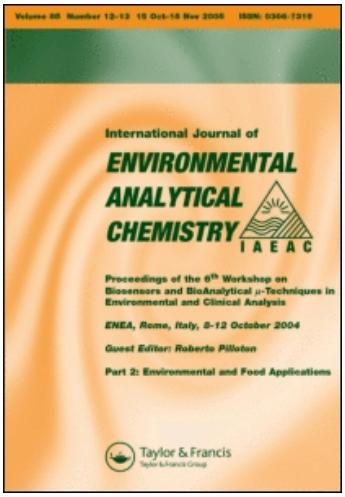

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Chromium speciation analysis by separation of Cr(III) from Cr(VI) on a XAD sorbent derivatized with shellac: a natural polymer

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A XAD-shellac sorbent, synthesized by the impregnation of the natural polymer shellac (purified product of the hardened resinous secretion of the lac insect *Kerria lacca*) on Amberlite XAD-16 copolymer backbone, has been developed for the separation of Cr(III) from Cr(VI), and preconcentration of Cr(III) from synthetic solutions and real samples. The preconcentration factor for Cr(III) was 75. All chromium determinations were made using the diphenyl carbazide spectrophotometric method after oxidizing Cr to chromate(VI) where necessary, and simultaneously with flame-AAS for confirmation. The dynamic breakthrough and batch capacities of this sorbent for Cr(III) were 0.3 and 0.9 mg g^{-1}, respectively, indicating that the ion-exchange mechanism was prevalent in the dynamic mode, whereas in the batch mode, the surface sites were also capable of exerting their chelating effects. When XAD-shellac was thoroughly washed with ammonium acetate solution prior to use in chromium speciation, the cationic (RH^+) surface sites were probably neutralized to yield free acetic acid, and the resulting resin did not retain CrO_4^{2-}. Thus, complete separation and speciation of Cr(III) from CrO_4^{2-} was possible using this sorbent. The shellac-coated sorbent decomposed in alkaline solution (i.e. over pH 7.5), and therefore the retained Cr(III) was eluted with dilute (0.025–0.050 M) HCl. Thus, Cr(III) in admixture with Cr(VI) could be separated and recovered, without interference from the hexavalent state. XAD-shellac was not successful for Cr preconcentration from seawater, but was efficiently used for synthetic and real electroplating wastewater and CRMs such as SO-2 soil, San Joaquin soil, BCR 145 R sewage sludge, with a recovery ratio for Cr(III)/Cr(VI) extending up to ≤98%.

Keywords: Chromium speciation; Cr(III) uptake; Chelating ion exchange; Shellac-XAD sorbent

1. Introduction

While Cr(III) may be considered as an essential trace element for the proper functioning of living organisms, e.g. for the maintenance of the glucose tolerance factor in the human body, Cr(VI) can be toxic and carcinogenic probably because of its high oxidation potential and small size. The toxic hexavalent chromium may be present in effluents from various industries such as plating, tanning, paint and

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pigment production, and metallurgy-contaminated natural waters. Since the evaluation of chromium toxicity in environmental and biological samples requires speciation studies, the number of papers on Cr separation and speciation analysis has increased significantly in recent years. For example, considering the literature published between 1983 and 1999 on chromium speciation, 24% are based on ion-exchange separations [1]. Atomic spectrometric techniques only measure total concentrations, necessitating the separation of Cr(III) and Cr(VI) prior to their detection. A unique approach is described using ion chromatography (IC) and inductively coupled plasma mass spectrometry (ICP-MS) for the determination of Cr(VI) in wastewater sludge incinerator emissions [2]. Quartz-fibre filters, spiked with an isotopically enriched (Cr-50 or Cr-53) chromate salt, were used to collect emission particulates. The enriched Cr(VI) isotope was used to monitor the reduction of Cr(VI) during sample collection using a pseudo-first-order reaction model and to calculate the rate of deposition of native Cr(VI) on the filters. At the end of the sampling period, the Cr(VI) was extracted from the filters with 0.1 M sodium hydroxide and determined by IC using postcolumn derivatization with 1,5-diphenylcarbohydrazide. To determine the ratio of enriched Cr(VI) to the native Cr(VI) emitted from the incinerator, an additional aliquot of the sample extract was preconcentrated by IC, and the isotopic composition of the Cr(VI) fraction determined by ICP-MS [2]. Once the chromium species are separated, they can be individually determined by different tecniques such as FAAS [3], ETAAS [4, 5], and ICP-AES [6, 7], which are not available for most conventional laboratories. A few examples of speciation pretreatment applicable to conventional laboratories are the separation and recovery of Cr(III) from tannery effluent with a weakly acidic carboxylic resin [8], recovery of Cr(VI) from acidic electroplating wastewater with a strongly basic anion exchanger [9], and the selective preconcentration of Cr(III) from natural waters on a poly (aminophosphonic acid) chelating resin [10], or a maleic acid-functionalized XAD sorbent [11], followed by FAAS [3] or diphenylcarbazide spectrophotometric [12] determination of chromium[11]. Other significant chelating sorbents used for selective Cr(III) uptake include those functionalized with quinolin-8-ol [13], Chelex-100 or Lewatit TP207 [14], polystyrene-divinylbenzene resins complexed with quinolin-8-ol [15], XAD-2 resin covalently bound to 5-palmitoyl-8-hydroxyquinoline [16]. Most of these resins were also used for Cr(VI) uptake after reduction of hexavalent chromium to the trivalent state [13–15].

When strategies for the separation and individual determination of chromium species in solution are considered as a whole [17–24], it may be deduced that one or the other (or both) oxidation states of chromium may be selectively retained on an ion-exchange column, while the other oxidation state requires a redox reaction prior to retention/elution by/from the same column. Previous strategies for solid-phase extraction (SPE) and speciation analysis of Cr have already been summarized by the authors in a previous article [11]. When Cr(III)-specific separation and determination is to be applied to Cr(VI), an aliquot of the sample should be subjected to preliminary reduction treatment with ascorbic acid [25], $NH_2OH \cdot HCl$ [26], ammonium ferrous sulphate [27], or Na_2SO_3 [28], and then be fed to the resin column.

In the light of the requirements for the search of simple and inexpensive methodologies to achieve separate retention of Cr(III) and Cr(VI)—the latter after reduction—by their individual elution and determination, this work has focused on the use of natural polymeric materials such as shellac as a Cr(III)-selective *O*,*O*-donor chelating ligand, which, when immobilized on an XAD sorbent, would behave as a

weakly acidic cation-exchange resin. Cr(III), being a hard Lewis acid, prefers hard Lewis bases like oxygen-donor ligands in accord with the Hard and Soft Acids and Bases (HSAB) theory of coordination chemistry. Shellac is a non-toxic natural polymer (a purified product of the hardened resinous secretion of the East Asian lac insect, *Kerria lacca*, scraped from the surfaces of trees inhabited by these insects) containing a number of hydroxy-carboxylic acids, namely aleuritic acid (a trihydroxy fatty acid), jalaric acid (a dihydroxyterpenoid), laccijalaric acid, butolic, and shelloic acid, enabling metal ion binding via the –COOH and –OH functional groups [29]. These typical carboxylic acids together with sesquiterpenoid compounds are the main molecules identified in fresh and old samples of the resin [30]. Shellac is completely non-toxic and can be even used in edible products. In preliminary experiments, shellac showed an affinity to bind Cr(III), and therefore a shellac-derivatized XAD resin was prepared in this work for selective uptake of Cr(III) from a mixture solution containing Cr(VI) as well as other elements. To the best of our knowledge, this work reports the first use of shellac for metal-speciation analysis.

2. Experimental

2.1 *Preparation and characterization of XAD-shellac sorbent*

The XAD-shellac sorbent (resin) was prepared by impregnating 1 g of Amberlite XAD-16 copolymer (previously washed with 1 M HNO_3, then with 1 M NaOH, and thoroughly with water, and dried) with 50 mL of shellac solution (1 g of purified shellac dissolved in 50 mL pure ethanol) with constant stirring at 25°C for 8 h. The shellac used in sorbent preparation was previously purified by dissolution in EtOH, filtration, and vacuum evaporation of the filtrate. The product was filtered off, washed with ethanol, and then dried for a week. The impregnated copolymer resin obtained was characterized by means of IR spectroscopy (see figure 1). The additional peaks in the IR spectrum of the XAD-shellac resin that do not appear in that of the XAD-16 copolymer are as follows: the wide band at $\nu(\text{OH}) = 3450\,\text{cm}^{-1}$ and the peak due to shellac carbonyl band at $(\text{–C=O}) = 1727\,\text{cm}^{-1}$.

The adsorptive saturation of XAD copolymer for shellac was determined by means of a Langmuir approach to adsorption data. For this purpose, 0.1–0.8 g (with 0.1 g increments) of shellac dissolved in 50 mL of EtOH was batch-contacted with continuous stirring for 4 h with 0.2 g of Amberlite XAD-16, and the supernatants of the equilibrated solutions were analyzed spectrophotometrically at 281 nm to find the adsorption density of shellac on XAD copolymer. The adsorption *versus* concentration (Langmuir isotherm) data were linearized—with regression analysis—to calculate the saturation level of shellac on XAD.

2.2 *Materials and methods*

All chemicals were purchased from E. Merck, Darmstadt and were of analytical reagent grade. Shellac was supplied from the local market as 'gomolac'. Chromium(III) and Cr(VI) solutions—each at $1000\,\text{mg}\,\text{L}^{-1}$ concentration—were prepared by dissolving the appropriate amounts of $CrCl_3 \cdot 6H_2O$ in 0.5 M HCl solution and of $K_2Cr_2O_7$ in

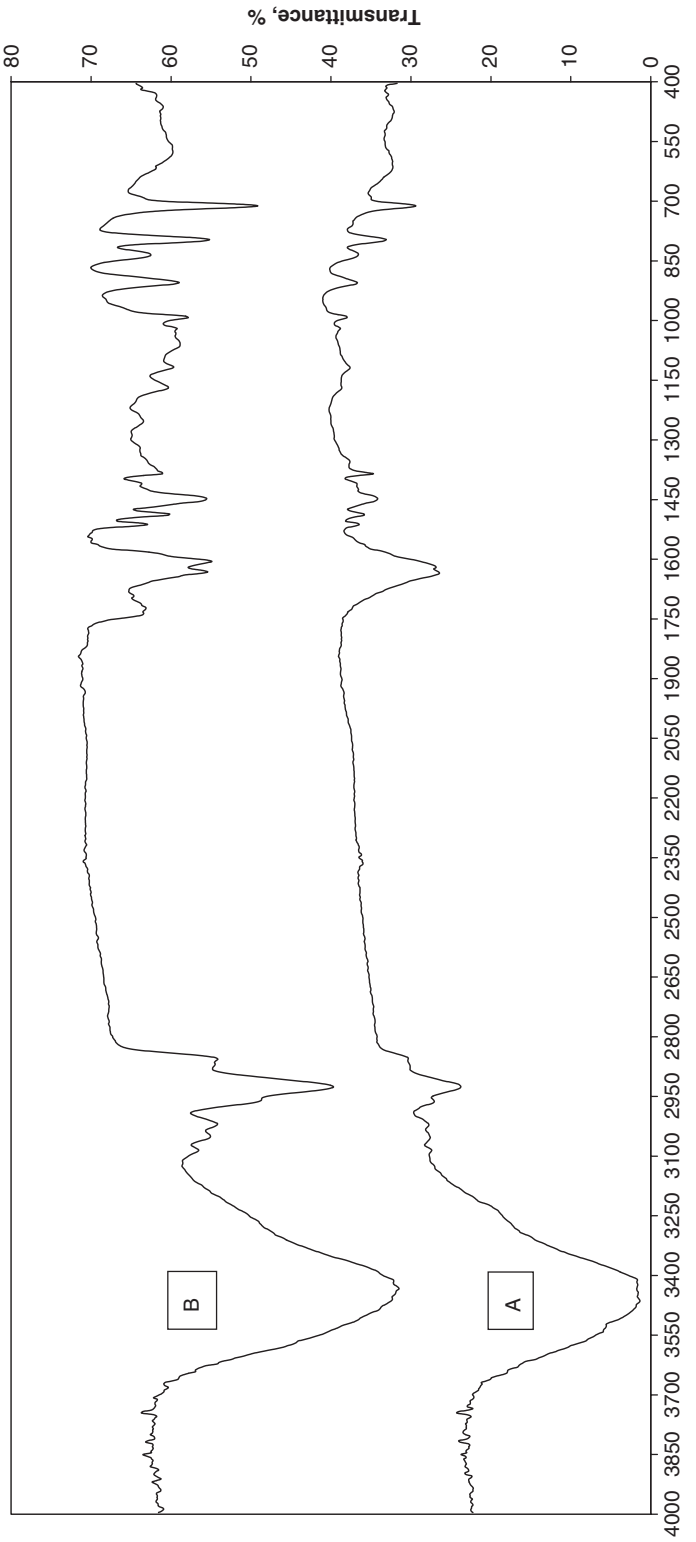

Figure 1. IR spectra of XAD copolymer and its shellac-derivatized resin.

distilled water, respectively. The stock solutions were standardized by complexometric (EDTA) and iodometric titrations and were used in the preparation of working solutions. The required pH adjustments were made by the use of 0.1 M (or more dilute) HCl and 0.1 M aqueous NH_3 solutions. A 0.05 M organic solution of the Cr(VI) reagent, diphenylcarbazide, was prepared by dissolving 0.6056 g in 50 mL of acetone.

The concentration of each metal solution was measured using a Varian SpectrAAFS-220 atomic absorption spectrometer with an air–acetylene flame. The findings for Cr were also confirmed using the diphenyl carbazide spectrophotometric method using a Cary 1 E UV-Vis spectrophotometer at a wavelength of 540 nm. All the pH measurements were performed with a Metrohm Herisau E-512 pH meter equipped with a glass electrode. The functional groups of the synthesized resin (for Cr preconcentration) were analyzed in KBr tablets by the aid of a Mattson 1000 FT-IR spectrometer. The resin was used in a glass burette of volume 25 mL and diameter 1 cm; 2.5 g of resin filled over a glass wool plug yielded a height of 10 cm.

The efficient form of the resin was the NH_4^+-form at pH 4.5. In the analysis of a $1\,mg\,L^{-1}$ Cr(III) + $50\,mg\,L^{-1}$ Cr(VI) mixture solution, this solution was first passed through the column at a flow rate of $1\,mL\,min^{-1}$, and trivalent chromium was retained. The hexavalent chromium originally not retained by the column was brought to pH 1 with 1 M H_2SO_4 and reduced to Cr(III) with 1 M Na_2SO_3, pH adjusted and diluted to $1\,\mu g$ Cr(III) mL^{-1}, thereby enabling retention by the resin. When elution was made in the dynamic (column) mode with 20 mL of 0.05 M HCl, a flow rate of $1\,mL\,min^{-1}$ was chosen. Here, two separate columns containing the same resin for the individual uptake of Cr(III) and Cr(VI) may be used.

The dynamic capacity of the resin for Cr(III) was calculated from the breakthrough curve obtained by passing 1 L of $1\,\mu g$ Cr(III) mL^{-1} at pH 4.5 through 10 cm of resin bed—in NH_4^+ form—at a rate of $1\,mL\,min^{-1}$, and integrating the upper portion of relative concentration *versus* eluate volume (breakthrough curve) until the concentrations in the fed solution and eluate were equal. The batch capacity was found by contacting 10 mL of $1-30\,\mu g\,mL^{-1}$ of Cr(III) solution with 0.1 g of resin at pH 4.5 for 2 h, measuring the equilibrium Cr concentrations in the filtrate, and mathematical treatment of adsorption data fitting to a Langmuir isotherm. The maximum preconcentration factor of the resin was found by adsorbing Cr(III) from 1.5 L of a 3.3 ng Cr(III) mL^{-1} solution, desorbing with 20 mL of the eluent mixture, and analyzing the eluate by AAS. For preconcentration experiments, 0.5 L of $10\,ng\,mL^{-1}$, 1.5 L of $3.3\,ng\,mL^{-1}$, and 2 L of $2.5\,ng\,mL^{-1}$ Cr(III) solutions, each freshly adjusted to pH 4.5, were passed individually through the resin bed at $1\,mL\,min^{-1}$, and each time, the retained Cr(III) was eluted with 20 mL of 0.05 M HCl at $1\,mL\,min^{-1}$. The final Cr(III) concentrations in the extracts were determined by both FAAS and diphenyl carbazide spectrophotometry. The repetitive usability of the resin was tested by batchwise contact of 10 mL of a $25\,\mu g\,mL^{-1}$ Cr(III) solution with 0.1 g sorbent at pH 4.5 and desorbing the retained Cr(III) with 0.05 M HCl. This procedure was repeated 24 times.

Synthetic solutions of possible interferent metal ions, i.e. alkali metal and ammonium cations, common anions, transition and heavy metals, were prepared at varying concentrations in a binary admixture with $1\,mg\,L^{-1}$ of Cr(III) in a total volume of 100 mL and the tolerance limits for these ions were determined, so as not to change Cr(III) retention at pH 4.5 by more than 1%. The eluant was 25 mL of 0.05 M HCl, and both adsorption and elution flow rates were fixed at $1\,mL\,min^{-1}$.

Common interferents of the diphenyl carbazide (DPC) colorimetric assay identified as Fe(III), Cu(II), and Hg(II) cations and VO_3^-, MoO_4^{2-}, and WO_4^{2-} anions by Llobat-Estelles [12] were tested in the developed assay as follows: 10 mL each of 100 mg L^{-1} stock solutions of VO_3^-, MoO_4^{2-}, and WO_4^{2-} (as sodium salts) were mixed; Cr(III) was added to yield a final concentration of 1 mg L^{-1}, the pH was adjusted to 4.5, the solution diluted to 100 mL with water, and then the solution passed through the NH_4Ac-saturated sorbent column at a rate of 1 mL min^{-1}. The retained Cr(III) was eluted with 25 mL of 0.05 M HCl and determined by DPC colorimetry. For the study of cation interference, 10 mL each of 100 mg L^{-1} stock solutions of Fe(III), Cu(II), and Hg(II) (as sulphate salts) was mixed; Cr(III) was added to yield a final concentration of 1 mg L^{-1}, 10 μL of pure thioglycolic acid (TGA) was added at a pH of 6.5 to mask the interferents, and finally the solution was diluted with water to 100 mL. The mixture was passed through the sorbent, and the retained Cr(III) was eluted, as described in the study of anion interference.

2.3 *Recommended procedure for Cr speciation analysis*

The water-soaked resin (XAD-shellac) of dry mass 2.5 g was filled in a 25 mL burette (of diameter 1 cm) supported over a glass wool plug and yielded a height of 10 cm. The resin column was thoroughly washed with 0.1 M ammonium acetate, and then with enough water. A suitable volume (up to 1.5 L) of a Cr(III) solution of concentration exceeding the quantitation limit of 3.3 ng mL^{-1} was brought to pH 4.5 using 0.1 M aqueous ammonia or HCl and passed through the resin bed at a flow rate not exceeding 1 mL min^{-1}. The column-retained Cr(III) was eluted with 20–25 mL of 0.05 M HCl at a flow rate not exceeding 1 mL min^{-1}, and analyzed by diphenylcarbazide spectrophotometry or flame-AAS. Cr(VI), if present in the original mixture, was not retained at all in the first column and existed totally in the solution leaving the column. This Cr(VI) solution was brought to pH 1 by the addition of 1 M sulphuric acid, and reduced to Cr(III) using 0.1 M sodium sulphite. After pH adjustment to 4.5, this solution was passed through a second resin column presaturated with ammonium acetate, and the retained Cr(III)—as the reduction product of Cr(VI)—was eluted and determined as described for original Cr(III).

2.4 *Analysis of complex samples*

Typical synthetic wastewater solutions (solutions A and B) were prepared according to the compositions indicated in the literature [31, 32] listed in table 1, and these synthetic solutions imitated Cr-plating industrial effluents and mixed plating rinse wastewaters widespread in India (Aligarh) and Malaysia. Each of these solutions was subjected to Na_2SO_3 reduction of the hexavalent chromium, adjusted to pH 4.5, and passed through the XAD-shellac resin to recover total Cr as Cr(III) as previously described. Solution A—containing free cyanide—was brought to pH 10 with 0.1 M NaOH, and the cyanide content (5.55 mg L^{-1} CN^- or 10.46 mg L^{-1} NaCN) of 1 L of solution was left to oxidize overnight with 7 mL of 0.1 M NaOCl. Then, the solution was acidified with H_2SO_4 and total Cr reduced with Na_2SO_3 as described earlier. The final solution containing Cr(III) was passed through the resin bed at pH 4.5. Solution B was prepared by adding 44 mg L^{-1} Cr(VI) and 4.5 mg L^{-1} Cr(III) to achieve a total Cr concentration

Table 1. Compositions of typical[a] Cr-electroplating wastewater samples synthetically prepared in the laboratory.

	Solution A [31]	Solution B [32]
Cu ($mg\,L^{-1}$)	–	
Ni ($mg\,L^{-1}$)	–	
Zn ($mg\,L^{-1}$)	7.36	
Cr(VI) ($mg\,L^{-1}$)	7.77	44
Na ($mg\,L^{-1}$)	–	
K ($mg\,L^{-1}$)	–	
Ca ($mg\,L^{-1}$)	–	
pH ($mg\,L^{-1}$)	6.63	3.1
Hardness (as $CaCO_3$)	63.76	
Cyanide ($mg\,L^{-1}$)	5.55	
Total Cr ($mg\,L^{-1}$)	8.25	48.5
COD[b] ($mg\,L^{-1}$)		100
TDS[c] ($mg\,L^{-1}$)	424	730

[a]Plating bath and mixed rinse effluents were typical of Indian and Malaysian Cr-plating industries, as indicated in literature sources [31, 32].
[b]COD was adjusted with glucose (COD: chemical oxygen demand).
[c]TDS was adjusted with Na_2SO_4 with compensation for $CaCO_3$ or total Cr where applicable (TDS: total dissolved solids).

of 48.5, and 113 $mg\,L^{-1}$ glucose was added to adjust a COD (chemical oxygen demand) value of 100 $mg\,L^{-1}$. The organic content of this solution was oxidized with UV-irradiated ammonium peroxydisulphate ($(NH_4)_2S_2O_8$) degradative procedure [33]. To 1 L of the synthetic solution were added 12.5 mL of 1 M $(NH_4)_2S_2O_8$ prepared in 0.1 M H_2SO_4 solution, and the sample was oxidized for 6 h under UV irradiation. When oxidation was complete, Na_2SO_3 reduction of total Cr was carried out in the already acidic (H_2SO_4-containing) solutions, pH adjusted to 4.5 with aqueous NH_3, diluted as required, and passed through the resin bed at a flow rate of 0.5 $mL\,min^{-1}$. All eluted Cr analyses (using 0.05 M HCl at a rate of of 0.5 $mL\,min^{-1}$) were carried out with FAAS and spectrophotometry.

A lyophilized standard sample of CRM-544 containing 26.8 $\mu g\,L^{-1}$ of Cr(III) and 22.8 $\mu g\,L^{-1}$ of Cr(VI) in 0.05 M carbonate ($H_2CO_3/NaHCO_3$) buffer at pH 6.4 was prepared in the laboratory according to the procedure described in the literature [34]. Since the salt tolerance of shellac-derivatized sorbent was not high, this solution was diluted to a final carbonate concentration of 250 $mg\,L^{-1}$ and passed through the sorbent column at a rate of 1 $mL\,min^{-1}$. After the Cr(VI)–Cr(III) reduction of the final mixture solution with Na_2SO_3 in acidic medium, the solution was passed through a second column, and the Cr recoveries of both Cr(III) and Cr(VI) species were reported.

As for certified reference materials (CRMs) analysis, SO-2 soil (containing $16 \pm 2\,\mu g\,Cr\,g^{-1}$), San Joaquin soil (NIST-SRM 2709) ($130 \pm 4\,\mu g\,Cr\,g^{-1}$), and sewage sludge BCR-145R ($307 \pm 13\,\mu g\,Cr\,g^{-1}$) reference materials were dried in a vacuum desiccator; the SO-2 soil was weighed 0.5 g, and the other two samples 0.1 g each. Five millilitres of hydrofluoric acid and 5 mL of perchloric acid were added to each sample, and evaporated three times at 200°C in a Teflon crucible placed on a sand bath. The last evaporation was made with $HClO_4$ alone. Aqueous ammonia (2 M) and H_2O_2 (5%) were added to oxidize the Cr content to Cr(VI) and evaporated to dryness. The residues were taken up with water, the precipitates containing ferric hydroxide were filtered and washed on the filter paper with water, and the washings were combined

with the filtrate. The clear solution was weakly acidified with H_2SO_4 and diluted to 100 mL with water. The sewage sludge BCR 145R sample was evaporated to dryness with two successive 5 mL portions of concentrated nitric acid; the residue was weakly acidified with H_2SO_4 and diluted to 100 mL with water. Twenty-five millilitre aliquots were withdrawn from the supernates of each reference sample solution, and the Cr(VI) contents of the solutions were reduced with 1 M sodium sulphite at pH 1 (pH adjustment being made with H_2SO_4 when necessary). The solution pH was brought to 4.5 by dropwise addition of 2 M aqueous ammonia and diluted to volume in a 100 mL flask with water. These solutions were passed through the resin column at 0.5 mL min^{-1} and eluted with 25 mL of 0.05 M HCl as described earlier. The Cr(III) contents of the eluates were analyzed with FAAS.

3. Results and discussion

The IR spectra of shellac-derivatized XAD sorbent (figure 1) confirms that impregnation is complete (the carbonyl band at 1725 cm^{-1} due to shellac carboxylic acids appears in the spectrum of derivatized sorbent). The Langmuir adsorption isotherm of shellac on XAD-16 copolymer (figure 2) demonstrates that about 84 mg of shellac g^{-1} resin is sorbed at saturation.

Amberlite XAD-16 was selected because it is highly stable in both acidic and basic solution, exhibits an adequate surface area, and is appropriate for column use with numerous repetitive cycles utilizing strong acidic eluents without degradation or loss

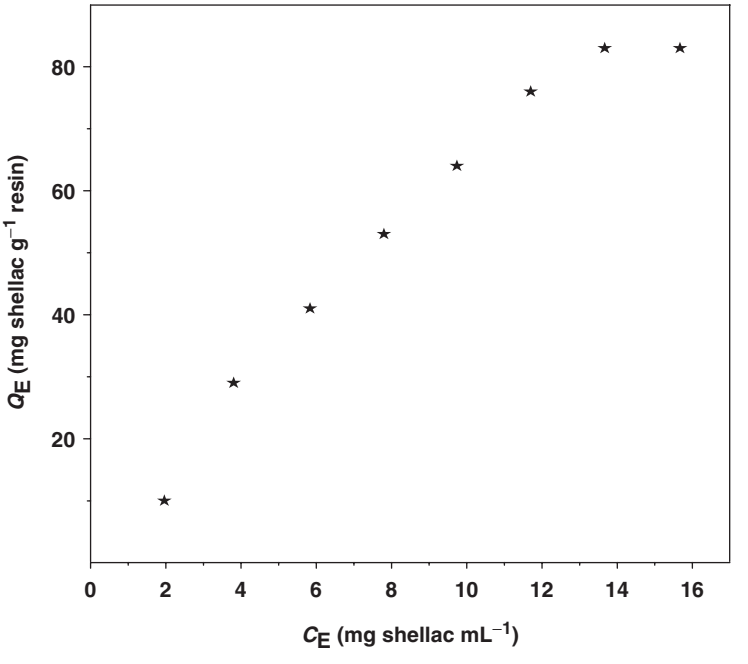

Figure 2. Adsorption isotherm of shellac on XAD-16.

of performance [35]. The suitability of XAD-16 to solid-phase extraction was attributed to its good physical and chemical properties such as porosity, uniform pore distribution, high surface area, and satisfactory adsorptive properties in terms of favourable surface chemistry [36].

Preliminary experiments showed that complex fractionation of shellac with sequential solvent extraction [37], where each resin constituent would show an affinity toward a different organic solvent, could not maintain its favourable Cr(III)-adsorptive properties when immobilized on a XAD copolymer. Since shellac was immobilized on XAD from its alcoholic solution, the simple procedure comprising EtOH dissolution, followed by filtration and vacuum evaporation of the filtrate, was chosen as the appropriate method of shellac purification.

The adsorption of Cr(III) on XAD-shellac sorbent (figure 3) as a function of pH shows that complete adsorption is achieved at pH 4.5. One hundred millilitres of 1 μg mL^{-1} Cr(III) was quantitatively retained by the sorbent, whereas 100 mL of 10 μg mL^{-1} Cr(VI) was not retained at all between pH 4 and 5, showing selectivity of sorbent to Cr(III) (see figure 3). Since hydrolytic equilibria of Cr(III)-species prevail at a higher pH, it is recommended that the working pH be maintained between pH 4.5 and 5.5 for efficient recovery. At this pH, up to 50 μg Cr(VI) mL^{-1} in the preconcentration/analysis of 1 μg Cr(III) mL^{-1} did not interfere, provided that the XAD-shellac sorbent be presaturated with NH_4Ac. This presaturation is thought to neutralize the cationic surface sites (RH^+) responsible for CrO_4^{2-} uptake with a favourable equilibrium reaction:

$$RH^+ + CH_3COO^- \leftrightarrow R + CH_3COOH.$$

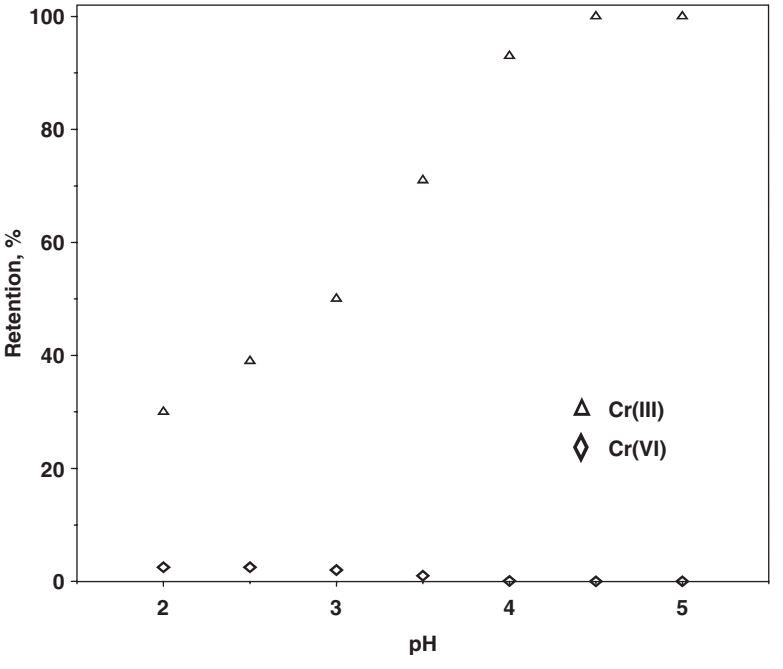

Figure 3. Retention of Cr(III) and Cr(VI) on the XAD-shellac sorbent as a function of pH (100 mL of 1 μg of Cr(III) mL^{-1}, 100 mL of 10 μg Cr(VI) mL^{-1}).

The formation of a weak acid (CH_3COOH) may shift the above equilibrium to the right, neutralizing surface RH^+, and thereby inhibiting anion retention. In this way, the derivatized resin is tailored to retain only the Cr(III) cation among different oxidation states of chromium, enabling Cr speciation analysis.

Batch adsorption studies carried out at the optimal pH of 4.5 for 2 h showed with the aid of a Langmuir isotherm that the batch capacity of XAD-shellac for Cr(III) is about 0.9 mg g^{-1} (figure 4). On the other hand, the breakthrough curve of Cr(III) for the derivatized sorbent studied in the dynamic column mode (figure 5) with adsorption and elution rates less than or equal to 1 mL min^{-1} yielded a dynamic capacity of 0.3 mg g^{-1}. The relative magnitudes of batch and dynamic capacities indicate that Cr(III) uptake by XAD-shellac is essentially through surface complexation (chelation ion exchange) of Cr(III) with the hydroxy carboxylic acid functional groups of shellac, and such reactions require time for equilibration. The derivatized sorbent probably behaves as a weakly acidic, chelating cation-exchanger resin toward Cr(III).

Since the batch capacity of the XAD-shellac sorbent was 0.9 mg Cr(III)/g, and at equilibrium, a maximal amount of 84 mg of shellac was shown to be adsorbed by the sorbent, the Cr(III)/shellac binding ratio on a molar basis was: (0.9/52)/(84/1500) = 17.3 μmol/56 μmol = 1 : 3.2. (The mean molar mass of shellac biopolymer was taken as 1500, as in most literature sources.) The Cu-binding capacities of dissolved organic matter (DOM) and bacterial extracellular polymers (BEP) were around 0.2 and 0.3 mmol g^{-1}, respectively [38], which were close to the Cr capacity of adsorbed shellac in the same units (i.e. 0.2 mmol Cr(III)/g of shellac sorbed on XAD). Naturally, this Cr(III) binding stoichiometry applies for XAD-bound shellac, which is the more

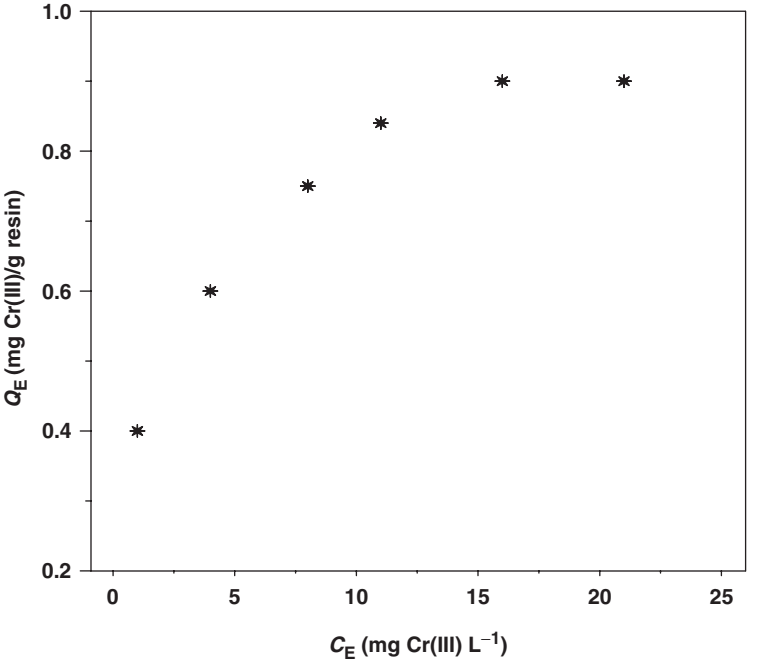

Figure 4. Langmuir adsorption isotherm of XAD-shellac sorbent for Cr(III) (pH: 4.5, 10 mL solution contacted with 0.1 g sorbent for 2 h).

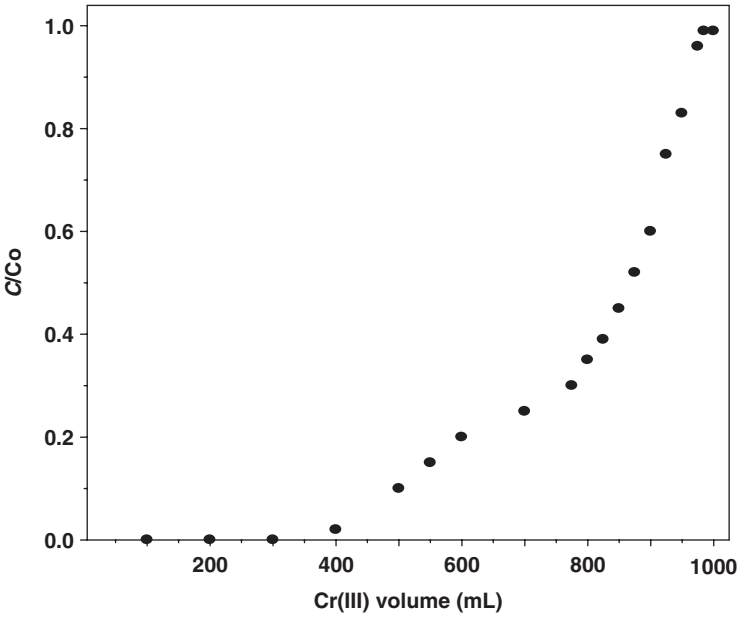

Figure 5. Breakthrough curve of Cr(III) for XAD-shellac sorbent.

important one in resin preconcentration applications, and not for pure shellac in ethanolic solution. Thus, some functional groups of shellac may have been used for anchoring to XAD resin, and the rest for Cr(III) binding. It should be borne in mind that free polymers in solution (e.g. polycarboxylates) may condense in the presence of metal ions when the charge density of the polymer exceeds a critical value [39]. Therefore, the maximal binding ratio of polymer to metal may not be easily found experimentally for polymers in solution, and the observed stoichiometries may not correspond to those found for adsorbed polymers.

The effect of interferences of common ions is depicted in table 2; alkali metal cations, ammonium, and common anions (the latter due to suppressing of cationic surface sites) do not interfere with the retention of $1\,mg\,L^{-1}$ Cr(III) at 250-fold (by mass) concentrations. However, certain transition metal cations interfere, as these ions are tolerated only at 1 : 1 mass ratios. Possibly, the hydroxy carboxylic acid functional groups of shellac also act as a strong chelating cation exchanger toward these cations at the optimal pH of Cr(III) retention. A good application of the method to complex samples would be soda (Na_2CO_3) precipitation of cationics, neutralization, Cr(VI) reduction with Na_2SO_3, and passage through the resin column such that common anions would not interfere with the determination of reduced chromium.

Study of common interferents to DPC colorimetry revealed that a mixture of cationic interferents containing tenfold Fe(III), Cu(II), and Hg(II)-after masking wth TGA at a mole ratio of 2 : 1 did not interfere with retention/colorimetric determination of Cr(III); however, the Cr(III) recovery remained at approximately 87.5%. On the other hand, anion interference was not observed as a mixture of tenfold VO_3^-, MoO_4^{2-}, and WO_4^{2-} yielded 98% Cr(III) recovery efficiency. These observations confirmed that typical interferents to DPC colorimetric assay of chromium did not significiantly inhibit preconcentration/determination of Cr(III) in the standard method practice.

Table 2. Study of interferences of common ions on the adsorption of Cr(III) on XAD-shellac sorbent (100 mL of 1 μg Cr(III) mL^{-1}).

Interfering ion	Concentration ($\mu g\,mL^{-1}$)	Cr recovery
Na^+	250	99.9
NH_4^+	250	100
Fe^{3+}	1	100
Cu^{2+}	1	100
Ni^{2+}	1	100
Cd^{2+}	1	100
Pb^{2+}	1	100
Ca^{2+}	1	100
Zn^{2+}	1	100
Mg^{2+}	1	100
Cl^-	250	99.9
NO_3^-	250	99.9
SO_4^{2-}	250	100
HCO_3^- [a]	250	100
CH_3COO^- [a]	250	99.3
$H_2PO_4^-$ [a]	250	100.1

[a]The pH of the binary solution is adjusted to pH 4.5, partially converting the weakly basic anion to its conjugate acid.

Table 3. Statistical data for comparison of the proposed method with reference methods (100 mL of 1 μg Cr mL^{-1} was used at pH = 4.5, $N = 5$).

Parameter	Reference method 1 (sorbent: XAD-oxinate)	Reference method 2 (sorbent: XAD-maleic)	Proposed method (XAD-shellac)
Cr(III) recovery (%)	99.98	99.96	99.94
SD (σ)	8.37×10^{-2}	8.94×10^{-2}	8.94×10^{-2}
Variance (σ^2)	7.0×10^{-3}	8.0×10^{-3}	8.0×10^{-3}
$t_{0.95}$ (df = 8)	$0.73 < 2.31$	$0.37 < 2.31$	–
$F_{0.95}$ ($df_1 = df_2 = 4$)	$1.14 < 9.61$	$1.0 < 9.61$	–
Cr(VI) recovery (%)	99.90	99.92	99.80
SD (σ)	0.187	0.130	0.158
Variance (σ^2)	3.50×10^{-2}	1.70×10^{-2}	2.50×10^{-2}
$t_{0.95}$ (df = 8)	$0.91 < 2.31$	$1.31 < 2.31$	–
$F_{0.95}$ ($df_1 = df_2 = 4$)	$1.4 < 9.61$	$1.47 < 9.61$	–

Table 3 shows that comparison of the means of the two samples (as Cr recovery, %) found via a pooled estimate of standard deviation led to the acceptance of the null hypothesis; the sample variances were also compared at the 95% significance level. These tests revealed that either sample means or variances (binary comparisons of the proposed method with XAD-oxinate or XAD-maleate singly) did not differ significiantly, and the XAD-shellac was as accurate and precise for trace Cr(III) preconcentration/determination as the XAD-oxinate [16] or XAD-maleate [11] sorbents.

Results of Cr analyses of reference materials with the proposed procedure (in comparison with declared amounts or findings of standard analytical methods), as depicted in table 4, confirm the accuracy of the XAD-shellac sorbent preconcentration method for complex reference samples. As for the synthetic lyophilized CRM-544

Table 4. Results of Cr analyses of complex samples by the XAD-shellac sorbent (in comparison with certified amounts or findings of standard analytical methods).

Sample	Certified amount ($\mu g\,g^{-1}$)	Result with standard method ($mg\,L^{-1}$)	Result with XAD-shellac sorbent
SO-2 soil	16 ± 2	–	$13 \pm 1\,\mu g\,g^{-1}$
San Joaquin soil	130 ± 4	–	$121 \pm 4\,\mu g\,g^{-1}$
BCR 145 R sewage sludge	307 ± 13	–	$286 \pm 11\,\mu g\,g^{-1}$
Cr plating-rinsing wastewater	–	Cr(III): $9 \pm 1\,mg\,L^{-1}$ Cr(VI): $260 \pm 8\,mg\,L^{-1}$	Cr(III): $9 \pm 1\,mg\,L^{-1}$ Cr(VI): $261 \pm 9\,mg\,L^{-1}$

Table 5. Operational stability of XAD-shellac resin over extended use (adsorption/elution cycles).

No. of cycles	Leakage of shellac[a] in 0.1 M NH_4Ac soln. $mg\,g^{-1}$-sorbent (%)	Leakage of shellac[a] in 0.05 M HCl eluent $mg\,g^{-1}$-sorbent (%)	Cr(III) sorption[b] capacity of sorbent $mg\,g^{-1}$-sorbent
5	2.5; (3.0)	1.0; (1.2)	0.89
10	2.0; (2.4)	0.45; (0.53)	0.86
15	1.0; (1.2)	0.05; (0.06)	0.85
20	0.06; (0.07)	0.025; (0.03)	0.85

[a]The total shellac leakage after 20 adsorption/elution cycles was 8.5%.
[b]Determined using 100 mL of $1\,mg\,L^{-1}$ Cr(III) solution. The operational capacity was measured under the experimental conditions without reaching saturation.

sample solution buffer, the efficiency of retention was 99.9 and 98.7% for original Cr(III) and hexavalent chromium-reduced Cr(III), respectively, provided that the total carbonate salt was reduced with dilution to less than $250\,mg\,L^{-1}$. The relative standard deviation for analyses carried out in pure solutions and real samples ranged between 0.2% (pure solution) and 3% (real sample soil). However, the proposed method could not be efficiently used for artificial seawater spiked samples, because salt interference could not be overcome due to the predominant cation-exchange mechanism of sorption of XAD-shellac. (The XAD-oxinate and XAD-maleate sorbents developed for Cr(III) preconcentration in the same laboratory [16, 11] was not adversely affected from salt interference because the chelation ion-exchange mechanism was predominant.) The shellac-derivatized sorbent could be effectively used over 20 adsorption–desorption cycles without significantly losing its batch capacity (table 5), provided that low adsorption-elution flow rates and weakly acidic conditions (without causing alkaline hydrolysis/decomposition of shellac) be maintained in recycling, and that the temperature not be raised above 40°C. In general, shellac is a fairly stable natural polymer, aged samples of which have survived even from 15th-century frescoes [40]. Shellac is reasonably stable in acidic-to-neutral media, with an increase in acid value and a decrease in ester value being observable upon mild alkali hydrolysis [41]. Experimental shellac leakage of sorbent after 20 adsorption cycles (with 0.1 M ammonium acetate buffer) was 6.67%, and leakage after 20 elution cycles (with 0.05 M HCl eluent) was 1.82%. Total shellac leakage after 20 adsorption/elution cycles was 8.5%, with a Cr(III) retention capacity loss of $\leq$6% (see table 5).

Alkaline eluant/leachant should not be used to prevent the hydrolytic decomposition of shellac. On the other hand, stronger acid solution—stronger than

0.05 M HCl—should not be used for desorption, because relatively strong acids cause the partial irreversible sorption of Cr(III) on weakly acidic resins [8, 9].

From a theoretical point of view, methods involving selective determination of a single valency of chromium followed by the determination of the other valency (or total chromium) after a redox conversion may be argued to be mathematically less suitable than methods enabling the simultaneous determination of both valencies of Cr because of the propagation of errors, and possible loss of information on chelated and organometallic forms of Cr [21]. However, such examples from the literature, capable of adsorbing and eluting both valencies of Cr at different pH such as alumina microcolumns associated with a FIA-ICP-AES analytical procedure [17], may require high elution volumes of mineral acid or base (aq. NH_3) to quantitatively remove the retained species, and therefore suffer from the resulting high LOD values significantly reducing the ability of the SPE to provide effective sample preconcentration.

The selectivity of most templated resins (gel-type polyethylene imine or imino-diacetate-functionalized Chelex-100) as well as of some hydroxamic acid or polyacrylamide-oxime resins for Cr over other transition-metal cations is not very high, with separation factors centering around 1.0 ± 0.5 [42]. Therefore, selectivity in recovery of Cr (III) may not be easily achieved. The optimal pH range of Cr(III) retention (i.e. pH 4.5–5.5) is also the range for the uptake of other transition and heavy metals, and this explains why low amounts of these interfering ions were tolerated (as low as $1\,mg\,L^{-1}$) in table 2.

4. Conclusion

The basic advantages of the developed method may be summarized as follows:

- high preconcentration factors and low detection limits for Cr(III), allowing direct applicability to natural waters without any appreciable salt contents;
- applicability to both valencies of chromium (i.e. directly to Cr(III), and indirectly to Cr(VI) after reduction of the latter with Na_2SO_3 in weak H_2SO_4 medium);
- applicability of simple and cost-effective DPC colorimetry to the resin column eluate;
- low-cost, non-toxic, and environmentally friendly nature of the shellac-derivatized sorbent as a natural material;
- extended use of the resin (i.e. a long operational life).

The figures of merit of the proposed preconcentration/determination of Cr(III) were as follows: preconcentration factor: 75, $LOD = 1\,ng\,mL^{-1}$ and $LOQ = 3.3\,ng\,mL^{-1}$, providing a high sensitivity. Cr(III) could be preconcentrated/separated from at least 50-fold Cr(VI) on a NH_4Ac-saturated sorbent. (The LOD and LOQ values, calculated as three and ten times the standard deviation of a blank, respectively, divided by the slope of the calibration line, were associated with the whole procedure comprising preconcentration and analytical determination.) Cr(VI) could be assayed separately after Na_2SO_3 reduction at pH 1. Although the developed sorbent is not useful for Cr(III) separation from brackish and sea water, the natural polymer used in derivatization, i.e. shellac, is easily accessible, inexpensive, and nontoxic, and can be coated on XAD copolymer backbone with an environmentally friendly procedure.

Also, the whole cycle of preparation, use, and disposal of the resin does not generate any hazardous chemical wastes. XAD-shellac was useful for assaying Cr in a number of standard reference samples and artificial electroplating wastewater. To the best of our knowledge, this is the first time shellac has been used to modify a sorbent for ionic speciation analysis.

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