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Th(IV) ion-imprinted polymer for selective solid-phase extraction of Th(IV) and its analytical applications

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ABSTRACT

A new Th(IV) ion-imprinted polymer (IIP) was synthesized for the separation and recovery of trace Th(IV) ion from river water sample. Th(IV) IIP was prepared by copolymerization of methyl methacrylate (monomer) and ethylene glycol dimethacrylate (cross-linker) in the presence of Th(IV)-thiosemicarbazide-4-vinyl pyridine ternary complex wherein Th(IV) ion is the imprint ion and is used to form the imprinted polymer. Thorium(IV) ion was eluted with 10 mL of 1 M HCl. The polymers have been characterized by surface area measurements, fourier transform infrared spectroscopy, microanalysis and scanning electron microscopy analysis. The adsorption capacity of the imprinted polymer was found to be 0.290 mmol g^{-1}, which is much higher than most of the reported IIPs. The optimum pH for quantitative enrichment is 4.0. The relative selectivity coefficient values of the imprinted polymer for Th(IV)/Pb(II), Th(IV)/Zn(II), Th(IV)/Cu(II), Th(IV)/Ni(II), Th(IV)/Cd(II) and Th(IV)/Co(II) are 37.13, 37.40, 30.34, 35.69, 37.63 and 36.28, respectively. The lowest concentration that could be determined by Arsenazo III spectrophotometric method below which the recovery becomes non-quantitative is 5 μg L^{-1}.

Keywords: Thorium(IV); ICP-MS; Ion-imprinted polymer; Arsenazo III; Thiosemicarbazide

1. Introduction

Thorium has widespread applications in variable areas, such as optics, radio, aeronautics and aerospace, metallurgy and chemical industry, and material fields, extensively [1]. Unfortunately, thorium not only has chemical toxicity like other heavy metals do, but also has radioactivity which can cause a large-scale permanent damage of bone, kidney and liver [2,3]. Thorium is extremely mobile and once entered into the living bodies will provoke inner irradiation (especially due to the γ-active decay products), resulting in cancer [4]. Various preconcentration and separation techniques have been employed for the separation and purification of thorium.

The traditional preconcentration and separation methods for heavy metals are liquid–liquid extraction [5], electrodeposition [6], ion exchange [7–10], extraction chromatography [11] and solid-phase extraction (SPE) [12]. Of all these preconcentration methods, the SPE is the most popular one because of flexible working conditions and simple procedures. The basic principle of SPE is the concentration and purification of analytes from solution by sorption on a solid sorbent.

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Several previous studies have been reported for the selective separation and preconcentration of Th(IV) ions from various analytical matrices using polymeric supports impregnated with selective organic extractant [13–16]. The SPE method using ion-imprinted polymers (IIPs) are the most popular methods for separation and preconcentration of trace metals [17–21].

IIPs have found extensive applications in analytical chemistry for preconcentration of metal ions and their separation from interfering constituents before determination. The selectivity of IIP arises from the memory effect of the polymer to the imprint ions. Ion imprinting is a rapidly developing technique for the preparation of polymeric materials that are capable of ion recognition for selective separation and identification. The metal cation can also serve as templates for imprinting cross-linked polymers. Suitable ligand groups are brought in contact with the cation to form a complex. This is then converted to metal ion selective polymer by the usual polymerization with suitable cross-linking agent. After the removal of the template metal ion, the metal ion-desorbed polymer showed specific and fast rebinding.

In this study, synthesis of a new Th(IV) IIP has been presented along with its analytical characteristics and applicability for determination of trace Th(IV) in river water sample. The adsorption capacity of developed IIP (0.290 mmol g^{-1}) is higher than the reported IIPs (0.155–0.279 mmol g^{-1}) [22–24]. The developed IIP is highly selective for Th(IV). The possessed SPE method is simple, convenient and accurate.

2. Experimental

2.1. Instrumentation

A Systronics double beam spectrophotometer-2203 (Ahmedabad, India) was used for spectrophotometric measurements. EI digital pH meter 111 (Chandigarh, India) was used for pH measurements. FT-IR spectra were recorded in the frequency range 4,000–400 cm^{-1} by KBr pellet method using Bruker FT-IR Vertex 70 (Germany). The microanalysis was carried out using Elementar Analysensysteme GmbH: vario EL V3.00. Temperature-controlled rotary shaking machine (IEC-56) was used for shaking. The scanning electron microscopy (SEM) micrographs of the adsorbents were obtained at 5.0 kV on a SUPRA 40 VP Field Emission Scanning Electron Microscopy (SEM) (USA). Inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo Fisher, Germany) was used for selectivity studies. The operating conditions of the ICP-MS are given in Table 1.

Table 1
The operating conditions of the ICP-MS

ICP-MS	Thermo Fisher Xseries 2
Plasma gas flow rate (L min^{-1})	14
Auxiliary gas flow rate (L min^{-1})	0.7
Nebulizer gas flow rate (L min^{-1})	0.94
RF power	1,403
Replicates	3
Gas	Argon
Mass monitored	^{58}Ni ^{59}Co ^{65}Cu ^{66}Zn ^{111}Cd ^{208}Pb

2.2. Reagents and materials

A stock solution (1,000 μg mL^{-1}) of Th(IV) was prepared by dissolving 2.457 g of thorium nitrate ($Th(NO_3)_4·4H_2O$) purchased from Thomas Baker, India in 1 mol L^{-1} HNO_3. Arsenazo III (Alfa Aesar, UK) solution was prepared by dissolving 0.1 g of reagent in 100 mL of demineralized water.

Thiosemicarbazide (C.D.H., India), 4-vinyl pyridine (Alfa Aesar, UK), ethylene glycol dimethacrylate (Merck, Germany), methyl methacrylate (C.D.H., India), 2-methoxy ethanol (Thomas Baker, India) and 2,2´-azobisisobutyronitrile (Merck, Germany) were used. All other reagents were of AR grade.

2.3. Synthesis of Th(IV) ion-imprinted and control polymers

The ternary complex of Th(IV) was prepared by stirring 2 mmol of thiosemicarbazide, 2 mmol of 4-vinyl pyridine and 1 mmol of thorium nitrate in 10 ml of 2-methoxy ethanol. The above ternary complex solution was then mixed with 12 mmol of methyl methacrylate (MMA) and 36 mmol of ethylene glycol dimethacrylate (EGDMA) and 50 mg of 2,2´-azobisisobutyronitrile. The polymerization mixtures were cooled to 0˚C and purged with N_2 for 10 min, sealed and thermally polymerized in an oil bath at 80˚C while stirring for 3 h. The bulk polymer was dried at 70˚C to remove the solvent (porogen). The polymer was first washed with acetone, followed by repeated wash with acetone and water mixture, gradually increasing amounts of water until only water was used. This procedure removed unreacted monomers. The resulting polymer was then dried, ground and sieved to obtain the IIP which is schematically represented in Fig. 1. Control polymer (CP) was similarly prepared by omitting the imprint ion.

2.4. Characterization studies

2.4.1. Surface area measurement

The surface area of the leached IIP (IIPL) and CP was measured by methylene blue adsorption method [25]. A standard solution of methylene blue ($0.0178\ g\ L^{-1}$) was prepared. A calibration curve for methylene blue was drawn ($\lambda_{max} = 600$ nm) by measuring diluents from standard stock. To calculate the surface area, 0.1 g of leached IIP and CP was treated with 25 mL of methylene blue solution. The treatment lasted until there was no further decrease in absorbance. The amount of methylene blue adsorbed was calculated based on concentration difference between the initial and equilibrium values, which were measured by spectrophotometry. The surface area of leached IIP and CP was also measured using BET method.

The CP/IIP were also characterized by FT-IR studies, SEM analysis and microanalysis.

2.5. General procedure for Th(IV) extraction

Aliquots of Thorium solution (25 mL) in the concentration range 0.043–0.431 mmol L^{-1} were treated with 0.1 g of polymer particles in the pH range 1–5 for 15 min. The pH of the solution was adjusted to desired values by adding the following buffers: sodium acetate/hydrochloric acid for pH (1–3) and sodium acetate/acetic acid for pH 4–5. At the end of predetermined time intervals, the polymer was separated by centrifugation and given a gentle wash with DMW to remove any unadsorbed Th(IV). Adsorbed Th(IV) ions were eluted by treatment with 10 mL of 1 M HCl. The concentration of thorium(IV) ion in the supernatant and eluent was determined spectrophotometrically using Arsenazo III method [26]. Suitable aliquots of eluent were taken and 2.5 mL each of conc. HCl and Arsenazo III were added and diluted to 25 mL. The absorbance of thorium (IV)–Arsenazo III complex was measured at 663 nm. The concentration

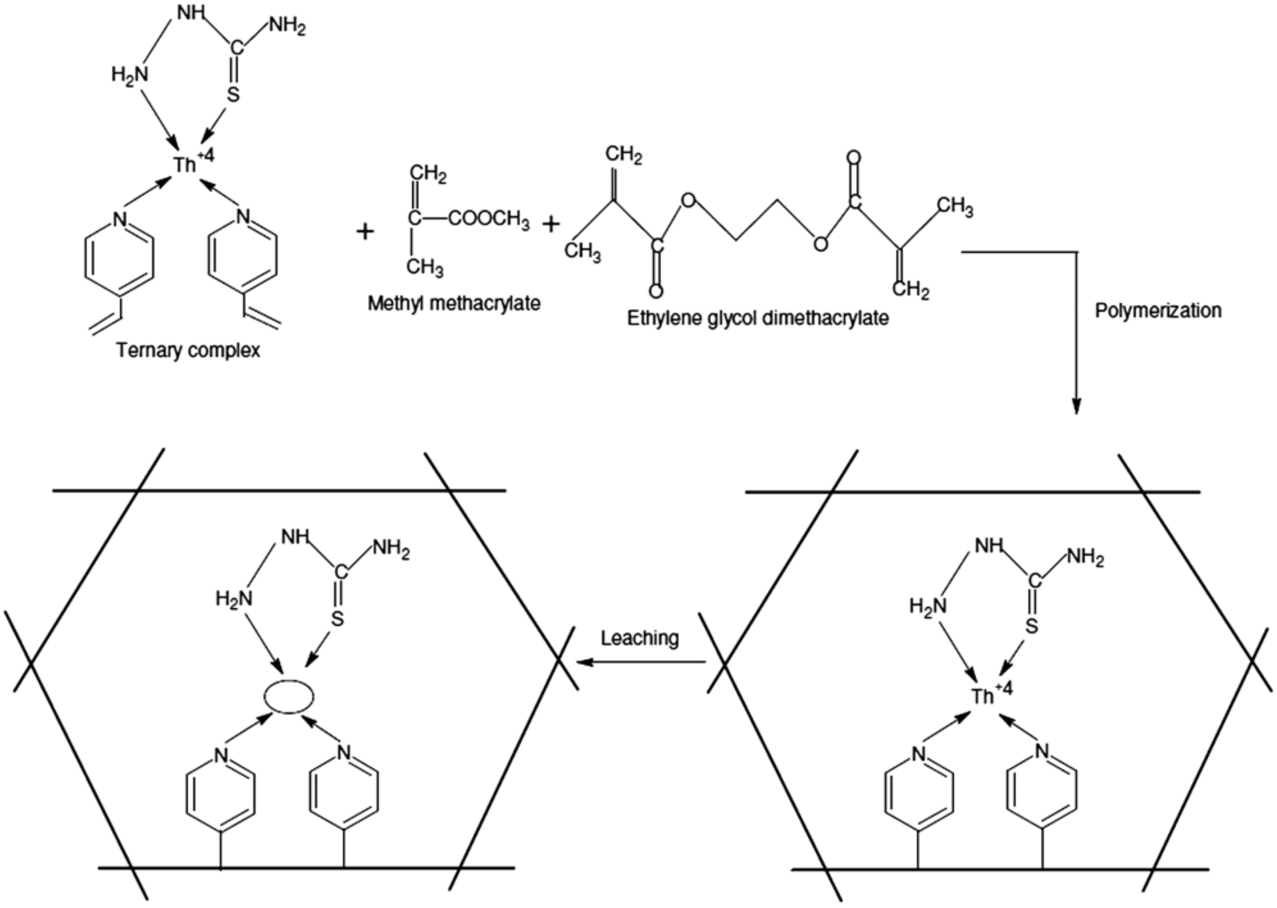

Fig. 1. Scheme of synthesis of Th(IV) IIP.

of other metal ions in the supernatant and eluent was measured by ICP-MS. The adsorption capacity, distribution ratio and selectivity factor of Th(IV) with respect to Pb(II), Zn(II), Cu(II), Ni(II), Cd(II) and Co(II) and relative selectivity factors were calculated using following equations:

$$q_e = (C_o - C_e)\ V\ /\ W \tag{1}$$

$$D = q_e /\ C_e \tag{2}$$

$$\alpha = D_{Th} /\ D_M \tag{3}$$

$$\alpha_r = \alpha_i /\ \alpha_n \tag{4}$$

where q_e represents the adsorption capacity (mmol g^{-1}), C_o and C_e are the initial and equilibrium concentrations of Th(IV) (mmol L^{-1}), W is the mass of polymer (g) and V is the volume of metal ion solution (mL), D is the distribution ratio (mL g^{-1}), α is the selectivity factor, D_{Th} and D_M represent the distribution ratios of Th(IV) and Pb(II), Zn(II), Cu(II), Ni(II), Cd(II) or Co(II), α_r the relative selectivity factor and D_i, D_n and α_i, α_n represent the distribution ratios and selectivity factors of IIP and CP, respectively.

3. Results and discussion

3.1. Characterization studies

3.1.1. Surface area measurement

The surface area of leached IIP and CP was calculated using the following equation:

$$A_s = \frac{G N_{AV} \varnothing 10^{-20}}{M M_W} \tag{5}$$

where A_s is the polymer surface area in $m^2\,g^{-1}$, G is the amount of methylene blue adsorbed (g), N_{AV} is the Avogadro's number ($6.02 \times 10^{23}\,mol^{-1}$), $\varnothing$ is the methylene blue molecular cross-section (197.2 Å^2), M_W is the molecular weight of methylene blue ($373.9\,g\,mol^{-1}$) and M is the mass of adsorbent (g). The surface area for leached IIP and CP are 514.0 and $320.0\,m^2\,g^{-1}$, respectively.

The BET surface area ($m^2\,g^{-1}$) for leached IIP and CP are 515.12 and 319.78, respectively.

3.1.2. FT-IR spectra

The FT-IR spectra of IIP (leached and unleached) and CP are shown in Fig. 2. The similarity in these IR spectra shows that these polymers have a similar backbone. In the FT-IR spectra of CP/leached IIP, the absorption peaks at 1,223/1,221 and 1,072/1,066 cm^{-1} belong to >C=S stretching vibrations. In case of unleached IIP, the absorption peaks of >C=S stretching vibrations are shifted towards lower wavenumbers (1,206 and 1,018 cm^{-1}) due to Th(IV)–thiosemicarbazide complex formation. Further, an absorption band obtained at 578 cm^{-1} in the FT-IR spectrum of IIP seems due to Th(IV)–N complexation. The N–H stretching frequency observed at 3,441–3,467 cm^{-1} shows that thiosemicarbazide remains intact in the polymer matrix after leaching.

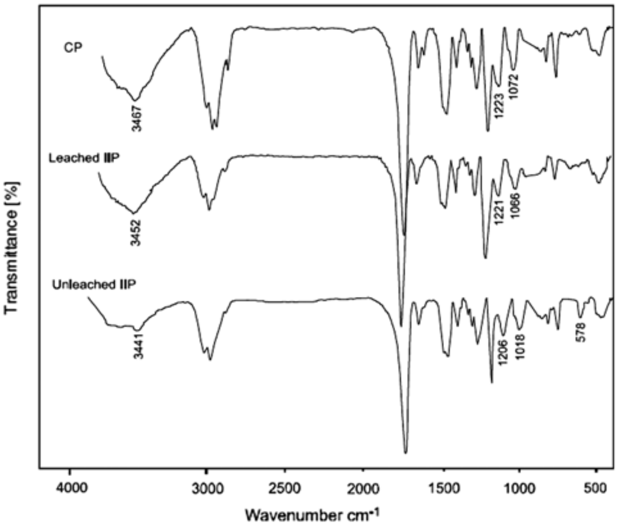

Fig. 2. FT-IR spectra of CP, unleached IIP and leached IIP.

3.1.3. Microanalysis experiments

The elemental composition of both control and imprinted polymers was much alike (Table 2). This confirms the IR spectral results that the ligands thiosemicarbazide and VP are intact in leached IIP and thorium ion alone is leached out during the process of leaching from the polymer matrix.

3.1.4. SEM analysis

SEMs of Th(IV) IIP and CP are shown in Fig. 3. The SEM image of CP (Fig. 3(B)) exhibited a fractured and irregular surface, while that of the IIP (Fig. 3(A)) was monoliths with particles packed together and a smoothly spherical surface, which is more beneficial to the homogeneous binding of template ions. Moreover, the surface of the Th(IV) IIP was porous, although the surface of CP was non-porous.

Table 2
Microanalysis data

	Calculated value (%)					Found value (%)				
Polymer	C	H	N	O	S	C	H	N	O	S
CP	60.38	7.30	0.96	30.33	1.03	60.28	7.31	0.97	30.28	1.16
IIP	58.31	7.29	1.13	32.29	0.98	58.33	7.29	1.13	32.18	1.07
IIPL	61.14	7.74	0.74	28.56	1.82	61.17	7.75	0.74	29.13	1.21

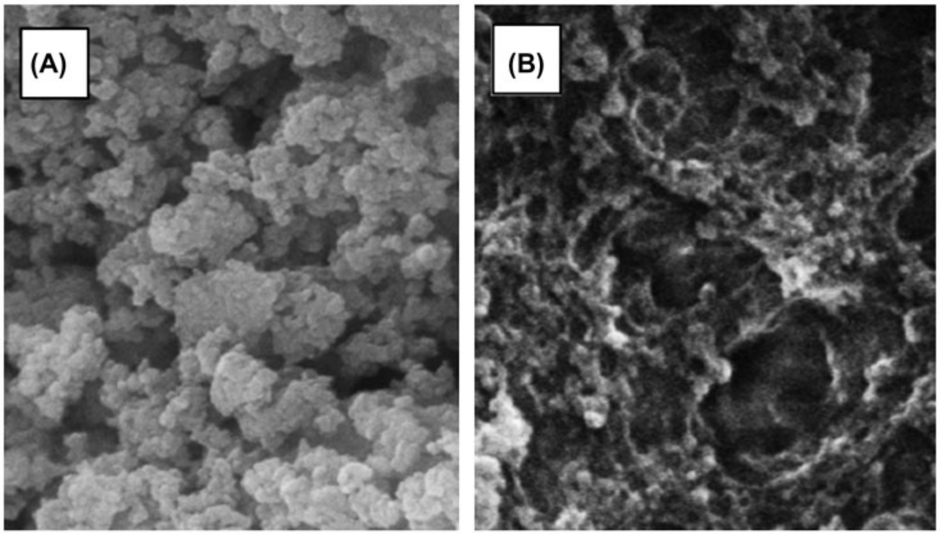

Fig. 3. SEM images of Th(IV) IIP (A) and CP (B). Both of the scale bars are 1 μm.

3.2. Adsorption capacity

The adsorption capacity increases with an increase in concentration of Th(IV) (pH 4.0) in both IIP and CP and reaches a plateau at 0.290 (IIP) and 0.176 (CP) mmol g^{-1} at concentration of 0.388 and 0.302 mmol L^{-1}, respectively (Fig. 4). The significant difference in adsorption capacities indicates the role of ion imprinting in determining the adsorption property of the adsorbent. Ion-binding cavities resultant from imprinting essentially activated the polymer surface for extensive ion uptake, whereas the interactions of CP, lacking ion-recognition ability, remained unspecific.

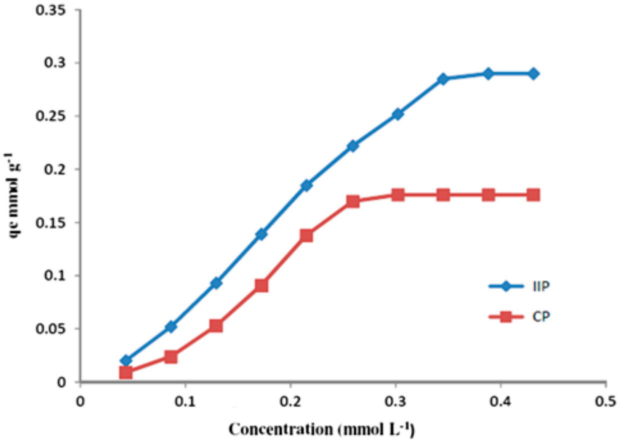

Fig. 4. Effect of concentration on the adsorption of Th(IV) on IIP and CP.

3.3. Effect of pH

The pH influence of the loading solution on the preconcentration of thorium was tested by shaking 0.1 g IIP or CP and 25 mL of thorium solution (0.388 mmol L^{-1}) for 15 min. Adsorption capacity of IIP is higher than CP at all the investigated pH values (Fig. 5). Decrease in adsorption capacity above pH 4.5 seems due to hydrolysis of thorium(IV) in both the polymers. The optimum pH was 4.0 and adjusted in all subsequent studies.

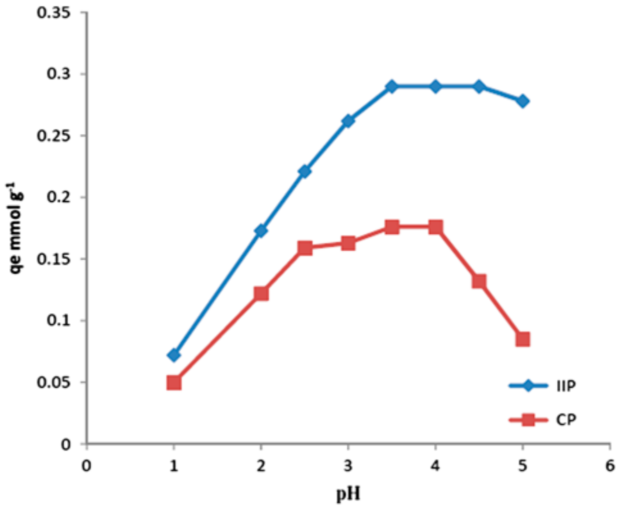

Fig. 5. Effect of pH on adsorption of Th(IV) ion on IIP and CP.

3.4. Selection of eluents and its concentration

The choice of the suitable elument is important for the analytical performance of the SPE procedure. In order to elute thorium adsorbed on the polymer, different eluents were tested (Table 3). The greater elution with 1 M HCl (>99.0%) in comparison to 1 M HNO_3 (89.8%) was observed and was used as an eluent for further studies. The effect of eluent volume on the Th(IV) desorption was evaluated. The quantitative elution was achieved with 10 mL of the eluent.

Table 3
Recovery (%) for Th(IV) from IIP using different eluents (0.1 g IIP; 0.1 μmol mL^{-1} Th(IV); 10 mL eluent solution)

Eluent	Recovery (%)
0.5 M HCl	78.0
1 M HCl	>99.0
1 M HNO_3	89.8
1 M H_2SO_4	68.1

3.5. Selectivity studies

The selected metal ions present in 25 mL of 100 μg L^{-1} were equilibrated with 0.1 g of CP or IIP. The concentrations of these elements in solution were determined by spectrophotometry or ICP-MS after elution with 10 mL of 1 M HCl. The distribution ratios and selectivity factors of Th(IV) ion with respect to other metal ions using CP and IIP are summarized in Table 4. The relative selectivity factor (α_r) values of Th(IV)/Pb(II), Th(IV)/Zn(II), Th(IV)/Cu(II), Th(IV)/Ni(II), Th(IV)/Cd(II) and Th(IV)/Co(II) are 37.13, 37.40, 30.34, 35.69, 37.63 and 36.28, respectively, which are greater than 1. It shows that Th(IV) can be determined even in the presence of Pb(II), Zn(II), Cu(II), Ni(II), Cd(II) and Co(II) interferences.

3.6. Calibration curve, accuracy and precision

The calibration was performed using four Th(IV) standards at different concentrations in the range of 25–200 μg L^{-1}. The obtained linear regression equation and correlation coefficient (r) for Th(IV) were $A = 1.0153\ C–2.9751$ and $r = 0.9998$, correspondingly, where A is the absorbance and C is the amount of Th(IV) in micrograms per one litre of sample solution. The lowest concentration that could be determined by Arsenazo III spectrophotometric method below which the recovery becomes non-quantitative is 5 μg L^{-1}. The accuracy and precision of the method were determined using seven replicate samples containing 50 μg L^{-1} Th(IV). The found average concentration of Th(IV) was 48.94 μg L^{-1} with relative standard deviation (% RSD) of 0.293%, indicating that the accuracy and reproducibility of this method are satisfactory for the concentration and recovery of Th(IV) in aqueous solutions.

Table 4
The selectivity parameters of Th(IV) IIP for Th(IV)

Metal ion	Analysis procedure	D_i	D_n	α_i	α_n	α_r
Th(IV)	Spectrophotometry	14,455.89	394.43	–	–	–
Pb(II)	ICP-MS	378.14	381.58	38.24	1.03	37.13
Zn(II)	ICP-MS	361.25	370.35	40.02	1.07	37.40
Cu(II)	ICP-MS	335.49	345.24	43.09	1.42	30.34
Ni(II)	ICP-MS	277.43	269.75	52.11	1.46	35.69
Cd(II)	ICP-MS	243.10	249.00	59.46	1.58	37.63
Co(II)	ICP-MS	222.59	219.92	64.94	1.79	36.28

3.7. Applications

The applicability of the method was tested to the river water sample (Shuklaganj, Kanpur). The standard addition method was applied to check the selectivity of the IIP for Th(IV) against matrix elements. A recovery test was performed by determining the spiked concentration in the sample in which $25\,\mu g\,L^{-1}$ of Th(IV) was added. The recovery of Th(IV) from river water was 98.9 ± 1.03%, which could make the procedure a relatively reliable method.

4. Conclusions

Th(IV) IIP has improved binding characteristics as observed in their highest capacity and selectivity compared to the IIPs reported in the literature. The maximum adsorption capacity of Th(IV) was about $0.290\,mmol\,g^{-1}$. The adsorption capacity for the template increased with increasing initial metal ion concentration. When the pH was increased to 4.0, the adsorption capacity was close to its maximum value. On the basis of the results obtained in this study, we believe that the synthetic imprinted adsorbent can be used for selective enrichment of trace amount of Th (IV) from river water sample.

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