Selective preconcentration of thorium in the presence of UO_2^{2+}, Ce^{3+} and La^{3+} using Th(IV)-imprinted polymer

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Abstract

We have prepared Th(IV) ion-imprinted polymers, which can be used for the selective preconcentration of Th(IV) ions, represented by uranium and lanthanides. *N*-methacryloyl-(L)-glutamic acid (MAGA) was chosen as the complexing monomer. In the first step, Th(IV) was complexed with MAGA and the Th(IV)-imprinted poly[ethylene glycol dimethacrylate-*N*-methacryloyl-(L)-glutamic acid] (Poly(MAGA-EDMA)) beads were synthesized by suspension polymerization. After that, the template Th(IV) ions were removed using 8.0 M HNO_3 solution. The breakthrough capacity was 40.44 mg Th(IV)/g beads. The relative selectivity coefficients of imprinted beads were 68, 97 and 116 for UO_2^{2+}, La^{3+} and Ce^{3+}, times greater than non-imprinted matrix, respectively. The Th(IV)-imprinted beads could be used many times without decreasing their breakthrough capacities significantly.
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1. Introduction

Thorium is important element not only in industrial applications but also in energy and environmental problems. Thorium and rare-earth elements often coexist in their minerals and in waste-water. However, the separation of thorium from rare-earth is difficult and limited because their compounds show similar properties to thorium [1]. Because of this, various separation techniques are employed for the separation and purification of thorium. Although liquid–liquid extraction has been widely used [2,3] it is time-consuming. Extraction chromatography [4,5], functionalized resins [6–8], biosorption [9] and different adsorbents [10] have been extensively used for the separation and preconcentration of thorium ions. The process of using adsorbents is effective method for metal ions by using metal-chelating resins prepared with con-

taining aminoacid monomer ligands [11–14] and for recovering thorium because of the high selectivity for thorium, the ease of handling and environmental safety. The solid-phase extraction methods using ion-imprinted polymers (IIP-SPE) are the most popular methods for separation and preconcentration for trace metals [15–19].

Molecular imprinting is a method for making selective binding sites in synthetic polymers by using molecular template. Metal cations can be used as templates for imprinting cross-linked polymers. Heavy metals can also be removed by using molecular imprinting method [20–22]. During the imprinting procedure, metal coordination was also used in many cases. Molecularly imprinted polymers prepared with metal–chelate monomers have been used to examine the roles of metal ion and ligand shape on binding selectivity [23–25].

In this study, an ion-imprinting polymer prepared with methacryloyl-(L)-glutamic acid (MAGA) was used for selective separation of thorium ions from aqueous solutions. Th(IV) ion, a typical hard acid, can form stable com-

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plexes with catechol, carboxylic acids and aminopolycarboxylic acids [9]. Glutamic acid was chosen because glutamic acid molecules are linked to the backbone through carboxyl groups are responsible for the thorium complexation. Strong complex formation occurs between carboxylic groups and thorium ions. Poly(MAGA-co-EDMA) metal-complexing beads were produced by a dispersion polymerization technique. After removal of Th(IV) ions, thorium solid-phase extraction on the Th(IV) ion-imprinting microbeads from aqueous solutions containing their different amounts, selectivity study of thorium versus other interfering metal ions mixture which are uranyl, lantan and cerium and distribution and selectivity coefficients were reported here.

2. Experimental

2.1. Reagents

L-Glutamic acid hydrochloride and methacryloylchloride were supplied by Sigma (St. Louis, MO) and thorium nitrate·hydrate by Fluka and used as received. Ethylene glycol dimethacrylate (EDMA) were obtained from Fluka A.G. (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at 4 °C until use. Azobisisobutyronitrile (AIBN) was also obtained from Fluka (Switzerland). Poly(vinylalcohol) (PVAL; MW: 10,000, 98% hydrolyzed) was supplied from Aldrich Chemical (USA). All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany).

All water used in the experiments was purified using a Barnstead (Dubuque, IA) ROpure LP reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANO pure organic/colloid removal and ion exchange packed-bed system.

2.2. Preparation of thorium(IV)-imprinted polymeric microbeads

2.2.1. Synthesis of N-methacryloyl-(L)-glutamic acid (MAGA) monomer

Details of the synthesis and characterization of N-methacryloyl-(L)-glutamic acid (MAGA) monomer was reported elsewhere [19].

2.2.2. Synthesis of the thorium(IV)-N-methacryloylglutamic acid monomer

MAGA (0.430 g, 2.0 mmol) was added into 15 mL of ethanol and thorium nitrate·hydrate (1.0 mmol) at room temperature slowly to this solution with continuous stirring. The solution was allowed to stir for 2 h and turned yellow. The yellow complex was filtered, washed with hot water and dried in a vacuum desiccator. Decomp: ≥350 °C; FT-IR (KBr, cm^{-1}) ν: 3400 and 3250 (−CONH−); 3095 (vinyl C−H stretch); 1680 (C=O carbonyl stretch); 1550 and 1420 (C=O carboxy-

late stretch, sym and anti-sym); 788 and 735 (O−Th−O vibrations).

The thorium-imprinted beads were prepared by dispersion polymerization technique. A typical suspension copolymerization procedure of Poly(MAGA-co-EDMA) beads was given as follows: the dispersion medium was prepared by dissolving 0.2 g polyvinylalcohol within 60 mL of distilled water. 0.06 g of 2,2′-azobisisobutyronitrile (AIBN) was dissolved within monomer phase 7.0 mL/1.0 mmol in 4.0 mL ethanol/12.0 mL (EDMA/MAGA-Th(IV)/toluene). This solution was then transferred into the dispersion medium placed in a magnetically stirred (at a constant stirring rate of 600 rpm) glass polymerization reactor (100 mL) which was in a thermostatic water bath. The reactor was flushed by bubbling nitrogen and then was sealed. The reactor temperature was kept at 70 °C for 6 h. Then the polymerization was completed at 90 °C in 3 h. After polymerization, the Poly(MAGA-co-EDMA) beads were separated from the polymerization medium. The residuals (e.g., unconverted monomer, initiator) were removed by a cleaning procedure. The resulting beads were treated with 50/50 methanol–water, pH 3, for 24 h to remove the templates. The template free polymers were treated with 8 M HNO$_3$ for 24 h to remove of thorium ion. Briefly, beads cleaned by washing solutions (i.e., a dilute HCl solution, and a water–ethanol mixture) and dried in a vacuum oven at 70 °C for 48 h. In the same way, non-imprinted beads were also prepared by using MAGA and EDMA.

2.2.3. Characterization of Poly(MAGA-co-EDMA) beads

The average size and size distribution of the beads were determined by screen analysis performed using Standart Test Sieves (Retsch GmbH & Co., Germany). The specific surface area of the beads was determined in BET apparatus. Water uptake ratios of the beads were determined in distilled water. The experiment was conducted as follows: initially dry beads were carefully weighed before being placed in a 50 mL vial containing distilled water. The vial was put into an isothermal water bath at a fixed temperature (25 °C) for 2 h. The bead sample was taken out from the water, wiped using a filter paper, and weighed. The weight ratios of dry and wet samples were recorded. The water content of the non-imprinted and the imprinted beads were calculated using the weights of beads before and after uptake of water. FT-IR spectra of the beads were obtained by using FT-IR spectrophotometer (Jasco Corporation, Made in Japan; FT-IR-300 E).

2.3. Procedure

The solid-phase extraction and preconcentration studies were carried out in a packed-bed system, with an internal diameter of 0.9 cm and height of 4.0 cm. In the first group of experiments, the effect of Th(IV) concentration on adsorption was studied. To study the adsorption capacities of Th(IV)-imprinted beads towards Th(IV) ions, the capacity

breakthrough curve of the column packed with 0.275 g of the stationary phase were obtained.

The breakthrough curve was obtained by pumping solution containing 10 mg/L at pH 3.0 through the column at flow rate of 2 mL/min, continuously collecting each 20 mL of the column effluent to determine of Th(IV) by ICP-OES, then plotting the extraction percentage against the total volume of effluent. The extraction percentage is equal to $(C/C_0) \times 100$, where C is the concentration of the column effluent and C_0 is that of the column influent. In the second group of experiments, the effect of pH on the adsorption of thorium ions on Th(IV)-imprinted beads was investigated. In the third stage of experiments, the effect of flow rate of the thorium solution was examined. For this purpose, 10 mg/L Th(IV) solutions were circulated at different flow rates, in the range of 0.5–5.0 mL/min.

Column packed with Th(IV)-imprinted solid phase sorbent is simply a piece of pipe, standing on its end filled with the material. Solution containing the Th(IV) ion of interest flows into one end of the pipe and out the other end. Much of the information needed to evaluate column performance is contained in plots of adsorbed thorium ion concentration or normalised concentration defined as the ratio of effluent thorium ion concentration to inlet thorium ion concentration as a function of flow time. Total amount of thorium ion sent to the column is calculated from the following equation:

$$\text{Total amount of thorium ion sent to the column} = \frac{C_0 F t}{1000} \quad (1)$$

where $C_0 =$ inlet thorium ion concentration (mg/mL), $F =$ flow rate (mL/min), $t =$ total flow time (min).

Maximum adsorption capacity (Q) is defined by Eq. (2) as the total amount of thorium ion adsorbed per gram of thorium(IV)-imprinted beads at the end of the total flow time.

$$Q = \frac{\text{total adsorbed quantity in the column}}{\text{amount of the imprinted beads in the column}} \quad (2)$$

Desorption of thorium ions adsorbed on Th(IV)-imprinted microbeads was realized by using 1.0 M HNO$_3$ and 0.5 M H$_2$SO$_4$ solutions. In order to test the reusability of Th(IV)-imprinted beads, Th(IV) adsorption–desorption procedure was repeated five times by using the same imprinted beads.

The experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin error.

The packed-bed column selective solid-phase extraction experiments of UO$_2$(II), La(III) and Ce(III) with respect to Th(IV) were conducted using imprinted and non-imprinted polymers.

Distribution (K_d), selectivity (k) and relative selectivity (k') coefficients of uranyl, lantan and cerium ions with respect to thorium ion were calculated according to the study by Say et al. [19].

Table 1
Operating conditions of the ICP-AES

Parameter	
RF power (W)	1450
Plasma gas flow rate (L min^{-1})	16
Auxiliary gas flow rate (L min^{-1})	0.2
Nebulizer gas-flow rate (L min^{-1})	0.55
Sample flow rate (mL min^{-1})	1.5
View height (mm)	15
View mode	Axial-radial
Read	Peak area
Source equilibration time (s)	15
Read delay (s)	60
Replicates	3
Background correction	2-point (manual point correction)
Spray chamber	Scott-type spray chamber
Nebulizer	Gem Tip Cross-Flow Nebulizer (HF resistant)
Detector	Segmented-array charge-coupled-device detector
Purge gas	Nitrogen
Shear gas	Air
Gas	Argon
Analytical wavelengths (nm)	Thorium 283.730
	Uranium 385.958
	Lanthanum 408.672
	Cerium 413.764

Standards were prepared from 1000 ppm stock solutions (Th NIST SRM 3159, U NIST SRM 3164, La NIST SRM 3127a, Ce NIST SRM 3110) and diluted with 3% HNO$_3$ solution.

The concentration of thorium and other ions in the aqueous phase, were measured using an Inductive Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (Perkin Elmer 4300 D/V Model). The operating conditions of the ICP-AES is given in Table 1.

3. Results and discussion

3.1. Properties of thorium(IV)-imprinted beads

In the suspension polymerization, the yield of spherical beads with a size range of 63–140 μm in diameter was found to be 94% (w/w) based on the monomers initially charged in the polymerization reactor. The specific surface areas were found to be 33.7 m^2/g for non-imprinted and 131.6 m^2/g for imprinted polymers. The equilibrium swelling ratios of the non-imprinted and imprinted beads are 25 and 43%, respectively. Compared with non-imprinted beads, the water uptake ratio of the Th(IV)-imprinted beads increased. Formation of metal ion cavities in the polymer structure introduced more hydrodynamic volume into the polymer chains, which can result in the uptake of more water molecules by polymer matrix. The amount of thorium ion which has obtained after the treatment of polymeric beads by methanol–water, 8 M of HCl was determined by ICP-OES and it was found that 0.94 mmol thorium has removed from the imprinted polymeric beads. This result was also supported by the elemental analysis results. The percentage of C, H and C was found to

be 54.24, 6.953 and 1.044 for unleached thorium, and 58.16, 7.117 and 1.190 for leached thorium, respectively. As seen from the data, when thorium ion is removed from the polymer, the amounts of C, H and N are high as expected.

As mentioned before, MAGA was synthesized as the ligand. In the first step, MAGA was synthesized from L-glutamic acid hydrochloride and methacryloyl chloride. Then, thorium ion was complexed with MAGA to get MAGA-Th(IV) complex monomer and polymerized with EDMA. Thorium(IV) and glutamic acid complex with subsequent inclusion of hydroxyl in the coordination sphere of thorium ion and cavities are occurred on the surface of beads which are highly cross-linked with suitable size and very selective to Th(IV) ion.

The characteristic vibration bands of MAGA-Th(IV) and Th(IV)-imprinted Poly(MAGA-co-EDMA) show similarity. FT-IR spectra of Th(IV)-imprinted Poly(MAGA-co-EDMA) beads is given below: FT-IR (KBr, cm^{-1}) ν: 3460 (−CONH−); 1732 (C=O carbonyl stretch); 1643 (amide I band); 1446 (amide II); 780 (O−Th symmetric vibration); The COOH band of MAGA in unleached polymer cannot be seen because of the complexing of COOH with Th(IV). In addition, the vibration band of O−Th has given as 787.4 cm^{-1} [26]. In leached polymer, a strong band around 3500 cm^{-1} was obtained because Th(IV) ions were removed from the structure and O−Th band was not observed. So, it can be said that the imprinting process has been done successfully.

3.2. Effect of initial thorium ion concentration on adsorption

The column effluent was continuously monitored for breakthrough of the Th(IV) ions on the thorium-imprinted beads by recording the effluent by ICP-OES measurements. The breakthrough curve was constructed by plotting the percent extraction ($C/C_0 \times 100$, C = concentration of Th(IV) ions of the column effluent, C_0 = Th(IV) concentration of the column influent) against the total volume effluent (Fig. 1, ▲). The breakthrough capacity, in milligrams of Th(IV)/g of Th(IV)-imprinted beads, was obtained by calculating the number of milligrams of thorium adsorbed by the Th(IV)-imprinted beads at breakthrough point. The thorium breakthrough column started after 560 mL. When the flow rate was at 2.0 mL/min the concentration of thorium ions in ef-
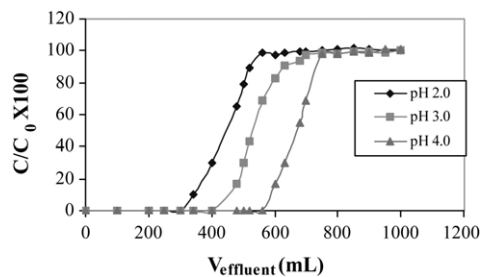
fluent was below 0.08 mg/L (125 times less than the initial concentration) to 520 mL. The course of the breakthrough curve indicated that thorium ions were effectively and relatively fast bonded to strong binding templates. The breakthrough capacity for Th(IV)-imprinted beads was 40.44 mg Th(IV)/g.

3.3. Effect of pH on thorium adsorption

Column capacity was determined for different pH values ranging from 2.0 to 4.0, using a 10.0 mg/L Th(IV) influent solution pumped through the column at a flow rate of 2.0 mL/min. The effect of pH on the Th(IV) adsorption of the Th(IV)-imprinted beads is also shown in Fig. 1. As can be seen in Fig. 1, for thorium-imprinted polymer, the optimum pH for maximum thorium binding capacity was found to be between pH 2.0 and 4.0 for Th(IV) ions. The Th(IV)-imprinted beads exhibited a high affinity in acidic conditions (pH 4.0) and when the pH of the solution was over 4.0, a precipitate was deposited. Therefore, it was necessary to use an adsorbent with which thorium could be quantitatively adsorption from the acidic solution, where no precipitate is expected to develop during the separation process [27].

3.4. Effect of flow rate on adsorption

The flow rate of the thorium solution through the packed-bed column is a very important parameter for controls the time of adsorption and separation process. The effect of flow rate on the adsorption of thorium ions in the packed-bed column was investigated by changing the flow rate between 0.5 and 5.0 mL/min. The initial metal ion concentration was kept constant at 10.0 mg/L and faster flow rates could not be investigated due to the back-pressure generated by the column. As seen from Fig. 2, the adsorption of thorium(IV) ions decreased from 40.44 to 15 mg/g with increasing flow rate as expected. At higher flow rates the contact time of thorium ions with the column material is shorter. The decrease in the breakthrough adsorption capacity by increasing flow rate is less significant up to 2.0 mL/min. These experimental results showed that the adsorption in this system is a rapid kinetic process.
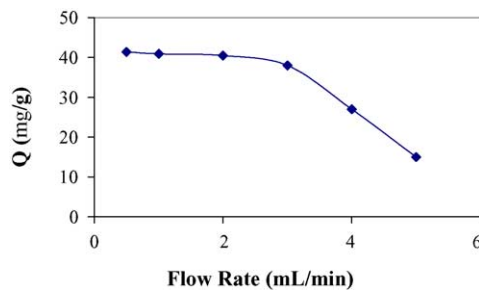

Fig. 1. The effect of pH on thorium binding capacity.

Fig. 2. The effect of flow rate on the adsorption of Th(IV)-ions.

Table 2
K_d, k and k' values of UO$_2$(II), La(III) and Ce(III) with respect to Th(IV)

Beads	Th^{4+} (mg/L)	UO$_2^{2+}$ (mg/L)	K_d (Th^{4+})	K_d (UO$_2^{2+}$)	k	k'
Non-imprinted	10	10	1183.4	7928	0.15	–
Th(IV)-imprinted	10	10	29303	2876	10.2	68
Beads	Th^{4+} (mg/L)	La^{3+} (mg/L)	K_d (Th^{4+})	K_d (La^{3+})	k	k'
Non-imprinted	10	10	1604	650	2.44	–
Th(IV)-imprinted	10	10	116647	492.5	237	97
Beads	Th^{4+} (mg/L)	Ce^{3+} (mg/L)	K_d (Th^{4+})	K_d (Ce^{3+})	k	k'
Non-imprinted	10	10	1890	2021	0.935	–
Th(IV)-imprinted	10	10	78365	721	108.7	116

3.5. Elution and reusability

Elution of thorium(IV) ions from the thorium(IV) imprinted microbeads in the column were made by passing of 1.0 M nitric acid, 1.0 M HCl and 0.5 M H$_2$SO$_4$ solution. It can be observed that, in the experimental conditions used, thorium(IV) ions could be quantitatively eluted with 1.0 M HNO$_3$, 1.0 M HCl and 0.5 M H$_2$SO$_4$ solution. Quantitative elution of thorium ions was possible passing 16.0 mL of these solutions and desorption ratios greater than 91.8, 94.4 and 96.9%, respectively. When H$_2$SO$_4$, HCl and HNO$_3$ are used as a desorption agent, the coordination spheres of chelated Th(IV) ions is disrupted and subsequently Th(IV) ions are released from the thorium templates into the desorption medium. In order to obtain the reusability of the Th(IV)-imprinted beads, adsorption–desorption cycles were repeated seven times by using the same imprinted beads. The breakthrough capacity of the recycled Th(IV)-imprinted beads can still be maintained at 92% level at the 7th cycle. It can be concluded that the Th(IV)-imprinted beads can be used many times without decreasing their breakthrough capacities significantly.

3.6. Selectivity studies versus UO$_2$(II), La(III) and Ce(III)

Competitive adsorption of Th(IV)/UO$_2$(II), Th(IV)/La(III) and Th(IV)/Ce(III) from their couple mixture was also investigated in a batch system. Th(IV)/UO$_2$(II), Th(IV)/La(III) and Th(IV)/Ce(III) was chosen as competitive elements because uranium, lantanium, cerium and thorium often coexist in their minerals, products and in even in waste-water. Due to their similar behavior, determination and separation of thorium is a problem in the presence of lantanium, cerium and uranium. Table 2 summarizes K_d, k and k' values of UO$_2$(II), La(III) and Ce(III) with respect to Th(IV).

A comparison of the K_d values for the Th(IV)-imprinted samples with the control samples for the Th(IV)-imprinted beads shows increase in K_d for Th(IV), while K_d decreases for UO$_2$(II), La(III) and Ce(III). The relative selectivity coefficient is a indicator to express an adsorption affinity of recognition sites to the imprinted Th(IV) ions. These results showed that the relative selectivity coefficients of the imprinted beads for Th(IV)/UO$_2$(II), Th(IV)/La(III) and Th(IV)/Ce(III) were 68, 97 and 116 times greater than non-imprinted matrix, respectively.

The Th(IV) cavity on the imprinted beads, occurred with the help of glutamic acid ligands, were arranged to match the charge, coordination number, coordination geometry and size to Th(IV). The recognition sites number on the ligand has an important role in ionic recognition. One mol Th(IV) make by 2 mol L-glutamic acid hydrochloride. Glutamic acid shows higher affinity to Th(IV) than La(III) and Ce(III), that may be due to the difference in coordination numbers for La(III), Ce(III) and Th(IV) (6, 6 and 8, respectively) and the number of donor atoms of glutamic acid is 4. The strong ligand MAGA shows higher affinity to Th(IV) than La(III) and Ce(III) and the ionic radius of UO$_2$(II) is larger than Th(IV) ions. Therefore, competitive adsorption studies [UO$_2$(II)/Th(IV), La(III)/Th(IV), Ce(III)/Th(IV)] showed that Th(IV)-imprinted beads are only selective to Th(IV) even in the presence of UO$_2$(II), La(III) and Ce(III).

There is no any Th(IV)-imprinted study in literature, so comparing of these results with other imprinted polymer study is impossible. But, some results that have obtained using resin and copolymer have compared. When a chelating resin, 11,23-disemicarbazono-26,28-dipropoxy-25,27-dihydroxy calyx[4]arene[8], a polymeric adsorbent such as divinylbenzene supported with o-vanillinsemicarbazone [28] and a polymer supported calix[6]arene hydroxomic acid [29] were used, the distribution coefficient (K_d) values for the determination of Th(IV) have found to be 3556, 5155 and 4635, respectively. These values are higher than K_d values of non-imprinted beads (1183.4) and lower than K_d values of imprinted beads (29,303). The K_d values of non-imprinted beads are low, because they have no any selectivity property on it. Since Th(IV)-imprinted beads have same size and shape cavity with Th(IV), the K_d value increase dramatically.

4. Conclusion

Solid-phase extraction (SPE) is more rapid, simple, economical and environmental-friendly preconcentration

method than the traditional liquid–liquid extraction. The main problem associated with SPE columns packed with ordinary stationary phases is low selectivity of the retention mechanism. A desired grade of selectivity may be obtained using columns packed with materials based on MIPs [30]. In the present work, a thorium(IV) imprinted polymer obtained by imprinting with Th(IV) ion as an ion-imprinted SPE beads spherical in shape were prepared by suspension polymerization. The adsorption is relatively fast and breakthrough capacity for Th(IV) ions was 40.44 mg Th(IV) per gram dry weight of beads. This fast adsorption equilibrium is most probably due to high complexation and geometric affinity between Th(IV) ions and cavities in the beads structure. The relative selectivity coefficient is an indicator to express an adsorption affinity of recognition sites to the imprinted Th(IV) ions. These results showed that the relative selectivity coefficients of the imprinted beads for Th(IV)/UO_2^{2+}, Th(IV)/La(III) and Th(IV)/Ce(III) were 68, 97 and 116 times greater than non-imprinted matrix, respectively. These results show that the produced IIP-SPE beads may be used in packed-bed chromatographic separation of thorium from Eskişehir monazite in future studies.

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