

Adsorption and Separation of U (VI), Co (II), and Dy (III) Metal Ions on Crown Synthetic Resin

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Abstract

Synthetic resins were combined 1-aza-12-crown-4 macrocyclic ligand with styrene divinylbenzene copolymer having 1%, 2%, 8%, and 16% crosslink by a substitution reaction. These synthetic resins were confirmed by chlorine content, elementary analysis, SEM, surface area, and IR-spectrum. As the results of the effects of pH, crosslink of synthetic resin, and dielectric constant of a solvent on metal ion adsorption for resin adsorbent, the metal ions showed high adsorption at pH 3 or over. Adsorption selectivity for the resin in ethanol solvent was the order of uranium (UO_2^{2+}) > cobalt (Co^{2+}) > dysprosium (Dy^{3+}) ion, adsorbability of the metal ion was the crosslink in order of 1%, 2%, 8%, and 16% and it was increased with the lower dielectric constant. In addition, these metal ions could be separated in the column with 1% crosslink resin by using nitric acid (pH 2.0) as an eluent.

Keywords: Adsorption, Separation, Macrocyclic Ligand, Styrene, DVB, Crosslink

1. Introduction

Crown compounds comprise alkali, alkaline earth metal, transition metal, heavy metal ions and stable complexes^[1] by the properties of donor atom forming a ring. A method for separating metal ions from these kinds of complexes was initiated from the studies on the equilibrium of a solvent extraction system^[2].

Grimsley *et al.*^[3] synthesized a chain of nitrogen-oxygen donor macrocyclic ligands, and examined complex formation of the ligands, transition metal ions and post-transition metal ions for finding the macrocyclic ligands to select specific metal ions and for verifying the causes to exist the selectivity.

Moreover, whereas a method to separate metal ions by using neutralization or precipitation gives a low separating effect due to high solubility of the metal ions and has some technical difficulties, another method to adsorb and separate the metal ions by using minerals is being used as a variety of forms because of easy application without requiring high technology or complicated equipment^[4].

Every country in the world caused exorbitant environment destruction during the courses of indiscreet energy development to secure energy sources. Some countries with insufficient natural resources strove to solve their energy-short problem through the undeveloped countries. Korea also has nearly empty natural resources, and maybe reaches a big deadlock in providing the energy in future if there is no epochal alternative plan. On account of this, one of perpetual solutions to preserve the environment as best as possible and to secure the production of energy is the advent of atomic energy industry using uranium. Korea holds 0.42-1.2%^[5] of uranium within coal of low quality in Goisan, waste of phosphatic fertilizer and so on, according to producing districts. Consequently, effective separation and withdrawal must be guaranteed without delay in respect of disposal of radioactive waste matter and natural resource preservation.

Bombieri *et al.*^[6] identified the structure of lanthanoid and uranium complexes through X-ray analysis, and verified that all oxygen atoms on a same plane are combined with uranium ions. Meanwhile, studies have been actively under way for preventing environmental contamination due to the loss of toxicant macrocyclic compounds possibly produced in the chromatography moving the solvent extraction or the macrocyclic compounds into a fixed phase or a mobile phase^[7], and for

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developing a separation method with an excellent separating effect. Blausius *et al.*^[8] synthesized resins by condensing various macrocyclic compounds and formaldehyde, or copolymerizing divinylbenzene and macrocyclic compounds containing vinyl radicals. They also substituted crown series for styrene-1,4-divinylbenzene (styrene-DVB), and studied the separation of metal ions by using these resins. And, crown series resin and metal ion adsorption are dependent on the characteristics of ion diameter-cavity radius.

Styrene^[9] is 2th petroleum in 4th class hazardous materials, as a colorless and toxic benzene derivatives, it has a distinctive smell. It dissolves in alcohol, ether and carbon disulfide is insoluble in water. It forms a colorless solid matter by polymerization.

On the other hand, the analysis of micro impurities in uranium dioxide is recognized as very important in the production and quality control of nuclear fuel appropriate to the atomic power generation. Especially, in senses of the lanthanoid elements having a large cross-sectional area absorbing neutrons and the resource collection, the separation and condensation of a very small amount of uranium should be necessarily studied in the field of separating nuclear fuel and nuclear substances.

Therefore, this study synthesized^[10,11] the chloromethylated styrene-DVB copolymer available to selectively separate and collect metal from transition metals. Hereupon, the chloromethylated copolymers were chemically combined with 1-aza-12-crown-4 (1-aza-12-C-4) macrocyclic ligand to produce a new functional resin, and then, the adsorption and separation^[12-16] of uranium (UO_2^{2+}), cobalt (Co^{2+}), and dysprosium (Dy^{3+}) ions were examined.

2. Experimental Section

2.1. Materials

1-aza-12-crown-4, uranium nitrate, dysprosium nitrate and styrene were purchased from Aldrich Co., special grade 1,4-divinylbenzene (55%), 1,4-dioxane and benzoyl peroxide were bought from Donggyeong Hwaseong, and cobalt nitrate, benzene, toluene, potassium iodide, dimethyl sulfoxide, etc. were used with general reagents.

An infrared ray spectrum was analyzed through Shimadzu IDP-440 A, surface area was measured using Nanoporosity-XQ of Miirae SI Co, SRM was using

Hitachi S-4800, and element analysis were performed using Model 1108 of Carlo-Erba Co. pH was measured through a calomel glass electrode of Corning pH meter 320, and a quantitative analysis of Cl^- was conducted by Orion chloride ion-selective electrode. Also, adsorption and separation of uranium (UO_2^{2+}), cobalt (Co^{2+}), and dysprosium (Dy^{3+}) ions were measured through ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer) Lab-test 710 type and Coleman spectrophotometer (350~750 nm).

2.2. Synthesis of Styrene-DVB Copolymer

For the synthesis^[10,11] of styrene-DVB copolymer, a 500 mL triple mouth flask equipped with a reflux condenser and a thermometer was connected with a nitrogen gas injection tube, and was installed with an apparatus to confirm the stirring speed. Distilled water 250 mL was added into the triple mouth flask. The added amount of resin was varied according to the crosslink such as follows : styrene 99 mL /DVB 1.8 mL for 1% of the crosslink, styrene 98 mL /DVB 3.6 mL for 2%, styrene 92 mL /DVB 14.4 mL for 8%, and styrene 84 mL /DVB 28.8 mL for 16%. Benzoyl peroxide 1 g as an initiation reagent, NaCl 10 g as stabilizer, gelatin 0.5 g and Arabic rubber 1.5 g were added and stirred at 1,200 rpm with being reacted at 90°C for 6 hours, and then cooled. Supernatant was removed, and the copolymer was washed with methanol, distilled water and methanol in order.

2.3. Chlorination of Copolymer

Styrene-DVB copolymer was dried at 110 °C for more than 12 hours, and 5 g of which and 100 mL of chloroether were swollen at room temperature for 2 hours in a 250 mL flask. Zinc chloride 2 g was dissolved in chloroether 25 mL, which was added to and placed in the flask. The supernatant was removed, and 100 mL of dioxan-distilled water mixture (70:30) was added to the flask and stirred for an hour for washing the copolymers during the stirring process. Then, the washed copolymers were dried at 50°C for 4 days.

2.4. Function Reaction of Copolymer

Each 2.83 g of chloromethylated 1%, 2%, 8%, and 16% styrene-DVB copolymers was mixed with 50 mL of benzene, and then stirred, refluxed and swollen at boiling temperature for 2 hours. After remaining ben-

zene was removed, 50 mL of toluene, 0.75 g of KI and 1.76 g of 1-aza-12-C-4 macrocyclic ligand were added, stirred and refluxed at 55°C for 30 hours under nitrogen condition, which was cooled at room temperature and filtered. The washing process was conducted with 2 M hydrochloric acid, distilled water, 1 M sodium hydroxide and distilled water in order. Finally, the copolymer was washed several times with methanol and then dried in the air, to get 1-aza-12-C-4-styrene-DVB resins (called resin or synthetic resin) having 1%, 2%, 8%, and 16% crosslink. The size of resin cavity was 300-400 mesh.

2.5. Experimental Method

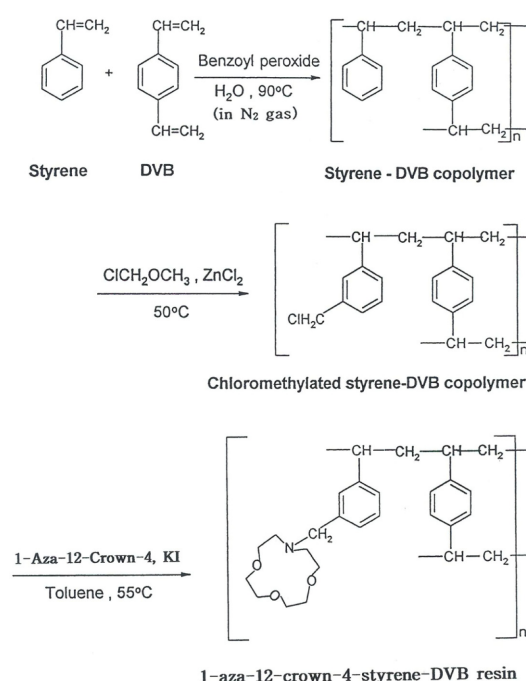
It was measured to take the content of chloro according to crosslink in the process of synthesizing the resin using chloride ion-selective electrode. It was confirmed that the synthesis of resins was IR-spectrum due to KBr disc method, the ultimate resins that each was composed of 1%, 2%, 8%, and 16% crosslink analyzed the content of elements like C, H, N, O using elementary analysis, SEM was used confirmed synthetic resin, and surface area was investigated.

Also, $\text{UO}_2(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, and $\text{Dy}(\text{NO}_3)_3$ solutions of 3.0 mM were controlled the pH by dilute nitric acid or sodium hydroxide to investigate the adsorption character of metallic ion according to pH, crosslink, and dielectric constant of solvent. The resin having 1% crosslink was added 1 g to each solution, and solutions were filtered after being stirred for two hours in room temperature. The adsorption amount of metal ions were quantitatively analyzed by ICP-AES under the dilute nitric acid. The separation of the metal ions were carried out by placing the resin adsorbed on the metal ions into a controllable column, pH 2.0 eluate was added using nitric acid and hydrochloric acid, the eluent was slowly taken out from the column, and the metal ions contained therein were quantitatively analyzed by ICP-AES.

3. Result and Discussion

3.1. Confirmation of Resin

Styrene-DVB copolymer was synthesized^[10,11] as shown in Scheme 1 through suspension polymerization in an aqueous solution with benzoyl peroxide as an initiation reagent that is commonly used to synthesize conventional polymerized-type ion exchange resin.



Scheme 1. Synthetic progress of resin.

Table 1. Chlorine contents of copolymer and composition of 1-aza-12-C-4-styrene-DVB resins with various crosslinked

Degree of crosslinking (%)	Copolymer		Resin		
	Cl (%)	C (%)	H (%)	N (%)	O (%)
1	12.35	72.92	8.37	3.32	11.39
2	11.86	76.96	8.38	3.26	11.40
8	10.13	77.17	8.46	2.90	11.47
16	10.01	77.38	8.54	2.54	11.55

To measure the content of chlorine according to crosslink during the copolymerization, HCl produced through heat hydrolysis was absorbed into distilled water, and the chlorine content was measured using chlorine ion-selective electrode as shown in Table 1. With the increase of the crosslink, the chlorine content was decreased. This can be understood by the fact that the increase of the crosslink increased the DVB content and consequently increased the crosslink density, and also the porosity according to the increase of the crosslink density of copolymers became lower and reduced the chlorine content during the substitution reaction.

In addition, Table 1 exhibited the results of the resin synthesis according to the size of crosslink and the ele-

mentary analysis. When the crosslink became increased, the nitrogen content was decreased. As the results shown like this, the increase of the crosslink also brought on the increase of the DVB content, which subsequently decreased the chlorine content during the substitution reaction because the porosity was lowered due to the increase of crosslink density. Consequently, this influenced the macrocyclic ligand to be displaced, and caused the decrease of the nitrogen content.

Table 2 is an IR-data obtained through KBr disc method. As a result that the chloromethylated styrene-DVB copolymer was combined with 1-aza-12-C-4, the 1-aza-12-C-4 was maybe displaced because there were no N-H peak near 3400 cm^{-1} and C-Cl absorption peak around 700 cm^{-1} . Moreover, the induction of the macrocyclic ligand brought stretching vibration peaks of strong and wide C-O-C and C-N-C in 1260 cm^{-1} , and a new stretching vibration peak of sharp C-N in 1030 cm^{-1} .

Table 2. IR-data of 1% crosslinked styrene-DVB copolymer (A), 1-aza-12-C-4 (B), and 1% crosslinked 1-aza-12-C-4- styrene-DVB resin(C)

Kinds of resin function group	Frequency (cm^{-1})		
	(A)	(B)	(C)
N-H	---	3400	---
Aromatic (C-H)	3100-3150	---	3100-3150
Aliphatic (C-H)	2900-2980	2800-2980	2850-2980
Benzene ring (CC)	1460-1520	---	1460-1520
C-O-C	---	1100-1200	1260
C-N-C	---	---	---
Mono Substitution (4 peaks)	1850-1980	---	1850-1980
C-Cl	700	---	---
C-N	---	---	1030

Table 3. Surface area and pore volume of 1-aza- 12-C-4-styrene-DVB resin

Degree of crosslinking (%)	Surface area (m^2/g)	Pore volume (cm^3/g)
1	14.18	0.0196
2	12.57	0.0171
8	5.87	0.0069
16	4.74	0.0022

The surface area was measured and the results are shown in Table 3 to determine porosity, one of the adsorption characteristics. The resins having 1%, 2%, 8%, and 16% crosslink degrees synthesized in this experiment were dried at 150°C for 30 minutes under reduced pressure, and the surface area was measured by nitrogen gas adsorption method at -190°C . As the degree of crosslink increased, surface area and pore volume tended to decrease, which was also reported by Howdle *et al*^[17,18].

On the other hand, electron micrographs of 1% copolymer and 1% resin were shown in Figure 1 and Fig. 2, respectively. Fig. 1 shown the spherical shape, but Fig. 2 shown the distorted shape of the hydrogen of the macrocyclic ligand, it can be seen that the particle shape

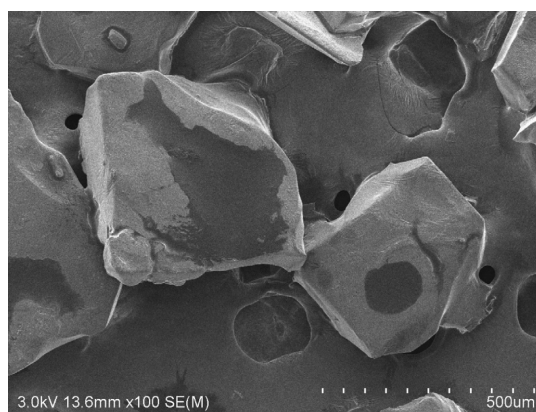


Fig. 1. SEM photograph of 1% crosslinked chloromethylated styrene-DVB copolymer.

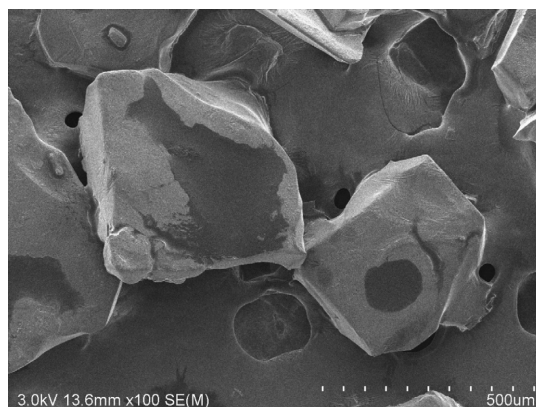


Fig. 2. SEM photograph of 1% crosslinked 1-aza-12-C-4-styrene-DVB resin.

was distorted while causing the substitution reaction with the chlorine atom of the styrene molecule. And, in the chloromethylation process, chloro ether acts as a chloromethylating agent and a solvent. The copolymers are greatly swollen chloroethers and the copolymers of 1% and 2% chloromethylated are light yellowish white, but in the case of copolymers of 8% and 16% they are light brown.

3.2. Effects of pH

To confirm the acidic zone possible to adsorb metal ions for the resin, uranium, dysprosium, and cobalt ions of 3.0 mM were stirred in ethanol solvent for 2 hours, and the adsorption characteristics was examined according to the pH changes of the resin representatively having 1% of crosslink as shown in Figure 1. The adsorbability of uranium ion became slowly increased and the stable complexes of uranium was rapidly increased at pH 3 or over. The adsorbability of cobalt ion was gradually increased between pH 3 and pH 4, and the stable complexes of cobalt was suddenly increased at pH 4 or over. This phenomenon can be explained by the assumption that because the crown resin is basic amine, the nitrogen atom of the resin becomes protonated in a strong acidic solution ($\text{pH} < 2$) and obstructs the adsorption of the metal cations, how-

ever, uranium and cobalt ions with the products generated from hydrolysis of the non-protonated resin form stable complexes^[12,19] and yield high adsorptivity in a weak acidic solution ($\text{pH} > 3$). On the other hand, dysprosium ion cannot form a complex even in a strong acidic zone, and the complex formation is not easy because +3 value rare earth element ions are strongly hydrated and this hydration energy^[20] should be overcome to form crown resin and complexes.

Moreover, these kinds of metal ions have the addition of covalent bonds by electrostatic bonding and nitrogen atom during the formation of resin and complexes regardless of the adsorbability, and accordingly, the metal ions easily reach the adsorption equilibrium only after 2 hours. On account of this, not only the conception of ion diameter-cavity radius but also the covalent bond between metal ions and resins and the hydration energy of metal ions react complicately in a case of crown metal complexes having nitrogen donor atom. The crown resin used in the current study was alkaline, and therefore, the adsorption experiment was performed only in the acidic solution under pH 6.

3.3. Effects of Resin Crosslink

Fig. 4 shown the adsorption amount of uranium ion investigated by using the resins having 1%, 2%, 8%, 8%,

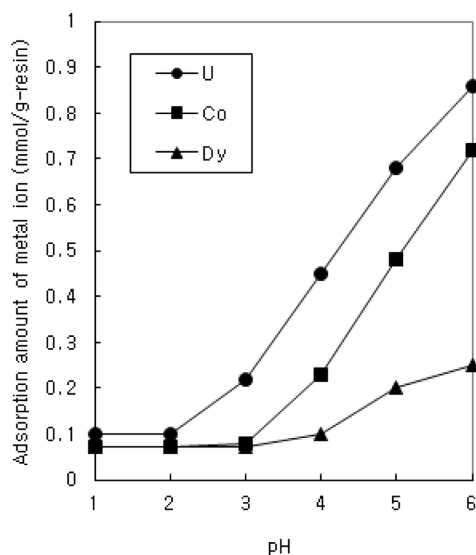


Fig. 3. Adsorption rate of UO_2^{2+} , Co^{2+} , and Dy^{3+} on 1% crosslinked 1-aza-12-C-4-styrene-DVB resin at various pH in ethanol (concentration: 3.0 mM, time: 2 h).

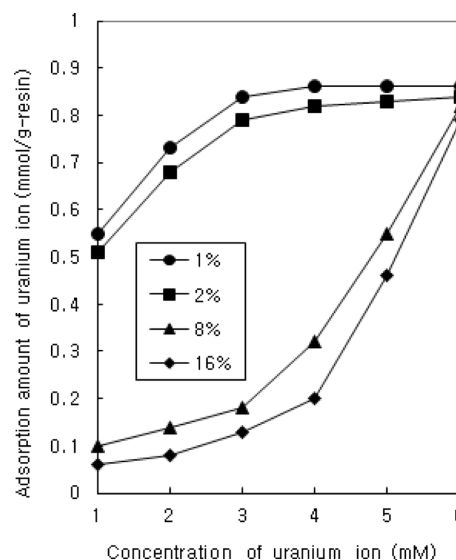


Fig. 4. Adsorption rate of UO_2^{2+} on 1%, 2%, 8%, and 16% crosslinked 1-aza-12-C-4-styrene-DVB resin at various concentration in ethanol (pH: 6.0, time: 2 h).

and 16% crosslink through a variation of uranium ion concentrations within a range from 1.0~6.0 mM by ethanol solvent.

As shown in Fig. 4, the resins having 1% and 2% crosslink adsorbed approximately 0.5 mmol/g in 1.0 mM whereas the resins having 3% and 6% crosslink adsorbed 0.10 mmol/g only. The result of the adsorption presenting as 1% \approx 2% > 8% \approx 16% resins can be considered due to the reason that the crosslink was dependent on the amount of DVB during the synthesis of styrene-DVB copolymers, and the resin crosslink density was decreased with the decrease of the DVB content, whereas the porosity becomes higher and the diffusion velocity of uranium ion into the resin was large in the 1% and 2% resins compared with the 8% and 16% resins. However, the 8% and 16% resins adsorbed at almost the same level as the 1% and 2% resins within the high range (6.0 mM) of uranium ion.

A point expressing the maximum adsorption observed in an adsorption curve of Figure 4 was the apparent capacity of resins. The apparent capacity of uranium ion for 1%, 2%, 8%, and 16% resins was 0.86, 0.84, 0.82, and 0.79 mmol/g, respectively.

3.4. Effects of Solvent Dielectric Constant

For verifying the adsorption effects of uranium ion according to different solvent kinds, the adsorption rate

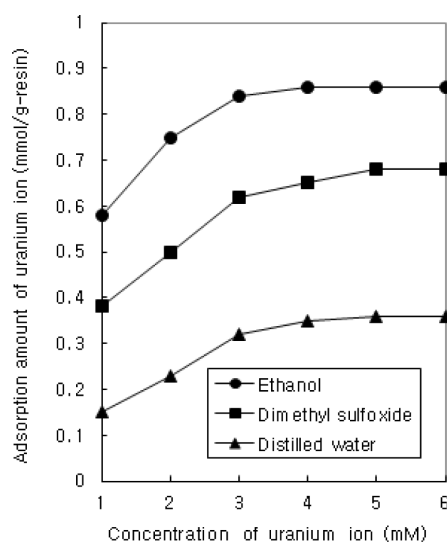


Fig. 5. Adsorption rate of UO_2^{2+} on 1% crosslinked 1-aza-12-C-4-styrene-DVB resin in ethanol, dimethyl sulfoxide, and distilled water (pH: 6.0, time: 2 h).

of uranium ion was examined in the solvents of distilled water (78.54), dimethyl sulfoxide (46.60), and ethanol (24.55) having different dielectric constants (ϵ , 25°C) as shown in Fig. 5.

The resins having 8% and 16% crosslink in Fig. 4 had generally lower metal ion adsorption rates than the resin having 1% crosslink. Therefore, the resin having 1% crosslink was selected from Fig. 5, and the adsorption rate of uranium ion was investigated under the varied uranium ion conditions controlled within a range from 1.0~6.0 mM and increased in an order of ethanol > dimethyl sulfoxide > distilled water. This is probably due to the reason that the power of electrostatic bond (the power of Coulomb) is larger as the dielectric constant value is smaller.

3.5. Separation of Metal Ions

Considering that the degree of adsorption of metal ions is inversely proportional to the size of the dielectric constant, ions may be separated or grouped separately using water or an organic solvent as an eluent. However, in the case of transition metals, it is difficult to separate them using water or an organic solvent because of the large adsorption at pH 4.0 or higher. HNO_3 and HCl solutions were prepared by adjusting the acidity of pH 2.0. The separation curves obtained from these results are shown in Fig. 6 and 7.

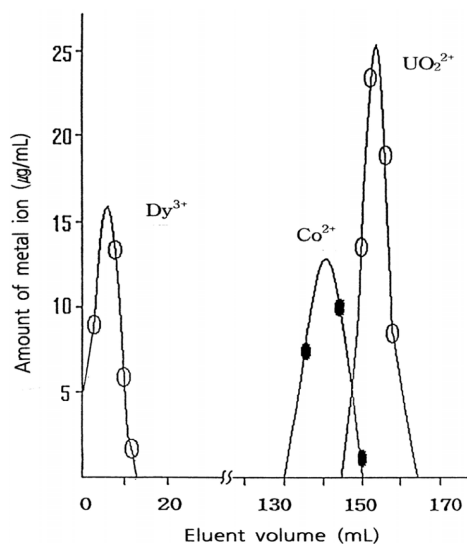


Fig. 6. Eluent curves of Dy^{3+} - Co^{2+} - UO_2^{2+} mixture, 1% crosslinked 1-aza-12-C-4-styrene-DVB resin, eluent: HCl (pH 2.0), eluent rate: 0.5 mL/min.

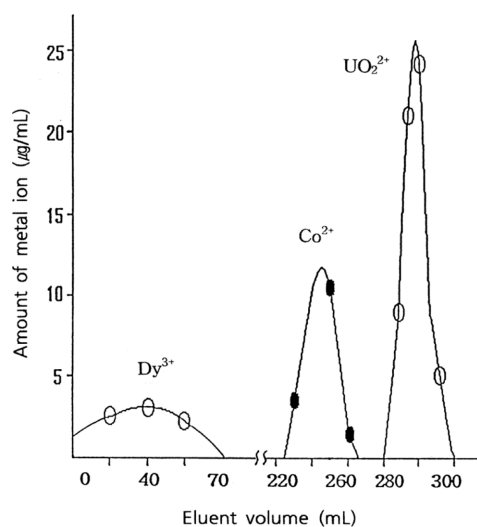


Fig. 7. Eluent curves of Dy^{3+} - Co^{2+} - UO_2^{2+} mixture, 1% crosslinked 1-aza-12-C-4-styrene-DVB resin, eluent: HNO_3 (pH 2.0), eluent rate: 0.5 mL/min.

In Fig. 6 and 7, some of the Dy^{3+} ions are attracted to the resin due to the ionic interaction, and some are not adsorbed, but stay on the top of the resin for a while and then flow down. When HCl of pH 2.0 was used as the eluent, the separation band of Co^{2+} and Dy^{3+} overlapped. However, when the HNO_3 eluate at pH 2.0 was used, the separation band was completely separated. Therefore, it was found that the most preferable method was the use of HNO_3 eluent. The recoveries of each metal ion were 12.7~15.5% for Dy^{3+} , 28.3~31.7% for Co^{2+} and 48.2~52.6% for UO_2^{2+} .

4. Conclusion

To selectively separate and collect metal ions, resin was synthesized and its adsorption and separation were examined according to diverse conditions. The results are as follows.

The increase of crosslink in synthetic resin leads to the increase of crosslink density but the lowering of porosity, and subsequently, the chlorine content was reduced. This course influences the macrocyclic ligand, which reduced the nitrogen content.

The nitrogen atom in synthetic resins was protonated under ethanol solvent and pH 2 or lower (strong acid) and inhibited the adsorption of metal ions, but metal ions showed high adsorptivity through the formation of

stable complexes with the products by the hydrolysis of non-protonated resins, at pH 3 or over (toward weak acid).

The metal ions adsorbability for the resin were shown to be uranium > cobalt > dysprosium ions, which was affected by a ratio of metal ion to resin cavity, covalent bond between metal ion and resin, and hydration energy of metal ions. Also, the electrostatic bond and the covalent bond by resin nitrogen atom were added when the resin and metal ion form complexes.

The resins having 1% and 2% crosslink have lower crosslink density and higher porosity due to the small amount of the DVB content than the resins with 8% and 16% crosslink. Accordingly, the diffusion velocity of metal ion into the resin was large even in a dilute solution, which makes it well to adsorb metal ion.

The adsorption rate of metal ion for the resin having 1% crosslink was ethanol > dimethyl sulfoxide > distilled water in order, and increased as the dielectric constant of the solvent becomes smaller.

On the other hand, as a result of separation for Dy^{3+} - Co^{2+} - UO_2^{2+} mixture solution, Dy^{3+} - Co^{2+} ion and UO_2^{2+} ion were completely separated and the elution order was Dy^{3+} , Co^{2+} , UO_2^{2+} ion sequential. The optimal elution condition was pH2.0 nitric acid.

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