LETTER TO THE EDITOR

Removal of mercury(II) and methylmercury from solution by tannin adsorbents

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Adsorption of mercury(II) and methylmercury by two tannin sorbents was investigated using radiotracers. High sorption capacities for mercury are registered for both sorbents at pH 7. For *Eucaliptus Saligna* Sm sorbent (ETS) the maximum sorption capacity was 1.2±0.2 mmol/g and for *Lysiloma latisiliqua* sorbent (LTS) was 8.5±0.2 mmol/g. Methylmercury adsorption maximum was recorded at pH 4 and in buffered solutions at pH2. This species can be recovered in the presence of mercury(II). Influence of different ions present in water was examined. High recoveries were reported for ETS in tap water samples but a decrease of uptake is observed for seawater.

Introduction

Mercury is a well-known heavy metal pollutant of the aquatic environment, which is transformed to other more toxic species as methylmercury. Many technologies were developed to avoid the throughput of mercury to the environment, however this element and its toxic species still cause many ecological problems due to wrong waste management by mining, electronic, chloro – alkali, etc. industries.

During the last years, there was a growing interest in the use of biomaterials for the sorption and preconcentration of heavy metals from water. Yeast biomass was tested for the speciation of methylmercury and Hg(II).[1] Plant derived materials as algae,[2] bark, leaves and roots[3] were also used with this purpose. In particular, bark is a waste of wood industry and is a potential source for the recovery of heavy metals, because it contains large amount of vegetable tannin.

Tannin forms chelates with metals due to the presence of a great number of adjacent hydroxyl groups in its molecule. Tannin is water-soluble but to use it as sorbent it must be immobilized. The immobilization of tanic acid and other tannins was reported.[4,5,6] Previous authors studied the sorption capacity for chromium(VI) by two tannin resins obtained from *Eucaliptus Saligna* Sm (ES) and *Lysiloma latisiliqua* (LL).[7]

The adsorption of mercury and methylmercury on these sorbents is investigated in this paper. ^{203}Hg and CH$_3$ ^{203}Hg Cl were used in the estimation of sorption properties.

Experimental

Adsorbent synthesis

The synthesis and characterization of tannin resin from *Eucaliptus Saligna* Sm (ETS) and *Lysiloma latisiliqua* (LTS) has been described elsewhere.[7] The character of the exchanging groups was estimated from titration curves. Glass bottles of 100 ml were filled with 50 ml of 1 m/l of NaCl and increasing amounts of NaOH 0.1 m/l. The content of each bottle was adjusted by the addition of deionized water in order to keep the same volume in each bottles. 0.15 g of airdried resin was added and shaked for 48 hours. After that, the pH of solutions was measured. The equivalence point on the basic site was determined by GRAN's method.[8]

Resin were analysed using neutron activation analysis. Known amounts of resin and comparator standard were irradiated under identical conditions in the IEA-R1 reactor of the "Instituto de Pesquisas Energéticas e Nucleares", (São Paulo, Brazil). For the measurement of Cu, Mg, Mn, V, Cl, Hg and Ti irradiation for 2 minutes with a neutron flux of 10^{11} n·cm^{-2}·s^{-1} was used. To analyse Hg, Rb, Cr, Sc, Sb, Zn, Fe, Co, Se, samples were irradiated for 30 minutes with a reactor flux of 10^{13} n·cm^{-2}·s^{-1}. The γ-ray spectra of samples and standards were recorded using a hyperpure Ge detector GEM 20190 connected to an ORTEC 4K multichannel analyser with a resolution of 1.81 keV at the ^{57}Co photopeak and 2.28 keV at the 1332.49 keV peak of ^{60}Co.

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Table 1. Neutron activation analysis of sorbents

Element	Nuclide	Half-life	E_γ, keV	Mass, $\mu g/g$ Resin ETS	Resin LTS
Hg	^{203}Hg	46.9 d	279.1	<D.L.	<D.L.
Hg	^{197}Hg	2.7 d	192	<D.L.	<D.L.
Cu	^{66}Cu	5.1 m	1039	17±2	36.0±3.0
Mg (843 keV)	^{27}Mg	9.45 m	-	<D.L.	260±14
Mg (1014 keV)	^{27}Mg	9.45 m	-	<D.L.	280±30
Mn	^{56}Mn	2.58 h	847.1	<D.L.	0.9±0.1
V	^{52}V	3.76 m	1434	<D.L.	0.36±0.05
Cl	^{38}Cl	37.29 m	1642	3230±50	3980±60

Adsorption experiment

^{203}Hg ($T_{1/2}$=46.6 days) and CH$_3$ ^{203}Hg Cl were obtained in the above mentioned reactor by the irradiation of reagent grade Hg(NO$_3$)$_2$ and methylmercury chloride. The radioactivity was measured by an SR-7 radiometer with a well type NaI (Tl) detector (Nuclear Enterprise).

Stock solutions containing the desired concentration of each species were prepared from Hg (NO$_3$)$_2$ and methylmercury chloride (CH$_3$HgCl) Merck respectively. Solutions of 100 mg/l were prepared diluting stock solutions. Aliquots of the radioisotope were added to obtain good background/signal rates.

Batch sorption experiments were conducted at room temperature by a previously described method.[7] 10 ml of labeled chromium solutions were shaken with the desired mass of resins during 24 hours. Three aliquots of 1 ml of the supernatant were collected and the radioactivity was measured in the detector.

Mercury and CH$_3$Hg$^+$ sorption was evaluated using the expression:

$$q = (1-I_f/I_0)C_i \, V/1000 \, m_r \qquad (1)$$

where q is chromium adsorption in mg/g, V is the volume of supernatant solution in ml, m_R is resin mass in g, C_i is the concentration of initial solution in mg/l, $R = 1-I_f/I_0$ is the fraction of sorbed metal and I_i and I_0 are activities in cps of 1 ml of the initial and final solutions.

Tap water samples were collected in our laboratory. Seawater was from Havana north coast. All water samples were filtered using a Millipore filter with 0.45 μm pore size. Labeled mercury aliquots were added to obtain solutions of 1000 mg/l. The pH was adjusted to 7 with 0.1 HNO$_3$ and batch experiments were carried out by suspending 0.06 g of resin.

Results and discussion

Neutron activation analysis of the sorbents is given in Table 1. As it can be seen mercury concentrations in resins are under the detection limits. Other elements as Zn and Cr were not detected using this method. The high chloride concentration observed was due to the purification procedures used. For that reason before all sorption studies, resins were washed with enough distillate water.

Figure 1 shows the sorption of Hg(II) in different synthesis steps of resin ETS. In this sorbent, tannins were immobilised onto cellulose by the method described in a previous work.[7]

In step "0" sorption of mercury onto spherical cellulose was studied and no adsorption was registered. The other intermediate products, epoxiactivated cellulose and hexanodiamine cellulose also do not adsorb mercury. Only when tannin is introduced in the step IV almost 100% all mercury in the solution is adsorbed. This means that tannin is the principal responsible in the adsorption of mercury.

The hydroxyls are the most important functional groups present in tannin molecules and the adsorption of cations in tannin resin can be explained by the metal chelation involving adjacent hydroxyl groups of the tannin phenolic molecules.[9] Figure 2 shows the possible structure of tannin chelate.

The titration curve for LTS is shown in Fig. 3. Typical titration curves for weakly acid cation exchanger with –OH functional groups were obtained.

From the titration curve dissociation constants of the functional groups were calculated. For LTS the resin a $pK_a = 9.6\pm0.2$ was obtained this constant is similar to that of 1,2-dihydroxybenzene which is 9.40. This means, that the protonation constants of the active groups in the resins are related to that of some model monomers, as cathecol in aqueous solution.
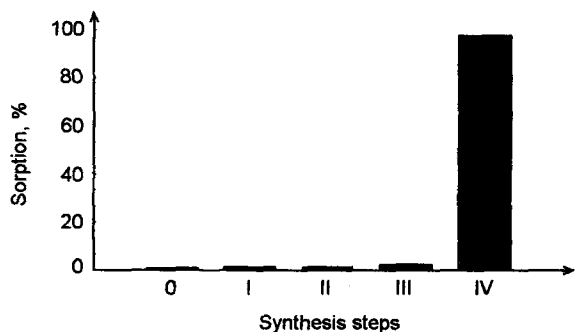
Fig. 1. Adsorption of Hg(II) in the synthesis of ETS.
Steps: 0-spherical cellulose, I – epoxiactivated cellulose,
II – introduction of space arm, III – epoxiactivated cellulose,
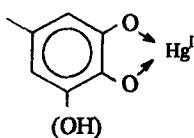IV – introduction of tannin

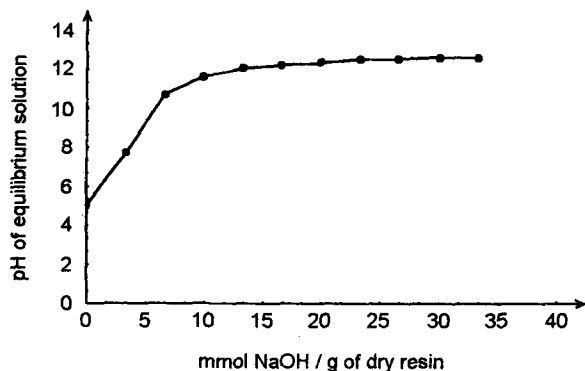*Fig. 2.* Structure of tannin chelate

Fig. 3. Titration curve of the LTS resin. Conditions: NaCl, 1 mol/l,
$V = 100$ ml, 0.15 g of resin

Figure 4 shows the influence of pH on the adsorption of both mercury species on tannin resins. The uptake of metal increases with pH. At pH bellow 2 the adsorption is very low and maximum values can be attained at pH 7. For CH_3Hg^+ maximum of adsorption is achieved at pH 4 and remains practically constant up to high pH values.

From Fig. 3 it can be seen that the groups involved in adsorption are very weak acids and their protonation increases with the pH. For that reason the extent of complex formation will depend upon the pH of the environment. The adsorption of CH_3Hg^+ in moderate acid solution is presumably due to the formation of more stable complexes of this species with the resins. The difference in adsorption of both species at pH 2 in the LTS resin suggest that the sorbent can be used for mercury speciation at this pH.

Figure 5 shows the recovery of CH_3Hg^+ in the presence of different amounts of mercury(II). The study was carried out using 0.01 g of LTS sorbent, 10 ml of radioactive CH_3Hg^+ and stable Hg(II). The solution was buffered using a formate buffer.

The results show that Hg(II) does not affect the retention of CH_3Hg^+ even when the ratio of $CH_3Hg^+/Hg(II)$ is 1:1 at pH 2 where the difference in adsorption of both species is larger. At a ratio of 1:10 a decrease of adsorption of approximately 10% was observed.
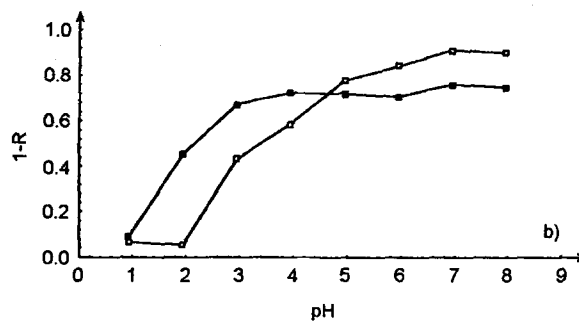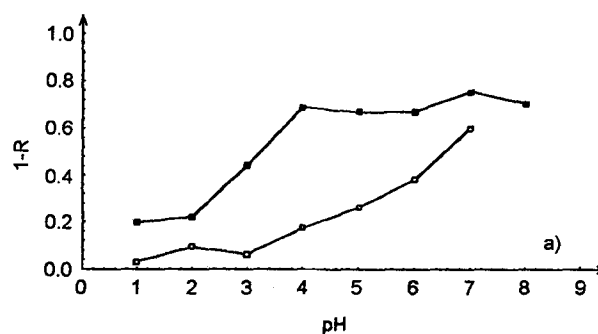

Fig. 4. Effect of solution pH on Hg(II) and CH_3Hg^+ uptake by tannin resin; a – ETS, b – LTS, □ MHg, ■ Hg(II)
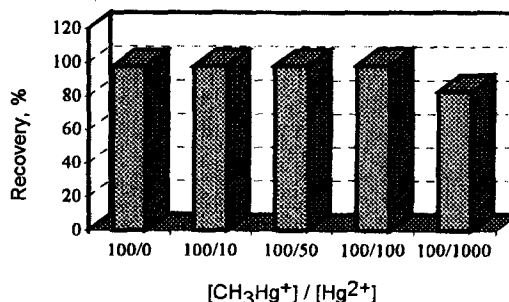

Fig. 5. Recovery of CH_3Hg^+ by LTS sorbent from mercury(II) buffered at pH 2 solutions
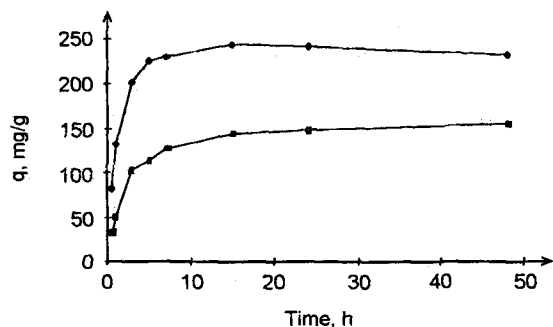
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Fig. 6. Extent of adsorption for Hg(II) at pH 2 and 298 K
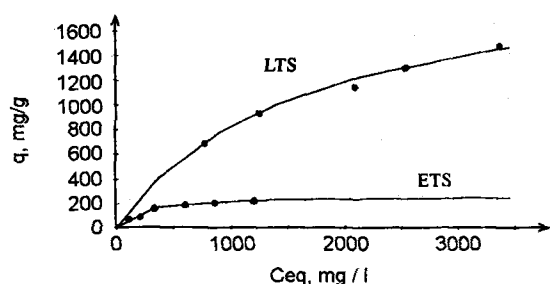as a function of time; ■ Hg(II) LTS, ◆ Hg(II) ETS

Fig. 7. Isotherms for Hg(II) at 298 K, pH 2; ● experimental data, – fit
using the Langmuir model

Table 2. Influence of the environment on the adsorption
of mercury species on ETS

Solution	Concentration, mg/l	Uptake decrement, %
NaCl	200	0
	500	4
	1000	15
	5000	25
	10000	52
	20000	86
	30000	93
Distilled water		–
Tap water		9
Seawater		76
Ca^{2+}	20	0
	40	0
	80	0
	100	0

The rate of uptake of Hg(II) and CH_3Hg^+ by the resins was investigated using 60 mg of resin in contact with 10 ml of radioactive solution of 1000 mg/ml for mercury and 100 mg/ml for methylmercury chloride at different times. Kinetic curves for Hg(II) are shown in

Fig. 6. For both sorbents the form of curves are similar. Accumulation of Hg(II) in the resins after 2 hours was almost 75% of its equilibrium uptake. At 24 hours the equilibrium was reached. For CH_3Hg^+ the behavior was similar. All following batch experiments were carried out using that equilibrium time.

It is well known that the stage determining the rate of the sorption process on chelating sorbents can be either diffusion in the polimeric matrix or complex formation. Matrices in tannin resins are hydrophilic macroporous copolymers in LTS and cellulose in ETS. Both matrices have the best kinetic characteristics.[10] The registered rates of uptake suggest that the relative low adsorption of mercury is due to the kinetics of sorption between tannin and metal.

Sorption isotherms for mercury(II) are presented in Fig. 7. Sorption isotherms were obtained using batch experiments sorbent masses between 0.02–0.1 g at 298 K and pH 7 in contact with 10 ml of 1000 mg/l solution. For LTS, more concentrate solutions were used due to the high sorption capacities for this resin. Data were fitted to the Langmuir equation:

$$q = q_{max} \cdot b \cdot C_f/(1+b \ C_f) \qquad (2)$$

where b is the Langmuir constant, C_f is the equilibrium concentration.

A high sorption capacity can be calculated from a reasonably well fitting Langmuir model. For ETS qmax was 1.2±0.2 mmol/g ($r = 0.994$) and for LTS 8.5± 0.2 mmol/g ($r = 0-998$). As observed for the adsorption of other metals[8] the sorption capacity of LTS was higher than the ETS capacity.

Different ions were tested for their effect on the uptake of Hg(II) by the tannin resin. As can be seen in Table 2, quantities of Ca^{2+} of 100 mg/l do not affect the sorption of Hg(II). However, the uptake decreased when chloride concentration increased. This is due to the high stability of mercury chloride complexes and this fact can explain the low recoveries of mercury in seawater. For LTS, the same behavior was observed.

Conclusions

Tannin resins are suitable sorbents for Hg(I) and CH_3Hg^+ removal. Adsorption of both species is pH dependent. High sorption capacities were registered for mercury(II) in LTS. At low pH, CH_3Hg^+ is better adsorbed that Hg(II). In buffered solutions, CH_3Hg^+ can be recovered in the presence of mercury(II). High concentration of chloride decreases the mercury uptake.

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