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Ebru Birlik[a]; Sibel Büyüktiryaki[b]; Arzu Ersöz[c]; Adil Denizli[d]; Rıdvan Say[bc]
[a] Department of Chemistry, Eskişehir Osmangazi Üniversitesi, Eskişehir, Turkey [b] BİBAM (Plant, Drug and Scientific Researches Center), Anadolu University, Eskişehir, Turkey [c] Department of Chemistry, Anadolu University, Eskişehir, Turkey [d] Department of Chemistry, Hacettepe University, Ankara, Turkey

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Selective Separation of Thorium Using Ion Imprinted Chitosan-Phthalate Particles via Solid Phase Extraction

Ebru Birlik
Department of Chemistry, Eskişehir Osmangazi University, Eskişehir, Turkey

Sibel Büyüktiryaki
BİBAM (Plant, Drug and Scientific Researches Center),
Anadolu University, Eskişehir, Turkey

Arzu Ersöz
Department of Chemistry, Anadolu University, Eskişehir, Turkey

Adil Denizli
Department of Chemistry, Hacettepe University, Ankara, Turkey

Rıdvan Say
BİBAM (Plant, Drug and Scientific Researches Center),
Anadolu University, Eskişehir, Turkey and Department of Chemistry,
Anadolu University, Eskişehir, Turkey

Abstract: We have studied a new method for the preparation of Th(IV)-imprinted chitosan-phthalate particles, which can considerably enhance the adsorption capacity and selectivity of thorium ions. In this study, chitosan-phthalate was used as the complexing monomer, Th(IV) as template, epichlorohydrin as crosslinking agent. Initially, chitosan was modified with phthalic anhydrides and complex formation occured between carboxylic acid functional groups and Th(IV) ions. Secondly, particles were crosslinked with epichlorohydrin. After the removal of Th(IV) ions, thorium solid phase

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Address correspondence to Ebru Birlik, Department of Chemistry, Eskişehir Osmangazi Üniversitesi, Fen-Edebiyat Fakültesi, Kimya Bölümü, Eskişehir, Türkiye. Tel./Fax: 0 (+90) 222 239 35 78; E-mail: ebirlik@ogu.edu.tr

extraction (SPE) on the Th(IV) ion-imprinted particles from aqueous solutions containing their different amounts, selectivity study of thorium versus other interfering metal ions mixture which are Fe^{3+}, La^{3+}, and Mn^{2+} and distribution and selectivity coefficients were reported here. A comparison of the selectivity coefficient of Th(IV)-imprinted chitosan-phthalate particles with the selectivity coefficient of non-imprinted polymers showed that the imprinted matrix for Th(IV)/Fe(III), Th(IV)/La(III) and Th(IV)/Mn(II) was 8.35, 8.75 and 10.81 times greater than non-imprinted matrix, respectively.

Keywords: MIP, SPE, ICP-AES, thorium determination, chitosan

INTRODUCTION

Thorium is widely distributed in the environment and occurs at low levels in water, soil, rocks, plants, and animals. Thorium is a typical lithophilic element and its geochemical behavior is very similar to the rare earth elements (especially cerium), zirconium, hafnium, and uranium (1). Rare earth element is a mine of new material and has very wide uses in industry. The geochemistry of thorium is simplified by the existence of just one valent state, 4+. Since thorium in solution is a highly charged cation it undergoes extensive interaction with water and many anion (2) to form complex compounds.

Thorium and uranium are present in nuclear fuel and its determination is of significance. Numerous methods have been described for its effective separation and preconcentration; procedures based on ion exchange (3, 4), solvent extraction (5–7), and solid phase extraction (SPE) (8–12) are among them. Solid phase extraction is now widely used for the preconcentration and clean up of various chemicals and for applications such as the removal of toxic or valuable subtances from a variety of predominantly aqueous solutions. The process of using adsorbents is an effective method for heavy metals by using metal chelating resins prepared using aminoacids monomer ligands (13–15) and for recovering of thorium because of the high selectivity for thorium, the ease of handling and environmental safety. The solid phase extraction methods using molecular imprinted polymers are the most used methods for the separation and preconcentration of trace metals (16–18). Molecular imprinting is a methodology for the introduction of selective recognition sites into highly cross-linked polymeric matrices, via the template-directed assembly of functionalized monomers into a polymer network (19–21). Generally, polymerization is carried out in the presence of a print molecule or template, which forms a complex with the constituent monomers. The subsequent removal of the template leads to the formation of cavities within the polymeric structure that function as specific recognition sites.

The chitosan, obtained through partial chitin deacetylation, contains a high percentage of reactive amino groups that favors its modification, and makes it highly selective when modified with chelating agents (22, 23). The adsorption characteristics of chitosan are due to the flexible structure of the polymer chain that enables it to adopt the appropriate configuration and its high hydrophilicity is due to the presence of hydroxyl groups. It is applied as an adsorbent for recovery and separation of various metal values in hydrometallurgy (24, 25) and for the removal of trace amount of toxic heavy metals from the enviroment (26).

The purpose of this study was to investigate in detail the selective separation of thorium ions from aqueous solution using Th(IV)-imprinted chitosan-phthalate particles. Chitosan was chosen because it has a large number of primary amino groups and hydroxyl groups at sixth position with high reactivity, while on the other hand it enables a variety of chemical modifications. Chitosan was modified with phthalic anhydrides and complex formation occured between carboxylic acid functional groups and Th(IV) ions. Then, the polymeric particle was crosslinked with epichlorohydrin. After the removal of Th(IV) ions, thorium adsorption on the Th(IV)-imprinted chitosan-phthalate particles from aqueous solutions containing their different amounts at different pHs and selectivity studies were done. Finally, the adsorption-desorption cycle was repeated 5 times by using the same Th(IV)-imprinted polymeric particles for removal of Th(IV) ions from aqueous solutions in order to investigate reusability of imprinted particles without any loosing of adsorption capacity.

EXPERIMENTAL

Materials

Chitosan, phthalic anhydride, and epichlorohydrin were supplied from Aldrich Chemical (USA) and thorium nitrate tetra.hydrate by Fluka and used as received. Lanthanium nitrate hegza.hydrate was also obtained from Fluka A.G.(Buchs, Switzerland). All other chemicals were of analytical reagent grade and purchased from Merck (Darmstadt, Germany).

Instrumentation

The concentration of thorium and other ions in the aqueous phase, was measured using a Inductive Coupled Plasma Optic Emission Spectrometer (ICP-OES) (Perkin Elmer 4300 D/V Model). The working wavelengths for Th(IV), Fe(III), Mn(II), and La(III), were chosen as 283.730 nm, 238.204 nm, 257.610 nm, and 408.672 nm, respectively.

The Jenway 3100 pH-meter was used to measure pH values.

Preparation of Chitosan Phthalate

Chitosan-phthalate was synthesized according to the procedure reported in Aiedeh and Taha's work (27). Chitosan (1.00 g, corresponding to approximately 6.20 mmols glucoseamine) was dissolved in the acetic acid aqueous solution (%1, 100 mL) at ambient temperature, and a solution of the phthalic anhydride (6.25 mmol) in pyridine (5 mL) was added dropwise with vigorous stirring. The reaction of pH was maintained at 7.0 by the dropwise addition of NaOH solution (1.0 M). NaOH addition was continued till the pH was stabilized. After 40 min the reaction was terminated by the addition of NaCl aqueous solution (%20, 200 mL). The resulting precipitate was filtered, washed with acetone and diethyl ether, and desiccated to give chitosan phthalate conjugates.

The IR spectra of the chitosan and chitosan-phthalate showed aromatic ring stretching in the 1580 cm^{-1}, amide carbonyl stretching in the range of 1659–1557 cm^{-1}, and carboxylic carbonyl stretching in the 1714 cm^{-1}, indicating the formation of amide links with phthalate. The selective acylation of the amino groups is probably due to their superior nucleophilic character compared to the surrounding hydroxyl groups (27).

Preparation of Th(IV) Imprinted Chitosan Phthalate

Chitosan phthalate (1 g) was dissolved in acetic acid (5%) and Th $(NO_3)_3 \cdot 4H_2O$ (2 g) was added slowly to this solution with continuous stirring at room temperature. It was poured, dropwise, into the dispersion medium, which was composed of mineral oil, petroleum ether (25 : 35, v/v), and an emulsifier (Tween-80). During this process, the dispersion medium was stirred with a mechanical stirrer at 1000–2000 rpm at room temperature. Ten minutes later, an additional 1 mL epichlorohydrin was added to the dispersion medium. Similary, 1 h later, another 1 mL was added to the medium, which was then stirred for a further 2 h. At the end of this period, the magnetic chitosan microspheres were collected using a magnet and washed consecutively with petrolium ether, sodium bisulfide, and acetone. The microspheres were then dried in an oven at 40°C for 2 days and kept in a vacuum desiccator for further analysis and use. After vacuum filtration, the yellow product of crosslinked Th(IV) complexed chitosan phthalate was washed with methanolic NaOH (%5 NaOH), 0.1 N H_2SO_4 and deionized water several times in clearly yellow turn. A light yellow product was obtained, after the removing of Th(IV) ions from the Th(IV)-complexed chitosan phthalate using aqueous 0.1 N H_2SO_4.

The IR spectra of the Th(IV)-imprinted chitosan-phthalate showed acid carbonyl stretching in the 1743.45 cm^{-1}, amide I. band in 1620 cm^{-1}, amid II. band in 1680 cm^{-1} aliphatic C-H stretching in the 1384,48 cm^{-1}, aromatic C=C stretching in 1456 and 1557 cm^{-1} and Th-O stretching in the 724.40 cm^{-1}. In the IR spectra of the Th(IV) ions removed from Th(IV)-imprinted chitosan-phthalate, Th-O stretching was not seen in the 724.40 cm^{-1}. That is to say, the selectivity cavity for thorium in the Th(IV)-imprinted chitosan-phthalate was formed.

Adsorption-Desorption Studies of Th(IV) Ions

Adsorption of Th(IV) aqueous solutions was investigated in batch experiments. The effects of the initial Th(IV) concentration, pH of the medium on the adsorption rate and adsorption capacity were studied. Nitrates of respective metal ions were used. Aqueous solutions (25 mL) containing different amounts of thorium ions (5–10 mg/L) were incubated both with 25 mg of Th(IV)-imprinted polymers at different pH (in the range of 2.0–4.0, which was adjusted with HNO_3 or NaOH at the beginning of the experiment and not controlled (afterwards) at 25°C performed in a temperature-control chamber), in the flask agitated magnetically at an agitation speed of 600 rpm. After the desired incubation periods (60 min), the aqueous phases were separated from the polymers by centrifugation (1000 rpm for 5 minutes), and the concentrations of the metal ions in these phases were measured by using ICP-OES. The amounts of metal ions adsorbed per unit mass of the polymers (mg metal ions/g polymer) were evaluated by using the following expression.

$$Q = [(C_o - C) \cdot V]/M \qquad (1)$$

Here, Q is the amount of ions adsorbed onto the unit amount of the polymer (μmol/g-polymer); C_o and C are the concentrations of the ions in the initial solution and in the aqueous phase after adsorption, respectively (mg/L); V is the volume of the aqueous phase (mL); and M is the amount of polymer (g).

Competitive metal ion adsorption from aqueous solutions containing 25 mL of 10 mg/L Fe(III)/Th(IV), Mn(II)/Th(IV), La(III)/Th(IV) were investigated by following a similar procedure described above. These studies were performed at a constant pH 3.0, and at 25°C using solutions containing different amounts of the respective ions.

Adsorbed Th(IV) ions were desorbed by treatment with 0.1 N H_2SO_4 solution. The Th(IV) adsorbed imprinted particles were placed in the desorption medium and stirred continuously at 600 rpm at room temperature for 3 h. The final Th(IV) concentration in aqueous phase was determined by ICP-OES. In order to test the reusability of Th(IV)-imprinted particles, Th(IV) adsorption-desorption procedure was repeated 5 times by using the same imprinted particles.

RESULT AND DISCUSSION

Adsorption Capacity of Th(IV)-Imprinted Polymer

Adsorption Rate

Figure 1 exemplifies adsorption rates of Th(IV) ions by Th(IV)-imprinted polymer as a function of time. The figure shows the changes in the metal

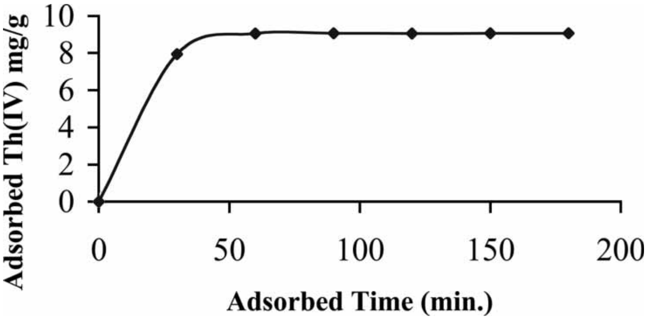

Figure 1. Adsorption rates of Th(IV) ions on the Th(IV)-imprinted polymer; Initial concentration of metal ions: 10 mg/L; pH: 3.0; T: 25°C.

ions adsorbed over time, which were calculated by using the expression given in equation (1). Note that these batch experiments were performed by using single (not multiple) solutions of the ions of interest. Adsorption conditions are given in the figure legend. It should be noted that there was no precipitation in these groups of experiments under the concentration and pH condition studied. Figure 1 shows that high adsorption rates were observed at the beginning, and then plateau values (i.e., adsorption equilibrium) are gradually reached within 60 minutes.

Several experimental data on the adsorption of various ions by chitosan have shown a wide range of adsorption rates. For example, Inukai et al. have investigated adsorption of germanium(IV) on the 2,3-dihydroxypropyl chitosan resin and particles and reported 5 h equilibrium adsorption time (28). Guo et al. used molecularly imprinted chitosan particles for the separation of hemoglobin and found 10 h as an equilibrium time (29).

Adsorption Capacity

In Fig. 2, the adsorption capacity of Th(IV) ions is seen. The amount of metal ions adsorbed per unit mass of the particles increased with initial concentration. The batch equilibrium experiments were studied at different Th(IV) ion initial concentration within the range 5.0–100.00 mg/L. The maximum adsorption (corresponding a 100 ppm Th(IV) ion initial concentration), which represents the saturation of active points Th(IV) ions on the polymers, was 264 μmol Th(IV)/g-polymer.

An adsorption isotherm is used to characterize the interactions of each molecule with the adsorbents. This provides a relationship between the concentration of the molecules in the solution and the amount of ion adsorbed on the solid phase when the two phases are at equilibrium. The Langmuir adsorption model assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which is capable of holding only one

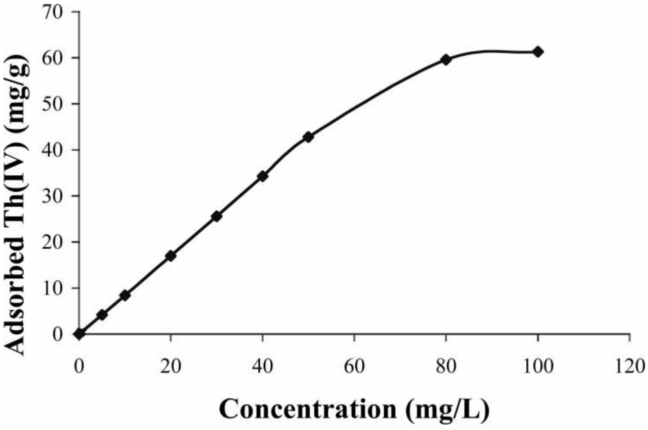

Figure 2. Adsorption capacity of Th(IV) ions on the Th(IV)-imprinted particles; pH: 3.0; T: 25°C.

molecule. These sites are also assumed to be energetically equivalent and distant from each other so that there are no interactions between the molecules adsorbed on adjacent sites.

During the batch experiments, adsorption isotherms were used to evaluate the adsorption properties. For the systems considered, the Langmuir model was found to be applicable in interpreting thorium adsorption by imprinted particles. The corresponding transformations of the equilibrium data for thorium ions gave rise to a linear plot, indicating that the Langmuir model could be applied in these systems and described by the equation

$$Q = Q_{max} b\, C_e/(1 + bC_e) \tag{2}$$

Where Q is the concentration of bound Th (IV) ions in the adsorbent (μmol/g-polymer), C_e is the equilibrium Th (IV) ions concentration in solution (μmol/L), b is the Langmiur constant (L/μmol) and, Q_{max} is the adsorption capacity (μmol/g). This equation can be linearized.

$$1/Q = (1/Q_{max} b)(1/C_e) + (1/Q_{max}) \tag{3}$$

The plot of $1/C_e$ versus 1/Q was employed to generate the intercept of $1/Q_{max}$ and the slope of $1/Q_{max}b$ (Fig. 3).

The maximum adsorption capacity (Q_{max}) data for the adsorption of Th(IV) ions was obtained from the experimental data. The correlation coefficient (R^2) was 0.9937 at pH 3.0. The Langmuir adsorption model can be applied in this affinity adsorbent system. It should be also noted that the maximum adsorption capacity (Q_{max}) and the Langmuir constant were found to be 2000 μmol/g (pH 3.0) and 0.0005 g/μmol, respectively. Theoretical Q_{max} is higher than calculated Q due to the accessibility of Th(IV) ions. Some Th(IV) cavities which formed during the imprinting process stayed

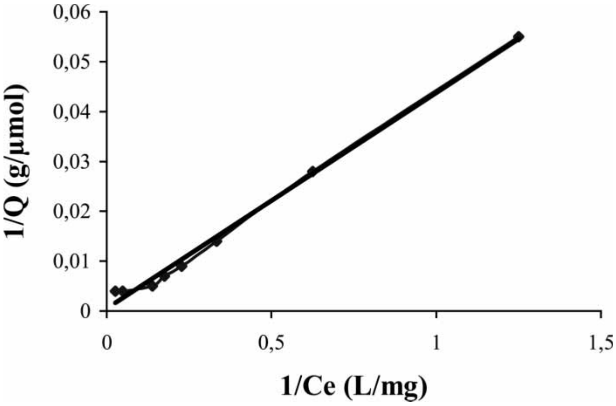

Figure 3. Langmuir adsorption isoherm of Th(IV)-imprinted particles.

inside the polymer matrix. Due to the diffusion or mass transfer limitations, Th(IV) ions do not reach these binding sites. Therefore, (Q_{max})theo is found to be higher than (Q_{max}) calculated.

Effect of pH

Metal ion adsorption on chelating adsorbents is pH-dependent. Ionization of the metal-complexing ligand and the stability of the metal-ligand complexes change with the pH (30). Furthermore, the precipitation of the metal ions are affected by the concentration and form of soluble metal species. The solubility of metal ions is governed by the concentration of hydroxide or carbonate ions. The precipitation of metal ions becomes significant approximately at pH 7.0 for all metal ions (31). The theoretical and experimental precipitation curves indicate that precipitation begins above this pH, and may also depend on the concentration of metal ions in the adsorption medium. Therefore, in our study, in order to establish the effect of pH on the adsorption of thorium ions onto imprinted polymers, the batch equilibrium studies were repeated at different pHs within the range 2.0–4.0. The effect of pH on the Th(IV)ions adsorption using Th(IV)-imprinted polymer is shown in Fig. 4.

The Th(IV)-imprinted polymers exhibited a high affinity in acidic conditions (pH = 3.0) and when the pH of the solution was over 4.0, a precipicate was deposited. Therefore, it was necessary to use an adsorbent with which thorium could be quantitatively adsorbed from the acidic solution, where no precipitate is expected to develop during the separation process (32).

Selectivity Studies

The competitive adsorption of Fe(III)/Th(IV), Mn(II)/Th(IV), La(III)/Th(IV) from their couple mixture was also investigated in a batch system.

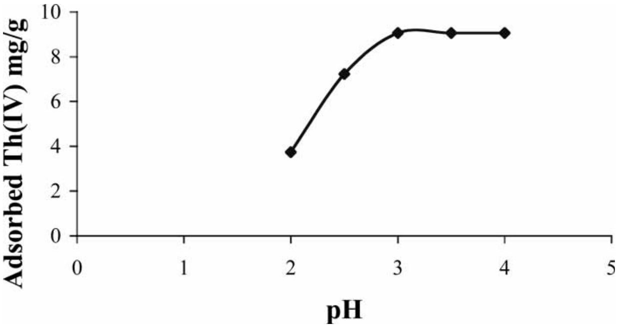

Figure 4. Effects of pH on Th(IV) adsorption; Th(IV) initial concentration: 10 ppm; T: 25°C.

Adsorption capacities of the Th(IV)-imprinted and non-imprinted particles for metal ions under competitive conditions (i.e. adsorption from solution containing 10 mg/L from each of Th(IV), La(III), Fe(III), Mn(II) ions) are given in Table 1.

The Th(IV) adsorption capacity of the Th(IV)-imprinted particles was much higher than that of other ions. The competitive adsorption capacity of the Th(IV)-imprinted particles for Th(IV) ions was also higher than non-imprinted particles. When they exist in the same medium, a competition will start for the same attachment sites. It can be concluded that the Th(IV) imprinted particles show the following metal ion affinity order under competitive conditions: Th(IV) > Mn(II) > La(III) > Fe(III) (Table 2). It should be noted that the imprinted microparticles showed excellent selectivity for the target molecule (i.e. Th(IV) ions) due to molecular geometry.

The distribution and selectivity coefficients of La(III), Fe(III), and Mn(II) ions with respect to Th(IV) ion were calculated as explained below.

$$K_d = [(C_i - C_f)/C_f] \text{ X (volume of the solution, mL)/} \times \text{(mass of microparticles, g)} \tag{4}$$

Table 1. Competitive adsorption of thorium and metal ions on the Th(IV)-imprinted and non-imprinted particles

Couple mixture (10 mg/L)	Adsorbed metal ions (mg/g)							
	Imprinted particles				Non-imprinted particles			
	Th (IV)	Fe(III)	Mn(II)	La(III)	Th (IV)	Fe(III)	Mn(II)	La(III)
Th (IV)-Fe(III)	9.81	9.58	—	—	9.10	9.73	—	—
Th (IV)-Mn(II)	9.89	—	7.70	—	8.98	—	7.64	—
Th (IV)-La(III)	9.80	—	—	8.26	9.26	—	—	9.12

Table 2. The effect of imprinting on selectivity

Particles	Th(IV) (mg/L)	Fe(III) (mg/L)	K_D (Th(IV))	K_D (Fe(III))	k	k′
Non-imprinted	10	10	10190.63	36383.17	0.28	
Th(IV)-imprinted	10	10	53614.96	22860.65	2.34	8.35
	Th(IV) (mg/L)	Mn(II) (mg/L)	K_D *(Th(IV))*	K_D *(Mn(II))*	k	k′
Non-imprinted	10	10	8803.92	3242.68	2.71	
Th(IV)-imprinted	10	10	98304.86	3353.50	29.31	10.81
	Th(IV) (mg/L)	La(III) (mg/L)	K_D (Th(IV))	K_D (La(III))	k	k′
Non-imprinted	10	10	12678.01	10380.44	1.22	
Th(IV)-imprinted	10	10	50948.05	4770.34	10.68	8.75

where K_d, C_i, and C_f represent the distribution coefficient the initial, and the final solution concentrations, respectively. The selectivity coefficient for the binding of a thorium ion in the presence of competitor species can be obtained from equilibrium binding data according to the Eqn. (5);

$$k = K_d(\text{Th (IV)})/K_d(X) \tag{5}$$

where k is the selectivity coefficient and X represents Fe(III), La(III), or Mn(II) ions. A comparison of the k values of the imprinted particles with those metal ions allows an estimation of the effect of imprinting on selectivity. A relative selectivity coefficient k′ (Eqn. (6)) can be defined

$$k' = k_{\text{imprinted}}/k_{\text{control}} \tag{6}$$

Desorption and Repeated Use

Desorption of the adsorbed Th(IV) ions from the imprinted particles was also studied in a batch experimental set up. Various factors are probably involved in determining the rates of Th(IV) desorption, such as the extent of hydration of the heavy metal ions and polymer microstructure. However, an important factor appears to be the binding strength. When H_2SO_4 was used as a desorption agent, the coordination sphere of chelated Th(IV) ions was distrupted and subsequently Th(IV) ions were released from the thorium templates into the desorption medium. In order to show the reusability of the Th(IV)-imprinted particles, the adsorption-desorption cycle was repeated 5 times by using the same imprinted particles and it was observed that the adsorption capacity was decreased only around 2%. The results showed that the Th(IV)-imprinted affinity particles can be used repeatedly without loosing significantly their adsorption capacities.

CONCLUSIONS

We have shown that Th(IV) imprinted chitosan phthalate particles are very selective for Th(IV) ions. For this purpose the naturally occurring polymer chitosan was modified with the phtahalic anhydrides. Th(IV)-imprinted chitosan phthalate sorbent was prepared by a molecular imprinting technique. The Th(IV) ion was removed from polymer particles by leaching with 1N H_2SO_4 which leave a cavity in the polymer particles. Th(IV)-imprinted chitosan phthalate sorbent is suitable for repeated use without considerable loss of adsorption capacity. A high adsorption rate was observed at the beginning of the adsorption process and saturation values are reached within 60 minutes. This adsorption time is rather good compared to literature. The sorbent is good enough for thorium determination in matrixes containing interferent ions, such as La(III), Fe(III) and Mn(II). The competitive adsorption capacity of Th(IV)-imprinted chitosan phthalate particles for Th(IV) ions is higher than non-imprinted particles. The K_d values for the Th(IV)-imprinted chitosan phthalate showed increase in K_d for Th (IV), while K_d decreases for La(III), Fe(III), and Mn(II) ions. It may be concluded from the results presented that Th(IV)-imprinted chitosan phthalate particles can be effectively used for the specific removal of Th(IV) ions from aqueous solutions by solid-phase extraction.

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