

Use of immobilized tannin adsorbent for removal of Cr(VI) from water

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Adsorption of Cr(VI) by two tannin sorbents is evaluated using radiotracers. Evaluation of the sorption process shows that the Cr(VI) – tannin molecule binding is the principal responsible for chromium adsorption. High sorption capacities were registered for both sorbents at pH 2. For *Eucalyptus Saligna* Sm sorbent (ETS) sorption capacity is 0.92 ± 0.03 mmol/g and for *Lysiloma latisiliqua* sorbent (LTS) is 3.8 ± 0.3 mmol/g. Influence of different ions present in water is examined. High sorption capacity is reported for LTS in sea and tap water samples. It represents 90–94% of adsorption in distilled water.

Introduction

Chromium is an important heavy metal pollutant of the aquatic environment. This element can be found in the environment in three oxidation states, but Cr(III) and Cr(VI) are the most important species. While Cr(III) is essential for life, because it participates in different metabolic processes, Cr(VI) is toxic. Its toxicity is related to the high oxidation potential of this species and its irreversible reaction with DNA. That is why, from an analytical point of view, it is important to monitor the individual chemical species and to find a system for the selective adsorption of Cr(VI).

Due to the fact that Cr(VI) may be present in aqueous solution in anionic forms, ion exchange is the most widely used method used for the recovery of this species. Synthetic anion organic^{1–2} and inorganic exchangers as alumina³ and silica⁴ were reported for the preconcentration of Cr(VI). Derivatized cellulose with anionic and cationic groups has been used for the separation of both chromium species previous flow injection analysis.⁵

Plant materials can be used in analytical preconcentration to raise the detection limit. One advantage of using plant derived materials for metal recovery, is that Ca^{2+} or Mg^{2+} and alkali ions do not interfere with the binding of heavy metals.⁶ Tannins are high molecular weight polyphenols that can be found in different parts of the trees but principally, in the bark. Tannins form chelates with metals due to the presence of a great number of adjacent hydroxyl groups in their molecules. They are water soluble and for using them as sorbent they must be immobilized.^{7,8}

In the early stage of this work, we studied the sorption capacity for metal recoveries of several forest species that grow in Cuba. Best results were obtained

with tannins from *Eucalyptus Saligna* Sm (ES) and *Lysiloma latisiliqua* (LL).^{9,10}

This paper describes the adsorption behavior of Cr(VI) on two sorbents from LL and ES tannins. The adsorption parameters were studied using ⁵¹Cr as a radiotracer. The simplicity and rapidity of the radiotracer methods allowed to perform a great number of experiments in a short time.

Experimental

Adsorbent synthesis

Eucalyptus Saligna Sm tannins were immobilized onto spherical cellulose. A well known method in affinity chromatography for ligand immobilization is the matrix epoxiactivation. Figure 1 shows the synthesis steps, that also include the interposition of space arm allowing solute-stationary phase interactions.

The employed matrix was spherical cellulose supplied by Cuba 9 Enterprise (Havana City, Cuba) that was a white colour powder with high porosity and good mechanical properties. The cellulose was sifted and the 0.075–0.16 mm fraction was used for immobilization.

A crude tannic extract was obtained from bark with water in a reactor with controlled temperature. The extract was filtered and concentrated in a hot plate to 15 mg/l. For matrix activation 1,2 epoxi-3 chloropropane, with a density of 1.18 kg/l from Riedel-de Haën was used. The activation mechanism also includes the use of 1,6-hexanodiamine from Sigma as space arm. Approximately 500 ml of tannin extract was mixed with 20 g of epoxiactivated cellulose in a reactor in nitrogen atmosphere at 313 K during 24 hours. The brown coloured sorbent was filtered and washed with 1 m/l HCl, distilled water and air dried.

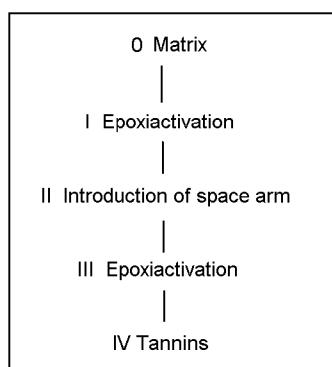


Fig. 1. ETS synthesis steps

Lysiloma latisiliqua B (LL) tannins were immobilized by non linear polycondensation with formaldehyde. Tannins were extracted from bark in a reactor with water at 363 K and lyophilised. The obtained product was characterized using STIASNY's method.¹¹ 64±3% of reactive phenols were detected in the tannic extract.

Spherical resins from LL were obtained as follows: tannic extract and formaldehyde of analytical degree from Merck were mixed in a reactor with controlled temperature and stirred during 3 hours. A solution of polyethylene in xilene of desired viscosity was used as dispersion medium to obtain spherical shape grains. The resin was separated from the reaction mixture, washed twice with xilene and water and air dried. Physical properties of the obtained sorbents are shown in Table 1.

Adsorption experiment

The ⁵¹Cr (*T*_{1/2}=27.7 days), supplied by the IEA-1 reactor of the Instituto de Pesquisas Energéticas e Nucleares, (Sao Paulo, Brazil) was used for sorption studies. Radioactivity was measured using an SR-7 radiometer with a well type NaI(Tl) detector from Nuclear Enterprise.

Stock solutions containing the desired concentration of Cr(VI) and Cr(III) were prepared from Merck K₂Cr₂O₇ and metallic Cr, respectively. Solutions of 100 mg/l were prepared diluting stock solutions. Aliquots of the radioisotope were added to obtain good background/signal rates. All reagents used were of analytical grade.

Table 1. Properties of resins

Material	Shape of particles	Size range, mm	Bulk density, g/cm ³	Swelling, g _{water} /g _{resin}
ETS	Spherical	0.075–0.16	0.66	0.15
LTS	Spherical	0.351–0.991	0.36	0.24

Batch sorption experiments were conducted at room temperature. 10 ml of labeled chromium solutions were shaken with the desired mass of resins during 24 hours. Three aliquots of 1 ml of supernatant were collected and the radioactivity was measured in the detector.

Chromium adsorption was evaluated using the expression:

$$q = \frac{V \cdot (C_i - C_f)}{m_R} \quad (1)$$

where *q* is chromium adsorption in mg/g, *V* is the volume of supernatant solution in liter, *m_R* is resin mass in g, *C_i* is the concentration of initial solution in mg/l, *C_f* is the concentration of final solution in mg/l.

C_f was calculated as follows:

$$C_f = \frac{C_i - I_f}{I_i} \quad (2)$$

where *I_i* and *I_f* are radioactivity in cps of 1 ml of the initial and final solutions.

The effect of the pH of the suspending medium was studied performing equilibrium sorption test at different pH values. The pH was adjusted with 0.1 mol/l NaOH and HNO₃. 0.03 g of each sorbent was weighed into individual 25 ml bottles and 10 ml of 100 mg/l of chromium radioactive solution has been added.

For kinetic experiments contact times of 0.5 to 72 hours were used. Batch experiments were also performed at 343 K in short contact times (from 5 to 50 min). The bottles were filled as described above and shaken in a water bath with controlled temperature.

Sorption isotherms were obtained using batch experiments by varying sorbent masses between 0.01–0.08 g at 298 K and pH 2.

The effect of NaCl on Cr(VI) adsorption was studied varying salt concentration from 200 to 30 000 mg/l at an initial concentration of 100 mg/l of Cr(VI). For Ca²⁺, concentrations from 20 to 100 mg/l of this cation were used.

Column studies

Column experiments were performed using a polypropylene column of 8 mm×100 mm with 2 g of resin and with a flow rate of 1 ml/min. Effluent aliquots of 1 ml were collected and the radioactivity was registered.

Cr(VI) desorption was studied in columns of polypropylene of 6 mm×20 mm. 2 ml of labeled Cr(VI) solution at pH 2 was passed through the column with a flow rate of 0.5 ml/min. The column was washed with distillate water until the effluent activity was near

background. The column was introduced in the detector and the initial activity was measured (I_i). The elution systems in Table 4 were used for Cr(VI) desorption with a flow rate of 1 ml/min and aliquots of 1 ml were collected. When the activity of aliquots was near background, the final column activity (I_f) was registered. Elution rates were calculated according to:

$$R = [1 - (I_f/I_i)] \times 100\% \quad (3)$$

Tap water samples were collected in our laboratories. Sea water was from Havana north coast and river water was from Almendares River in Havana, Cuba. All water samples were filtered using a Millipore filter with 0.45 μ m pore size. Labeled Cr(VI) aliquots were added to obtain solutions of 100 mg/l of Cr(VI), the pH was adjusted to 2 with 0.1 HNO₃ and batch experiments carried out by suspending 0.03 g of each resin. Some water properties are shown in Table 2.

Table 2. Properties of used water

Water	Conductivity, μ S/cm	Salinity, $^{\circ}$ Be
Distilled water	0.5	0
Tap water	730	0.1
River water	798	0.1
Sea water	52.6*	3.4

* mS/cm.

Results and discussion

Figure 2 shows the adsorption behavior of Cr(VI) and Cr(III) on both sorbents at different pH values. The batch procedure was used to obtain adsorption data in mg/g. The radioactivity of supernatant solutions was measured and the chromium adsorption was evaluated using Eq. (1).

The sorption of both species, Cr(VI) and Cr(III) is pH dependent. However, their behavior is quite different, Cr(VI) anion has an adsorption maximum at pH 2 and then the sorption capacity decreases as pH increases. ETS practically does not adsorb Cr(VI) at pH > 8 and LTS adsorbs 1/5 of the maximum adsorption. This behavior of Cr(VI) at low values is similar to that reported for the adsorption of this species by biomass.⁶

At pH 2, Cr(III) uptake is low for both sorbents and grows till pH near hydrolysis (4.05). At higher pH values the Cr(OH)₃ precipitates and sorption experiments can not be done. This increment of metal uptake with pH in tannin resins was already reported for other cations as Hg²⁺, Cd²⁺^{9,10} and UO₂²⁺.^{7,10}

Due to the fact that immobilized tannins were obtained from crude extracts and not from chemical pure reagents their chemical structure can not be clearly

known. However, it is evident that *Eucalyptus Saligna* Sm tannin is a mixture of 60–70% of hydrolyzable tannins and the other 30% are condensed tannins formed for proanthocyanidines of resorcinolic origin. The *Lysiloma latisiliqua* B tannins are mainly condensed tannins of resorcinolic type.¹²

Although carboxylic and amine groups could be present in the tannin structure, the hydroxyls are the most important functional groups present and can be expected that they are responsible for metal binding.⁷

The adsorption of Cr(III) and other cations on tannin resins can be explained by metal chelation involving adjacent hydroxyl groups of the tannin phenolic molecules. This complexes become more stable at higher pH values as phenols are very weak acids and the protonation of R-OH groups increases with the pH value.

It is not clear what the mechanism of binding the Cr(VI) anion is. The results in Fig. 3 suggest an important participation of the tannin molecules in the binding. Here the adsorption of Cr(VI) in different synthesis steps is examined.

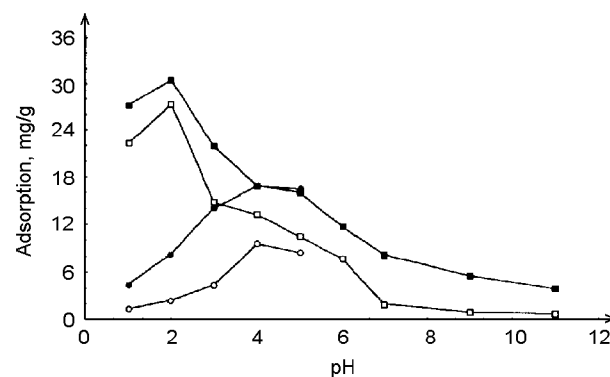


Fig. 2. Effect of solution pH on Cr(VI) and Cr(III) uptake by tannin resins, ■ Cr(VI)LTS, □ Cr(VI)ETS, ● Cr(III)LTS, ○ Cr(III)ETS

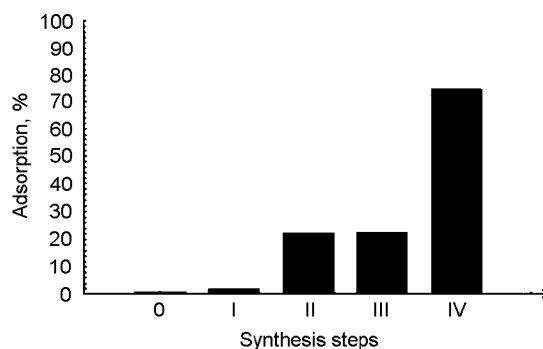


Fig. 3. Adsorption of Cr(VI) in the synthesis steps of ETS. Steps: 0 – spherical cellulose, I – epoxiactivated cellulose, II – introduction of space arm, III – epoxiactivated cellulose, IV – tannin added

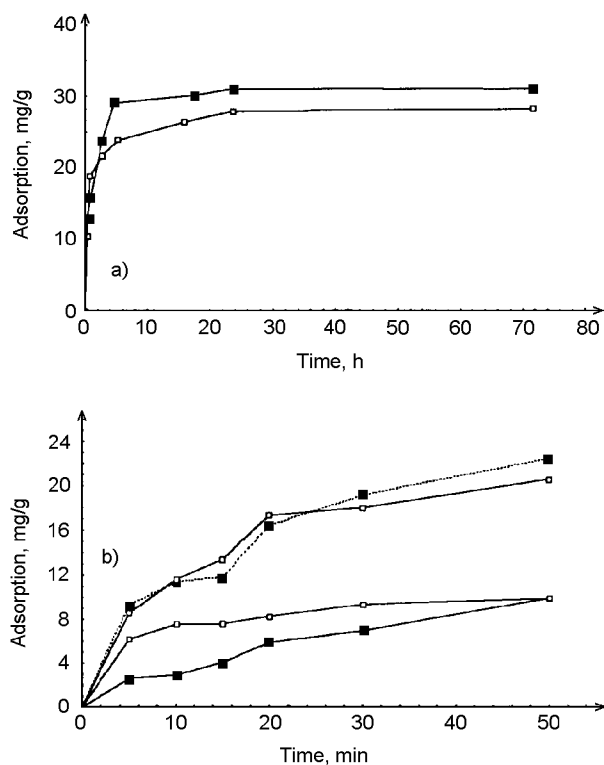


Fig. 4. Adsorption of Cr(VI) at pH 2 as a function of time; a – long contact times, b – short contact times; ■ Cr(VI)LTS, □ Cr(VI)ETS; — 298 K, ----- 343 K

No adsorption is registered when Cr(VI) solutions are in contact with the spherical cellulose and epoxiactivated cellulose in the steps 0 and I of Fig. 3. However, when the space arm is introduced the derivatized cellulose starts to retain the ion. Hexavalent chromium in diluted solutions is present in several anionic forms³ and the adsorption in the second and third step is due to an ion exchange mechanism on the amine groups of the 1,6 hexanodiamine. The derivatized cellulose from step II has an adsorption capacity of 0.16 ± 0.02 mmol/g of dry resin. This value is comparable with that reported for commercially available cellulose with quaternary amine functional groups.⁵

The adsorption of Cr(VI) ions in step II and III of Fig. 1 is approximately 1/3 of the adsorption of the sorbent obtained after the addition of the tannin molecules (step IV). The great increment of the uptake after the addition of tannin demonstrated that the principal responsible of the adsorption is in fact the tannin molecule. This explains the similar behavior of adsorption of both sorbents with the pH value despite that they were synthesized using different methods. The difference in uptakes of chromium(VI) and (III) species at pH 2 suggests that sorbents can be used for chromium speciation.

The sorption kinetic curves shown in Fig. 4 are characterized by three regions; a rapid initial uptake, deceleration and a plateau corresponding to equilibrium conditions.

As shown above, the shape of adsorption curves at different pH values does not depend on the immobilization reaction or on the type of tannin used. In contrast, the kinetic curves are different for each sorbent.

For LTS at 298 K the adsorption grows linearly, and after 50 minutes the 32% of Cr(VI) in its equilibrium capacity at 72 hours (Fig. 4a.) has been adsorbed. On the other side, ETS adsorbs around 30% of its ultimate uptake very rapidly (less than 10 min) and after that the sorption grows very slowly to reach equilibrium.

This behavior shows that two mechanisms account in the binding of Cr(VI) in ETS. One rapid, that can be related to ion exchange in the anionic exchange groups of the 1,6 hexanodiamine and an other slower which is the interaction between metal and tannin molecules. When the temperature of the system increases (Fig. 4b) the shape of both kinetic curves become similar, and the Cr(VI) uptake increases more rapidly. This indicates that the binding of Cr(VI) with tannin is favoured by temperature.

Figure 5 shows the adsorption isotherm for both sorbents. Experimental data were fitted using the Freundlich equation:¹²

$$q(\text{mg/g}) = K_F \cdot C_{\text{eq}}^{\alpha} \quad (4)$$

where K_F is the Freundlich constant, α the Freundlich exponent and C_{eq} the concentration of Cr(VI) in equilibrium supernatant solution.

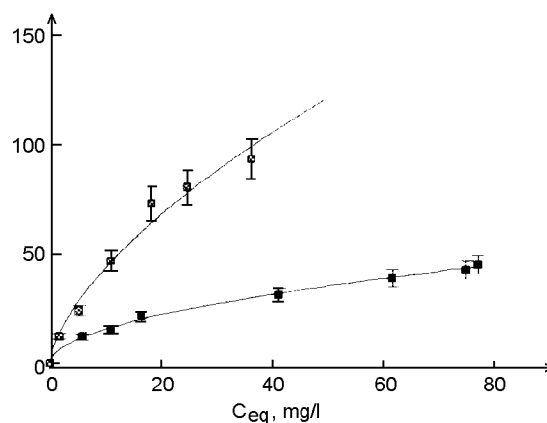


Fig. 5. Freundlich isotherms for Cr(VI) at 298 K, pH2; ■ ETS, □ LTS

Table 3. Freundlich isotherm parameters

Resin	K_F	α	χ^2	q_{max} , mmol/g
LTS	8.69	0.680	0.894	3.8 ± 0.3
ETS	4.90	0.496	0.810	0.92 ± 0.09

Table 4. Scatchard parameters

Resin	Equilibrium constant	Total Cr(VI) adsorption sites, mmol/g
ETS	2.2±0.3	1.11±0.08
LTS	2.8±0.5	3.0±0.3

The curvature and Freundlich parameters in Table 3 indicate a favourable sorption process, the maximum sorption capacities calculated as upper limit solid phase concentration are also shown.

The Scatchard plot, which can be used to obtain binding parameters and calculate equilibrium constants¹³ is shown in Fig. 6. The plot q/C_{eq} versus q is a straight line and its slope $-K_{eq}$ is the equilibrium constant value. The x axis intercepts represent the mmol of total Cr(VI) adsorption sites per gram of resin (P_0). The Scatchard model assumes that the binding is a simple reversible bimolecular reaction that obeys mass action laws. Though it is not clear at this time which model correctly describes the Cr(VI) tannin adsorption process, some binding parameters can be used for qualitative analysis.

Table 4 shows the Scatchard parameters. As seen, there is not difference between the equilibrium constants of Cr(VI) adsorption for ETS and LTS. This indicates similar binding mechanism for both materials. However, LTS has 3 times more binding sites than the ETS resin. This can be related with the immobilization method. In ETS, the anchoring of tannin ligands in the cellulose structure is limited by the epoxiactivated sites, whereas in LTS the body of resin grain is formed by polycondensed tannin molecules and it can be expected that more sites are available for the Cr(VI)-tannin interaction.

Figure 7 shows the sorption of Cr(VI) when NaCl is in the supernatant solution. For Cr(VI) adsorption on LTS, any influence of NaCl in a wide concentration

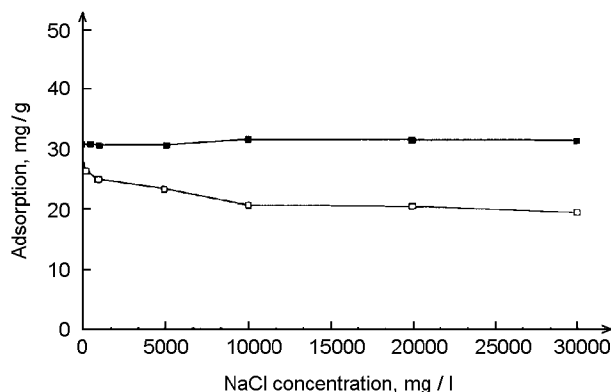


Fig. 7. Influence of NaCl on Cr(VI) adsorption; ■ LTS, □ ETS

range is observed. However, for ETS, the adsorption of Cr(VI) decreases as the concentration of salt in supernatant solution increases, but only until a certain NaCl concentration, after which an increase in salt concentration do not produce any change in Cr(VI) adsorption. For large NaCl values the Cr(VI) adsorption was 69.25% of the uptake in distilled water.

This behavior of Cr(VI) adsorption on ETS corroborates that two mechanisms are present in the Cr(VI) uptake. Approximately 30% of chromate anions compete with the Cl^- for the ionogenic groups of 1,6 hexanodiamine and the other 70%, which is binding to tannin, is retained by the sorbent even in high NaCl concentrations.

Breakthrough capacities were calculated using the binding profile from Fig. 8. For ETS 0.608 mmol/g was the breakthrough capacity calculated as 50% of equilibrium binding capacity. For LTS the same column experiments were conducted and 1.85 mmol/g was the breakthrough capacity. From Fig. 8, it can be seen that approximately 100 ml of a 100 mg/l solution of Cr(VI) can pass through this small column before the breakthrough value is exceeded.

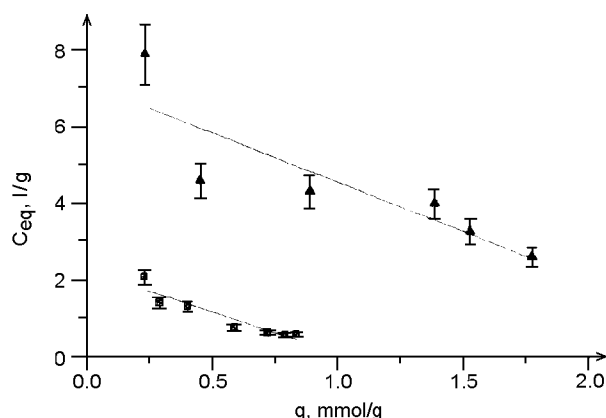


Fig. 6. Scatchard plot for Cr(VI); ■ ETS, ♦ LTS

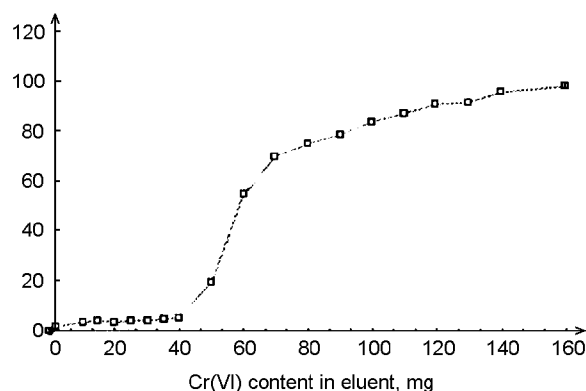


Fig. 8. Breakthrough curve for Cr(VI) adsorption on ETS

Table 5. Elution of Cr(VI) from columns

Elution system	Recovery, %	Recovery, %
HONH ₃ Cl 10% Oxalic acid 0.02 m/l	32.6	–
HONH ₃ Cl 10% EDTA 0.5 m/l	32.6	–
HONH ₃ Cl 10% EDTA 0.25 m/l	75.3	51.5
363 K, pH 5		
HONH ₃ Cl 10% EDTA 0.25 m/l	73.28	47.0*
363 K, pH 6		

* 328 K.

Table 6. Cr(VI) uptakes in real water samples

Water sample	Sorption capacity, mg/g	Sorption capacity,* mg/g
	ETS	LTS
Distilled water	27.4±0.3	30.9±0.3
Tap water	17.7±0.2(0.64)	28.9±0.3(0.94)
River water	14.9±0.1(0.55)	24.6±0.2(0.80)
Sea water	17.6±0.2(0.64)	27.0±0.3(0.90)

* In parentheses Cr(VI) uptake in water/Cr(VI) uptake in distilled water.

In Table 5, recoveries of chromium with the more successful elution system is given. With other elution agents as Na₂CO₃ (5%), phosphate buffer at pH 9, carbonate buffer at pH 9 and ascorbic acid the recoveries were smaller.

Looking at Fig. 1 it can be suggested that if Cr(VI) adsorption is pH dependent, an increase of the pH can desorb the metal from the column. However, using elution systems with pH > 9 the recoveries were always less than 30% for ETS and even smaller for LTS. The desorption strategy has to use a combination of reducing and complexing agents. Hydroxylammonium chloride was selected as reducing agent and oxalic acid and ethylenediaminetetraacetic acid (EDTA) as complexing agents.

At room temperature small recoveries were registered with the chosen eluents. Only at 363 K recoveries were improved. But even in this condition only 50–75% of chromium could be removed. This suggest a strong binding reaction between Cr(VI) and tannin molecules.

Cr(VI) uptakes in real water samples are shown in Table 6. For ETS, the adsorption capacities in tap and sea water are similar, though salinity of sea water is 34 times greater. This behavior is in agreement with the results obtained in interference experiments, where after some salt concentration in the supernatant solution, the Cr(VI) adsorption remains constant.

In contrast, in river water the sorption was less than expected. At pH 2, Cr(VI) is a good oxidation agent and it is possible that an oxidation – reduction process reduces the quantity of Cr(VI) in river, which has high content of organic matter. High sorption capacities were registered for sea and tap water using LTS. This suggests that this material can be used successfully for preconcentration of chromium from these samples.

Conclusions

The anchoring of tannin molecules on cellulose increases sorption of Cr(VI). Tannin resins, with high sorption capacity, are suitable sorbents for Cr(VI) removal from natural water. The resins selectively adsorb Cr(VI) in the presence of high salt contents.

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