



Destination of chromium residue from exhausted biosorbents used in effluent treatment

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ABSTRACT

This study analyzes the destination of biosorbents prepared from Araucaria, eucalyptus and pine forest residues, after application in chromium biosorption from synthetic solutions and industrial electroplating effluent. The used biosorbents were submitted to characterization, waste classification, regeneration and recovery tests. Pine presents the best biosorption performance (98% Cr removal in 2 h contact time) in both synthetic solutions and industrial effluent tests. All the biosorbents became hazardous waste after contact with synthetic solutions and effluent containing chromium, making suitable disposal or reuse in another process. Acid regeneration resulted in low Cr recovery yields indicating also difficulty in the reuse of biosorbent. Incineration proved to be promising, since it generated chromium oxide, a compound of commercial interest, and the heat generated can also be used in the process, reducing the costs of effluent treatment.

Keywords: Forest residues; Biosorption; Chromium recovery

1. Introduction

Several studies have been proposed to remove chromium species (hexavalent and trivalent) from synthetic solutions, using a huge variety of biosorbents [1–9]. The application of biosorption on chromium removal from industrial wastewater is more restricted due to its greater complexity [3,10,11]. However, the viability and competitiveness of biosorption in front of the usual processes (for example: chemical precipitation) have been demonstrated [3]. Despite this, the commercial application of these greener processes has not yet spread, due to some factors such as disponibility (related to seasonal production of biomasses), variable chemical composition and performance, difficulties and cost associated to metal recovery, biosorbent regeneration or destination [12,13]. Among the several types of lignocellulose biosorbents, a special interest is focused on forestry

waste due to their huge quantities, worldwide availability and good performance on metal sorption.

Investigating the characteristics of metal-loaded biosorbents with a view to their final destination is relevant, whether through regeneration, recovery or disposal of this waste [14]. The usefulness of biomass as a biosorbent depends not only on its biosorption capacity, but how easily it can be regenerated or recovered [3,13,15]. However, most research tends to focus solely on performance, without considering the final destination of the material used [3,16,17]. In addition, exhaust biosorbents generally become hazardous waste because of the high concentration of toxic elements. In this way their disposal can generate cost and negative impacts to the environment.

The choice of destination depends on the metal accumulation mechanism; however, since biomass is inexpensive and the metals to be recovered are valuable, destructive

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recovery processes, such as incineration and/or acid/alkaline dissolution, may be economically feasible [12,13]. When bound to the surface of a biosorbent through physical adsorption, the adsorbate can be desorbed via a simple, nondestructive physical–chemical method using chemical eluents [4,13]. In many cases, dilute acids or mineral bases enable efficient biosorbent desorption, but can also cause severe structural damage to the biosorbent, thereby reducing biosorption capacity [3]. Additionally, desorption yield may be lower when the adsorption mechanism is the result of chemical interaction [12]. As such, given the implications of the final destination of the biosorbent, the choice of biomass type is important for whole process viability.

The pyrolysis and calcination of wastes containing chromium have been proposed as a viable alternative to the destination of this kind of residues, besides their potential use as alternative compounds to substitute some raw materials [13,14,16,18–20]. For instance, Dettmer et al. [20] found that ash generated in the controlled burning of leather processing residues contains 50–60 wt% chromium oxide. Therefore, it could be used as a Cr source in the tanning process itself. It was also shown that metal-loaded biosorbents can generate concentrates with metallurgical potential by heating treatments [11,13]. As biosorbents are combustible materials, their use as alternative fuel has also been proposed [21,22]. However, no attention has been paid to the influence of contaminants, from both the biosorbent itself and the treated effluent, on the quality of the biosorbed recovered metals.

In this context, the present study assessed alternative destinations, whether through regeneration, recovery or disposal; for Araucaria, eucalyptus and pine biosorbents after biosorption of chromium (VI) and (III) present in both synthetic solutions and industrial effluents.

2. Materials and methods

2.1. Materials

The biosorbent materials used in this study were from Araucaria (*Araucaria angustifolia*), pine (*Pinus elliottii*) and eucalyptus (*Eucalyptus* spp.) forest waste. Cone shells from Araucaria, pine trees and eucalyptus bark were used in this work. Pine cone shells were used whole, whereas only the dried wings or 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), grounded in an industrial blender (LO 4.0 Visa) and sieved to obtain a powder with particle size <250 µm. Pine cones were further ground to obtain a sample with particle size <44 µm, for comparison with the activated carbons tested.

Commercial steam-activated carbon (SAC, Brascarbo, CarboActiv V Plus) and chemically activated carbon (CAC, Clarimex, CAE Plus) were also used in chromium adsorption and recovery tests for comparison with biosorbents. Activated carbons were selected for being the most widely used material in the adsorption treatment of metal-containing effluents [23]. After preparation, all sorbents were placed in sealed plastic vials and stored in the dark, under controlled temperature (23°C ± 3°C) and humidity (50% ± 10%). Characterization experiments of burned

Cr-loaded biosorbents employed commercial Cr(III) oxide (Labsynth, Brazil, 99%) as reference.

2.2. Biosorption tests

The biosorption experiments conditions used were previously optimized [1,2] and are shown in Table 1. The process consists of two sequential steps. In the first step, the biosorbents (10 g L⁻¹, <250 µm) were placed in contact with 100 mL Cr(VI) solutions (20 mg L⁻¹ prepared from K₂Cr₂O₇ and adjusted for pH 2.0) and stirred for 15 min, when all Cr(VI) present were reduced to Cr(III) and/or removed from solution. In the second step of biosorption, the pH was adjusted to 5.0 and the suspension was kept under agitation for 24 h. The same procedure was applied to the industrial effluent, which was obtained in a wastewater treatment plant of an electroplating factory being collected directly at the inlet [2]. At the end of contact time, solutions were filtered and analyzed for total chromium and Cr(VI), and Cr(III) content was calculated by difference, as described in section 2.4.

2.3. Destination tests

2.3.1. Waste classification

The waste generated in chromium biosorption was classified according to Brazilian Leaching of Solid Waste Standard [24]. The maximum contaminant level (MCL) for chromium in the leachate extract is 5 mg L⁻¹. As such, any waste that exceeds this limit is considered hazardous.

2.3.2. Exhausted biosorbents regeneration and metal recovery tests

The final destination of chromium-loaded biosorbents was studied in stages, as shown in Fig. 1. The solids obtained in chromium removal tests were dried (60°C until constant mass). Biosorbent regeneration was tested by desorption using 0.8 and 2.0 mol L⁻¹ hydrochloric acid with contact times of 24 and 48 h under constant magnetic agitation (400 rpm)

Table 1
Test conditions chromium(VI) reduction and chromium(III) removal in synthetic solutions and industrial effluent in batches

Parameters	Values (range)
Dosing of adsorbent (g L ⁻¹)	0.5–15
Particle size of adsorbent* (µm)	<250
Contact time (h)	0.3 up to 32
Stirring speed (rpm)	120
pH in the Cr(VI) reduction tests	2.0
pH in the Cr(III) removal tests	5.0
Temperature (°C)	23 ± 3
Initial concentrations (mg L ⁻¹)	
<u>Synthetic Solutions</u>	
Chromium (III)	10–800
<u>Industrial effluent</u>	
Chromium (III)	8.5
Chromium (VI)	21.1

*Pine biosorbent was also tested at lower size granulometry (<44 µm).

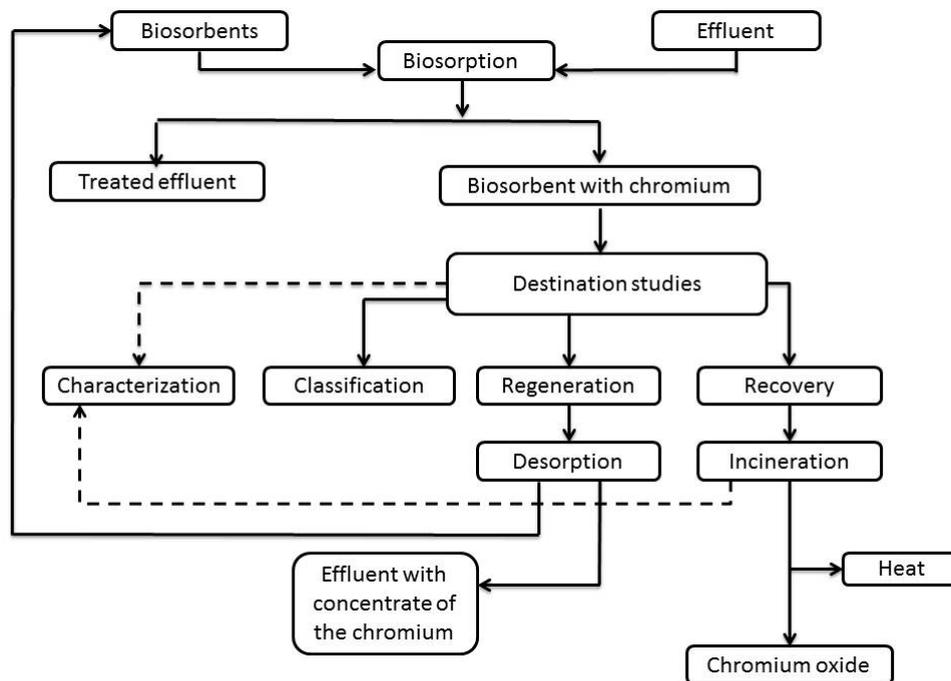


Fig. 1. Schematic of the chromium biosorption and the destination procedures of the exhausted biosorbents evaluated in this study.

following literature procedures [4,23]. Desorption tests at basic medium were not performed because previous works about the leaching behavior of studied biosorbent, indicated great solubilization of organic matter in alkaline pHs [1,23].

Recovery tests by incineration were performed in a muffle furnace (Lavoisier 440d) at 550°C for 4 h, in line with the standard procedure [25] and the results obtained in thermogravimetric analyses (TGA) (section 3.4.2).

2.4. Characterization

A detailed characterization of the raw and chromium-loaded biosorbents was performed by scanning electron microscopy with energy dispersive spectroscopy, Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and X-ray fluorescence (XRF), following procedures described by Santos [1,2,10,23]. The thermal stability and degradation behavior of the solid samples were evaluated by TGA under oxygen atmosphere using a thermal analyzer (SDT Q600, TA Instruments, USA) with temperature increase of 20°C min⁻¹ up to 1,000°C. The residues obtained after incineration of the chromium-loaded solids were also characterized using these same techniques.

The concentration of chromium species on liquid samples was determined following standard procedures described in detail elsewhere [1]. 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 Chemicals, Brazil). The Cr(VI) concentration was determined by the diphenylcarbazide method [26] in a Micronal B442 spectrophotometer (Brazil). Cr(III) content was calculated based on the difference between total chromium and Cr(VI). Industrial effluent was characterized following standard procedures [27]

and the evaluated parameters are presented in Table S1 (supplementary materials).

3. Results and discussion

3.1. Biosorption tests

Table 2 shows the results of biosorption tests for Cr(VI) reduction and Cr(III) removal in both synthetic solutions and industrial effluent. The tests were conducted to compare

Table 2
Comparative results for batch tests of chromium(VI) reduction and chromium(III) removal in synthetic solutions and industrial effluent

Sorbents	Concentration (mg L ⁻¹)			
	Synthetic solution		Industrial effluent	
	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)
Initial concentration	18.7	0	21.1	8.5
Final concentration				
Araucaria	0	1.4	0	1.7
Eucalyptus	0	7.4	0	3.1
Pine	0	0.8	0	0.8
Pine*	0	0.4	–	–
Carbon SAC*	0	4.8	0	6.4
Carbon CAC*	0	0.4	0	0

Conditions: Sorbents: 10 g L⁻¹ and Particle size <250 µm. Reaction starts with pH 2 for Cr(VI) reduction and removal, adjusted to pH 5 after 15 min for Cr(III) removal for 24 h; T 23°C ± 3°C; shaking at 120 rpm.

*Particle size < 44 µm.

the biosorption performance of Araucaria, eucalyptus and pine biosorbents with the performance of activated carbon samples, as well as to obtain chromium-loaded material for further final destination studies.

Pinus was the only biosorbent that removed chromium (0.8 mg L^{-1}) below the environmental limit (1.0 mg L^{-1} [28]) after 24 h of contact time. In addition, Pinus samples with lower particle size ($<44 \mu\text{m}$) achieved environmental limit after 2 h of contact, with Cr(III) removal of 98%. Araucaria, although not reaching the environmental limit, presented a lower residual Cr(III) concentration (1.4 mg L^{-1}) than eucalyptus (7.4 mg L^{-1}). The steam activated carbon (SAC) presented similar Cr(III) removing performance (0.4 mg L^{-1}) as the Pinus sample with same particle size ($<44 \mu\text{m}$). On the other hand, the CAC presented the worst performance, indicating that this sorbent is not recommended for the removal of chromium under the conditions used.

The results obtained with the effluent were similar to those reported for the synthetic solutions, with CAC and Pinus (particle size $<250 \mu\text{m}$) presenting the highest removals of 100% and 97%, respectively. The concentration of total chromium in the effluent (29.6 mg L^{-1} : 21.1 mg L^{-1} Cr(VI) + 8.5 mg L^{-1} Cr(III)) was higher when compared with its concentration in the synthetic solution (18.7 mg L^{-1}). In addition, several other metals are present in the effluent (Table S1), which could compete with chromium in the biosorption process. Therefore, the biosorbents performance under real conditions is remarkable. These results suggest the feasibility of biosorbents application, especially Pinus, on effluent treatment in a commercial scale.

It is also worth noting that part of the solubilized Cr(VI) was reduced into Cr(III), as evidenced by the increase of trivalent chromium concentration in the first 15 min of reaction (data not shown). This behavior has already been verified in other studies [2,3] and is often misunderstood. When Cr(III) concentration is not monitored in biosorption experiments, the disappearance of Cr(VI) from the solution is incorrectly considered as a complete removal of the metal hexavalent form.

3.2. Classification of chromium-containing waste

The waste generated after biosorption was characterized using the leaching test [24] to classify the residues. Table 3 displays the results of leaching tests for Araucaria, eucalyptus and pine biosorbents loaded with chromium. The total chromium content recorded in the leachate extracts exceeded the established MCL for nonhazardous substances. Based on these results, the waste obtained after chromium

biosorption should be sent to industrial landfills or reused in other processes.

3.3. Regeneration of chromium-containing waste

The possibility of regenerating biomass used in chromium biosorption was assessed by desorption tests using HCl solutions [4,23]. The adsorbents used in these tests were obtained after contact with the industrial effluent. Table 4 shows the results obtained as recovery percentages from the adsorbed chromium.

Under mild desorption conditions (Test 1: 0.8 mol L^{-1} , 24 h) the Cr-loaded biosorbents exhibited low chromium recovery, with more significant results for eucalyptus (28%). The best recovery results were obtained using Cr-loaded activated carbons, with total recovery (100 %) of the metal adsorbed onto SAC and lower, yet significant, recovery for CAC (63 %).

In light of the low recovery percentages recorded for the biosorbents, more severe conditions (Test 2) were applied, increasing both contact time to 48 h and acid concentration to 2 mol L^{-1} . A significant increase on chromium recovery was observed, with eucalyptus releasing 61% of the chromium adsorbed. Araucaria and pine also exhibited better recoveries (40%–42%) under these conditions. However, these preliminary tests indicated that chromium is more strongly bonded to the lignocellulosic surface of the biosorbents when compared with activated carbons. During biosorption process, Cr(VI) is reduced to Cr(III), mainly in the surface of biosorbent, which then chemically bonds to the biomass [1]. Park et al. [11] obtained 67%–76% chromium recovery and 98% zinc recovery through desorption tests

Table 4
Percentage of total chromium recovered by acid desorption of the adsorbents used in the industrial effluent treatment

Adsorbents	% Cr recovered	
	Test 1	Test 2
Araucaria	19	40
Eucalyptus	28	61
Pine	21	42
Carbon SAC	104	Not tested
Carbon CAC	63	Not tested

Test 1: HCl 0.8 mol L^{-1} ; dosage 10 g L^{-1} ; contact time 24 h; Test 2: HCl 2.0 mol L^{-1} ; dosage 10 g L^{-1} ; contact time 48 h.

Table 3
Leaching tests of residues of biosorbent containing chromium

Parameter	Residues Cr-loaded biosorbents		
	Araucaria	Eucalyptus	Pine
Loading – mg Cr g^{-1}	26.9	17.8	20.2
Leached – total chromium (mg L^{-1})	17.12	17.65	7.12
Residue classification	Hazardous	Hazardous	Hazardous

Maximum limit in the leach extract is 5 mg L^{-1} [24].

using different biosorbents. This indicates that biosorbent may not be completely regenerated by Cr desorption. These authors suggest burning as an alternative for chromium recovery, an economically appealing and energy-saving method that produces highly concentrated chromium and reducing storage costs.

3.4. Recovery of chromium-containing waste

3.4.1. Thermogravimetric analysis

The thermal stability and degradation behavior of the solid samples were evaluated by TGA under controlled conditions (O_2 , $20^\circ C \text{ min}^{-1}$). The thermograms for raw and Cr-loaded biosorbents are shown in Fig. 2. The raw biosorbents degraded mainly in two stages. The first stage of decomposition started at around $260^\circ C$, corresponding to lignocellulosic materials decomposition, and the second stage began at $450^\circ C$, corresponding to complete decomposition. These results are in agreement with those reported in the literature [21,22,29]. Above $550^\circ C$, no event is observed for all analyzed samples, indicating that this temperature could be used in the incineration of Cr-loaded biosorbents.

Table 5 displays the partial biosorbent mass loss values and thermal decomposition temperature. TGA identified an initial stage of mass loss in all biosorbents due to water loss, varying from 10.39% to 13.53% for chromium-loaded Araucaria and eucalyptus, respectively. Primary mass loss occurred in two stages in all the biosorbents, except chromium-loaded pine. Decomposition temperature declined for all the chromium-loaded biosorbents, confirming a change in the structure of the compounds. The temperature decreases observed were $92^\circ C$ for Araucaria, $67^\circ C$ for pine and $22^\circ C$ for eucalyptus.

TGA also provided an estimation of the gross calorific value (GCV, $J \text{ g}^{-1}$) of the biosorbents. Table 6 shows the GVC values recorded in this study and, for comparison purposes, those reported in the literature for wood and coal. The obtained GCV indicate that the biosorbents show potential as fuel sources. Thus, waste regeneration by incineration may produce energy that could be used making biosorption a more competitive process in an industrial scale application.

In order to evaluate the chromium recovery from Cr-loaded biosorbents, the material was burned ($550^\circ C$) in a furnace to eliminate water and organic matter and to concentrate metal under the oxide form. After burning,

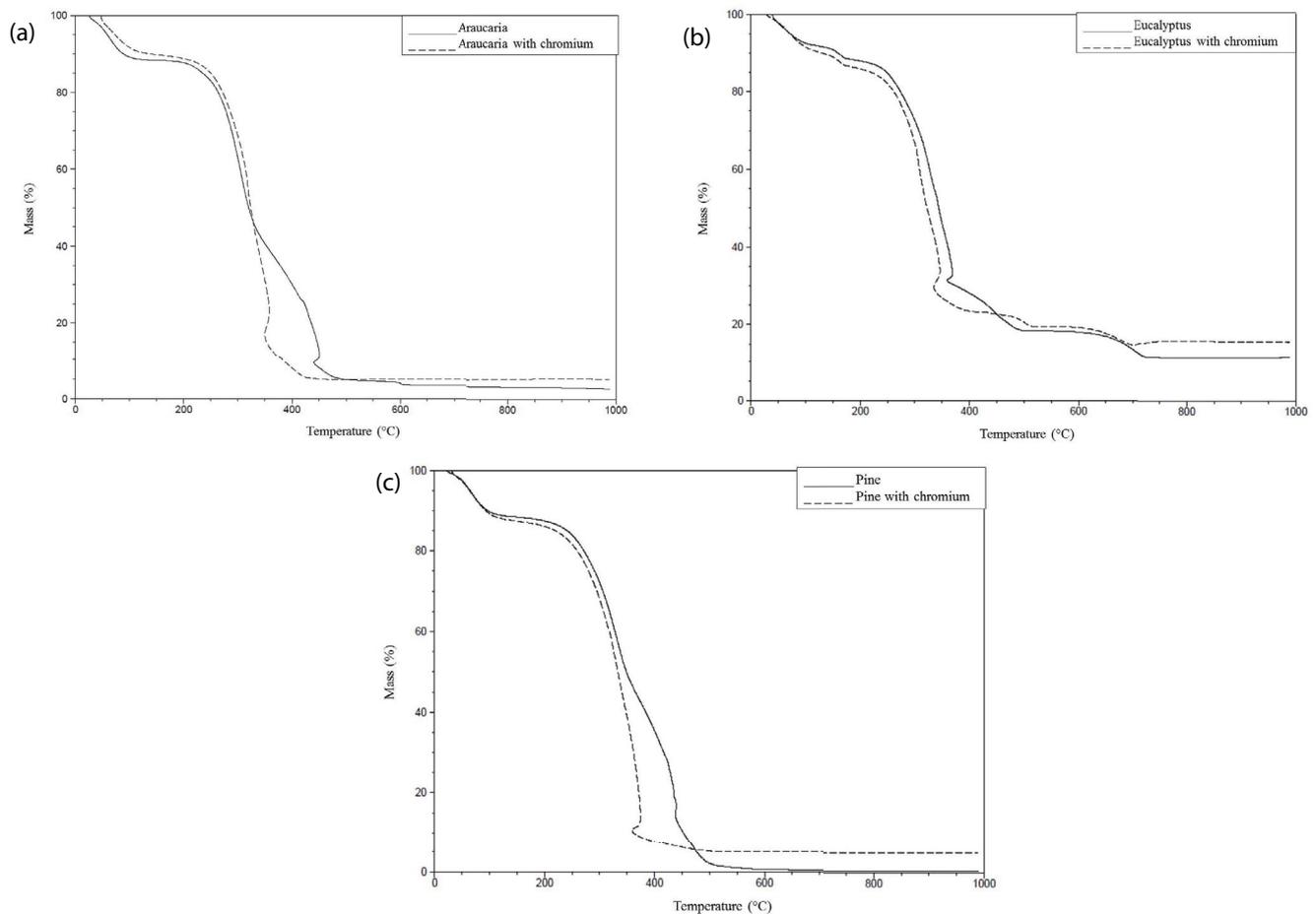


Fig. 2. Images of the products, Cr-loaded samples of (a) Araucaria, (b) eucalyptus and (c) pine obtained after incineration at $550^\circ C$. An image of a commercial grade chromium(III) oxide sample (image d) is presented for comparison.

Table 5
Thermogravimetric analysis (TGA) results of raw and Cr-loaded biosorbents

Biosorbents	% Mass loss				T (°C) Decomp.
	H ₂ O	1st stage	2nd stage	Residue	
Raw Araucaria	11.59	50.42	33.42	2.67	450.47
Cr-loaded Araucaria	10.39	52.16	32.48	5.14	358.06
Raw eucalyptus	11.58	58.36	11.72	11.31	368.78
Cr-loaded eucalyptus	13.53	40.34	26.62	15.22	346.18
Raw pine	11.42	45.40	42.60	0.45	439.88
Cr-loaded pine	12.52	82.60	–	4.94	372.89

the ashes obtained from Cr-loaded Araucaria (Fig. 3a) and pine (Fig. 3c) presented a bright green color, very similar in appearance to the commercial compound (Fig. 3d), suggesting the formation of chromium(III) oxide. On the other hand, the product obtained from eucalyptus presented a pale green color, suggesting a different chemical composition. In order to determine the purity of the chromium oxide formed, as well as, the possible contaminants present, the ashes were characterized in detail by FTIR, XRD, XRF and MEV-EDS (Fig. S1).

3.4.2. Characterization of the ashes of the used biosorbents obtained by incineration

The ashes obtained in recovery tests by incineration (550°C for 4 h) for both raw and Cr-load biosorbents were characterized in detail. Fig. 4 depicts the results of FTIR analyses of the loaded and burned biomasses, as well as, a sample of commercial chromium(III) oxide used as a standard for comparison. After burning, significant changes were observed in the three biosorbents spectra, demonstrating that changes occurred after incineration of the organic matrix. The FTIR spectra of Araucaria and pine were similar to those of the commercial chromium(III) oxide spectrum, suggesting that this compound is formed after these biomasses are burned. This similarity was not observed for eucalyptus, possibly due to the formation of another compound or a mixture of compounds.

XRD was used to better assess the compounds obtained after burning the chromium-loaded biosorbents and commercial chromium(III) oxide compound was also adopted as standard (Fig. S2). The diffractograms for Araucaria and pine showed chromium oxide as the major element, similar to the diffractogram for commercial chromium(III) oxide, iron oxide as a minor element for Araucaria, and traces of silicon oxide for Araucaria and pine. XRD was useful to explain the complexity of eucalyptus compounds formed. Calcium compounds were the major element, followed by chromium oxide and traces of silicon oxide. These data corroborate the results of FTIR analysis, indicating that the compounds obtained after burning eucalyptus showed a greater variety of elements.

XRF was employed for quantitative chemical analysis to assess the purity of synthetic solution and industrial effluent Cr-loaded biosorbents ashes produced. Table 7 shows the percentages of the elements found after incinerating Araucaria, eucalyptus and pine, as well as the commercial chromium(III) oxide. The results of XRF analysis of

Araucaria and pine compounds identified chromium oxide as the main compound obtained after biomass incineration, with 88% and 81% in tests using the synthetic solution, respectively. The lower percentages (37% for Araucaria and 31% for pine) recorded after testing with industrial effluent were expected, given the difference in chromium content between the Cr(III) solution and industrial wastewater, resulting in solids with different loadings. For the eucalyptus compound, chromium oxide percentages after biosorption testing in synthetic solution and industrial wastewater were similar (41% and 31%).

The elements Fe, Pb and S were also observed in the compounds obtained after contact with industrial effluent, possibly originated from the effluent itself. A particularly noteworthy feature was the solubilization of certain elements present in the ashes of the raw biosorbent, which were not observed after biosorbent contact with the chromium solution or the effluent. A typical example is K for Araucaria (86%) and pine (23%). In eucalyptus, calcium oxide (76%) declined after contact with the chromium solution (51%), reaching low levels (3%) after contact with the effluent. Quantification of silicon oxide (33%) by XRF in pine ash corroborated the XRD results, indicating the presence of silicon oxide in the diffractogram. By contrast, the presence of sulfur oxide (6%) as a contaminant of the Cr(III) standard observed by XRF was not confirmed by XRD, likely due to the lower sensitivity of the latter technique. The remaining oxides quantified by XRF, such as manganese and phosphorous, exhibited low percentages (less than 10%).

Table 6
Calorific values of tested biosorbents and other fuels

Fuels	Low calorific value (dry base)	
	(J g ⁻¹)	(cal g ⁻¹)
Raw Araucaria	10,969	2,624
Cr-loaded Araucaria	10,280	2,459
Unwashed eucalyptus	7,928	1,897
Chromium-loaded eucalyptus	7,104	1,700
Unwashed pine	11,705	2,800
Chromium-loaded pine	10,562	2,527
Wood [32]	20,000	4,785
Bituminous coal [33]	30,000	7,177

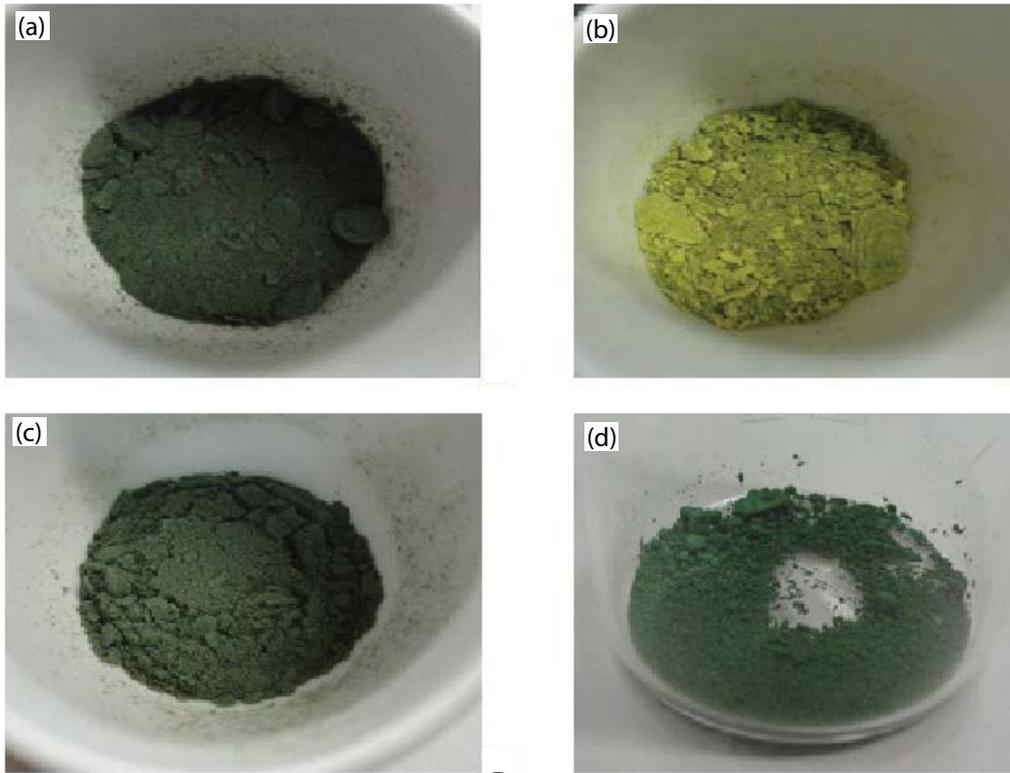


Fig. 3. TGA thermograms of the raw and Cr-loaded biosorbents: (a) Araucaria, (b) pine and (c) eucalyptus. Metal-loaded samples obtained in the biosorption tests using Cr(VI) synthetic solutions.

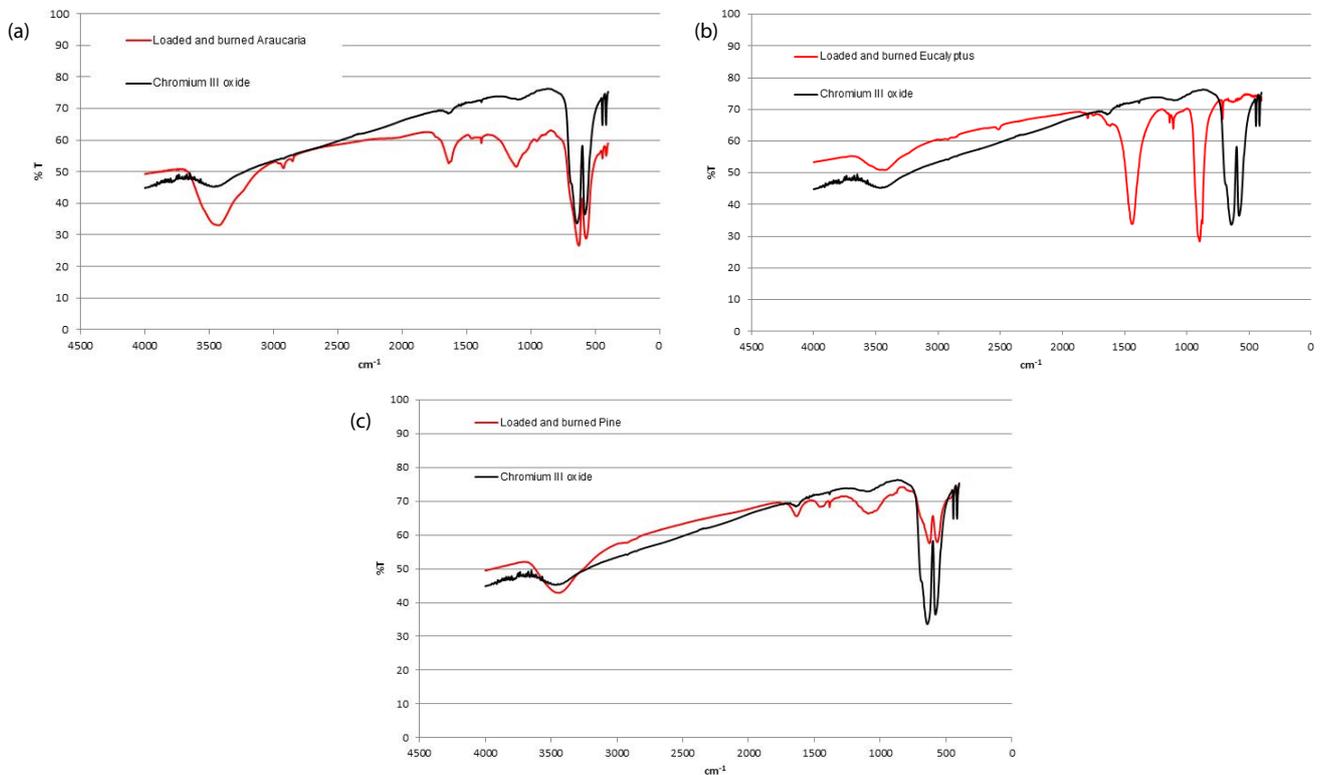


Fig. 4. FTIR spectra of the Cr-loaded samples of (a) Araucaria, (b) pine and (c) eucalyptus obtained after incineration at 550°C, and (d) a commercial grade chromium(III) oxide sample.

Table 7
Chemical composition (% wt.) of the calcinated samples of raw and Cr-loaded biosorbents

Oxides	Araucaria			Eucalyptus			Pine			Cr ₂ O ₃ *
	1	2	3	1	2	3	1	2	3	
Cr ₂ O ₃	Nd	88	37	Nd	41	31	Nd	81	31	93
Fe ₂ O ₃	Nd	Nd	14	1	Nd	9	6	1	14	Nd
PbO	Nd	Nd	9	Nd	Nd	7	Nd	Nd	7	Nd
SO ₃	6	1	19	1	Nd	36	5	1	18	6
K ₂ O	86	Nd	1	5	Nd	Nd	23	Nd	Nd	Nd
CaO	Nd	Nd	2	76	51	3	16	Nd	1	Nd
SiO ₂	Nd	1	3	4	2	3	33	8	10	Nd
MgO	1	Nd	Nd	5	Nd	Nd	5	Nd	Nd	Nd
MnO	1	7	2	3	3	2	Nd	6	2	Nd
P ₂ O ₅	4	2	9	1	Nd	6	4	1	10	Nd
Remaining	2	1	4	4	3	3	8	2	7	1

1 – Before contact; 2 – After contact with synthetic solution Cr(III); 3 – After contact with effluent;

*Commercial chromium(III) oxide for comparison; nd – not detected.

The ashes characterization results demonstrate the possibility of reusing the metals, particularly chromium (approximately 40%), in addition to lead and iron (about 15%).

According to research by Della et al. [30], residual oxides can be used to manufacture a variety of materials, including ceramic stains, providing technological, economic and ecological benefits. In studies by Abreu [31] after purification and calcination, chromium waste from tanning industry was incorporated into ceramic stains, producing material with good color and texture characteristics. In general, chromium recovery by incineration of biosorbents loaded with this metal indicates the potential reuse of residues from biosorption as sources of chromium in the form of chromium(III) oxide.

4. Conclusions

The application of standard waste classification tests indicated that all the biosorbents became hazardous waste after contact with synthetic solutions and effluent containing chromium. These results corroborate the need to ensure a suitable final destination for this waste. Among the alternatives tested, acid desorption aiming at reusing the biosorbents and obtaining a solution with a high chromium content did not produce good results, with regeneration efficiency varying from 19% to 61%. By contrast, incineration of the chromium-loaded biosorbents to obtain chromium(III) oxide seems viable. The biosorbents in contact with the synthetic solution generated waste containing 80% chromium oxide. Purity tests indicate compounds containing about 40% chromium and 15% lead and iron, after biosorption tests with industrial effluent. Despite its lower purity, chromium can be used as a precursor source of metals in the production of pigments or composites.

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References

- [1] F.A. Santos, L. Alban, C.L.C. Frankenberg, M. Pires, Characterization and use of biosorbents prepared from forestry waste and their washed extracts to reduce/remove chromium, *Int. J. Environ. Sci. Technol.*, 13 (2016) 327–338.
- [2] F.A. Santos, M. Idrees, M. Silva, P.H.E. de Lima, N. Bueno, F. Nome, H.D. Fiedler, M. Pires, Cr(III) biosorption by forest wastes from *Araucaria angustifolia* and *Pinus elliottii*: biosorbent surface characterization and chromium quantification by spectrofluorimetry in micellar medium, *Desal. Wat. Treat.*, 51 (2013) 5617–5626.
- [3] D. Park, Y.S. Yun, J.M. Park, The past, present, and future trends of biosorption, *Biotechnol. Bioprocess Eng.*, 15 (2010) 86–102.
- [4] J.C.P. Vaghetti, E.C. Lima, B. Royer, J.L. Brasil, B.M. da Cunha, N.M. Simon, N.F. Cardoso, C.P.Z. Noreña, Application of Brazilian-pine fruit coat as a biosorbent to removal of Cr(VI) from aqueous solution-kinetics and equilibrium study, *Biochem. Eng. J.*, 42 (2008) 67–76.
- [5] K.K. Krishnani, X. Meng, C. Christodoulatos, V.M. Boddu, Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk, *J. Hazard. Mater.*, 153 (2008) 1222–1234.
- [6] B. Singha, S.K. Das, Biosorption of Cr(VI) ions from aqueous solutions: kinetics, equilibrium, thermodynamics and desorption studies, *Colloids Surf., B*, 84 (2011) 221–232.
- [7] S. Nag, A. Mondal, N. Bar, S.K. Das, Biosorption of chromium (VI) from aqueous solutions and ANN modelling, *Environ. Sci. Pollut. Res.*, 24 (2017) 18817–18835.
- [8] A.K. Panda, R.K. Singh, D.K. Mishra, Thermolysis of waste plastics to liquid fuel: a suitable method for plastic waste management and manufacture of value added products – a world prospective, *Renewable Sustainable Energy Rev.*, 14 (2010) 233–248.
- [9] A.K. Bhattacharya, T.K. Naiya, S.N. Mandal, S.K. Das, Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents, *Chem. Eng. J.*, 137 (2008) 529–541.
- [10] F.A. dos Santos, M.J.R. Pires, M. Cantelli, Treatment of effluent from galvanoplasty by biosorption of chromium and iron with cone scales from the *araucaria angustifolia*, *Rev. Esc. Minas*, 64 (2011) 499–504.

- [11] D. Park, Y.-S. Yun, J.H. Jo, J.M. Park, Biosorption process for treatment of electroplating wastewater containing Cr(VI): laboratory-scale feasibility test, *Ind. Eng. Chem. Res.*, 45 (2006) 5059–5065.
- [12] I.S. Bădescu, D. Bulgariu, I. Ahmad, L. Bulgariu, Valorisation possibilities of exhausted biosorbents loaded with metal ions – a review, *J. Environ. Manage.*, 224 (2018) 288–297.
- [13] S. Lata, P.K. Singh, S.R. Samadder, P.K. Singh, S.R. Samadder, Regeneration of adsorbents and recovery of heavy metals: a review, *Int. J. Environ. Sci. Technol.*, 12 (2015) 1461–1478.
- [14] P. Staroń, Z. Kowalski, A. Staroń, M. Banach, Thermal treatment of waste from the meat industry in high scale rotary kiln, *Int. J. Environ. Sci. Technol.*, 14 (2017) 1157–1168.
- [15] S.V. Vassilev, D. Baxter, C.G. Vassileva, An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types, *Fuel*, 117 (2014) 152–183.
- [16] A. Dettmer, K. Guerra, P. Nunes, M. Gutterres, N.R. Marcílio, Production of basic chromium sulfate by using recovered chromium from ashes of thermally treated leather, *J. Hazard. Mater.*, 176 (2010) 710–714.
- [17] J. Torras, I. Buj, M. Rovira, J. de Pablo, Chromium recovery from exhausted baths generated in plating processes and its reuse in the tanning industry, *J. Hazard. Mater.*, 209–210 (2012) 343–347.
- [18] M.A. Abreu, S.M. Toffoli, Characterization of a chromium-rich tannery waste and its potential use in ceramics, *Ceram. Int.*, 35 (2009) 2225–2234.
- [19] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, An overview of the composition and application of biomass ash. Part 1. Phase-mineral and chemical composition and classification, *Fuel*, 105 (2013) 40–76.
- [20] A. Dettmer, K.G.P. Nunes, M. Gutterres, N.R. Marcílio, Obtaining sodium chromate from ash produced by thermal treatment of leather wastes, *Chem. Eng. J.*, 160 (2010) 8–12.
- [21] A. Ronda, M. Della Zassa, M.A. Martín-Lara, M. Calero, P. Canu, Combustion of a Pb(II)-loaded olive tree pruning used as biosorbent, *J. Hazard. Mater.*, 308 (2016) 285–293.
- [22] M.A. Martín-Lara, G. Blázquez, A. Ronda, M. Calero, Kinetic study of the pyrolysis of pine cone shell through non-isothermal thermogravimetry: effect of heavy metals incorporated by biosorption, *Renewable Energy*, 96 (2016) 613–624.
- [23] F.A. Santos, Performance and Conformity Biosorbents Produced from Forest Residues and its Application in Chromium Treatment of Electroplating Industrial Effluent, Thesis, Post-Graduation Program in Materials Engineering and Technology Pontifical Catholic University of Rio Grande do Sul, Porto Alegre, Brazil, 2013.
- [24] ABNT - Brazilian Association for Technical Standards, ABNT NBR 10005:2004 Procedure for Obtention Leaching Extract of Solid Wastes, 2004.
- [25] ABNT - Brazilian Association for Technical Standards, ABNT NBR 10664:1989 Waters - Determination of Residues (Solids) - Gravimetric Method, 1989.
- [26] ABNT - Brazilian Association for Technical Standards, ABNT NBR 13738:1996 Water - Hexavalent Chromium Determination - Diphenylcarbazide Colorimetric Method, 1996.
- [27] APHA, Standard Methods for Examination of Water and Wastewater, Am. Public Heal. Assoc., Washington, DC, USA, 2012.
- [28] CONAMA, National Council of Environment. Resolution CONAMA 430/2011, Effluent Release Conditions and Standards, Brasilia, Brazil, 2011.
- [29] G. Blázquez García, M. Calero De Hocés, C. Martínez García, M. Teresa, C. Palomino, A.R. Gálvez, M. Ángeles Martín-Lara, Characterization and modeling of pyrolysis of the two-phase olive mill solid waste, *Fuel Process. Technol.*, 126 (2014) 104–111.
- [30] V.P. Della, J.A. Junkes, I. Kuhn, H.G. Hiella, D. Hotza, By-product utilization of metallic recovering of stainless steel slags in the ceramic pigments synthesis; raw material characterization, *Cerâmica*, 51 (2005) 111–116.
- [31] M.A. Abreu, By-product utilization of metallic recovering of stainless steel slags in the ceramic pigments synthesis; raw material characterization, Thesis, Sao Paulo University, 2006.
- [32] B. Günther, R. Barkowski, M. Rosenthal, K. Gebauer, C.-T. Bues, Calorific value of selected wood species and wood products, *Eur. J. Wood Prod*, 70 (2012) 755–757.
- [33] S.U. Patel, B. Jeevan Kumar, Y.P. Badhe, B.K. Sharma, S. Saha, S. Biswas, A. Chaudhury, S.S. Tambe, B.D. Kulkarni, Estimation of gross calorific value of coals using artificial neural networks, *Fuel*, 86 (2007) 334–344.

Supplementary Information

Table S1
Characterization of the industrial electroplating effluent used

Parameter	Unit	Values
pH		1.80
Dissolved oxygen	mg O ₂ L ⁻¹	0.90
Conductivity	mS cm ⁻¹	6.26
Color	mg Pt-Co L ⁻¹	40
Turbidity	NTU	0.26
UV _{254nm}	cm ⁻¹	5.15
COD	mg O ₂ L ⁻¹	220
Cr(VI)	mg L ⁻¹	50.0
Cr(III)	mg L ⁻¹	24.0
Cr total	mg L ⁻¹	74.0
Ni	mg L ⁻¹	0.42
Fe total	mg L ⁻¹	36.20
Na	mg L ⁻¹	16.45
Al	mg L ⁻¹	5.71
Pb	mg L ⁻¹	0.51
Zn	mg L ⁻¹	7.73
Cu	mg L ⁻¹	3.39
Mg	mg L ⁻¹	3.23
Mn	mg L ⁻¹	0.26
K	mg L ⁻¹	10.98
Ca	mg L ⁻¹	12.29

nd – not detected.

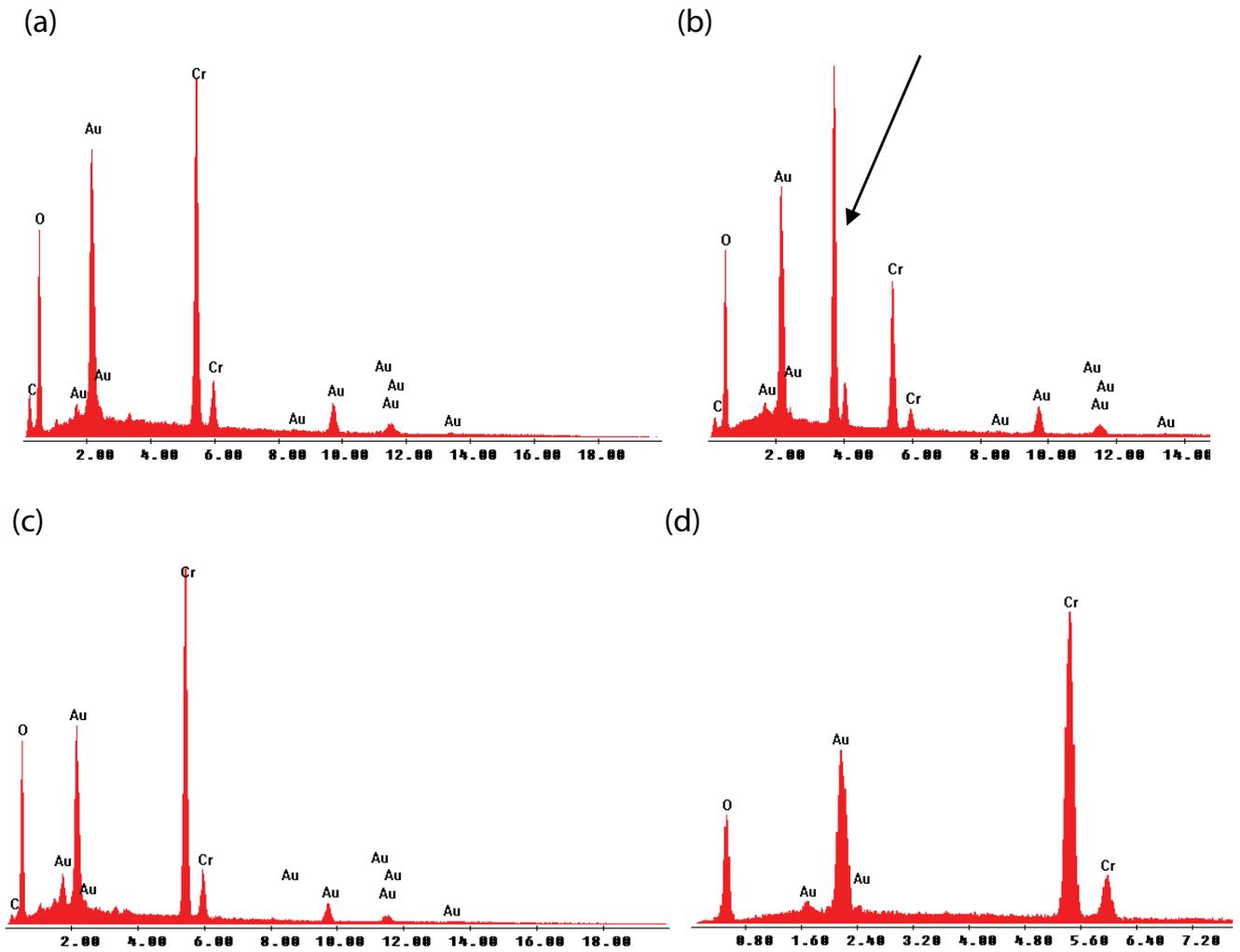


Fig. S1. EDS spectra of chromium-loaded biosorbent burning products (a) Araucaria, (b) Eucalyptus, (c) Pine, and a spectrum of commercial (d) chromium(III) oxide.

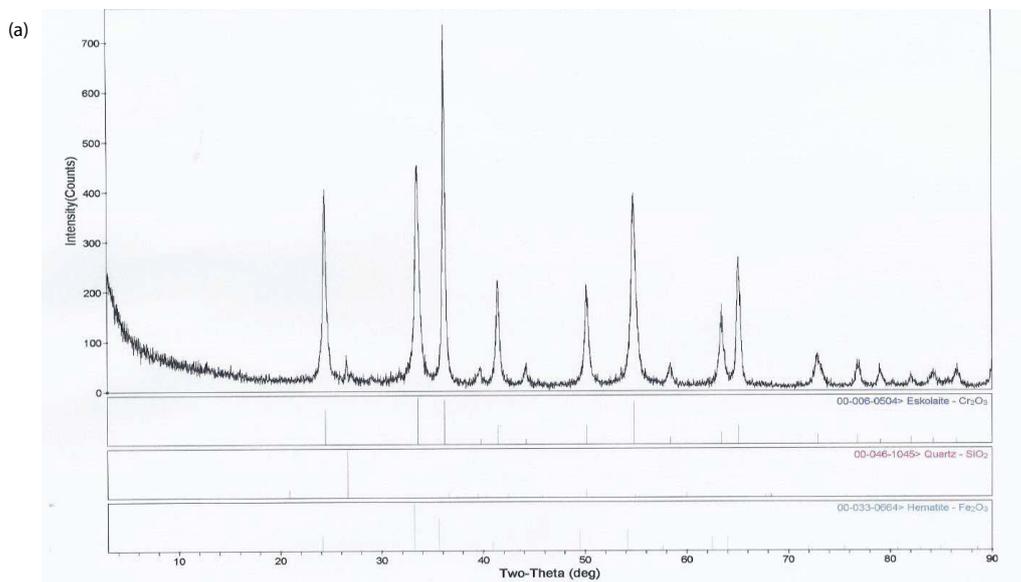


Fig. S2. continued

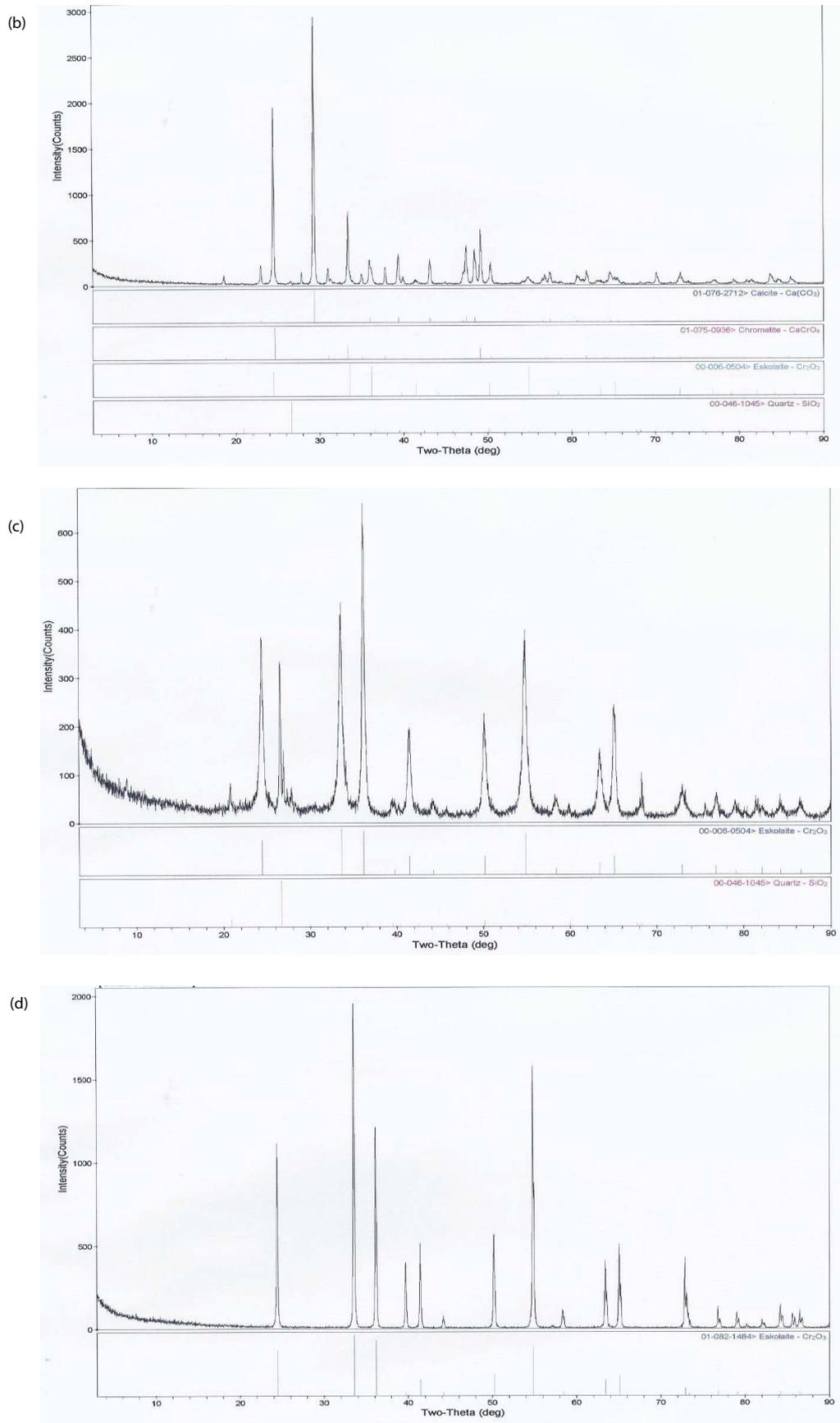


Fig. S2. XRD spectra of chromium-loaded (a) Araucaria, (b) eucalyptus and (c) pine samples after burning in a muffle furnace at 550°C and (d) commercial chromium(III) oxide.