A Chelating Resin Containing 2-(2-Thiazolylazo)-5-dimethylaminophenol as the Functional Group: Synthesis and Sorption Behavior for Some Trace Metal Ions

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A new polystyrene-divinylbenzene resin containing 2-(2-thiazolylazo)-5-dimethylamino-phenol (TAM) functional groups has been synthesized and its sorption behavior for nineteen metal ions, including Zr(IV), Hf(IV) and U(VI) has been investigated by batch and column methods. The chelating resin showed high sorption affinity for Zr(IV) at pH 1-5 and U(VI) at pH 4. Some parameters affecting the sorption of the metal ions have been detailed. The breakthrough and overall capacities were measured under optimized conditions. The overall capacities of Zr(IV), Th(IV) and U(VI), which showed higher than the other metal ions, were 0.90, 0.84 and 0.80 mmol/g. respectively. The elution order of metal ions at pH 4 was evaluated as Zr(IV) > Th(IV) > U(VI) > Cu(II) > Hf(IV) > W(VI) > Mo(VI) > In(III) > Sn(IV) > Cr(III) > V(V) > Fe(III). Quantitative recovery of most metal ions except Zr(IV) was achieved using 2 M HNO₃. Desorption and recovery of Zr(IV) was successfully performed with 2 M HClO₄ and 2 M HCl.

Key words : Chelating resin, 2-(2-Thiazolylazo)-5-dimethylaminophenol, Sorption behavior, Column method

Introduction

Recently, for high sensitivity, good reproducibility and a wide dynamic concentration range inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) have been widely selected as the technique of choice to perform the analysis of trace amounts of metal ions. However, separation and preconcentration of trace levels of metal ions are indispensable because spectral interference is found in the intensively complex atomic emission spectra of matrices of various sample. such as metal alloys and ores. Many separation techniques using solvent extraction and ion exchange chromatoraphy have been applied to this the purpose. Ion exchange is a popular method owing to its applicability to both preconcentration and separation. But, for the lack of selective separation, a new method using various chelating resins has worked.[1-6] This method has good sorption ability of ion exchange in the trace and ultra trace concentration range.[1] A study on the synthesis and sorption characterization of chelating resins available for interesting metal ions has been extensively carried out.[4-7] Lee and others reported that TAR-XVI has a relatively high sorption selectivity for U(VI) and rapid sorption.[7] And we previously reported that polystyrenedivinylbenzene resin containing 1-(2-thiazolylazo)-2-naphthol (TAN) has a high sorption affinity for Zr(IV) and Hf(IV) at pH 2.[8]

Interest has been shown in any fractionation between Zr and Hf in geochemistry and cosmochemistry. Because the change in the Zr/Hf ratio may be interpreted as a reflection of a change in the geochemical or cosmochemical environment.[9-10] But Zr and Hf have very similar chemical properties due to their identical atomic and ionic radii and the sorption behavior of Zr is very similar to Hf, which makes them difficult to separate from each other.

This paper describes the synthesis, characterization and metal sorption characteristics of new chelating sorbent, XAD-16-TAM. obtained by the introduction of 2-(2-thiazolylazo)-5-dimethyl-aminophenol (TAM) as a complexing functional group into polystyrene-divinylbenzene copolymer. Amberlite XAD-16. The commercially available Amberlite XAD copolymers have been widely used as absorbents suitable for reconcentration of multielements from aqueous solution.[5-8,11,12] These polymers have the advantages of having a high surface area. uniform pore distribution and rigid porous structure. Because XAD-16 resin has the largest surface area (800 m²/g) in XAD series. it was used as matrix of chelating sorbent. On the basis of selective chelate forming for Zr and Hf, we had paid attention to TAM, which acts as a tridentate ligand toward metal ions and a metal-indicator in complexometric titrations.[13-15]

In this study, a new chelating sorbent was synthesized by coupling TAM with a diazotized XAD-16. The chelate formation of metal ion with TAM is shown in Figure 1. For the selective separation of Hf(IV), Zr(IV) and U(VI) from a material related to the nuclear fuel cycle, sea water, wastewater and geological material. the sorption and desorption behaviour of XAD-16-TAM on the nineteen metal ions, including Zr(IV), Hf(IV) and U(VI) were investigated by batch and column methods.

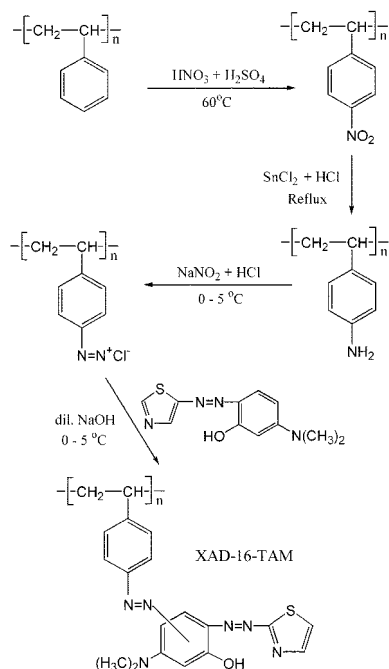*Corresponding Author. Fax: +82-2-968-6584; e-mail: wonlee@khu.ac.kr

Figure 1. Schematic diagram for Synthesis of XAD-16-TAM chelating resin.

Experimental Section

Apparatus. The concentrations of metal ions were determined by inductively coupled plasma atomic emission spectrometer (IRIS/AP, Thermo-Jarrel Ash). Functional groups of intermediates and a final chelating resin taken in the synthesis process were identified with a FT-IR spectrometer (IFS 28, Bruker). Elemental analysis was carried out using elemental analyzer (Eager 200, CEst).

Materials. Amberlite XAD-16 resin (wet density: 1.02 g/mL, surface area: 800 m^2/g, ave. pore diameters 100 purchased from Aldrich (USA). The 100-200 mesh resin was washed with H$_2$O-methanol (70/30, v/v), 2 M NaOH-methanol (50/50, v/v), H$_2$O-methanol (50/50, v/v), 2 M HCl-methanol (50/50, v/v), THF-methanol (50/50, v/v), acetone, methanol and finally with H$_2$O-methanol (50/50, v/v). The resin was dried in a vacuum oven at 60 °C and stored in a polyethylene bottle. 2-(2-thiazolylazo)-5-dimethylaminophenol (TAM) was purchased from Sigma. XAD-16-TAM chelating resin was prepared as described previously.[7,8] Metal ion solutions were prepared by diluting ICP standard solutions (1000 µg/mL, Accu Standard). All the chemicals were used analytical reagent grade. Water was obtained from the Milli-Q/-RO reagent water purification system (Millipore Ltd.).

Chemical stability of the resin. 1-5 M HCl and NaOH solutions were added to the polyethylene bottle containing 30 mg of XAD-16-TAM. It was shaken continuously for 7 days, filtered off and washed with distilled water until neutral. After drying, the sorption capacity for Cu(II) was measured by using the batch equilibrium method.

Sorption studies. The sorption behavior of XAD-16-TAM for Zr(IV), Th(IV), U(VI), Cu(II), Hf(IV), W(VI), Mo(VI), In(III), Sn(IV), Cr(III), V(V), Fe(III), Ta(V), Nb(V),

Co(II), Mn(II), Ni(II), Pb(II), Zn(II) were studied by batch and column methods.

Effect of pH on the sorption of metal ions. Fifty milligrams of the resin were shaken with 50 mL of the mixed solution containing 10 µg/mL of each metal ion at pH 1-6. The pH of the solution was adjusted to the desired value with hydrochloric acid or ammonia solution. After 24 hrs, the residual concentrations of the metal ions were measured by ICP-AES.

Kinetics of the sorption of metal ions on XAD-16-TAM. Thirty milligrams of the resin were shaken with 30 mL of 0.01 M acetate buffer solution (pH 3) containing 10 µg/mL of the Zr(IV). Aliquots of the solutions were withdrawn at various intervals and the residual concentration of the Zr(IV) was measured.

Effect of masking agent on the sorption of metal ions. Fifty milligrams of the resin were shaken with 50 mL of 0.01 M acetate buffer solution (pH 4) containing 10 µg/mL of each metal ion and 0.5-10 mM of the ethylenediamine-tetraacetic acid (EDTA), cyclohexanediaminetetra acetic acid (CDTA) and nitrilotriacetic acid (NTA) as a masking agent, respectively. After 24 hrs, the residual concentrations of the metal ions were measured

Breakthrough experiment. For the column experiment, 5 µg/mL of the mixed metal solution buffered to pH 4 was passed through polyacryl column (0.4 × 5 cm), packed with 100 mg of the resin suspended in distilled water and preconditioned with the 0.01 M acetate buffer solution (pH 4). The solution was eluted at a flow rate of 0.2 mL/min. The effluent fractions were collected in 5 mL portions and analyzed for the presence of the metal.

Desorption studies. The mixed metal solution containing 5 µg/mL of each metal ion was prepared with 0.01 M acetate buffer solution (pH 4). 5 mL aliquot was passed through the column of XAD-16-TAM at a flow rate of 0.2 mL/min. After washing with 5 mL of 0.01 M acetate buffer (pH 4) and 5 mL of distilled water, the metal ions sorbed on the chelating resin were desorbed with 20 mL of 0.1-2 M HCl, HNO$_3$, and HClO$_4$ at a flow rate of 0.1 mL/min. The effluent fractions were collected in 3 mL portions and analyzed for the presence of the metal.

Results and Discussion

Characteristics of XAD-16-TAM chelating resin. For the identification of functional groups, infrared spectra of the intermediates, the TAM monomer, and XAD-16-TAM chelating resin were analyzed by KBr pellet method, and the positions of absorption bands corresponding to the functional groups are listed in Table 1. XAD-16-NO$_2$ exhibited two strong bands at 1526 and 1350 cm^{-1}, which are characteristics of nitro groups. However, these bands decreased in the infrared spectrum of XAD-16-NH$_2$ and a strong band due to amine groups were observed at 1626 cm^{-1}. This means that NO$_2$ groups bonded to the XAD-16 reduced to NH$_2$. In the spectrum of XAD-16-TAM, the absorption bands at 1490 and 1400 cm^{-1} due to the C=C and C=N stretching vibration

Table 1. Analytical data of the intermediates, synthesized resin and TAM monomer

	IR spectrum of functional group (cm^{-1})				mmol of functional group g resin		
	vN-O	vN-H	vC-C (thia.)	vC-N (thia.)	-NO$_2$[a]	-NH$_2$[b]	-TAM[c]
XAD-16 resin	–	–	–	–			
XAD-16-NO$_2$	1526 (s)				5.96		
	1350 (s)						
XAD-16-NH$_2$	–	1626 (s)				3.85	
XAD-16-TAM			1490 (m)	1400 (m)			1.21
TAM monomer			1490 (vs)	1400 (vs)			

thia.: thiazole group. m: medium, s: strong. [a]elemental analysis, [b]non-aqueous titration method.

of the thiazole group in TAM molecule were observed. From these results, it could be confirmed that TAM molecule was bonded to the XAD-16 resin. The data of elementary analyses of the synthesized resin are listed in Table 1. The amount of TAM in the resin was 1.21 mmol/g.

The chemical stability was evaluated by measuring the change of sorption capacity for Cu(II) after successive contact of XAD-16-TAM with acidic and alkaline solutions in the various concentration range. As a result, the chelating resin was stable in acidic and alkaline solutions below 5 M and could be reused over 5 times.

Sorption of metal ions on XAD-16-TAM resin. The sorption of metal ions on chelating resin is dependent on the pH of the sample solution due to competitive reaction between chelate forming groups and hydrogen ions in the solutions. The effect of pH on the sorption of nineteen metal ions in the pH range 1-6 was examined by a batch method and the results are presented in Figure 2 and Figure 3. The sorption percent of Zr(IV) was above 90% at pH 1-5. U(VI) was above 88% at pH 4. But the maximum sorption percentage of Hf(IV) was 79% at pH 3. The optimum pH was 4 for Cu(II), Th(IV), Mo(VI) and W(VI). 5 for Nb(V) and V(V) and 4-5 for Ta(V), Fe(III), Sn(IV), Cr(III) and In(III). The
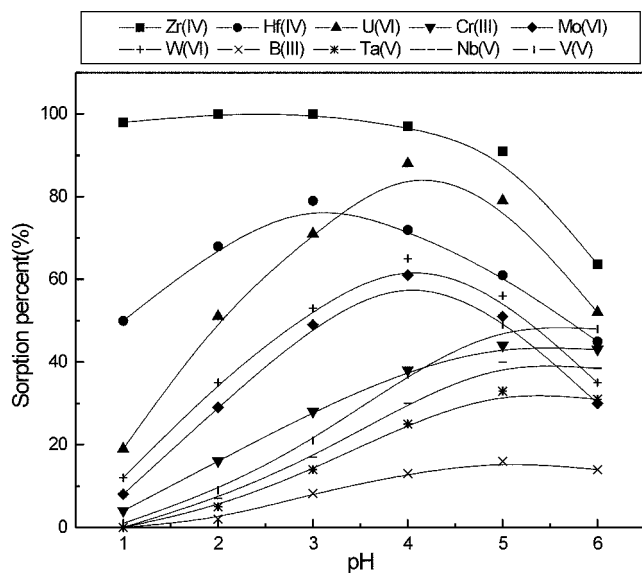

Figure 3. Effect of pH on sorption of metal ions with XAD-16-TAM chelating resin. Resin weight: 50 mg, Conc. of metal ions: each 10 μg/mL/50 mL, Shaking time: 24 hrs.
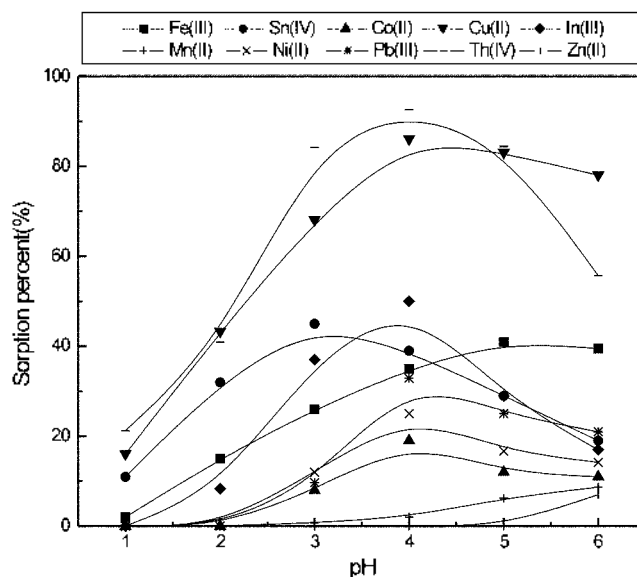
selectivity order of metal ions was evaluated as follows: Zr(IV) > Th(IV) > U(VI) > Cu(II) > Hf(IV) > W(VI) > Mo (VI) > In(III) > V(V) > Sn(IV) > Cr(III) > Fe(III) > Nb(V) > Ta(V) > Pb(II) > Ni(II) > Co(II) > Mn(II) > Zn(II). This order was in good agreement with that of Irving-Williams series[16] and also the stability constants of the chelates formed between TAM and the metal ions.[17]

Mechanism and kinetics of the sorption. Kinetics of the sorption was studied using Zr(IV), which showed the best sorption affinity for the resin. As shown in Figure 4, the sorption was fast and the time taken to reach equilibrium was about 2 hr. This demonstrates that XAD-16-TAM was suitable for the ion chromatographic separation of the metal ions studied.

According to earlier reports,[18-21] the exchange reaction, which is the sorption procedure of metal ions, was regarded as taking place through two mechanisms of film diffusion and particle diffusion. The rate-determining step is particle diffusion. diffusion through the ion-exchange particle, in the following equations derived by Boyd. *et al.*[22]

Figure 2. The effect of pH on sorption of metal ions with XAD-16-TAM chelating resin. Resin weight: 50 mg, Conc. of metal ions: each 10 μg/mL/50 mL, Shaking time: 24 hrs.

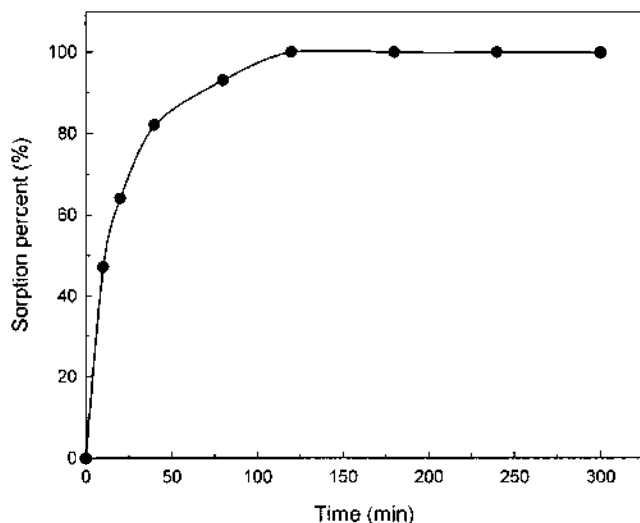$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \qquad (1)$$

Figure 4. Sorption equilibrium of XAD-16-TAM chelating resin according to shaking time. Resin weight: 30 mg, Conc. of metal ion: Zr(IV) 10 μg/mL/30 mL, Matrix: pH 3, 0.01 M HAc-NH₄Ac buffer solution.

Where, F is (the amount of exchange at time t)/(the amount of exchange at infinite time) and B is sorption rate. The equation (2) between F and time t developed by Boyd. *et al.* expresses this relationship

$$-\ln(1-F) = k_d t \qquad (2)$$

Where, k_d is sorption rate constant. From the equation (1) and (2). equation (3) is obtained.

$$-\ln(1-F) = cBt = k_d t \qquad (3)$$

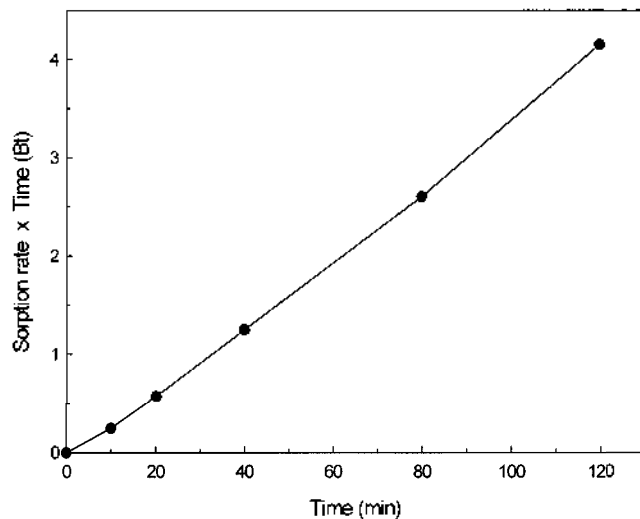Where, c is a constant. Therefore. if a linear plot of Bt *vs.* t is obtained, the rate-determining step can be expected as

Figure 5. Sorption rate of XAD-16-TAM chelating resin according to shaking time. Resin weight: 30 mg, Conc. of metal ion: Zr(IV) 10 μg/mL/30 mL, Matrix: pH 3, 0.01 M HAc-NH₄Ac buffer solution.

particle diffusion.

In the present study, F was obtained from the sorption percent change of Zr(IV) according to the shaking time and Bt was obtained from F value. Reichenberg[23] gives values of Bt for each F values. As shown in Figure 5. the plot of Bt *vs.* t was linear. Therefore, it can be seen that the rate-determining step is diffusion through the particle.

Effect of masking agent on the sorption of metal ions. In this work. applicability of masking agents such as CDTA, EDTA. and NTA to further selective separation of metal ion from a mixed-metal solution was investigated. The results are illustrated in Figures 6-8. As shown in Figure 6, when 2-5 mM of CDTA were added. the sorption percentages of Fe(III). Cr(III) and Ta(V) were less than 30%. When the amount added was more than 5 mM. the sorption percentages of most ions containing Zr(IV). Hf(IV) and Th(V) decreased. But, CDTA had little effect on the sorption of U(VI) for the addition of 5 mM CDTA. The effect of EDTA on sorption of metal ions is shown in Figure 7. When the amount of EDTA added exceeded 2 mM. Mn(II) and Ni(II) did not sorb entirely, and Co(II). Ta(V). Nb(V) and V(VI) did not sorb at amounts of EDTA that exceeded 5 mM. Adding 10 mM EDTA. the sorption percentage of Pb(II), Fe(III). Cr(III) and Sn(IV) was less than 10%. And according to the result of the previous paper.[8] the sorption percentage of Zr(IV) was more than 80% for 5 mM EDTA. This indicate that EDTA can be effectively used as a masking agent for the selective separation of Zr(IV) from the other metal ions. In Figure 8. the metal ions except for U(VI) did not sorb in more than over 5 mM NTA. Zr(IV). Th(IV), Hf(IV) and Cu(II) had low sorption percentage of less than 30%. in 10 mM NTA solution. But. the sorption percentage of U(VI) was 80% for 5 mM NTA. So U(VI) can separate
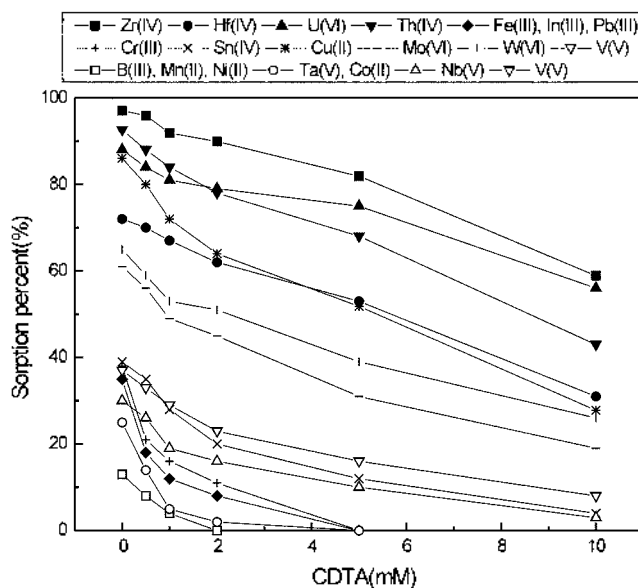

Figure 6. The Effect of CDTA concentration on sorption of metal ions with XAD-16-TAM chelating resin. Resin weight: 50 mg, Conc. of metal ions: each 10 μg/mL/50 mL, Matrix: pH 4, 0.01 M HAc-NH₄Ac buffer solution, Shaking time: 24 hrs.
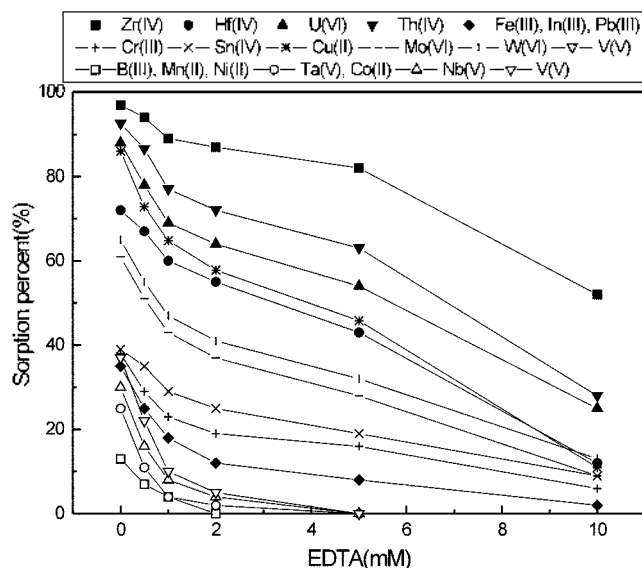
Figure 7. The effect of EDTA concentration on sorption of metal ions with XAD-16-TAM chelating resin. Resin weight: 50 mg, Conc. of metal ions: each 10 μg/mL/50 mL, Matrix: pH 4, 0.01 M HAc-NH₄Ac buffer solution. Shaking time: 24 hrs.
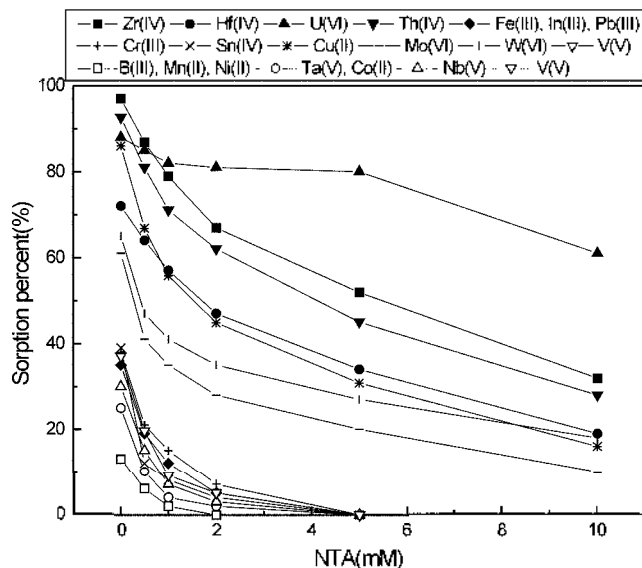

Figure 8. The effect of NTA concentration on sorption of metal ions with XAD-16-TAM chelating resin. Resin weight: 50 mg, Conc. of metal ions: each 10 μg/mL/50 mL, Matrix: pH 4, 0.01 M HAc-NH₄Ac buffer solution, Shaking time: 24 hrs.

selectively from other coexisting metal ions. using 5 mM NTA solution. From these results. the masking effect of NTA for most of the metal ions except U(VI) was very large. The masking effect of CDTA and EDTA was similar but for more than 5 mM. the masking effect of EDTA was large.

Column breakthrough studies. In the present work, the metal sorption capacity of XAD-16-TAM was measured to estimate how large a quantity of the chelating resin would be needed for quantitative recovery of an interesting metal ion from an aqueous solution. For the optimum chromatographic condition, the effect of a flow rate on the sorption of metal
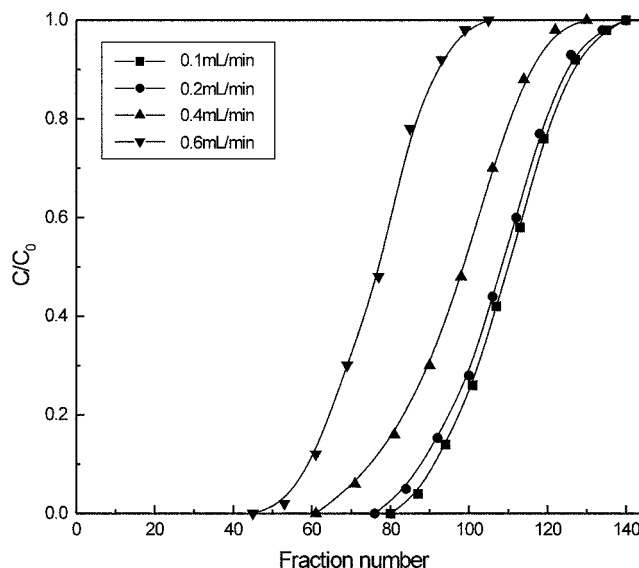

Figure 9. The effect of flow rate on sorption of metal ion with XAD-16-TAM chelating resin. Resin weight: 50 mg, Conc. of metal ion: Cu(II) 10 μg/mL, Matrix: pH 4, 0.01 M HAc-NH₄Ac buffer solution, 1 Fraction: 5 mL.

ions was investigated with Cu(II). showing a high sorption percentage respectively. Overall capacity was calculated by measuring amount of Cu(II) sorbed on XAD-16-TAM at the point where C/C_0, *i.e.*, the Cu(II) concentration ratio of the effluent to influent, was 0.5 on the breakthrough curves, and breakthrough capacity, C/C_0 was 0.01. As shown in Figure 9, the breakthrough and overall capacity decreased with an increasing flow rate from 0.1 to 0.6 mL/min. This is probably because retention time of metal ion on the chelating resin increased with decreasing flow rate. But the capacities at the flow rate of 0.1-0.2 mL/min showed little difference.
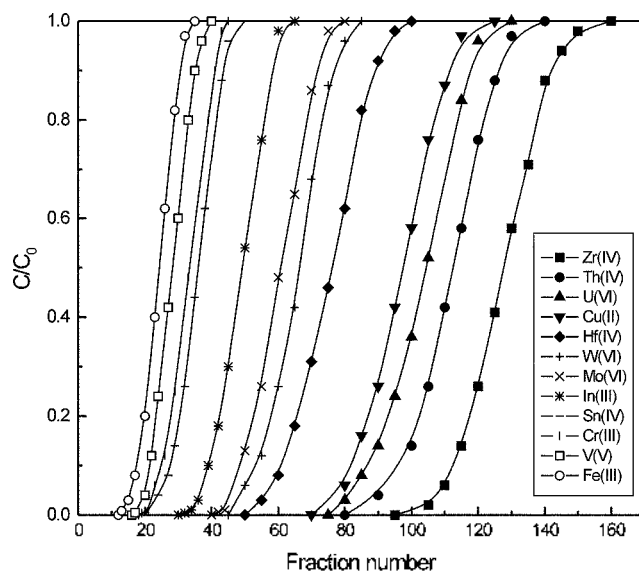

Figure 10. The breakthrough curves of metal ions with XAD-16-TAM chelating resin. Resin weight: 100 mg, Conc. of metal ions: each 5 μg /mL, Matrix: pH 4, 0.01 M HAc-NH₄Ac buffer solution, Flow rate: 0.2 mL/min, 1 Fraction: 5 mL.

Table 2. Breakthrough capacity and overall capacity of metal ions with XAD-16-TAM chelating resin

Metal ion	Breakthrough capacity	Overall capacity
	mmol g resin	
Zr(IV)	0.72	0.90
Th(IV)	0.66	0.84
U(VI)	0.62	0.80
Cu(II)	0.60	0.79
Hf(IV)	0.49	0.65
W(VI)	0.43	0.58
Mo(VI)	0.39	0.54
In(III)	0.31	0.43
Sn(IV)	0.22	0.32
Cr(III)	0.21	0.31
V(V)	0.20	0.30
Fe(III)	0.18	0.28

Resin weight: 100 mg. Conc. of metal ions: each 5 μg mL. Matrix: pH 4, 0.01 M HAc-NH$_4$Ac buffer solution. Flow rate: 0.2 mL min. 1 Fraction: 5 mL.

Therefore, the optimum flow rate was 0.2 mL/min for shorter elution time. For a flow rate of 0.2 mL/min. breakthrough curves of the twelve metal ions. such as Zr(IV), Th(IV), U(VI), Cu(II), Hf(IV), W(VI), Mo(VI), In(III), Sn(IV), Cr (III), V(V), Fe(III), are shown in Figure 10. The inflections of the breakthrough curves showed good symmetry for a volume corresponding to one half of the initial concentration (C$_t$/2). This indicated that it should be possible to separate selectively these metal ions from the mixture of metal ions using XAD-16-TAM.[24] The resulting breakthrough and overall capacities are listed in Table 2. The elution order of metal ions was evaluated as Zr(IV) > Th(IV) > U(VI) > Cu(II) > Hf(IV) > W(VI) > Mo(VI) > In(III) > Sn(IV) > Cr(III) > V(V) > Fe(III) at pH 4. The breakthrough capacity and overall capacity of Zr(IV), which were higher than the

Table 3. The desorption of metal ions on various desorption agents with XAD-16-TAM chelating resin

Metal ion	Recovery (%)		
	2 M HClO$_4$	2 M HCl	2 M HNO$_3$
Zr(IV)	100	98	25
Th(IV)	92	100	95
U(VI)	77	75	100
Cu(II)	26	43	100
Hf(IV)	95	100	100
W(VI)	90	34	70
Mo(VI)	88	28	74
In(III)	34	50	100
Sn(IV)	57	25	100
Cr(III)	43	26	100
V(V)	51	88	58
Fe(III)	48	45	100

Resin weight: 100 mg. Conc. of metal ions: each 5 μg/mL. Sorption flow rate: 0.2 mL min. Desorption flow rate: 0.1 mL min. Desorption agent volume: each 15 mL.

other metal ions, were 0.72 and 0.90 mmol/g. The breakthrough capacity of U(VI) was 0.80 mmol/g, this value was higher than for XAD-16-TAN in a previous study.[8] respectively. U(VI) was more selectively sorbed on the chelating resin and the ratio of breakthrough capacity to overall capacity was 0.78. These results show that XAD-16-TAM was used effectively for the separation and condensation of U(VI).

Desorption of metal ions. For the quantitative recovery of trace metal ions and reuse of resin. characteristics of desorption were investigated with desorption agents, such as HClO$_4$, HCl and HNO$_3$ at a flow rate of 0.1 mL/min. The results listed in Table 3 show that Zr(IV) and Hf(IV) were at least 95% recovered by elution with 2 M HCl and 2 M HClO$_4$. With HCl, the high desorption percent was considered because Zr(IV) and Hf(IV) formed a stable complex of ZrCl$_6^{2-}$ and HfCl$_6^{2-}$ with Cl$^-$. In 2 M HNO$_3$ solution, recovery percentage of Zr(IV) was 25%. This result was attributed to Zr(IV)'s low stability constant of complex with NO$_3^-$ (log K$_{1l}$ = 0.8). Most of the metal ions, except Zr(IV), were completely recovered using 2 M HNO$_3$. As shown in these results. we expect that Zr(IV) can be separated selectively from other metal ions.

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