Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Singh, Dhruv Kumar and Srivastava, Meenakshi(2005) 'Diethylenetriaminepentaacetic Acid Impregnated Ceralite IR 400 for Transition Metal Complexation: Implication for Separation and Recovery', Separation Science and Technology, 40: 10, 2053 — 2065
To link to this Article: DOI: 10.1081/SS-200068466
URL: http://dx.doi.org/10.1081/SS-200068466

Separation Science and Technology, 40: 2053–2065, 2005

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200068466

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Diethylenetriaminepentaacetic Acid Impregnated Ceralite IR 400 for Transition Metal Complexation: Implication for Separation and Recovery

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Abstract: The impregnation of diethylenetriaminepentaacetic acid (DTPA) onto an anionic strong base resin Ceralite IR 400 is described. Mixing DTPA solution with Ceralite IR 400 in water carried out the procedure. The maximum impregnation is 1.164 mmol of DTPA/g of Ceralite IR 400. The DTPA impregnated resin was used for transition metal-DTPA complexation. The distribution coefficients (K_d) of 15 metal ions were determined in demineralized water, 0.05 M ammonium acetate solution and acetate buffers (pH = 2, 4, and 6). On the basis of significant difference between distribution coefficients of metals M_1 and M_2 ($K_{dM1}/K_{dM2} \geq 3$), the quantitative separations were tried on the Pyrex glass column (30 cm long and 0.4 cm i.d.), packed with 1 g of DTPA-Ceralite IR 400 resin. The separations achieved are: Cu(II)–Zn(II)–Ag(I), Mn(II)–Pt(IV)–Zr(IV), Ni(II)–Pt(IV), Ni(II)–Fe(III), Co(II)–Fe(III), Ni(II)–Zn(II), Cu(II)–Au(III) and Mo(VI)–Cr(VI). The break through curves were studied for ziroconium. By increasing the impregnated amount of DTPA from 0.100 to 1.164 mmol/g of Ceralite IR 400, column capacity increased from 106.69 to 1261.13 mmol Zr/l of DTPA-resin. DTPA impregnated Ceralite IR 400 resin can be applied for the removal of zirconium(IV) from aqueous solutions (100 μg/l to 5 mg/l). Zirconium, preconcentrated on resin can be recovered quantitatively (97.2–99.8%) with 2 M HCl as eluting reagent. The proposed column technique is

Received 6 October 2004, Accepted 8 April 2005
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also successful for the removal and recovery of zirconium from synthetic seawater with almost the same efficiency.

Keywords: Column liquid chromatography, DTPA-impregnated Ceralite IR 400, transition metal ions, separation, recovery

INTRODUCTION

There is a growing need in the field of separation and water remediation to pursue effective adsorbents to separate and to remove or preconcentrate toxic heavy and transition metal ions. Zirconium and its salts generally have low systemic toxicity. Zirconium is unlikely to present a hazard to the environment. The adsorbents presently in use generally involve inorganic ion exchangers (1–3) or some biological sources (4). Ion exchange resins (5, 6) and chelating resins (7–9) are well known for separation and recovery of toxic heavy and transition metal ions from contaminated water (10) and in tap water treatment. Recently, the feasibility of in situ groundwater remediation using permeable reactive barriers (PRBs) containing various resins has been reported (11). The practicability of using solvent impregnated resins (SIRs) for in situ groundwater remediation is that they combine the advantages of ion-exchange resin and solid-liquid extraction technology with solvent extraction chemistry (12).

Metal chelating resins (adsorbed or chemically bonded chelates) have recently been found to be of great utility for the preconcentration and separation of trace metals from different matrices (13–16). The metal ions are trapped by the chelating resins more efficiently than the simple ion-exchange resins.

DTPA is widely used because of its ability for chelating different metal ions. DTPA is a chelating reagent that sequesters metal ions so they cannot combine with other ingredients in the product. It is used in soaps as a water softener, and to protect dyes and perfumes from combining with metals in solution. Ceralite IR 400(Cl^-) ion-exchange resin is a strongly basic gel type resin with quaternary ammonium functionality and commercially is being applied as an anion exchanger.

Several complexion cation exchangers with EDTA or DTPA complexon groupings attached through the amide to the polymer matrix of bead cellulose or of the methacrylate type are prepared (17). In spite of low total capacity, cation exchangers with immobilized DTPA have distribution coefficients higher by an order of magnitude than a commercial iminodiacetic resin. A chelating resin based on phenol-formaldehyde copolymer containing DTPA as functional species has also been studied (18).

In this paper we describe a simple pathway to impregnate DTPA on a strong-base anion-exchange resin, Ceralite IR 400. The column of DTPA impregnated Ceralite IR 400 resin has been applied for the quantitative separation of metal ions and removal of zirconium from aqueous solutions. Metal

ion adsorption and elution properties from the DTPA-Ceralite IR 400 columns are presented. The method has also been applied for the recovery of zirconium from synthetic seawater.

EXPERIMENTAL PROCEDURES

Materials and Reagents

Prior to impregnation, Ceralite IR 400 resin was powdered, sieved (60–100 mesh), and washed extensively with distilled-demineralized water, 1 : 1 methanol/H_2O, 1 : 1 methanol/CH_2Cl_2, and CH_2Cl_2, respectively. The purified Ceralite IR 400 was dried under vacuum at room temperature to constant weight. The solutions of DTPA and metal ions solutions were prepared in demineralized water. Ag(I), Au(III), Cr(VI), Ru(III), Zr(IV), and Pt(IV) were determined spectrophotometrically (19) and other metal ions were estimated volumetrically by EDTA. All the reagents were of analytical grade.

Apparatus

An electric rotary shaking machine IEC-56 was used for shaking. A Systronic digital pH meter type 335 was used for pH measurements. A Bausch and Lomb Spectronic 20 was used for spectrophotometric measurements.

Impregnation of DTPA on Ceralite IR 400

Approximately 1 g Ceralite IR 400 in Cl^- form (60–100 mesh) was mixed thoroughly with water containing required amounts of DTPA. The mixtures were shaken for 24 h at 150 rpm, to reach equilibrium. The resin was filtered and washed with demineralized water until the washings were free from DTPA. The filtrate and washings were analyzed for unadsorbed DTPA by back titration with standard solution of zinc using Eriochrome Black T as an indicator. The amount of DTPA impregnated on Ceralite IR 400 was calculated from the difference between the initial amount of DTPA taken in solution and the amount of DTPA found in the filtrate and washings.

Distribution Studies

The distribution coefficients (K_d) of 15 metal ions were determined by a batch process (1) after equilibrium had been attained by shaking 20 mL of metal ion solutions (0.005 M) with 0.1 g of impregnated resin for 4 h.

$$K_d(\text{mL/g}) = \frac{\text{Amount of metal ion in resin phase/g}}{\text{Amount of metal ion in solution phase/mL}}$$

The K_d values were determined in demineralized water, 0.05 M ammonium acetate solution and in acetate buffers (pH = 2, 4 and 6).

Separation

The separations were performed on a Pyrex glass column (30 cm long and 0.4 cm i.d.), packed with 1 g of DTPA impregnated resin. Before loading the mixture of transition metal ions, a 0.05 M ammonium acetate buffer (pH = 7) was passed through the column for 30 min at a flow rate of 1 mL/min. Then the mixture of metal ions (pH ~7) was loaded onto the column.

Procedure for Preconcentration and Recovery

For the experiments of preconcentration and recovery of zirconium from very dilute aqueous solutions, DTPA impregnated resin was packed in a Pyrex glass column (10 cm long and 1 cm i.d.) to a height of 2 cm. Aqueous solutions containing 50 μg of zirconium (pH ~5) were passed through the column at the flow rate of 2–3 mL/min. The zirconium adsorbed in the column was eluted out with 40 mL of 2 M HCl and determined spectrophotometrically with Alizarine Red (19).

Breakthrough Experiments

The impregnated DTPA-Ceralite IR 400 resin (1 g) was slurry packed into a Pyrex glass column (30 cm long and 0.4 cm i.d.) fitted with glass wool as bed support. Before the zirconium binding experiment was performed, a 0.05 M ammonium acetate buffer (pH = 7) was passed through the column for 30 min at a flow rate of 1 mL/min. Then Zr(IV) solution (100 ppm) was passed through the column at a flow rate of 1 mL/min. A total of 10 mL fractions of the effluent were collected and analyzed spectrophotometrically. After the effluent concentration had mostly reached the influent concentration, the passage of Zr(IV) solution was stopped. The zirconium adsorbed in the bed volume of the column was eluted with 2 M HCl and analyzed spectrophotometrically.

RESULTS AND DISCUSSION

Effect of pH and Concentration on Impregnation

Because the impregnation of DTPA on Ceralite IR 400 (Cl^-) was performed with aqueous solutions, pH seems an important factor that can influence the

process of impregnation. The deprotonation of COOH groups present in DTPA molecule is favored in basic solutions. Consequently, the bases increase the moles of DTPA anions and in turn strengthen the interactions with quaternary ammonium cations present in Ceralite IR 400. However, the bases also act to reduce the impregnation of DTPA due to competitive binding of both OH^- with quaternary ammonium cations. Therefore, the maximum impregnation was observed in neutral solution of DTPA. As shown in Fig. 1, the impregnated DTPA increases with increasing concentration of DTPA in aqueous phases. Theoretically, the maximum amount of impregnated DTPA should reach a saturation value of the Cl^- counter ions in the resin (3.8 mmol/g of Ceralite IR 400), but the solubility of DTPA in water and steric hindrance are limiting steps in the impregnation process. On the basis of maximum adsorption capacity, the resin sample loaded with 1.164 mmol of DTPA/g of resin was chosen for further studies unless otherwise stated.

Distribution Studies

The results of distribution studies summarized in Table 1 show that Zr(IV), Ag(I), Au(III), Pt(IV), Fe(III), Hg(II), Zn(II), Cr(VI), and Ru(III) are strongly retained by the DTPA impregnated resin and Mn(II), Cu(II),

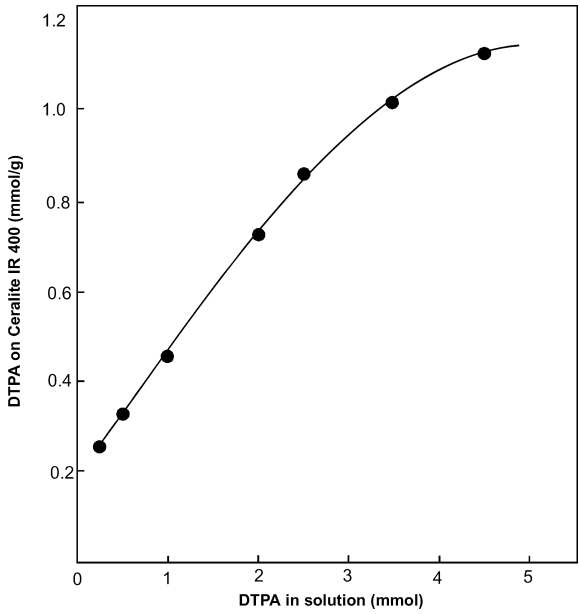

Figure 1. The variation of impregnated DTPA on Ceralite IR 400 with the initial DTPA in neutral solutions.

Table 1. Distribution coefficients of transition-metal ions on DTPA impregnated Ceralite IR 400

Metal ions	pH = 2	pH = 4	pH = 6	Demineralized water (pH = 6.8)	0.05 M ammonium acetate (pH = 7)
Zr(IV)	286	942	2140	2464	2500
Hg(II)	54	164	208	400	397
Ag(I)	523	860	1022	1150	—
Au(III)	128	422	610	726	728
Pt(IV)	438	505	608	675	678
Fe(III)	176	210	385	536	531
Zn(II)	163	219	302	340	350
Cr(VI)	102	186	294	300	323
Ru(III)	42	102	188	220	222
Mn(II)	20	82	85	95	96
Cu(II)	34	41	43	62	64
Mo(VI)	20	32	38	44	50
Cd(II)	6	20	30	36	35
Ni(II)	8	21	34	36	40
Co(II)	7	20	40	42	46

Mo(VI), Cd(II), Ni(II), and Co(II) are partially adsorbed. The reason for selective sorption and desorption of certain types of metal ions can be attributed to the large difference in the stability constants of metal-DTPA complexes. The K_d values observed in demineralized water and 0.05 M ammonium acetate are almost identical, probably due to similar solubility of metals in both the systems. However, a decrease in K_d was observed with the decrease in pH (acidic solutions). This may be explained on the basis of the combined effect of weaker metal-complex formation and desorption of metal ions in the acidic solutions. The maximum adsorption of metal ions (highest K_d) was observed at pH $\sim$7.

Separation

The mixtures containing the metal ions having significant difference in distribution coefficients ($K_{dM1}/K_{dM2} \geq 3$) were tried on the column of DTPA impregnated Ceralite IR 400 and those whose quantitative separations were achieved experimentally are listed in Table 2. The sequential elution of the different metal ions adsorbed on the resin bed of the column is based on the nature and strength of acid solution used as an eluent, which probably decides the stability of metal-DTPA complexes as well as solubility of metal ions. The order of elution and eluents for the separation of Cu(II)–Zn(II)–Ag(I) and Mn(II)–Pt(IV)–Zr(IV) are illustrated in Fig. 2. The elution

Table 2. Quantitative separations of transition metal ions achieved on the columns of DTPA-Ceralite IR 400 resins

Mixture No.	Metal ions	Eluents	Volume of effluent (mL)	Metal ions loaded (mmol × 10^3)	Metal ions recovered (mmol × 10^3)	Error (%)
1	Cu(II)	A	40	102.0	102.5	+0.5
	Zn (II)	B	50	105.0	104.6	−0.3
	Ag(I)	C	40	100.0	98.8	−1.0
2	Ni(II)	D	30	106.0	106.0	0.0
	Pt(IV)	E	40	88.0	87.6	−0.4
3	Mn(II)	D	30	106.0	106.0	0.0
	Pt(IV)	E	40	88.0	87.6	−0.4
	Zr(IV)	F	40	108.0	108.5	+0.4
4	Ni(II)	D	30	102.0	102.3	+0.3
	Fe(III)	E	40	106.0	105.7	−0.3
5	Co(II)	D	30	104.0	104.5	+0.5
	Fe(III)	E	40	106.0	105.7	−0.3
6	Ni(II)	D	30	102.0	102.3	+0.3
	Zn(II)	E	30	105.0	104.6	−0.3
7	Cu(II)	A	40	102.0	102.5	+0.5
	Au(III)	E	30	109.0	107.8	−1.1
8	Mo(VI)	D	30	100.0	100.4	+0.4
	Cr(VI)	F	40	98.0	97.7	−0.3

A = 0.01 M HNO_3, B = 0.1 M HNO_3, C = 1 M HNO_3, D = 0.01 M HCl, E = 1 M HCl, F = 2 M HCl.

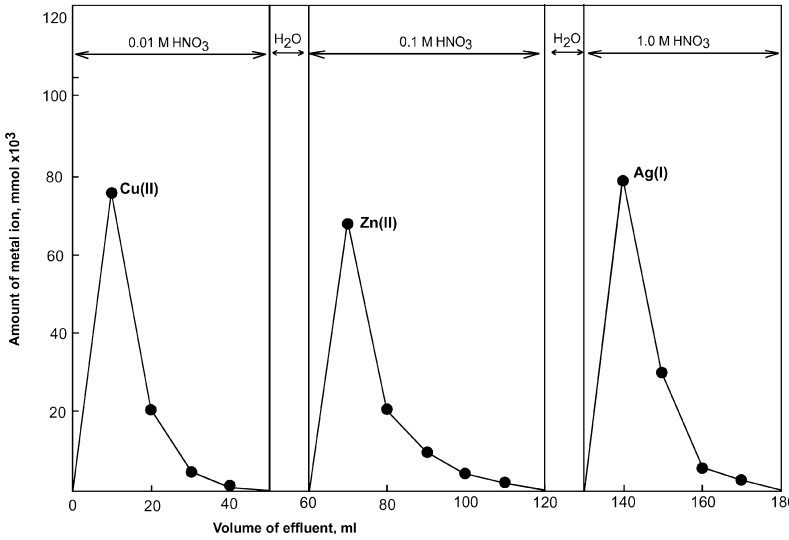

Figure 2a. Separation of Cu(II), Zn(II) and Ag (I).

curves show that the separation of metal ions is clear and the chromatograms are sharp. The volume of eluent required for the quantitative elution of the individual metal ions was 30–50 mL. The percent error in these experiments lies in the range -1.1 to $+0.5$.

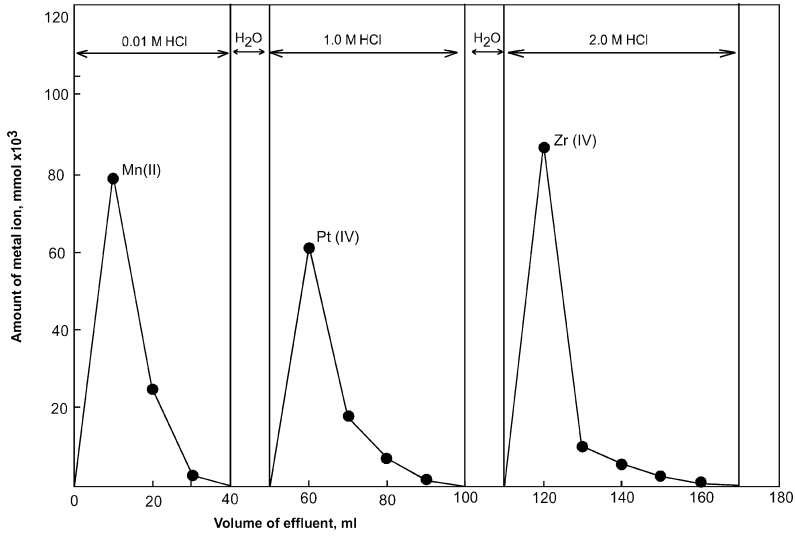

Figure 2b. Separation of Mn(II), Pt(IV), and Zr(IV).

Effect of Impregnated DTPA on Zirconium Binding

Conditioning of column by 0.05 M ammonium acetate buffer causes a slight extraction of DTPA from the resin. The extracted DTPA was tested by the addition of $FeCl_3-K_3[Fe(CN)_6]$ solution to form a green-blue colored complex $Fe^{II}-[Fe(CN)_6]^{III}$ as a consequence of reduction of $Fe^{(III)}$ into $Fe^{(II)}$ by DTPA (lone pair on N atoms). After passing 20 mL of the buffer solution through the columns, no DTPA was detected and columns were ready for zirconium complexation. The final impregnated DTPA on resin was calculated by subtracting the extracted amount of DTPA during conditioning from the initial impregnated amount of DTPA (Table 3). The effect of impregnated DTPA on zirconium binding was determined for 0.100, 0.456, 0.870, and 1.164 mmol of DTPA/g of Ceralite IR 400, passing Zr(IV) influent solution (100 ppm) through the columns loaded with 0.80 mL of various DTPA-resins at a flow rate of 1 mL/min. The breakthrough curves (zirconium effluent concentration vs. bed volume (BV); where, BV = Volume of effluent/Volume of resin bed) are plotted in Fig. 3. Depending upon the amount of impregnated DTPA, the breakthrough curves show differences in breakthrough points as well as in shape. The first curve for impregnated 0.100 mmol DTPA/g of Ceralite IR 400 shows that 60 BV of Zr(IV) (corresponding to 0.053 mmol Zr) could be passed through the column without any trace being detected in the effluent and the curve rises quickly during $60 \sim 150$ BV. In the other three curves for 0.456, 0.870, and 1.164 mmol DTPA/g of resin the breakthrough points appear after 360, 750, and 980 bed volumes, respectively (corresponding 0.317, 0.660, and 0.862 mmol Zr, respectively) and the curves rise slowly, suggesting that strong binding of DTPA with zirconium takes place. The total amount of zirconium bound (i.e., column capacity) mmol/l of DTPA-Ceralite IR 400 was calculated according to the following equation (20):

$$C_S = \frac{(C_m^o V - \int_o^v C_{mdv})}{V'}$$

Where C_s is the zirconium bound to the column material (mmol/l) after V mL of zirconium solution passed through the column C_m^o is the molar influent concentration. C_m is the column effluent concentration, and V' is the volume of DTPA Ceralite IR 400 used in mini-columns. The column capacity and other related informations used in the calculation and discussion are listed in Table 3. Assuming 1 : 1 Zr-DTPA complex, the actual amount of bound zirconium (mmol/l) is in all cases smaller than that of calculated zirconium binding. It reveals that there are some numbers of sites on the resin that are not available for zirconium complexation. The results of elution of zirconium from the DTPA-Ceralite columns reveal that the recoveries are quantitative (Table 4).

Table 3. Column capacity of DTPA-Ceralite IR 400 resin[a] for different amounts of impregnated DTPA

Column no.	DTPA impregnated on Ceralite IR 400 (mmol/g)	Remaining DTPA on Ceralite IR 400 after conditioning with 0.05 M ammonium acetate (mmol/g)	Experimental column capacity of DTPA-Ceralite IR 400 resin for zirconium (mmol/l)	Theoretical[b] column capacity of DTPA-Ceralite IR 400 resin for zirconium (mmol/l)
1	0.100	0.098	106.69	111.36
2	0.456	0.452	489.37	513.64
3	0.870	0.864	956.56	981.82
4	1.164	1.160	1261.13	1318.18

[a]Volume of resin taken in columns = 0.08 mL.
[b]The calculation is based on the assumption of a 1 : 1 complex between zirconium and DTPA.

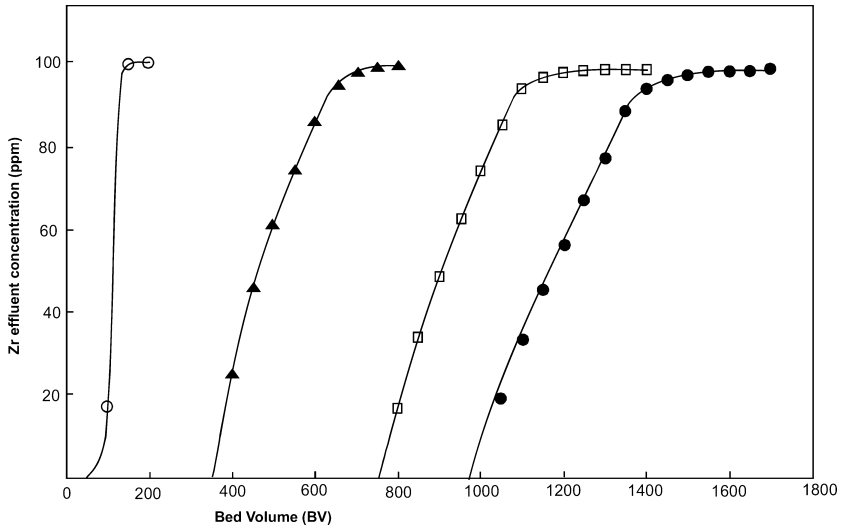

Figure 3. Breakthrough curves of zirconium (100 ppm, pH 7) binding to various amounts of impregnated IR 400 DTPA on Ceralite (○) 0.098 mmol DTPA/g of Ceralite IR 400, (▲) 0.452 mmol DTPA/g of Ceralite IR 400, (□) 0.864 mmol DTPA/g of Ceralite IR 400, (●) 1.160 mmol DTPA/g of Ceralite IR 400.

The results of preconcentration and recovery of known amount of Zr(IV) from distilled water samples are presented in Table 5. The applicability of the preconcentration method was further assessed by the recovery of a known amount of zirconium added to synthetic seawater samples. The seawater samples were prepared according to the composition given in the literature (21). A known amount (50 μg) of zirconium was added to the water samples of different volumes. The results shown in Table 5 reveal that the recoveries of zirconium are nearly quantitative from aqueous solutions. The presence of salts in synthetic seawater has no significant effect on the removal and recovery of zirconium(IV).

Table 4. Recoveries[a] of zirconium from the columns

Column no.[b]	Zr (mmol)/l of resin	Recovered Zr (mmol)/l of resin	Zr recovery (%)
2	489.37	482.31	98.56
3	956.56	938.77	98.14
4	1261.13	1221.78	96.88

[a]40 mL of 2 M HCl was used to elute zirconium.
[b]Column no. as mentioned in Table 3.

Table 5. Zirconium recovered from different volumes of water

Water	Volume[a] of solution passed (mL)	Zirconium recovered (%)
Distilled water	10	99.8
	100	98.6
	300	98.4
	500	97.2
Seawater	100	97.2
	300	96.6
	500	95.2

[a]Each volume contains 50 μg of zirconium.

CONCLUSION

A simple procedure for preparing DTPA impregnated Ceralite IR 400 has been presented. The chelating resin Ceralite IR 400 impregnated with DTPA has been studied for transition metal-DTPA complaxation. The developed resin columns have been applied for the quantitative separations of Cu(II)–Zn(II)–Ag(I), Mn(II)–Pt(IV)-Zr(IV), Ni(II)-Pt(IV), Ni(II)-Fe(III), Co(II)-Fe(III), Ni(II)-Zn(II), Cu(II)-Au(III), and Mo(VI)-Cr(VI). The use of resin has also been demonstrated for the preconcentration and recovery of zirconium from dilute aqueous solutions. The presence of salts in seawater has no significant effect in these experiments. The adsorbed zirconium on the resin bed can be quantitatively eluted with 2 M HCl. The adherence of DTPA is stable in acids up to 4 M. The chelating can be applied for the separations and recoveries of metal ions with almost same chelating efficiency for three cycles.

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