

Adsorption of Rare Earth Metal Ion on N-Phenylaza-15-Crown-5 Synthetic Resin with Styrene Hazardous Material

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Abstract

Resins were synthesized by mixing N-phenylaza-15-crown-5 macrocyclic ligand attached to styrene (2th petroleum in 4th class hazardous materials) divinylbenzene (DVB) copolymer with crosslink of 1%, 2%, 6%, and 12% by substitution reaction. The synthesis of these resins was confirmed by content of chlorine, element analysis, thermo gravimetric analysis (TGA), surface area, and IR-spectroscopy. The effects of pH, equilibrium arrival time, dielectric constant of solvent and crosslink on adsorption of metal ions by the synthetic resin adsorbent were investigated. The metal ions were showed fast adsorption on the resins above pH 4. The optimum equilibrium time for adsorption of metallic ions was about two hours. The adsorption selectivity determined in ethanol was in increasing order uranium (VI) > zinc (II) > europium (III) ions. The uranium ion adsorbed in the order of 1%, 2%, 6%, and 12% crosslink resin and adsorption of resin decreased in proportion to the order of dielectric constant of solvents.

Key words: *n*-Phenylaza-15-crown-5, Rare Earth, Styrene, Resin, Adsorption

1. Introduction

Grimsley *et al.*^[1] synthesized a chain of nitrogen-oxygen donor (cryptand) 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^[2].

Bombieri *et al.*^[3] 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^[4], and for developing a separation method with an excellent separating effect.

Blausius *et al.*^[5] synthesized resins by condensing various macrocyclic compounds and formaldehyde, or copolymerizing divinylbenzene and macrocyclic compounds containing vinyl radicals. They also substituted cryptand series for styrene-1,4-divinylbenzene (styrene-DVB), and studied the separation of metal ions by using these resins. And, cryptand series resin and metal ion adsorption are dependent on the characteristics of ion diameter-cavity radius.

Styrene^[6] 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.

Macrocyclic compounds comprise alkali, alkaline earth metal, transition metal, heavy metal ions and stable complexes^[7] 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

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on the equilibrium of a solvent extraction system^[8].

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%^[9] 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.

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] the chloromethylated styrene-DVB copolymer available to selectively separate and collect rare earth metals from mineral materials. Hereupon, the chloromethylated copolymer was chemically combined with N-phenylaza-15-crown-5 (N-P-15-C-5) macrocyclic ligand to produce a new functional resin, and then, the adsorption^[11-17] of uranium (VI), zinc (II), and europium (III) ions was examined.

2. Experimental Section

2.1. Materials

N-phenylaza-15-crown-5, uranium nitrate, europium 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 Co., and zinc nitrate, benzene, toluene, potassium iodide, etc. were used with general reagents.

An infrared ray spectrum was analyzed through Shimadzu IDP-440 A, element analysis was performed using Model 1108 of Carlo-Erba Co., and pH was measured through a calomel glass electrode of Corning pH meter 320. A quantitative analysis of chlorine was conducted by Orion chloride ion-selective electrode, thermo gravimetric analysis (TGA) was using TA-250 of TA Co., and surface area was measured through Nanoporosity-XQ of Mirae SI Co.. The uranium (VI), Zinc (II), and europium (III) 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] 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 crosslinks such as follows : styrene 99 mL/DVB 1.8 mL for 1% crosslink, styrene 98 mL/DVB 3.6 mL for 2%, styrene 94 mL/DVB 10.8 mL for 6%, and styrene 88 mL /DVB 21.6 mL for 12%. 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 7 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 for more than 10 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 3 days.

2.4. Function Reaction of Copolymer

Each 2.83 g of chloromethylated 1%, 2%, 6%, and

12% styrene-DVB copolymers was mixed with 50 mL of benzene, and then stirred, refluxed and swollen at boiling temperature for 2 hours. After remaining benzene was removed, 50 mL of toluene, 0.75 g of KI and 2.67 g of N-P-15-C-5 macrocyclic ligand were added, stirred and refluxed at 55°C for 24 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 N-P-15-C-5-styrene-DVB resin (after called resin) having 1%, 2%, 6%, and 12% crosslinks. The size of resin cavity was 200-400 mesh.

2.5. Experimental Method

It was measured to take the content of chlorine according to crosslink in the process of synthesizing the resin using chloride ion-selective electrode. It was confirmed that the synthesis of resins was a IR-spectrum due to KBr disc method and the ultimate resins that each was composed of 1%, 2%, 6%, and 12% crosslinks analyzed the content of elements C, H, N, O using elementary analysis. And thermogravimetric analysis and surface area were measured. Also, $\text{UO}_2(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, and $\text{Eu}(\text{NO}_3)_3$ 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, equilibrium arrival time, crosslink, and dielectric constant of solvent.

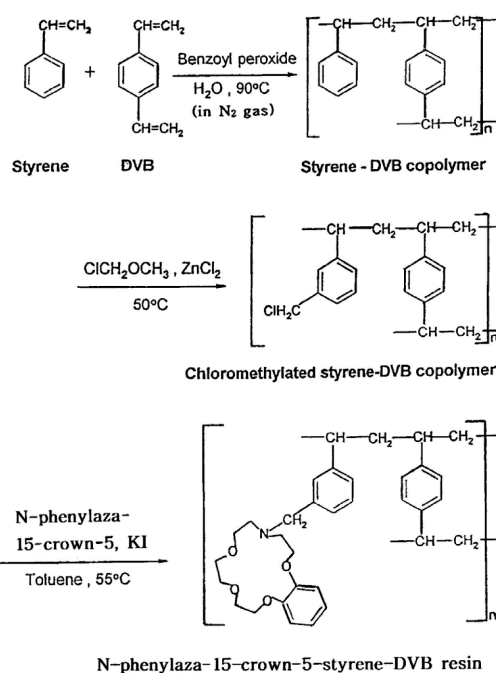
The resin having 1% crosslink was added 1 g to each solution, and solutions were filtered after being stirred for 2 hours in room temperature. Each ion of uranium, zinc, europium ions were quantitatively analyzed using ICP-AES under the circumstances of dilute nitric acid.

3. Results 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.

To measure the content of chlorine according to crosslinks during the copolymerization, HCl produced through heat hydrolysis was absorbed into distilled



Scheme 1. Synthetic process of resin.

Table 1. Chlorine contents in copolymer (chloromethylated styrene-DVB)

Degree of crosslink (%)	Cl (%)
1	12.35
2	11.86
6	10.18
12	10.06

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.

Table 2 is an IR-data obtained through KBr disc method. As a result that the chloromethylated styrene-DVB copolymer was combined with N-P-15-C-5, the N-P-15-C-5 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

Table 2. IR-data of 1%, 2%, 6%, and 12% crosslinked styrene-DVB copolymer (A), N-P- 15-C-5 (B), and 1% crosslinked resin (C)

Kinds of resin function group	Frequency (cm ⁻¹)		
	(A)	(B)	(C)
N-H	---	3400	---
Aromatic (C-H)	3000-3200	---	3000-3200
Aliphatic (C-H)	2800-2900	2800-2900	2800-2900
Benzene ring (C=C)	1450-1520	---	1450-1520
C-O-C C-N-C	---	1100-1200	1250
Mono Substitution (4 peaks)	1800-2000	---	1800-2000
C-Cl	700	---	---
C-N	---	---	1020

strong and wide C-O-C and C-N-C in 1250 cm⁻¹, and a new stretching vibration peak of sharp C-N in 1020 cm⁻¹.

Chloroether acts as chloromethylation agent and solvent in a chloromethylation process. Because the copolymers having 1% and 2% crosslinks were greatly swollen by chloroether, the copolymers lost a round shape and turned into a distorted shape due to the gelation during the reaction. The chloromethylated copolymers express a light yellowish white color when the crosslink is low, but the copolymers of 6% and 12% crosslinks are shown to be light brown.

In addition, Table 3 exhibited the results of the resin synthesis according to the size of crosslink and the elementary 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

Table 3. Compositions of resins with crosslink

Degree of crosslink(%)	C (%)	H (%)	N (%)	O (%)
1	76.86	8.01	2.72	12.41
2	76.98	8.03	2.56	12.43
6	77.21	8.08	2.24	12.47
12	77.38	8.13	1.97	12.52

to the increase of crosslink density. Consequently, this influenced the macrocyclic ligand to be displaced, and caused the decrease of the nitrogen content.

On the other hand, the result of thermo gravimetric analysis (TGA) is shown in Fig. 1 and Fig. 2, in order to know the thermo-stability of synthetic resins. As Fig. 1 represents the pyrolysis curve of chloromethylated styrene-DVB copolymer with 1% crosslink, which explains this copolymer is combined with these two groups styrene and DVB, according to the change of weight loss by 90.5% in a range of 330~450°C and by 8.3% in a range of 450~840°C.

Also, Fig. 2 shown the pyrolysis curve of synthetic resins with 1% crosslink, it is known that N-P-15-C-5 loses its weight by 25.0% in a range of 240~315°C, and styrene loses by 61.0% in a range of 315~440°C and

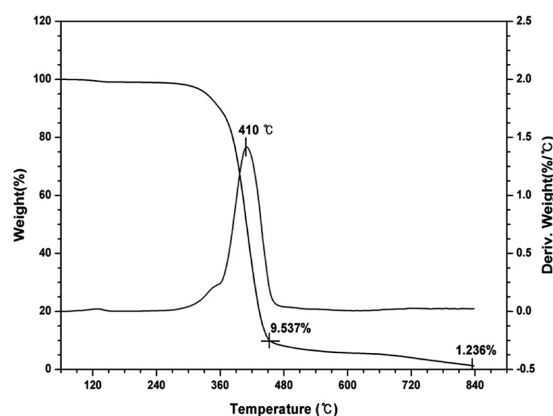
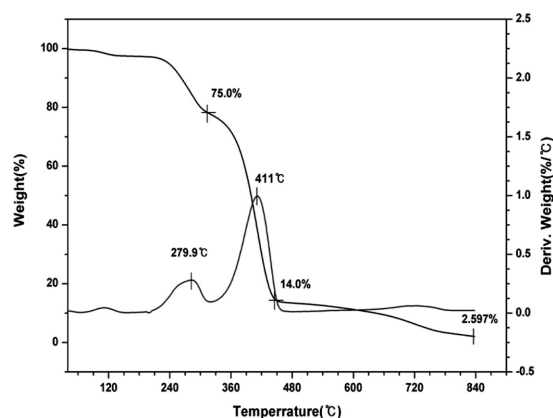

Fig. 1. TGA curve of 1% crosslinked chloromethylated styrene-DVB copolymer.

Fig. 2. TGA curve of 1% crosslinked resin.

Table 4. Surface area and pore volume of resin

Degree of crosslink (%)	Surface area (m ² /g)	Pore volume (cm ³ /g)
1	14.61	0.0240
2	12.96	0.0193
6	8.73	0.0131
12	7.11	0.0084

DVB loses by 11.4% beyond the degree of 440°C. This fact shows synthetic resins consist of N-P-15-C-5, styrene and DVB. Resins with 2%, 6%, and 12% crosslinks had similar conclusions as 1% crosslink. Thus, synthesized resins in this study become stable with the thermo for their having above 240°C of pyrolysis temperature that is more higher compared to the melting point of macrocyclic ligand (46–49°C), which matches up with the character of resins that Blasius *et al.*^[5] reported.

The surface area was measured in Table 4 to know the porosity of resin, one of absorptive property. After decompressing and drying the resin composing 1%, 2%, 6%, and 12% of crosslink made in this experiment in 150°C for 30 minutes and the surface area was exhibited under the circumstances of nitrogen adsorption method and -190°C by using Nanoporosity-XQ that the surface area and pore volume got lower as the degree of crosslink got bigger, which was reported in the study of Howdle *et al.*^[18,19].

3.2. Effects According to pH

To confirm the acidic zone possible to adsorb metal ions for the resin, uranium, europium, and zinc ions of 3.0 mM were stirred in ethanol solvent for 2 hours, and the adsorption characteristics were examined according to the pH changes of the resin representatively having 1% of crosslink as shown in Fig. 3.

The adsorbability of uranium ion became slowly increased at pH 2–3 and the stable complexes of uranium were rapidly increased at pH 3 over. The adsorbability of zinc ion was gradually increased at pH 3–4 and the stable complexes of iron was suddenly increased at pH 4 over. This phenomenon can be explained by the assumption that because the cryptand resin is basic amine, the nitrogen atom of the resin becomes protonated in a strong acidic solution (pH<2) and obstructs the adsorption of the metal cations, however, uranium and zinc ions with the products generated

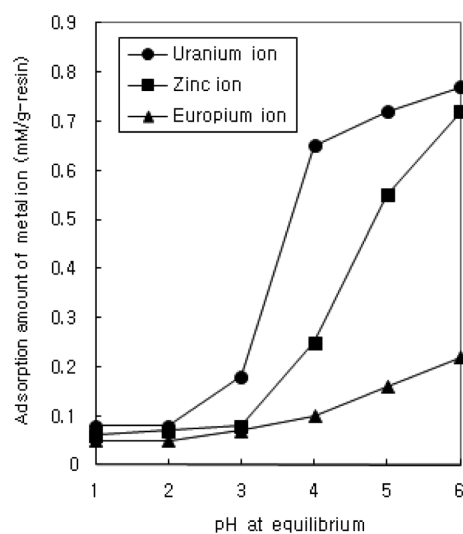


Fig. 3. Adsorption amount of U (VI), Zn (II), and Eu (III) ions on 1% crosslinked resin with pH in ethanol (concentration : 3.0 mM, time : 2 h).

from hydrolysis of the non-protonated resin form stable complexes^[12] and yield high adsorptivity in a weak acidic solution (pH>3). Besides, adsorption amount of uranium ion had influenced on hydro uranium precipitation in water solution at pH 4 over. On the other hand, europium ion cannot form a complex even in a strong acidic zone, and the complex formation is not easy because +3 value rare earth metal ions are strongly hydrated and hydration energy^[20] should be overcome to form cryptand resin and complexes. The cryptand resin used in this study was alkaline, and therefore, the adsorption experiment was performed only in the acidic solution under pH 6.

3.3. Effects According to Equilibrium Arrival Time

One of necessities to be resin is to quickly reach the adsorption equilibrium. Accordingly, Fig. 4 showed the adsorption equilibrium time of uranium, europium and zinc ions of 3.0 mM taken to reach the resin having 1% crosslink in ethanol solvent of pH 6. The adsorptivities were as large as 77% and 68% each for uranium and zinc ions easily forming resin and complexes^[12], but 22% for europium ion that did not form the cryptand resin and complexes well. Also, the adsorbability of each metal ion to the resin showed to decrease in an order of uranium > zinc > europium ions. In investigating the ratios of the size of U (2.38 Å), Zn (2.08 Å), and

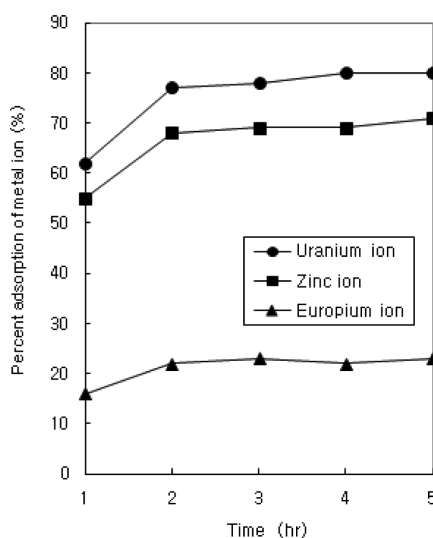


Fig. 4. Adsorption rate of U (VI), Zn (II), and Eu (III) ions on 1% crosslinked resin with time in ethanol (concentration : 3.0 mM, pH : 6.0).

Eu (2.41 Å) ions to the resin (2.7 Å) by a theory^[21] that the electrostatic attraction is very large and forms the stable complexes well when the ratios of the metal ion size to the resin cavity is between 0.7~0.9 the ratios were 0.88 (U), 0.77 (Zn), and 0.89 (Eu) and seemed to form the complexes very well, however, europium ion showed low adsorption owing to an influence of hydration energy. Moreover, these kinds of metal ions have the addition of covalent bonds by electrostatic bonding and resin nitrogen atom during the formation of 1% 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 cryptand-type metal complexes having nitrogen donor atom.

3.4. Effects According to Resin Crosslink

Fig. 5 shows the adsorption amount of uranium ion investigated by using the resins having 1%, 2%, 6%, and 12% crosslinks through a variation of uranium ion concentrations within a range from 1.0~6.0 mM by ethanol solvent.

As shown in Fig. 5, the resins having 1% and 2% crosslinks adsorbed approximately 0.5 mM/g in 1.0 mM

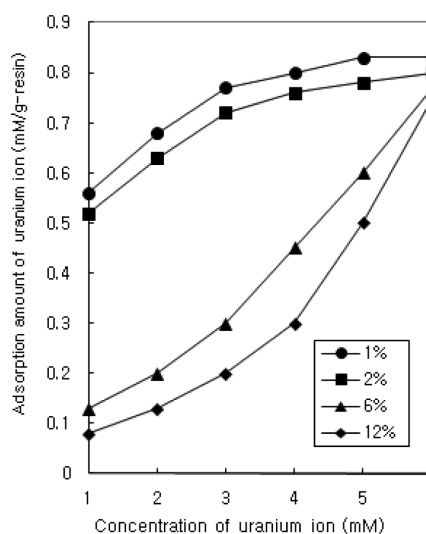


Fig. 5. Adsorption amount of U (VI) ion on 1%, 2%, 6%, and 12% crosslinked resin with concentration in ethanol (time : 2 h, pH : 6.0).

whereas the resins having 6% and 12% crosslinks adsorbed 0.10 mM/g only. The result of the adsorption presenting as 1% \approx 2% > 6% \approx 12% resins can be considered due to the reason that the crosslink is dependent on the amount of DVB during the synthesis of styrene-DVB copolymers, and the resin crosslink density is decreased with the decrease of the DVB content, whereas the porosity becomes higher and the diffusion velocity of uranium ion into the resin is large in the 1% and 2% resins compared with the 6% and 12% resins. However, the 6% and 12% 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 Fig. 5 is the apparent capacity of resins. The apparent capacity of uranium ion for 1%, 2%, 6%, and 12% resins were 0.83, 0.80, 0.77, and 0.75 mM/g, respectively.

3.5. Effects According to Solvent Dielectric Constant

For verifying the adsorption effects of uranium ion according to different solvent kinds, the adsorption rates of uranium ion were examined in the solvents of distilled water (78.54), nitrobenzene (34.82), and ethanol (24.55) having different dielectric constants (ϵ , 25°C) as shown in Fig. 6.

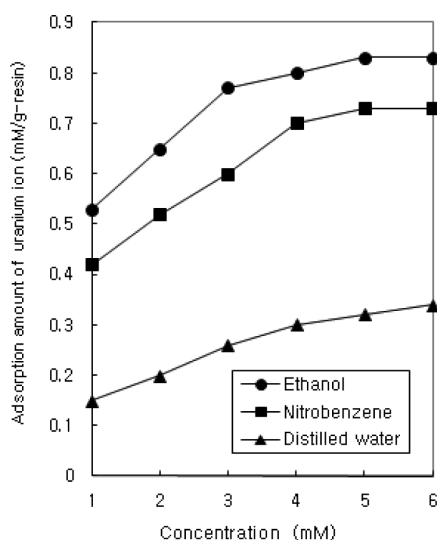


Fig. 6. Adsorption amount of U (VI) ion on 1% crosslinked resin in ethanol, nitrobenzene, and distilled water (time : 2 h, pH : 6.0).

The resins having 6% and 12% crosslinks in Fig. 5 had generally lower metal ion adsorption rates than the resin having 1% crosslink. Therefore, the resin having 1% crosslink was selected from Fig. 6, and the adsorption rates of uranium ion were investigated under the varied uranium ion conditions controlled within a range from 1.0–6.0 mM and increased in an order of ethanol > nitrobenzene > distilled water. This is probably due to the reason that the power of electrostatic bond (the power of Coulomb) is large as the dielectric constant value is smaller.

4. Conclusion

To selectively separate and collect rare earth metal ion, resin with styrene hazardous material was synthesized and its adsorption was 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 is reduced. This course influences the macrocyclic ligand, which reduced the nitrogen content. And the synthetic resin was stability under 240°C.

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). Besides, adsorption amount of uranium ion had influenced on hydro uranium precipitation in water solution at pH 4 over.

The metal ion adsorbability for the resin was shown to be uranium > iron > lutetium ions, which is 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 are added when the resin and metal ion form complexes, and therefore, the adsorption equilibrium can be quickly reached only 2 hours passed.

The resins of lower crosslink have lower density and higher porosity due to the small amount of the DVB content than the resins of high 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 rates of metal ion for the resin having 1% crosslink were ethanol > nitrobenzene > distilled water in order, and increased as the dielectric constant of the solvent becomes smaller.

In a series of results, solid membrane resin of macrocyclic compounds with styrene hazardous material is considered to use collect and separate metal ions in minimal matters.

References

- [1] P. G. Grimsley, L. F. Lindoy, H. C. Lip, R. J. Smith, and J. T. Baker, "Synthesis of new 14-, 15- and 16-membered crown compounds containing oxygen and nitrogen heteroatoms", *Aust. J. Chem.*, Vol. 30, pp. 2095-2098, 1977.
- [2] J. D. Kim, "Extraction characteristics of heavy metals for soil washing of mine tailings-contaminated soil according to particle size distribution", *J. Korean Chem. Soc.*, Vol. 19, pp. 98-104, 2008.
- [3] G. Bombieri and G. Depaoli, "Crown ether complexes of actinide elements (an x-ray study of the conformational change of the crown ether within the $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ (18-crown-6) molecule)", *J. Inorg. Nucl. Chem.*, Vol. 40, pp. 799-802, 1978.
- [4] T. Hayashita, J. H. Lee, S. Chen, and R. A. Bartsch, "Selective column concentration of alkali-metal cat-

- ions with a crown ether carboxylic acid resin”, *Anal. Chem.*, Vol. 63, pp. 1844-1847, 1991.
- [5] E. Blasius and P. G. Maurer, “Darstellung von austauschern mit kryptanden als ankergruppen”, *Makromol. Chem.*, Vol. 178, pp. 649-657, 1977.
- [6] J. T. Kim, “Adsorption of uranium (VI) ion on synthetic resin adsorbent with styrene hazardous materials”, *J. Korean Ind. Eng. Chem.*, Vol. 20, pp. 165-171, 2009.
- [7] K. W. Chi, Y. S. Ahn, K. T. Shim, H. Huh, and J. S. Ahn, “Synthesis of diazacrown ethers containing phenolic side arms and their complex with divalent metal ions”, *Bull. Korean Chem. Soc.*, Vol. 23, pp. 688-692, 2002.
- [8] H. K. Frensdorff, “Salt complexes of cyclic polyethers. Distribution equilibria”, *J. Am. Chem. Soc.*, Vol. 93, pp. 4684-4688, 1971.
- [9] Y. G. Ha, “Decomposition of monazite sand”, *J. Korean Chem. Soc.*, Vol. 23, pp. 136-140, 1979.
- [10] H. Egawa, T. Nonaka, and M. Ikari, “Preparation of macroreticular chelating resins containing dihydroxyphosphino and/or phosphono groups and their adsorption ability for uranium”, *J. Appl. Poly. Sci.*, Vol. 29, pp. 2045-2055, 1984.
- [11] J. T. Kim, “Adsorption characteristics and elution behavior of rare earth metals by new synthetic resins with macrocyclic compounds”, Chosun University, M. S. Dissertation, Gwangju, Korea, 1987.
- [12] M. Y. Suh, T. Y. Eom, and I. S. Suh, “Chromatographic behavior of cryptand [2,2] modified resin on metal cations”, *Bull Korean Chem. Soc.*, Vol. 8, pp. 366-372, 1987.
- [13] K. Joe, E. H. Lee, K. W. Kim, and K. Song, “Adsorption of an uranyl ion onto a divinylbenzene amidoxime resin in sodium carbonate solutions”, *Anal. Sci. Tech.*, Vol. 21, pp. 326-331, 2008.
- [14] K. C. Kang, S. S. Kim, M. H. Baik, S. H. Kwon, and S. W. Rhee, “Sorption of aqueous uranium(VI) ion onto a cation-exchangeable K-birnessite colloid”, *Anal. Sci. Tech.*, Vol. 23, pp. 566-571, 2010.
- [15] J. T. Kim, “Adsorption characteristics of uranium (VI) ion on OenNdien resins with styrene hazardous material”, *Appl. Chem. Eng.*, Vol. 22, pp. 697-702, 2011.
- [16] J. T. Kim, “Adsorption of uranium (VI) ion on 1-aza-12-crown-4 synthetic resin with styrene hazardous material”, *J. Chosun Natural Sci.*, Vol. 6, pp. 104-110, 2013.
- [17] J. T. Kim, “Adsorption characteristics of Al (III), Ni (II), Sm (III) ions on resin with styrene hazardous material in reinforcement water fire extinguishing agent”, *J. Chosun Natural Sci.*, Vol. 6, pp. 151-157, 2013.
- [18] S. M. Howdle, K. Jerabek, V. Leocorbo, P. C. Marr, and D. C. Sherrington, “Reversibly collapsible macroporous poly (styrene-divinylbenzene) resins”, *Polymer*, Vol. 41, pp. 7272-7277, 2000.
- [19] S. H. Kim, “Adsorption characteristics of heavy metal ions on 1-aza-18-crown-6- styrene-DVB synthetic resin”, Dongshin University, Ph. D. Dissertation, Naju, Korea, 2008.
- [20] J. A. Dean (Ed), “Lange's handbook of chemistry”, 13th, McGraw-Hill Book Company, New York, pp. 9-30-9-65, 1985.
- [21] C. J. Pedersen, “Crystalline salt complexes of macrocyclic polyethers”, *J. Am. Chem. Soc.*, Vol. 92, pp. 386-391, 1970.