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Synthesis, Characterization, and Metal Extractive Behavior of Functionalized AXAD-16 Polymeric Matrix Using Oxyacetone Acetamide

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ABSTRACT

A new metal chelating polymer has been synthesized using Amberlite XAD-16 (AXAD-16) polymer matrix, chemically modified using oxyacetone acetamide as the functional group. The resin was characterized by Fourier transform-infra red (FT-IR) studies, elemental analysis, and thermogravimetric analysis. The metal extractive efficiency of the functionalized resin matrix was examined and it was found that the synthesized resin showed high selectivity and preconcentrating ability toward trace heavy metal ions. Various physiochemical and kinetic factors operating on the quantitative metal ion extraction were studied and optimized. It was found that quantitative metal ion sorption was possible in the pH range of 5.0–7.0, 3.0–4.0, 5.0, and 6.0–7.0 for U(VI), Th(IV),

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Pb(II), and Cd(II), respectively. The developed resin showed faster exchange rates and a high metal exchange capacity value of 202, 185, 179, and 86 mg g^{-1} for U(VI), Th(IV), Pb(II), and Cd(II), respectively. The newly synthesized resin possesses improved metal extraction efficiency as revealed by the flow rate and kinetic studies, with complete metal ion saturation effective in <15 min, with a $t_{1/2}$ value of <5 min, for all the metal ions of interest. The ion-selective behavior of developed resin was tested using various interfering electrolyte and metal ion species and was found to have greater tolerance toward these matrix species in the process of quantitative trace metal ion recovery down to the parts per billion ppb level. A high preconcentration factor value of 400 was achieved for U(VI), Th(IV), and Cd(II), respectively, and 500 in the case of Pb(II). The developed method was tested on its metal preconcentration ability, using synthetic and real samples. The system showed reproducibility and reliability in analytical data, with an rsd value of <4.1% on triplicate measurements.

Key Words: Metal ion; AXAD-16; Resin; Desorption.

INTRODUCTION

With the growing interest and extensive usage of metal ions in the field of catalysis and in electronic and electrical industries, metal ion contamination in various water resources has become an increasing nuisance, which ultimately calls for environmental awareness.[1] As a result, separation and concentration of trace metal ions has become an increasing area of research interest. However, accurate analysis of metal ions, especially at their trace levels, is one of the most difficult and complicated analytical tasks and often demands for powerful analytical tools with a high degree of versatility, specificity, sensitivity, and accuracy.[2] But even highly sophisticated detection systems demand a preconcentration or sample cleanup step to facilitate selective extraction and sequential separation of analytes prior to their detection, in order to avoid matrix interferences.[3]

Several separation techniques have been developed in the past for this purpose, including the use of liquid–liquid extraction (LLE), ion-exchange resins, co-precipitation techniques, etc. Of these, the use of LLE has remained as the preferred technique for several years due to its high selectivity behavior.[4] However, due to several technical problems like huge organic waste disposal, large solvent requirements, etc., the use of solid-phase extractants (SPE) has turned out to be a more eminent and promising technique. Among the different types of SPE adsorbents reported, such as the use of activated carbon, silica gel, keiselghur, cellulose, porous glass beads, ion-exchange resins, etc., the development of synthetic ion-exchange resins drastically accelerated the growth of trace metal recovery. But these ion-exchange resins have poor ion selectivity and moderate exchange kinetics. Because of this, the use of styrene-based chelating polymeric sorbents and their application in the field of separation science has increased substantially in recent years. The main advantages of styrene resins are their high chemical and mechanical stability, high ion selectivity and sorptive capacity, and faster kinetics.[5] Numerous chelating sorbents have been developed based on styrene-divinyl polymers, and their applicability to metal ion extraction has been studied.[2,5,6] Chelating polymers based on AXAD (a styrene-divinyl copolymer) resin has gained significant importance in recent years due to their commercial availability and flexibility to chemical modification.[7–22] Based on these aspects, a new chelating polymeric resin has been synthesized; it uses amberlite XAD-16 (AXAD-16) polymeric matrix, chemically modified through a series of chemical reaction, to result in a chelating polymer with carbonyl-ether linkage, which favors selective heavy metal extraction. The metal extractive behavior of the resin matrix toward actinide and post-transition metal ions and the influence of various experimental parameters operating on the process of resin-phase metal ion sorption were studied using both static and dynamic equilibration techniques. The developed method, when applied to synthetic and real samples, showed high preconcentration values added to faster exchange kinetics, greater metal loading capacity, and ion-selective behavior, which were found much superior to the values reported to date in the literature.

EXPERIMENTAL

Instrumentation

Characterization of the resin matrix was performed using a Bruker IFS 66V model FT-IR spectrometer (Bruker, Ettlinger, Germany) for functional group identification. The chemically modified resin at each stage of its synthesis was analyzed using an Elementar Vario EL model CHNPS elemental analyzer (Elementar Americas, Inc., NJ, USA). Water-regaining capability (hydrophilicity) of the chelating sorbent was investigated using a Perkin–Elmer thermal analyzer (Perkin Elmer Life and Analytical Sciences Inc., CA, USA). Metal ion estimations were done using a Shimadzu UV-3100 model spectrophotometer (UV-Vis Spectrophotometer, Shimadzu Scientific Instruments, Inc., Columbia, USA) and a Hitachi F-4500 model fluorescence spectrophotometer (Hitachi High-Technologies, Berkshire, UK) for U(VI) and

Th(IV). In the case of Pb(II) and Cd(II), a Varian SpectrAA-20 model flame atomic absorption spectrometer was employed (FAAS, Varian Techtron, Springvale, Australia). An Orbitex-DS model mechanical shaker (Scigenics, Chennai, India) operated at 200 rpm was employed for static studies. Solution pH adjustments were performed using a Digisun DI-707 model pH meter (Instruments and Equipments, Mumbai, India).

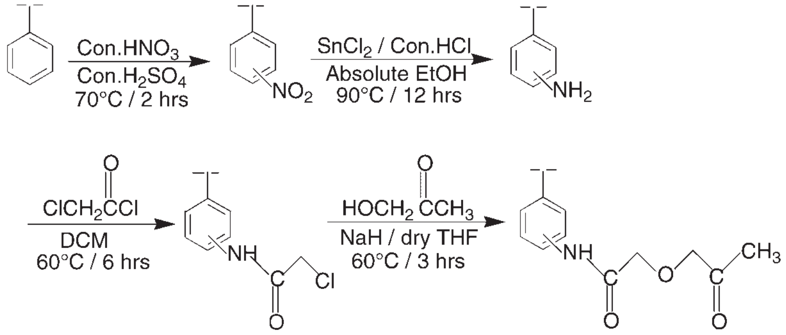
Chemicals and Reagents

Standard metal ion stock solutions were prepared by individually dissolving exact amounts of $UO_2(NO_3)_2 \cdot 6H_20$, $Th(NO_3)_4 \cdot 5H_2O$ (Fluka) and $Pb(NO_3)_2$, and $3CdSO_4 \cdot 8H_2O$ (E-Merck) in slightly acidified double-distilled water. Chemicals like hydroxyacetone and chloroacetyl chloride were purchased from Fluka. Amberlite XAD-16 resin beads (20–50 mesh, surface area 825 $m^2\,g^{-1}$, bead size 0.3–1.2 mm) were procured from Fluka.

Reagents like stannous chloride, ethanol, hydrochloric acid, nitric acid, sulfuric acid, tetrahydrofuran (THF), and dichloromethane (DCM) were obtained from E-Merck. For pH adjustments, chloroacetic acid–acetic acid (pH 1–3), sodium acetate–acetic acid (pH 4–6), ammonium acetate-ammonia (pH 7–8), and ammonium chloride–ammonia (pH 9–10) were used as buffer solutions. All chemicals and reagents mentioned were of analytical reagent (AR) grade.

Synthesis of the Chelating Polymer

The AXAD-16 resin beads were purified prior to functionalization using 4 M HCl followed by 2 M NaOH to remove both basic and acidic impurities. The resin beads were water-washed until the washings showed neutral pH followed by filtrations and vacuumization. Ten grams of the resin beads were nitrated using 35 cm^3 of nitrating mixture (10 cm^3 conc. HNO_3 and 25 cm^3 conc. H_2SO_4) at 70°C for 2 hr, followed by amination using 40 g $SnCl_2$, 45 cm^3 HCl, and 50 cm^3 absolute ethanol at 90°C for 10 hr. The aminated resin was washed with 2 M NaOH until the washings showed absence of tin. The resin was water-washed to neutral pH, vacuum-dried, and further reacted with chloroacetyl chloride (15 cm^3) in dry DCM at 60°C for 6 hr. The resin beads were purified and treated with hydroxyacetone, using sodium hydride in dry THF, at 60°C for 3 hr. The synthesis involved in the development of the chelating resin is depicted in Sch. 1.



Scheme 1.

Methods Adopted in the Process of Metal Extraction and Preconcentration

Static Equilibration (Batch) Method

The metal extractive behavior of the chelating resin was studied in pilot scale, using 50 mg of resin beads equilibrated with metal ion solution of known concentration at 200 rpm for 60 min using a mechanical shaker. The optimum conditions that facilitate quantitative metal sorption to the resin phase were initially studied using this method. Desorption of metal ions and their subsequent preconcentration were effective using either 4 M HCl

Table 1. Optimized experimental parameters for metal ion sorption and desorption.

Experimental parameters	U(VI)	Th(IV)	Pb(II)	Cd(II)
pH range	5.0–7.0	3.0–4.0	5.0	6.0–7.0
$t_{1/2}$ (minutes)	2.0	2.5	2.1	4.8
Metal sorption capacity (mmol g^{-1})	0.859	0.797	0.894	0.768
Concentration of HCl/ HNO$_3$ for desorption	4 M	4 M	4 M	4 M
Average % recovery	98.9	99.1	99.8	98.8
Sample flow rate (cm^3 min^{-1})	10–12	10–12	12–14	6–8
Lower limit of detection (ng cm^{-3})	5.5	5.2	6.0	4.5

or HNO_3 of 10 cm^3 volume. Metal ion estimation was possible using Arsenazo-III and Thoron spectrophotometric methods for U(VI) and Th(IV), respectively; in the case of Pb(II) and Cd(II), flame atomic absorption spectrometry (FAAS) technique was adopted. The metal-desorbed resin beads were water-washed and reused. The optimized experimental parameters for metal ion sorption and desorption are listed in Table 1. Similar batch studies conducted using nonfunctionalized AXAD-16 resin beads showed no metal extractive behavior.

Column Dynamic Method

A glass column of dimension (14 × 0.6 cm i.d.) was packed with 1 g of preconditioned resin beads by slurry method. The resin beads were preconditioned by soaking in optimum buffer solution for 60 min prior to packing. The resin bed (~5 cm) was water-washed prior to passage of sample solution, and the sample flow rates for individual analytes were as listed in Table 1. Estimation processes were carried out using FAAS and spectrophotometric methods for respective analytes. For trace level estimation of U(VI) concentration obtained from synthetic and real samples, a spectrofluorimetric procedure using H_3PO_4 medium[23] was adopted.

RESULTS AND DISCUSSION

Characterization of the Chelating Resin

IR Spectra

The spectral bands of the chelating matrix at 3376, 2925, 1389, 1150 and 1698, and 1620 cm^{-1} corresponds to N–H, C–H, C–N, C–O–C, and C=O stretching vibrations, respectively. The presence of the CH_2–Cl band at 710 cm^{-1} in the third step and its subsequent disappearance in the final step of synthesis, followed by the appearance of C–O–C and C=O spectral bands at 1150 and 1698 cm^{-1}, proved the completion of the reaction scheme. A red shift of 10–15 cm^{-1} was observed at C–O–C, and C=O stretching vibrations, indicating their active participation, were observed in the process of metal ion complexation, which was also confirmed by Far IR studies.

CHN and Thermal Analysis

The percentage values of C 70.11, H 6.42, and N 5.89, obtained from CHN analysis for the functionalized resin, in comparison with the theoretical values of C 66.95, H 6.44, N 6.00 confirms the presence of at least one ligand moiety per repeating unit of the polymeric backbone. Similarly, each stage of the reaction scheme was characterized by elemental analysis in order to study the extent of ligand functionalization.

Thermal studies showed a weight loss of 4.27% up to 110°C for the functionalized resin matrix soaked in water for 4 hr (which was filtered and air-dried, prior to analysis), compared with overunsoaked resin matrix. The data shows the resin's better water regaining capacity, thereby enhancing its hydrophilicity and ultimately resulting in faster metal-exchange kinetics.

Batch Method Metal Extraction Studies

Characteristic Influence of Solution pH

Influence of solution pH on the metal extractive efficiency of the polymeric matrix was investigated over a wide pH range (1–7). For this study, 50 mg resin was equilibrated with an individual metal ion concentration (10 $\mu g\,cm^{-3}$) of

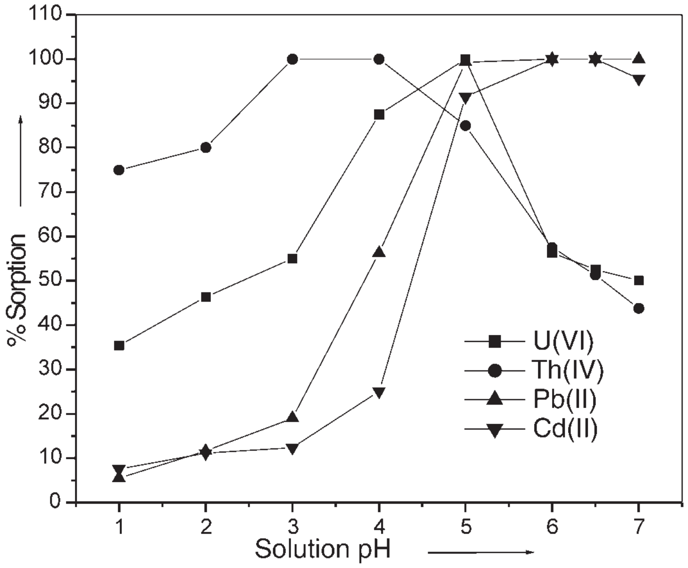


Figure 1. Metal extraction efficiency as a function of solution pH. Volume and concentration of metal ion solution—50 cm^3, 10 $\mu g\,cm^{-3}$. Amount of resin used—50 mg.

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50 cm^3 volume for 60 min at 200 rpm using a mechanical shaker. The plot of extraction efficiency as a function of solution pH (as shown in Fig. 1) shows distinct variation in its extractive property for all the analytes of interest. This can be attributed to the competition that exists between the formations of a more stable neutral metal–ligand polymer complex over other stable forms of the analyte species in the solution state that exist at various pH conditions.

Kinetic Studies

The rate of metal ion exchange between phases was investigated using individual metal ion solutions of concentration (40 cm^3, 12.5 μg cm^{-3}), equilibrated with 50 mg of resin over a series of time intervals, as indicated in Fig. 2. Extraction of 100% was observed for all analytes within 15 min. The kinetic properties of the chelating resin are mainly attributed to the physical properties of the polymeric matrix. The rate of metal ion-phase transfer was faster due to the enhanced hydrophilic character of the functionalized resin, which was reflected by $t_{1/2}$ values, where time duration of <5 min was sufficient for 50% metal ion sorption for all the analytes, thereby drastically reducing the time of metal ion analysis. The values obtained from kinetic

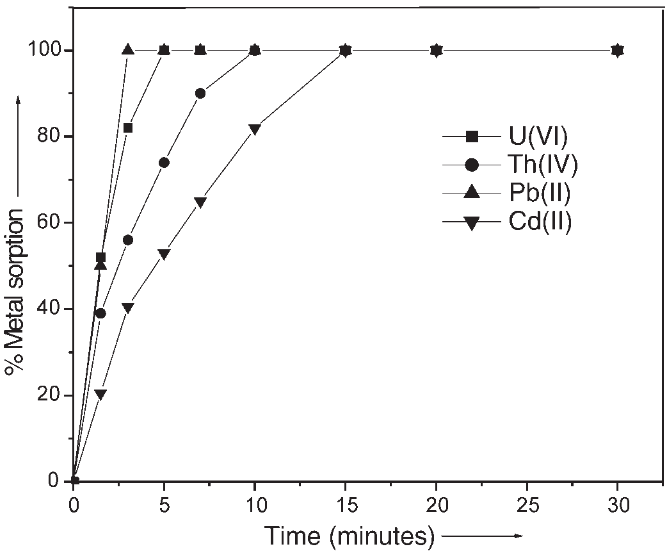

Figure 2. Kinetic studies on metal phase equilibration. Volume and concentration of metal ion solution—40 cm^3, 12.5 μg cm^{-3}. Amount of resin used—50 mg.

studies were twice or sometimes even three times above the values reported in the literature for other chelating resin matrices.[11–13,16–24]

Metal loading Capacity of the Resin Matrix

The extent of metal ion saturation to the chelating resin matrix was studied by saturating excess amounts of metal ion solution (100 cm^3, 125 $\mu g\,cm^{-3}$) with 50 mg of resin for 6 hr. High metal sorption values of 202, 185, 179, and 86 $mg\,g^{-1}$ were obtained for U(VI), Th(IV), Pb(II), and Cd(II), respectively. These values were found to be far more superior to reported literatures values due to the macroporous structure of the polymeric matrix, which ultimately facilitates greater ligand functionalization, thereby not only increasing the number of chelating sites but also favoring greater chelating site accessibility.

Table 2. Resin tolerance toward interfering electrolytes/metal ion species.

	Metal ions[a]			
	U(VI)	Th(IV)	Pb(II)	Cd(II)
Tolerance limits for electrolytes (mol dm^{-3})				
NaCl	0.86	0.86	0.61	0.73
KNO_3	0.48	0.47	0.41	0.40
$NaSO_4$	0.30	0.30	0.29	0.28
Na_3PO_4	0.30	0.30	0.30	0.36
NaF	0.51	0.54	0.68	0.82
CH_3COO^-	0.36	0.34	0.32	0.39
CO_3^{2-}	0.14	0.15	0.34	0.40
Ca^{2+}	0.71	0.85	0.81	0.88
Mg^{2+}	0.45	0.44	0.39	0.31
Tolerance limits for interfering metal ions (mmol dm^{-3})				
Mn(II)	3.9	3.8	3.4	3.2
Co(II)	3.6	3.7	3.0	3.0
Cu(II)	3.4	3.4	3.1	3.0
Fe(II)	4.1	4.2	3.3	3.1
Ni(II)	3.9	4.0	3.7	3.6
Zn(II)	3.3	3.3	3.0	3.1
Hg(II)	7.1	6.9	5.9	5.2

[a] Volume and concentration of metal ion solution—35 cm^3, 1.43 $\mu g\,cm^{-3}$. Amount of resin used—50 mg.

Interfering Electrolyte/Metal Ion Tolerance

The selectivity of the chelating resin depends on the nature of chemically active groups present in the resin matrix. In order to study the resin's ion-selectivity behavior and also its tolerance toward various electrolytes and metal ion species, individual analyte solutions (35 cm^3, 1.43 $\mu g\,cm^{-3}$) were equilibrated with 50 mg of resin in the presence of large concentrations of electrolyte/metal ions species. The concentrations of these matrices species, up to which no interference or quantitative analyte loss was observed, are shown in Table 2. The results show the superior metal complexing behavior of the resin matrix toward actinides and post-transition metal ions, even in the presence of huge concentrations of interfering electrolytes and more common transition metal ions. It is important to note that the metal sorption values obtained were much superior to other developed chelating resins reported in literature. However, the values were not that much higher when compared to some of the conventional ion-exchange resins, which lack selectivity, making the newly developed resin more superior.

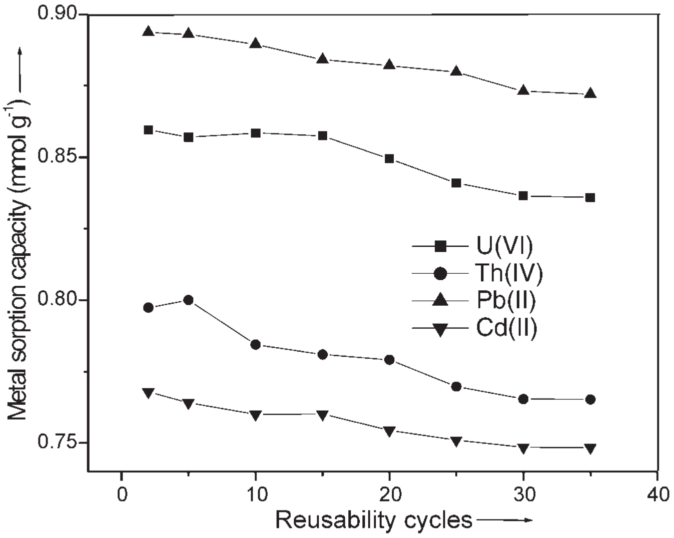

Figure 3. Regenerative character of the resin matrix. Volume and concentration of metal ion solution—100 cm^3, 125 $\mu g\,cm^{-3}$. Amount of resin used—1000 mg.

Lower Limit of Metal Ion Detection

Sensitivity of the developed method was studied using analyte solutions in the concentration range (30 cm^3, 0.01–0.0001 μg cm^{-3}) equilibrated with 50 mg of resin. The results obtained for each analyte (listed in Table 1) show the possibility of quantitative metal preconcentration, even at parts per billion levels.

Reusability and Chemical Stability

Accuracy and reproducibility in analytical data were often challenged when reusing the same resin. In order to study these effects, 50 mg of resin beads was equilibrated with metal ion solution (100 cm^3, 125 μg cm^{-3}). After the desorption and estimation process, the results were tested for reproducibility, and it was found to be within 3.1% rsd over 30 cycles (as depicted in Fig. 3) of continuous usage. Similarly, the durability of the resin matrix was tested using acid concentrations up to 4–6 M HCl/HNO$_3$, and it was found that the resin never showed any significant change in its extractive behavior, proving its high chemical stability.

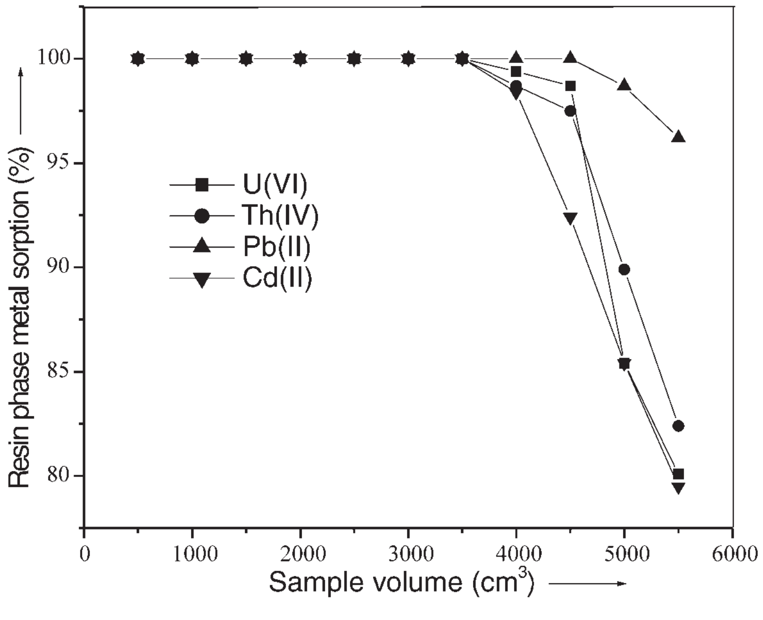

Figure 4. Effect of sample breakthrough volume on metal ion sorption. Amount of individual metal ion added—50 μg. Amount of resin used–1000 mg.

Dynamic Mode of Metal Ion Equilibration

Breakthrough Volume Studies

Sample breakthrough volume for individual analytes was estimated using sample solution of varying volumes, each containing 50 μg of individual metal ions, which was passed through the preconditioned resin bed. Breakthrough curves (Fig. 4) for all analytes were obtained only after 4000 cm^3 of sample passage, showing the resin's greater metal preconcentration ability, which was possible due to features like faster kinetics, ion selectivity, and better ligating site accessibility. As a result, a preconcentration factor value of 400 was obtained for U(VI), Th(IV), and Cd(II), respectively, and, in the case of Pb(II), it was found to be 500, with a metal ion recovery value of >97.9%. Metal ion desorption was carried out using 10 cm^3 of eluant at a flow rate of 2 $cm^3\,min^{-1}$, thereby reducing the time of metal ion analysis.

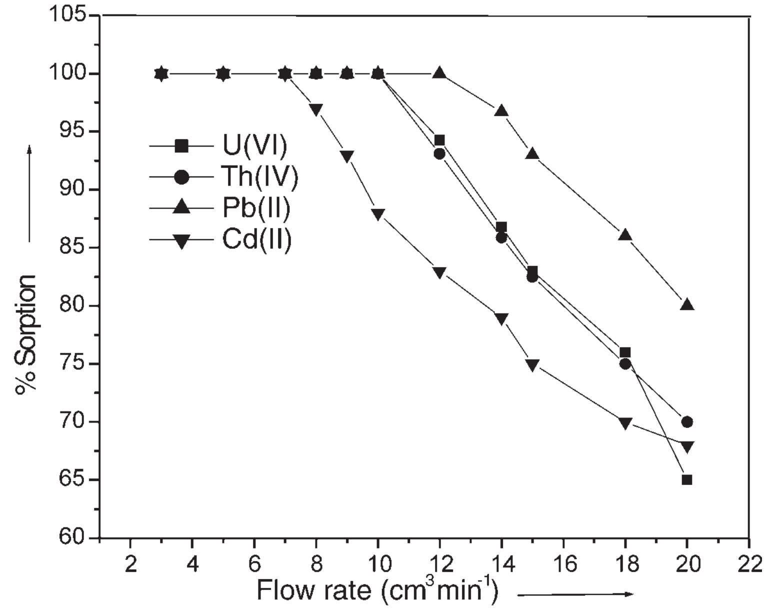

Figure 5. Influence of sample flow rate toward metal ion extraction volume and concentration of metal ion solution—1000 cm^3, 1 $\mu g\,cm^{-3}$). Amount of resin used—1000 mg.

Sample Flow Rate Studies

The influence of sample flow rate on the extent and rate of metal ion exchange to the polymeric matrix was studied under different flow rate conditions, as shown in Fig. 5. The metal ion solution ($1000\,cm^3$, $1\,\mu g\,cm^{-3}$) containing individual amounts of analytes was passed through the resin bed; the plot shows that a flow rate of $10-12\,cm^3\,min^{-1}$ was optimium for $>95\%$ metal sorption in the case of actinide ions and a flow rate of 6–8 and $12-14\,cm^3\,min^{-1}$ in the case of Cd(II) and Pb(II), respectively, thereby, providing favorable evidence to kinetic studies on the degree of metal ion phase exchange.

APPLICATIONS

Synthetic Seawater

Synthetic seawater composition ($2\,dm^3$) was prepared following standard procedures.[25] To the composite mixture, $10\,\mu g$ of U(VI), Pb(II), and Cd(II) were spiked, and the sample was passed through the preconditioned resin

Table 3. Extraction of metal ions from various water resources.

Sample nature	Source (state)/ year of sampling	Metal ions (concentrations in $\mu g\ dm^{-3}$) U(VI) (rsd %)[a]	Pb(II) (rsd %)[a]	Cd(II) (rsd %)[a]
Seawater-1	Chennai (T.N.)[b]/2003	5.82 (3.34)	1.65 (3.49)	2.01 (3.48)
Seawater-2	Mahabalipuram (T.N.)/2002	6.65 (3.12)	2.08 (3.40)	1.82 (3.36)
River water	Godavari (A.P.)[c]/2002	—	14.82 (3.21)	2.17 (3.12)
Tap water-1	IIT, Chennai (T.N.)/2003	—	27.14 (2.95)	2.15 (3.14)
Tap water-2	Guindy, Chennai (T.N.)/2003	—	30.14 (4.0)	3.12 (3.84)
Well water-2	Adyar, Chennai (T.N.)/2003	4.25 (3.15)	16.21 (2.56)	2.12 (2.74)

[a] Data obtained on triplicate analysis.
[b] Tamil Nadu.
[c] Andhra Pradesh.

column under optimized experimental conditions. The sorbed metal ions were desorbed and analyzed spectrofluorimetrically for U(VI) and using FAAS for Pb(II) and Cd(II). The results obtained on triplicate measurements showed a recovery of $>98.4\%$ with an rsd value of $<3.1\%$, proving its ability to preconcentrate metal ions from high saline conditions with a high degree of selectivity.

Preconcentration of Metal Ions from Various Water Samples

Individual water samples of $4\,\text{dm}^3$ obtained from various sampling sources (mentioned in Table 3) were passed through a 0.2-micron membrane filter prior to column passage to remove particulate materials and also passed without any dilution for metal extraction. The sorbed metal ions were desorbed with $10\,\text{cm}^3$ of suitable eluant and estimated by spectrofluorimetric and FAAS technique. The accuracy and reproducibility was cross-checked by spiking $20\,\mu\text{g}$ of individual metal ions into the water samples; the resulting values were within 3.5% rsd.

Extraction of Thorium from Monazite Sand (Travancore, India)

A 0.1-g sample of monazite sand was digested with concentrated H_2SO_4 initially at a low temperature (30°C) followed by vigorous heat treatment up to 250°C for 4 hr. The precipitate was filtered and redissolved in minimal volume of dilute HCl. The resulting solution was pH-adjusted and passed through the resin bed under optimum experimental conditions. After desorption, the amount of thorium extracted was estimated spectrophotometrically and found to be $80.3\,\text{mg g}^{-1}$. The data were further confirmed by standard addition technique, the values of which were within 4.1% rsd for triplicate measurements. The exact content of thorium in monazite sand sample was well established by standard chemical analysis methods using inductively coupled plasma-atomic emission spectrometry (ICP-AES) as the detection tool, which was found to be $81.0\,\text{mg g}^{-1}$. The close agreement of the obtained results to that of the certified value proves the reliability and accuracy of the developed method.

CONCLUSIONS

The newly developed chelating polymer showed excellent metal extractive behavior toward actinides and specified post-transition metal ions from samples of acidic to near neutral pH conditions. The developed method possessed high ion selectivity and superior preconcentration efficiency toward trace-level analytes. It is noteworthy to mention that a very high metal loading capacity value was observed, which was far more superior to other literature-reported chelating resin matrices. The metal phase exchange behavior was found to be rapid, thereby making it highly suitable and applicable to real sample systems, even at very high flow rates, thereby reducing the time of analysis. Stripping of metal ion from the sorbent phase was also very rapid, even with a minimum volume of eluant. Reusability, high chemical stability, and wide range of pH applicability were some of the highlighting features of this new chelating resin. The system was found to be eco-friendly because the constituent elements are C, H, O, and N, which result in complete incineration, and more importantly, it has a simple synthetic route.

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