57) and sodium hydroxide (basic pH 12.67). In the natural medium, araucaria extracts exhibited the smallest pH variation (5.64–6.40). In the first wash cycle, both the pine (pH 4.92) and eucalyptus extracts (pH 4.44) presented lower pH values. Subsequent wash cycles showed an increase in pH for both biosorbents (pH $\sim$ 5.2), though still in a more acidic range than the araucaria. The differences observed may be related to the acidic and basic species solubilized during washing. The quantity and strength of the surface acidic groups (Table 1) partially explain this behavior. Araucaria showed the lowest number of acid sites (1.06 mmol g^{-1}), consistent with the slight pH variation of its extracts, which remained close to the pH of the medium.

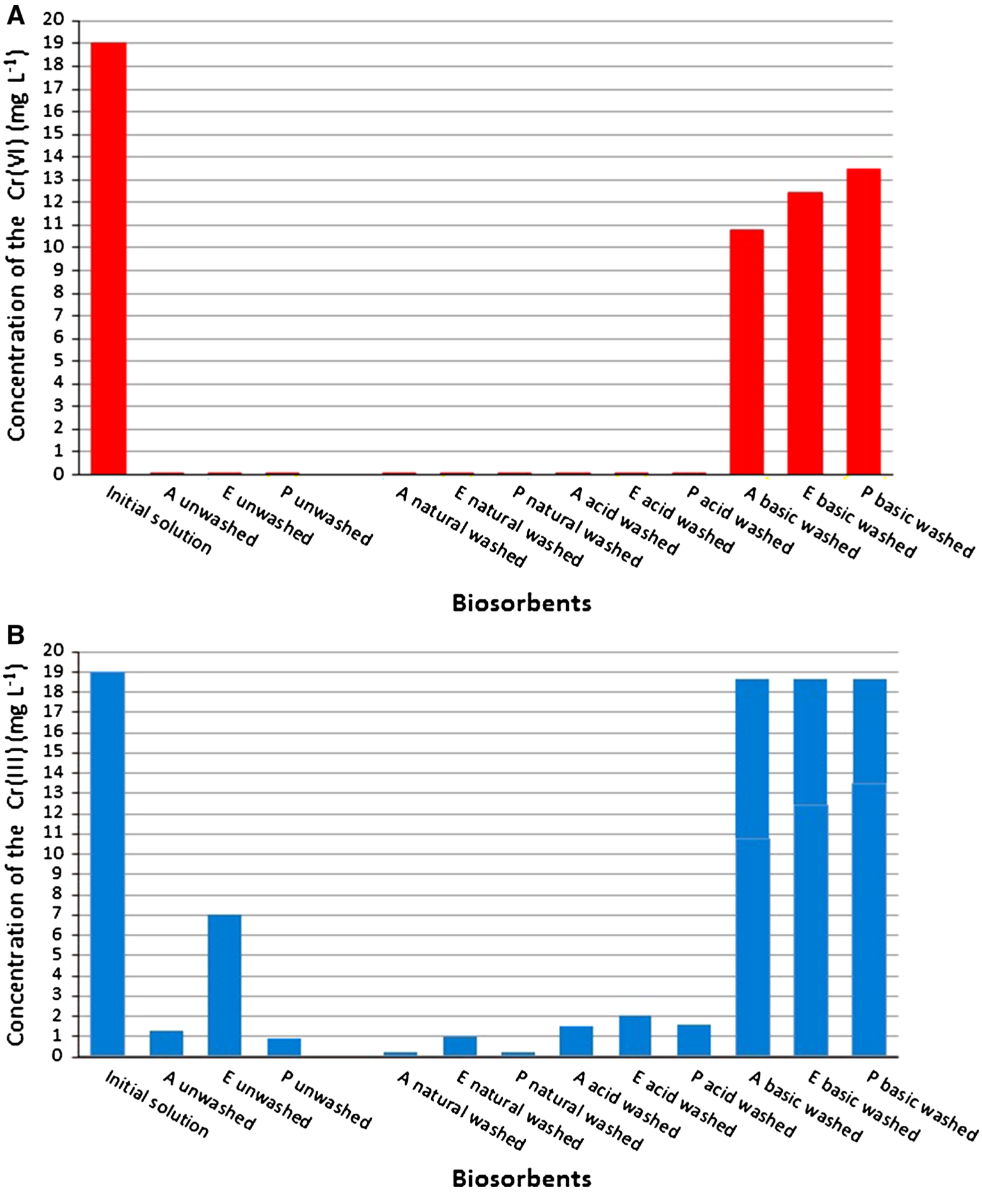

Fig. 3 Final concentrations of the **a** Cr(VI) and **b** Cr(III) in biosorption tests with unwashed biosorbents (*A* araucaria, *E* eucalyptus, *P* pine) and biosorbents washed with natural, acidic and basic media. Discharge limits for Cr(VI) and Cr(III) are indicated by *dotted lines*

Araucaria extracts in natural medium exhibited a greater concentration of electrolytes (0.41 mS cm^{-1}), five times higher than the other biosorbents. This result is important and suggests that the use of these biosorbents without pretreatment might ultimately transfer unwanted ionic compounds to the treated wastewater, affecting treatment efficiency.

On the other hand, absorbance at UV_{254nm}, measured in first washing cycle was significantly higher in eucalyptus extracts (7.23 cm^{-1}) compared with araucaria (3.01 cm^{-1}) and pine (1.43 cm^{-1}). These results likely indicate the presence of high concentration of soluble compounds with differentiated characteristics. UV_{254nm} absorption levels decreased in following cycles (second and third cycles, results not shown), though still exhibiting high values, particularly for araucaria and eucalyptus. However, there was a sharper decline in the UV_{254nm} parameter in the fourth cycle and, as a result, no further washing cycles were performed. Surprisingly,

Table 4 Characterization of the aqueous extracts of the biosorbents and of a commercial activated carbon

Extracts	UV_{254nm} (cm^{-1})	Polyphenols (mg L^{-1} gallic acid)
First cycle		
Araucaria	3.40	1.21
Eucalyptus	23.2	1.89
Pine	2.00	0.54
Activated charcoal	0.0	nm
Blend (first + second + third + fourth cycles)		
Araucaria	1.42	0.47
Eucalyptus	7.64	1.30
Pine	0.68	0.18

Conditions: dose 10 g L^{-1}, 5-h contact per cycle, 145 rpm, T 22 °C

nm not measured

the ash content (Table 1) was the parameter that best relates to UV_{254nm} absorption values, especially for eucalyptus.

As expected, in acid and basic media there were no significant variations in pH and conductivity for the extracts along washing cycles, since extractors H_2SO_4 (0.05 mol L^{-1}) and KOH 0.1 mol L^{-1} dominate the pH and conductivity of the medium. The extracts obtained in basic medium exhibited highest values for UV_{254nm} absorption, with eucalyptus stood out as the most significant levels in all media. These results are expected and are widely reported in the literature. These extracts were not fully characterized, because it was not considered when preparing the biosorbents since the biosorption of the relevant metals, such as chromium, occurs in the acidic range (pH 2–5).

On the other hand, acidic medium seems to be the weakest extractor if UV_{254nm} absorption is used as a criterion. However, TOC and COD data were very similar in acid and natural pH media for araucaria and pine, and a slightly lower for eucalyptus in acid medium. These results indicate more complex extraction behaviors. Total organic load are similar for each biosorbent in both natural and acidic media. However, the composition of the solubilized (extractable) species depends of the medium used. UV_{254nm} absorption levels do not follow this trend. This easily obtained parameter seems not be reliable for estimation of the DOM in our system. Despite this handicap, the UV_{254nm} is an important complementary parameter as will be seen in the discussions that follow.

Biosorption tests

Figure 3a, b shows the reduction of Cr(VI) and removal of Cr(III), respectively, by unwashed and washed biosorbents. The reaction conditions were chosen based on previous study (Santos 2013) for a real electroplating effluents ($[Cr(VI)]_0 = 19$ mg L^{-1}, pH < 2). The first stage (Fig. 3a) occurs at pH 2 and involves Cr(VI) reduction to Cr(III), and the second stage (Fig. 3b) consists of Cr(III) removal by biosorption at pH 5.

A very fast (<15 min) and complete reduction of Cr(VI) to Cr(III) occurs after contact with unwashed biosorbents, as well as washed biosorbents in both natural and acid media. In these conditions, the Cr(VI) discharge limit recommended by the Brazilian environmental legislation (0.1 mg L^{-1}; CONAMA 2011) is easily achieved.

However, biosorbents washed in basic medium are not able to efficiently reduce Cr(VI) presenting conversions <40 %, even after long reaction time (8 h). As the pH of the reaction medium is kept acid (pH 2 up to pH 5), lower reactivity could be related to biosorbent lost of actives moieties during strong alkaline washing.

The Cr(III) that has been generated in the first stage of the reaction and that was not bounded to biosorbent remaining free in solution must be removed to meet its environmental limit (1.0 mg L^{-1}; CONAMA 2011). For that, a second reaction stage was performed (Fig. 3b). The biosorbents washed in natural media presented greatest removal efficiency (>95 %), and Cr(III) discharged emission limit was achieved. Despite the significant removal (>90 %) of Cr(III) by the biosorbents washed in acid medium, they showed worse performance than unwashed ones. It is worth mentioning the pine, with the best performance, and the eucalyptus with poor removal (<60 %). These different behaviors are probably related to biomasses characteristics, previously discussed. The pine cones seem to be the most promising biosorbent for chromium removal, which could even be used without prior washing.

To better understand the mechanism of biosorption, X-ray photoelectron spectroscopy was used to determine

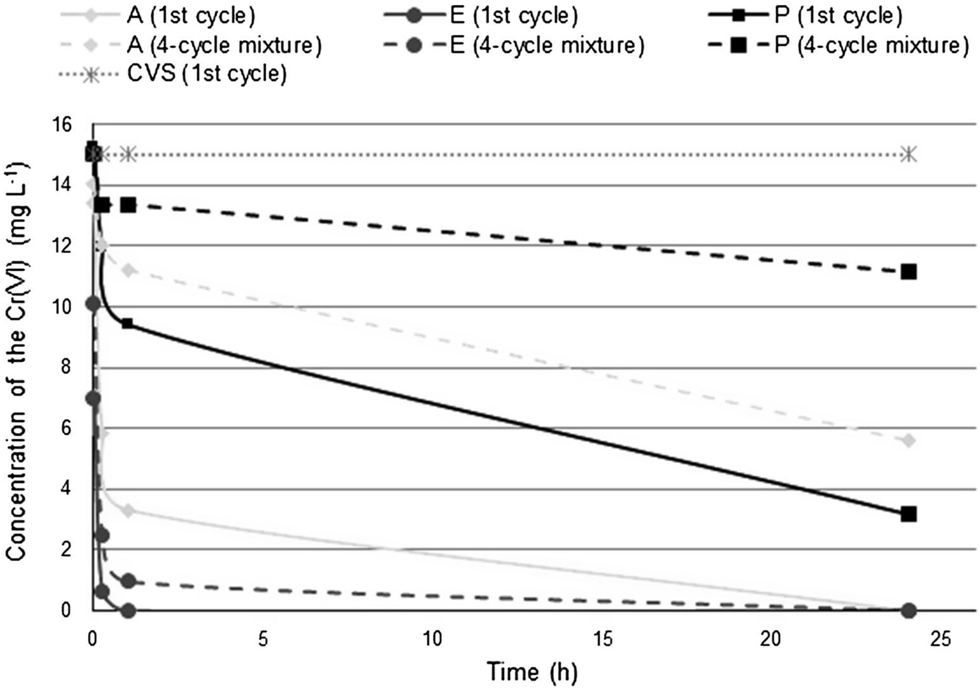

Fig. 4 Profiles of Cr(VI) concentration in function of the time contact with sorbent extracts. $[Cr(VI)]_0 = 15\ mg\ L^{-1}$, pH 2

the valence of chromium when bonded to the biomass. Araucaria was used as a model biosorbent for this analysis. According to the XPS results presented in Figure S4 (Suppl. Material), prior to contact with the synthetic chromium solution, the araucaria spectra did not show any peak in the wide range of binding energies analyzed. However, after contact peaks appear at binding energies of 590 and 580 eV, which coincide with peaks observed for chromium(III) standards. Park et al. (2004) report that Cr(VI) in synthetic wastewater is completely reduced to Cr(III) when the effluent is placed in contact with biomass. Part of the converted Cr(III) remains in solution, and part stays bonded to the biomass. Cardea-Torresdey et al. (2002) found that, even when bonded to a by-product, Cr(VI) is easily reduced to Cr(III) by positively charged clusters and is subsequently adsorbed by available carboxylic groups. These groups are present in significant numbers in araucaria, as determined by Boehm titration.

Reactivity of the extracts

The aqueous extracts obtained in biosorbent washing were used for Cr(VI) reduction testing. These tests were carried out to estimate the influence of the reaction in the liquid phase and compare it with the heterogeneous reaction in the presence of solids. Extracts from the first washing cycle in natural medium were used because they exhibit significant concentrations of extractable material (Table 3) and a suitable pH range. Blend of all extracts (first up to fourth) were also used to evaluate the performance under more diluted conditions, more similar to that found in industrial applications.

Initially, a characterization (UV_{254nm} absorption and polyphenol content) of these biosorbent extracts as well as one obtained by activated charcoal washing was performed (Table 4). As expected, blend extracts presents lower organic loads but still significant comparing with extract of activated charcoal. In fact, the absence of extractable material is a compliance parameter widely used for charcoal absorbent. In contrast, eucalyptus extract presents the highest UV_{254nm} absorption for both single and blended extracts (7.64–23.2 cm^{-1}). These values are 5 up to 12 times higher than those found for pine and araucaria. However, polyphenol contents of eucalyptus extracts (1.30–1.89 mg L^{-1} expressed as gallic acid) are close to that of the araucaria extracts (0. 41–1.21 mg L^{-1}) and slightly higher than those measured for pine (0.18–0.54 mg L^{-1}). As previously suggested, these data are related to the likely differences in composition between the biosorbents under study, which will probably impact their reactivity in the presence of Cr(VI).

The extracts were mixed with synthetic solutions (1:1, v/v) containing Cr(VI), and after pH adjust to 2.0, metal concentration was monitored in different reaction times up to 24 h. The obtained concentration profiles of Cr(VI) are shown in Fig. 4. All tested extracts can reduce Cr(VI) to Cr(III) but with different reactivity, while the activated carbon sample is unreactive. As expected, first washing cycle extracts are more reactive than diluted blend extracts. The eucalyptus extracts are the most efficient in reducing Cr(VI) to Cr(III). After 30 min of contact with first cycle, extract Cr(VI) was completely reduced (<0.01 mg L^{-1}, LOD) well below the emission limit (0.1 mg L^{-1}). For its bend extract, a longer contact time (24 h) is necessary.

A significant reactivity was also observed for first cycle extract of araucaria toward Cr(VI) with reduction >80 %. However, the Cr(VI) emission limit was not achieve, requiring a longer reaction time (>24 h). Pine and araucaria blend extracts presented weaker Cr(VI) reduction capacity. The complex observed behaviors are probably related to the presence of organic material which is readily oxidizable. Several compounds present in the extracts could exhibit this ability.

Figure S5 shows correlations between the initial rate of Cr(VI) reduction, calculated by a decrease in its concentration in the first 30-min reaction, and the concentration of polyphenols and UV_{254nm} absorbance (Table 4). A linear correlation (R^2 0.93) was observed between the content of polyphenols in extracts and their ability to reduce Cr(IV). The correlation with absorbance at UV_{254nm} is more complex (exponential trend with R^2 0.90), indicating a clear differentiation between the extracts of eucalyptus and the extracts of other two biosorbents. This behavior can be best checked when the correlation is done separately (segment of straight lines in Figure S5). Surprisingly, the eucalyptus extracts are relatively less reactive than the araucaria and pinus extracts, for which small variations of UV_{254nm} (3 cm^{-1}) cause very rapid reduction of Cr(VI) (14 mg L^{-1} h^{-1}). To obtain the same effect, an increase 25 times higher in the UV_{254nm} absorption of the eucalyptus extract is necessary. However, the huge amount of organic matter solubilized from eucalyptus, although less reactive, can continue reducing metal for a long time, allowing achieve stringent environmental limits [0.1 mg L^{-1} of Cr(VI)].

The data set presented in this study proved the significant solubilization of compounds during biosorbents pretreatment (washing) and during the biosorption. These compounds, especially those belong to organic matter, play a relevant role on reduction of Cr(VI), frequently negligence in the literature.

Conclusion

The three biosorbents, obtained from forestry waste of araucaria, eucalyptus and pines, are characterized in detail. Measured values are in the expected range of lignocellulosic biomass. However, eucalyptus distinguished from the others in several aspects that may influence the biosorption process (i.e., amount and type of both organic and inorganic solubilizable compounds). These differences could be attributed to the varied physiological functions that the eucalyptus bark and the cones of the araucaria and pinus perform in live trees.

The wash extracts obtained by the application of different extractor media to biosorbents, present great differentiation in the assessed parameters. Total organic load are similar for biosorbent in both natural and acidic media. However, the composition of the solubilized (extractable) species depends of the medium used. Unfortunately, the easily obtained UV_{254nm} absorption seems not be reliable for estimation of the DOM in the studied system. However, it remains a complementary parameter to polyphenols content, to estimate the reduction capacity of these extracts.

The biosorbents tested confirmed good performance to reduce/remove chromium. The reduction of Cr(VI) to Cr(III) biosorption is a very quick reaction, under tested conditions (i.e., pH 2,) in presence of both washed and unwashed biosorbents, with exception of basic medium washing. The washing process is necessary, and the more favorable is the natural media. The extracts can be used in the treatment as the initial step process in reducing the hexavalent chromium to trivalent. The washed biosorbents can be used for removal of trivalent chromium, in combination ensuring availability. Thus, the tested biosorbents/extracts have potential for application in the treatment of wastewater containing chromium at least in similar levels to those studied.

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