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ADSORPTION OF METAL BY IMMOBILIZED TANNINS

ABSTRACT: Simultaneous adsorption of thorium, europium,iron, cerium, and neodymium by immobilized tannins was studied at different pH values. Tannic materials have excellent ability to adsorb selectively thorium at pH 5. The rest of the elements could be isolated in group at pH 7.

INTRODUCTION

Tannins and many biopigments were used to adsorb uranyl ions with a high selectivity [1-3] from aqueous samples.On the other hand, the use of different tannic matrixes for adsorption of iron [6] and oxovanadium (IV) [7] was reported. Mitra and coworkers made studies on ion exchange resins based on chemically modified naturally occurring tannins [8]. Some authors describes the pressumible structure of metal- tannin complexes as showed in the figure 1.

Therefore, to date, the use of different vegetable tannins in optimal adsorption conditions of studied metals simultaneously has not been reported. The use of natural, ubiquitous, inexpensive product such as tannins for controlling environmental contamination by micropollutans has not been discussed.

In this paper we discuss the adsorption of metals from multielemental neutron activated samples by immobilized tannins of Eucaliptus saligna Sm., Schinopsis Lorentzii (Quebracho), and tannic acid, using different column supports.

EXPERIMENTAL

500 mg of previously analyzed basnesite mineral sample (Ba - 24.27%, Ca - 1.3%, Fe - 1.2%, Sr - 0.22%, SiO2 - 10%, Th - 0.017%, Ce - 7.5%, Nd - 2.69%, Eu - 0.062%) [8] was irradiated in a TRIGA MARK III reactor (1 MW) during 40 hours ($2.7 \cdot 10^{13}$ neutrons$\cdot$cm$^{-2}\cdot$s^{-1}). After 20 days, the sample was partially dissolved with concentrated nitric acid. The filtrate and paper filter washes were transferred to a volumetric flask (25 mL).

Synthesis of Tannic Sorbents

The stationary phases were prepared using spherical, porous cellulose (100-200 μm) obtained from C.P. "CUBA-9", Quivican and powdered chitin from Pharmaceutical Laboratory, "Saul Delgado", Havana.

Sulphited tannins of Schinopsis Lorentzii (QTS) wereimmobilized on chitin by adsorption from 3% aqueous solution.

Crude extract from Eucalyptus saligna bark Sm. was chemically bonded to epoxyactivated cellulose (CEU) using a method similar to [3]. Tannic acid was immobilized on chitin (QAT) [4] and on spherical cellulose (CAT) by the same method described in [5].

Adsorption Procedures

5 g the prepared dry sorbents were put in chromatographic columns (50x8 mm) which were washed with 50 mL of 0.2 mol/L NaCl in order to test the stability of tannins' binding spectrophotometrically (270-280 nm).

The radioactive test solutions were prepared by diluting 400 μL of the original nitric acid filtrate in 50 mL of phosphoric - acetic buffer solution of different pH values and were passed through the columns at flow of 0.5 mL/min.

The phosphoric - acetic buffer was chosen in order to do less extensive the hydrolysis of the metals in studied system and to achieve the formation of tannin - metal complexes.

No macroscopic changes were showed during the sample preparation at the experimental conditions. The columns were ashed with 10 mL of buffer prior to measure the radioactivity. An Intertechnique HPGe gamma detector was used, and the presence of ^{59}Fe (1099 keV), ^{141}Ce (145.26 keV), ^{147}Nd (530.37 keV), ^{152}Eu (1408 keV), ^{233}Th (^{233}Pa 312 keV) was controlled. The peak's area calculation was carried out by software INNOVAT.

The adsorption ratio of each metal was calculated in relation to the peak area average of 400 μL aliquot deposited on 0.5 g of sorbent. It can be written as follows:

$$A\% = \frac{A_s}{A_o}$$

where, Ao: total radioactivity average of analyzed metal in 400 μL aliquot of initial filtrate, deposited (for measurements geometry) on 0.5 g of adsorbent, As: average radioactivity of analyzed metal, adsorbed by 0.5 g of adsorbent at indicated pH value.

In order to know the role of the unmodified sorbents (chitin, spherical cellulose) on metals adsorption, test solutions were passed through columns filled with these materials at different pH values.

RESULTS AND DISCUSSION

Selective Adsorption of Metals by Immobilized Tannins.

The adsorption ratios of metals by the studied sorbents are showed in table 1.

TABLA 1 **Adsorption (A%) of metals by immobilized tannins.**

pH 2					
Sorbent	Eu	Th	Fe	Ce	Nd
QTS	38.0±1.6	52.0±3.0	15.0±1.0	43.0±2.4	46.4±2.3
QAT	15.7±1.2	12.0±0.3	7.3±0.2	14.2±0.4	18.0±1.6
CEU	16.2±2.6	23.6±3.2	9.7±1.8	14.8±1.9	18.2±1.6
CAT	15.0±1.1	11.1±0.7	15.3±1.5	14.2±0.8	18.6±1.8

pH 5					
QTS	7.2±0.5	84.0±5.3	18.0±2.7	8.0±0.6	8.4±2.7
QAT	9.3±0.5	84.0±4.1	18.0±0.7	8.0±0.3	8.6±0.7
CEU	48.0±3.8	84.0±6.0	26.1±2.3	44.3±2.2	51.2±3.4
CAT	15.0±2.0	67.0±1.0	15.6±2.2	14.2±1.8	18.0±2.0

pH 7					
QTS	75.4±3.8	56.1±4.2	73.0±3.1	80.0±4.2	86.5±3.4
QAT	75.4±6.8	56.1±3.8	73.0±5.8	80.0±7.3	86.0±4.2
CEU	73.2±4.9	72.3±4.8	62.0±3.6	86.2±3.2	88.0±6.8
CAT	88.3±7.8	44.2±3.6	97.0±7.3	98.6±11.2	89.5±9.7

pH 9					
QTS	66.4±2.5	66.2±3.2	43.4±3.4	77.6±3.7	76.0±2.7
QAT	67.0±3.0	68.0±4.0	61.5±4.8	67.6±7.7	82.4±6.8
CEU	47.2±2.3	20.1±0.8	59.4±4.0	86.3±6.8	93.1±8.3
CAT	35.4±1.6	68.0±4.0	61.5±3.2	67.1±1.7	82.4±5.3

The adsorption of the metal ions at pH 2 was not significant except for the case of sulphited tannins from Schinopsis Lorentzii. The weak acid properties of functional groups of tannins are responsible for non significant interaction with metals.

The presence of sulfite and sulphidryl groups in a modified structure of Schinopsis Lorentzii tannins [10] probably is the cause of adsorption of metal ions in QTS columns at pH 2.

At about pH 5, thorium adsorption in all systems is maximum as showed in the table 1 while for the rest of the metals, the adsorption is minimum so, at this pH the adsorption selectivity for thorium is very high and his adsorption behavior is similar to the adsorption behavior of uranyl ions at this pH value according to [1 -3].

For thorium and uranyl ions the stability constants of hydroxy complexes are very high [11] in comparison with the other studied metals, so at quite low pH values is more probable for them the occurrence of extensive hydrolysis and the formation of oxocation or oxohydroxocation complexes, which are adsorbed by tannic resins selectively.

The CEU matrix at pH higher than 5 shows quite high levels of adsorption for each metal, probably because of the additional presence of many kinds of different polyhydroxyphenolic structures which are able to retain or adsorb metals. The Eucalyptus tannins are formed by phenolcarboxylic acids and derivatives of polyhydroxyphenolic flavonoids and their polycondensated in comparison with Schinopsis Lorentzii tannins which belong to the condensed tannins [10].

The adsorption at pH 7 was maximum for the majority of studied metals except thorium. The theoretical precipitation point (pH) of cerium, europium and neodymium hydroxides are about 8 - 9 [12]. Probably , the adsorption attains its maximum value when the metal atom is accompanied by atoms of oxygen forming oxo or oxohydroxo cation complexes, just before practical hydroxide precipitation.

The experiments at pH 9 show a decrease in adsorption values of metals. Probably, the reasons are the hydrolysis of polyphenolic materials, partial degradation of tannins [10] and high extension of metal hydrolysis.

The adsorption of metals on unmodified sorbents was not significant therefore, it can be supposed that the adsorption process only occur because of interaction between metal and tannin, and that the stationary phase can't be considered as a filter of hydrolyzed metal particles.

CONCLUSIONS

The different tannic matrixes studied have excellent ability to adsorb thorium from aqueous solutions at pH 5 in presence of many other metal ions.

The adsorption behavior of thorium at the experimental conditions is very similar to that of uranyl ions reported by other authors. The behavior of others 5f-elements could be study in the future.

The rest of the elements are adsorbed at pH 7 and this suggests that tannic materials could be used to remove heavy metals from contaminated natural waters.

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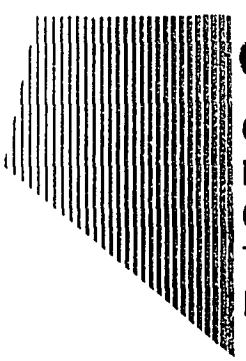

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