SORPTION OF METHYLMERCURY AND MERCURY FROM AQUEOUS SYSTEMS USING TANNIN SORBENTS.

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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) 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 specie can be recovered in 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 aquatic environment, which is transformed to other more toxic species as methylmercury. Many technologies were developed for avoid throughout of mercury to the environment, however this element and its toxic species still causes many ecological problems due to wrong waste management of industries like mining, electronic, chloro - alkalis, etc.

In the last years, there is a growing concern regarding 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 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 form chelates with metals due to the presence of a great number of adjacent hydroxyl groups in their molecules. Tannin are water-soluble and to use them as sorbent they must be immobilized. The immobilization of tanic acid and other tannin was reported[4,5,6]. Authors studied sorption capacity for chromium(VI) recovery of two tannin resins obtained from *Eucaliptus Saligna* Sm (ES) and *Lysiloma latisiliqua* (LL) [7].

The adsorption of mercury and methylmercury on these sorbents was 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) have been described elsewhere[7]. The character of the exchanging groups was estimated from titration curves. Glass bottles of 100ml were filled with 50mL of 1m/l of NaCl and increasing amounts of NaOH 0.1M. The content of each bottle was adjusted by the addition of deionized water in order to keep the same volume in each bottles. 0.15g of air-dried resin was added and shaked 48 hours. After that, pH of solutions was measured. The equivalence point on the basic site was determined by the Gran´s method.[8]

Resins were analysed using Neutron Activation Analysis. Known amounts of resins and comparator standards 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 of 2min with neutron flux of 10^{11} n/cm^{2}s was used. To analyse Hg, Rb, Cr., Sc, Sb, Zn, Fe, Co, Se, samples were irradiated 30min with a reactor flux of 10^{13} n/cm^{2}s. The γ-ray spectra of samples and standards were recorded using hyperpure Ge detector GEM 20190 connected to ORTEC 4K multichannel analyser with resolution of 1.81keV at the [57]Co photopeak and 2.28keV at the peak 1332.49keV of [60]Co

Adsorption experiment

The [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 analytical - reagent grade $Hg(NO_3)_2$ and methylmercury chloride. Radioactivity was measured using SR-7 radiometer with a well type NaI(Tl) detector from Nuclear Enterprise.

Stock solutions containing the desired concentration of each specie were prepared from $Hg(NO_3)_2$ and methylmercury chloride (CH_3HgCl) respectively, from Merck. Solutions of 100mg/L were prepared diluting stock solutions. Aliquots of radioisotope were added to obtain good background/ signal rates.

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

Mercury and CH_3Hg^+ sorption was evaluated using expression:

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

Where q is mercury 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;

$R = 1- I_i / I_{0i}$ 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 laboratories. Seawater was from Havana north coast. All water samples were filtered using Millipore filter with 0.45µm pore size. Labelled mercury aliquots were added to obtain solutions of 1000mg/L, pH was adjusted to 7 with 0.1M HNO_3 and NaOH. Batch experiments carried out by suspending 0.06g of resin.

Results and discussion

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

Table 1. Neutron Activation Analysis of sorbents.

Element	Nuclide	T½	Eγ (kev)	Mass (µg/g)	
				Resin ETS	Resin LTS
Hg	^{203}Hg	46.9 d	279.1	< D.L.	< D.L.
Hg	^{197}Hg	2.7d	192	< D.L.	< D.L.
Cu	^{66}Cu	5.1 min	1039	17± 2	36.0±3.0
Mg	^{27}Mg	9.45 min	844-	< D.L.	260± 14
Mg	^{27}Mg	9.45 min	1014	< D.L.	280± 30
Mn	^{56}Mn	2.58 h	847,1	< D.L.	0.9± 0.1
V	^{52}V	3.76 min	1434	< D.L.	0.36± 0.05
Cl	^{38}Cl	37.29 min	1642	3230 ± 50	3980± 60

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 previous work[7].
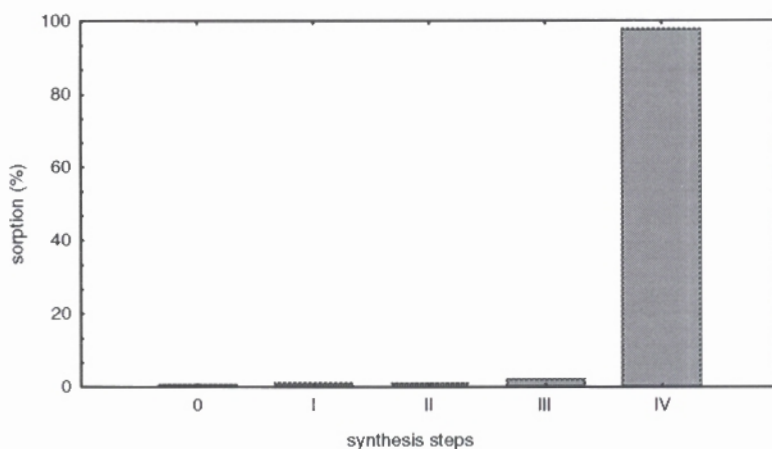

Figure 1. Adsorption of Hg (II) in the synthesis of ETS

Steps: 0-Sphericall Cellulose. I- epoxiactivated cellulose. II Introduction of space arm.
III epoxiactivated cellulose. IV Introduction of tannin

In step "0" sorption of mercury onto spherical cellulose was studied and no adsorption was registered. The others intermediate products, epoxiactivated cellulose and hexanodiamine cellulose also do not adsorb mercury. Only when tannin is introduced in the step IV almost 100% of all mercury in solution is adsorbed. Thent 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] . Fig. 2 shows the possible structure of tannin chelate.
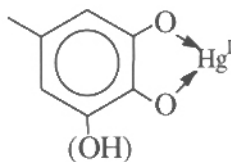
Figure 2 Structure of tannin chelate.

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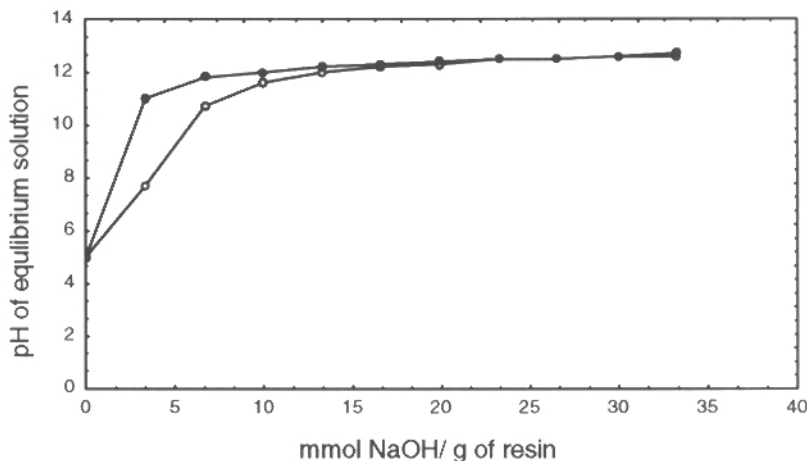

Figure 3 Titration curve of LTS resin.
Conditions: NaCl, 1M, V =100mL, 0.15 g of resin.

From titration curve dissociation constants of functional groups were calculated. For LTS resin pK_a = 9.6 ± 0.2 was achieved, this constant is similar to those 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.

Figure 4 shows the influence of pH on the adsorption of both mercury species on tannin resins. The uptake of metal increase 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.
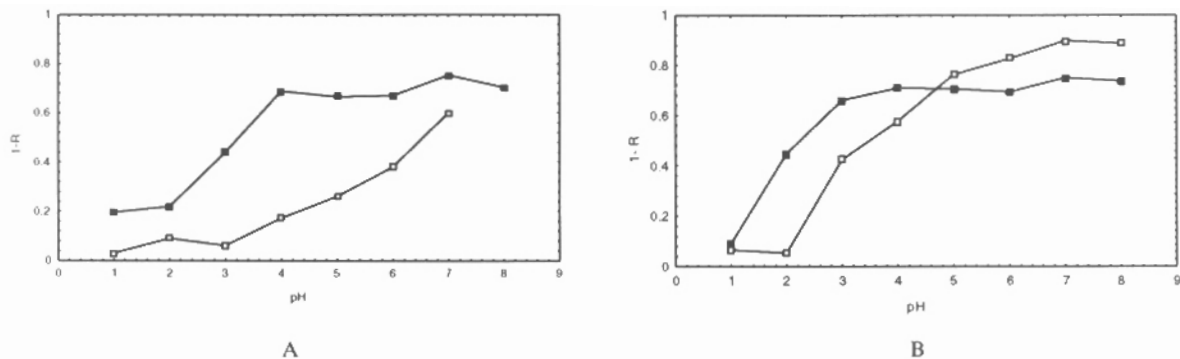
Figure 4 Effect of solution pH on Hg(II) and CH$_3$Hg$^+$ uptake by tannin resin.
A: ETS B: LTS , ■MHg, □ Hg(II)

From Figure 3 can be seen that 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$_3$Hg$^+$ in moderate acid solution is presumably due to the formation of more stable complexes of this specie with the resins. The difference in adsorption of both species at pH 2 in resin LTS suggest that this sorbent can be used for mercury speciation at this pH.

Figure 5 shows the recovery of CH$_3$Hg$^+$ in presence of different mercury(II) amounts. The study was carried out using 0.01g of LTS sorbent and 10mL of radioactive CH$_3$Hg$^+$ and stable Hg(II). Solution was buffered using formate buffer.
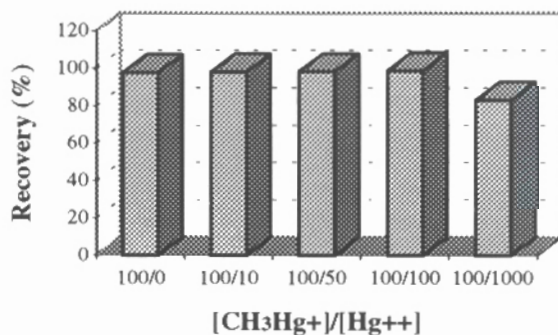

Figure 5 Recovery of CH$_3$Hg$^+$ by LTS sorbent in mercury(II) buffered at pH 2 solutions.

The results show that Hg(II) do not affect retention of CH$_3$Hg$^+$ even when the ratio of CH$_3$Hg$^+$/Hg(II) is 1:1 at pH 2 where the difference in adsorption of both species is larger. At ratio 1:10 a decrease of adsorption of approximately 10% was observed.

The rate of uptake of Hg(II) and CH$_3$Hg$^+$ by resins was investigated using 60mg of resin in contact with 10mL of radioactive solution of 1000mg/mL for mercury and 100mg/mL for methylmercury chloride at different times. Kinetic curves for Hg(II) are shown in Figure 6. For

both sorbent the form of curves are similar. Accumulation of Hg(II) in the resins after 2h was almost 75% of its equilibrium uptakes. At 24h the equilibrium was reached. For CH_3Hg^+ the behaviour 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 reaction. Matrices in tannin resins are hydrophilic macroporous copolymer in LTS and cellulose in ETS, both matrices have the best kinetic characteristics[10] . The registered rates of uptakes suggest that the relative low adsorption of mercury is due to the kinetic of sorption reaction between tannin and metal.
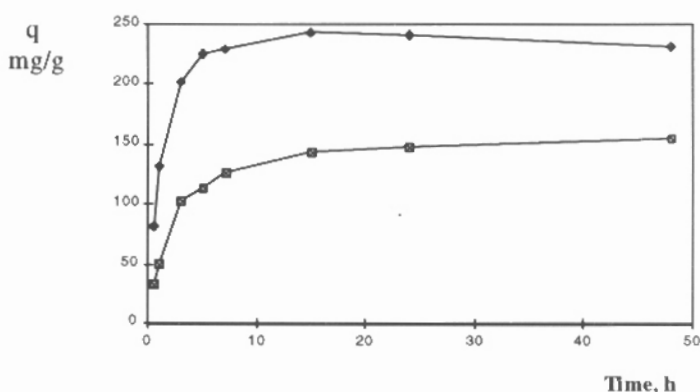

Figure 6 . Extent of adsorption for Hg (II) at pH 2 and 298 K as function of time.
■ Hg (II) LTS, ♦ Hg(II) ETS

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

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

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

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 was 8.5 ± 0.2 mmol/g (r = 0.998). As was observed for the adsorption of other metals[8] the sorption capacity of LTS was higher than ETS capacity.
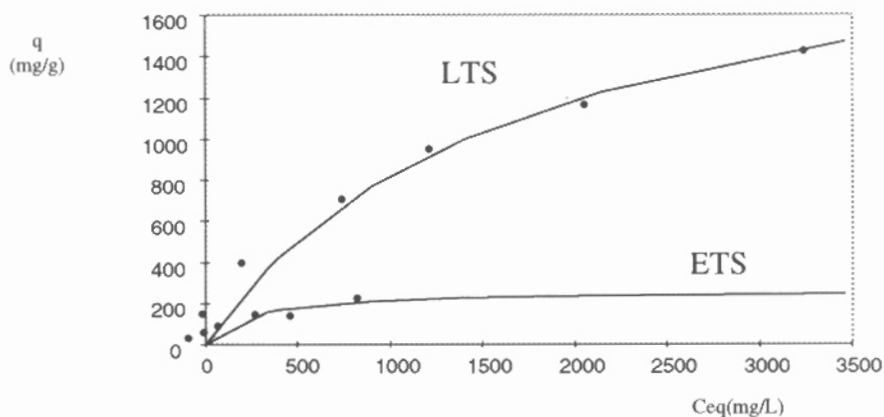
Figure 7 Isotherms for Hg (II) at 298 K, pH 2.

• experimental data, — fit using Langmuir model

Different ions were tested for their effect on the uptake of Hg(II) by tannin resin. As can be seen in Table 3, quantities of Ca^{2+} of 100mg/L do not affect the sorption of Hg(II). However, the uptake decreased when chloride concentration increased due to the high stability of chloride complexes with mercury, this fact can explain the low recoveries of mercury in seawater. For LTS, same behaviour was observed.

Table 3. Influence of environment in 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

Conclusions

Tannin resins are suitable sorbents for Hg(II) 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 presence of mercury(II). High concentration of chloride decreases the mercury uptakes.

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