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Adsorption Characteristics of U ranium (VI) Ion on Cryptand Synthetic Resin Adsorbent

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Abstract

Cryptand resins were synthesized by mixing 1-aza-18-crown-6 macrocyclic ligand with styrene divinylbenzene copolymer having 1%, 2%, 5%, and 10% 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 uranium ion adsorption for resin adsorbent, the uranium ion showed high adsorption at pH 3 or over. Adsorption selectivity for the resin in methanol solvent was the order of uranium (UO_2^{2+}) ＞calcium (Ca^{2+}) ＞neodymium (Nd^{3+}) ion, adsorbability of the uranium ion was the crosslink in order of 1%, 2%, 5%, and 10% and it was increased with the lower dielectric constant.

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

1. Introduction

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%[1] 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.

Crown compounds comprise alkali, alkaline earth metal, transition metal, heavy metal ions and stable complexes[2] 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[3].

Grimsley et al.[4] synthesized a chain of nitrogen donor (called 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[5].

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 devel-

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oping 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-divinyl benzene (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 is soluble in alcohol, ether, and carbon disulfide but 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.

In this study, the chloromethylated styrene-DVB copolymer, which is able to selectively separate and collect uranium ion from transition metals has been synthesized[10,11]. Hereupon, the chloromethylated copolymers were chemically by mixing with 1-aza-18-crown-6 (1-aza-18-C-6) macrocyclic ligand to prepare a new functional resin, and then, the adsorption characteristics[12-18] of uranium (UO_2^{2+}), calcium (Ca^{2+}), and neodymium (Nd^{3+}) ions were examined.

2. Experimental Section

2.1. Materials

1-Aza-18-crown-6, uranium nitrate, neodymium nitrate, and styrene were purchased from Aldrich Co., special grade, and 1,4-divinylbenzene (55%), 1,4-dioxane and benzoyl peroxide were bought from Donggyeong Hwaseong. Calcium nitrate, benzene, toluene, potassium iodide, dimethyl sulfoxide, etc. were used with general reagents.

An infrared spectrum was measured with Shimadzu IDP-440 A. Surface area was measured using Nanoporisity-XQ of Miirae SI Co. SRM and element analysis was measured with Hitachi S-4800 and Model 1108 of Carlo-Erba Co., respectively. 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 electrod. Also, adsorption and separation of uranium (UO_2^{2+}), calcium (Ca^{2+}), and neodymium (Nd^{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, 500 mL three neck 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. 250 mL distilled water was added into the 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 95 mL /DVB 9.0 mL for 5%, and styrene 90 mL /DVB 18.0 mL for 10%. 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. After dried, styrene-DVB copolymer (5 g) were swollen in 100 mL of chloroether in 250 mL flask at room temperature for 2 hours. Zinc chloride (2 g) dissolved in 25 mL of chloroether was added to 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 to wash 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%, 5%, and 10% 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 2.63 g of 1-aza-18-C-6 macrocyclic ligand were added, stirred, and refluxed at 55°C for 36 hours under nitrogen condition. The mixture 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-18-C-6-styrene-DVB resins (called resin or synthetic resin) having 1%, 2%, 5%, and 10% crosslink. The size of resin cavity was 200-400 mesh.

2.5. Experimental Method

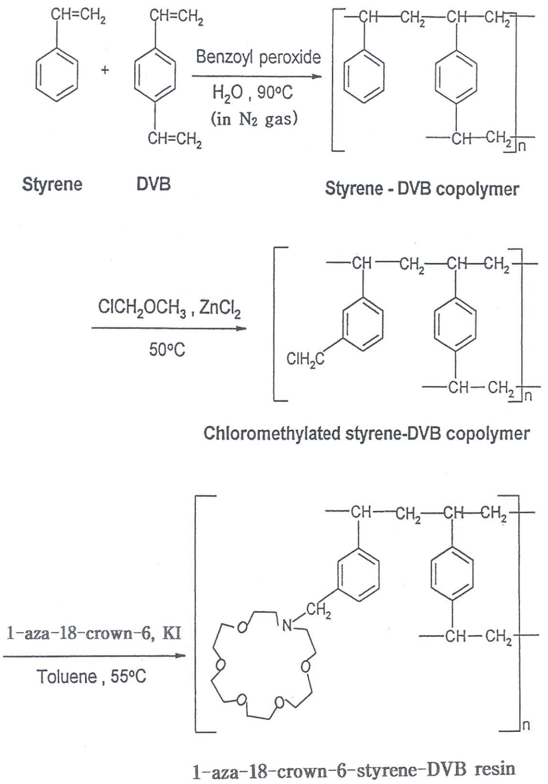
The content of chlorine was measured in the process of synthesizing the resin with chloride ion-selective electrode. The product resins composed of 1%, 2%, 5%, and 10% crosslink were confirmed by IR-spectrum with KBr disc method and their elemental analysis for C, H, N, O, The surface of synthetic resin was characterized by SEM.

Also, $UO_2(NO_3)_2$, $Ca(NO_3)_2$, and $Nd(NO_3)_3$ solutions of 3.0 mM were controled 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 uranium ion was quantitatively analyzed by ICP-AES under the dilute nitric acid.

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. Synthesis of Styrene-DVB copolymer.

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 for the degree of crosslink and the elementary analysis. When the crosslink increased, the nitrogen content decreased. As the results, the increase of the crosslink also brought on the increase of the DVB content, which subsequently decreased the chlorine content during the substitution

Table 1. Chlorine contents of copolymer and composition of 1-aza-18-C-6-styrene-DVB resins with various crosslinked

Degree of crosslinking (%)	Copolymer	Resin			
	Cl (%)	C (%)	H (%)	N (%)	O (%)
1	12.35	73.05	8.51	2.75	15.69
2	11.86	73.08	8.52	2.69	15.71
5	10.21	73.11	8.55	2.56	15.78
10	10.08	73.21	8.61	2.38	15.80

Table 2. IR-data of 1% crosslinked styrene-DVB copolymer (A), 1-aza-18-C-6 (B), and 1% crosslinked 1-aza-18-C-6-styrene-DVB resin(C)

Kinds of resin function group	Frequency (cm^{-1}) (A)	(B)	(C)
N-H	---	3400	---
Aromatic (C-H)	3100-3140	---	3100-3140
Aliphatic (C-H)	2950-2980	2800-2980	2900-2980
Benzene ring (CC)	1450-1520	---	1450-1520
C-O-C C-N-C	---	1100-1200	1250
Mono Substition (4 peaks)	1850-1980	---	1850-1980
C-Cl	650	---	---
C-N	---	---	1020

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 IR-data obtained through KBr disc method. As a result that the chloromethylated styrene-DVB copolymer was combined with 1-aza-18-C-6, the 1-aza-18-C-6 was displaced because there were no N-H peak near 3400 cm^{-1} and C-Cl absorption peak around 650 cm^{-1}. Moreover, the induction of the macrocyclic ligand brought strong and wide stretching vibration peaks of C-O-C and C-N-C in 1250 cm^{-1}, and a new sharp stretching vibration peak of C-N in 1020 cm^{-1}.

The surface area was measured and the results are shown in Table 3 to determine porosity for the adsorption characteristics. The resins having 1%, 2%, 5%, and 10% crosslink degrees 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, pore diameter decreased, but the surface area and the number of porosity increased. Similar results were also reported by Howdle[12] et al.

Table 3. Surface area and pore diameter of 1-aza-18-C-6-styrene-DVB resin

Degree of crosslinking (%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Ave. pore diameter (nm)
1	5.63	0.0196	5.0
2	5.98	0.0171	4.8
5	11.64	0.0069	4.3
10	15.18	0.0022	4.1

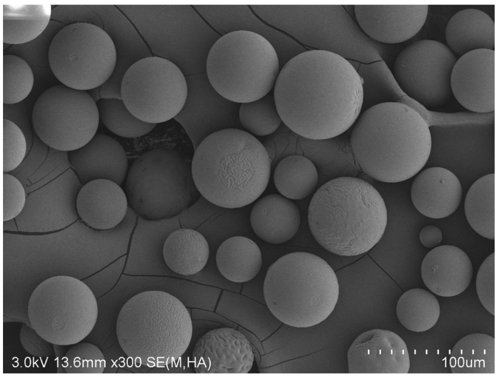


Fig. 1. SEM photograph of 1% crosslinked chloro -methylated styrene-DVB copolymer.

On the other hand, electron micrographs of 1% copolymer and 1% resin were shown in Fig. 1 and Fig. 2, respectively. Fig. 1 shows the spherical shape, but Fig. 2 shows the distorted shape of the hydrogen of the macrocyclic ligand. It can be seen that the particle shape 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 chloromethylate agent and a solvent. The copolymers are greatly swollen chloroethers. The copolymers of 1% and 2% chloromethylated are light yellowish white, but in the case of copolymers of 5% and 10%, they are light

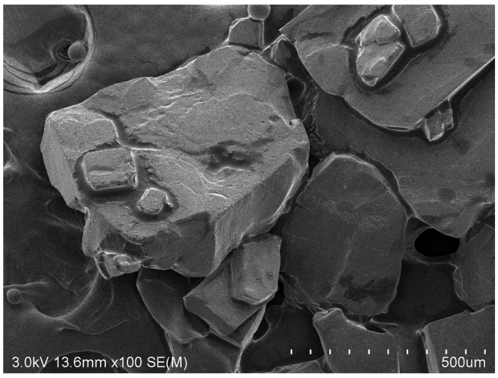


Fig. 2. SEM photograph of 1% crosslinked 1-aza -18-C-6-styrene-DVB resin.

brown.

3.2. Effects of pH

To confirm the acidic zone possible to adsorb metal ions for the resin, uranium, neodymium, and calcium ions of 3.0 mM were stirred in methanol 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 Fig. 3. The adsorbability of uranium ion slowly increased and the stable complexes of uranium was rapidly increased at pH 3 or over. The adsorbability of calcium ion was gradually increased between pH 3 and pH 4, and the stable complexes of calcium was suddenly increased at pH 4 or 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 calcium ions with the products generated from hydrolysis of the non-protonated resin form stable complexes[13,14] and yield high adsorptivity in a weak acidic solution ($pH>3$)[15-20]. On the other hand, neodymium 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[21] should be overcome to form cryptand 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 cryptand metal complexes having nitrogen donor atom. The cryptand 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%, 5%, and 10% crosslink[16-20] through a variation of uranium ion concentrations within a range from 1.0~6.0 mM by methanol 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 5% and 10% crosslink adsorbed 0.10 mmol/g only. The result of the adsorption presenting as 1%≈2% > 5%≈10% 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

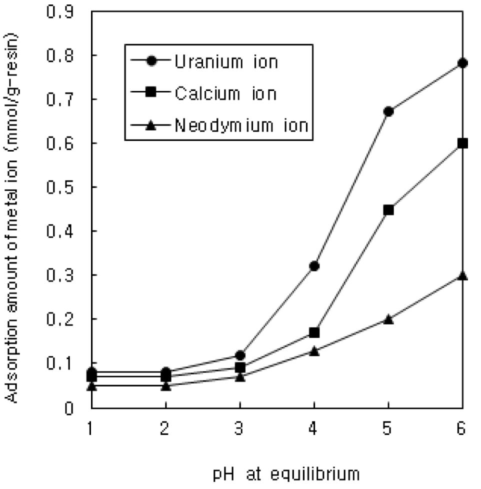


Fig. 3. Adsorption rate of UO_2^{2+}, Ca^{2+}, and Nd^{3+} on 1% crosslinked 1-aza-18-C-6-styrene-DVB resin at various pH in methanol (concentration : 3.0 mM, time : 2 h).

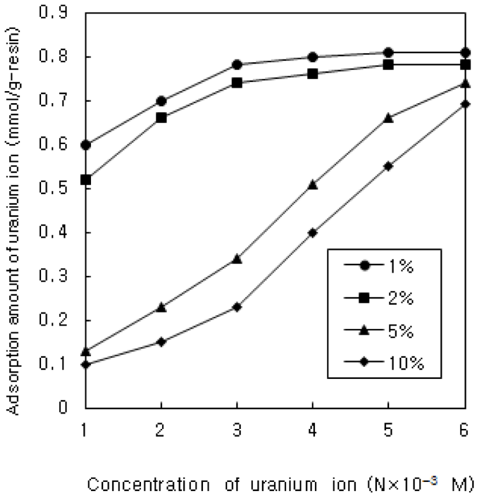


Fig. 4. Adsorption rate of UO_2^{2+} on 1%, 2%, 5%, and 10% crosslinked 1-aza-18-C-6-styrene-DVB resin at various concentration in methanol (pH : 6.0, time : 2 h).

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 5% and 10% resins. However, the 5% and 10% 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. 4 was the apparent capacity of resins. The apparent capacity of uranium ion for 1%, 2%, 5%, and 10% resins was 0.81, 0.78, 074, and 0.68 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 of uranium ion was examined in the solvents of distilled water, nitrobenzene, and methanol having different dielectric constants[15-20] as shown in Fig. 5.

The resins having 5% and 10% crosslink in Fig. 4 had generally lower uranium 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 methanol > nitrobenzene > 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.

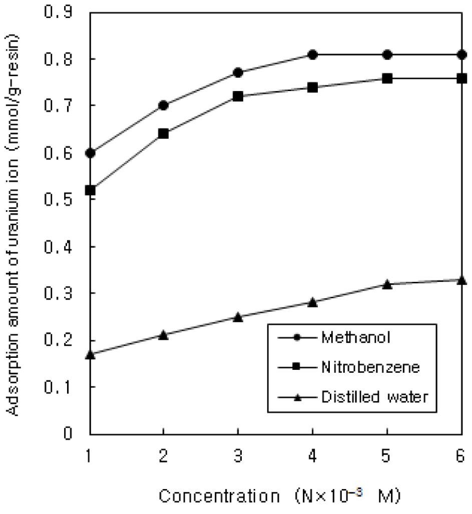


Fig. 5. Adsorption rate of UO_2^{2+} on 1% crosslinked 1-aza-18-C-6-styrene-DVB resin in methanol, nitrobenzene, and distilled water (pH : 6.0 time : 2 h).

4. Conclusion

To selectively separate and collect uranium ion, resin was synthesized and adsorption characteristics 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 was reduced. This course influences the macrocyclic ligand, which reduced the nitrogen content.

The nitrogen atom in synthetic resins was protonated under methanol 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 > calcium > neodymium 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 5% and 10% crosslink. Accordingly, the diffusion velocity of uranium ion into the resin was large even in a dilute solution, which makes it well to adsorb uranium ion.

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

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