Crown ether-type organic composite adsorbents embedded in high-porous silica beads for simultaneous recovery of lithium and uranium in seawater

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	作成者: TACHIBANA, Yu, TANAKA, Masahiro, NOGAMAI, Masanobu
	メールアドレス:
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1　　　　　　　　　　　　　**Title page**

2　**Names of the authors:** Yu Tachibana[a], Masahiro Tanaka[b], Masanobu Nogami[c]

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5　**Affiliations and addresses of the authors:** [a]Department of Nuclear System Safety

6　Engineering, Graduate School of Engineering, Nagaoka University of Technology, 1603-

7　1, Kamitomioka-machi, 940-2188 Nagaoka-shi, Niigata, Japan

8　[b]National Institute for Fusion Science, 322-6, Oroshi-cho, 509-5292 Toki-shi, Gifu, Japan

9　[c]Department of Electric and Electronic Engineering, Kindai University, 3-4-1, Kowakae,

10　577-8502 Higashiosaka-shi, Osaka, Japan

11　**E-mail address of the corresponding author:** yu_tachibana@vos.nagaokaut.ac.jp

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Crown ether-type organic composite adsorbents embedded in high-porous silica beads for simultaneous recovery of lithium and uranium in seawater

Yu Tachibana[a], Masahiro Tanaka[b], Masanobu Nogami[c]

[a]*Department of Nuclear System Safety Engineering, Graduate School of Engineering, Nagaoka University of Technology, 1603-1, Kamitomioka-machi, 940-2188 Nagaoka-shi, Niigata, Japan*

[b]*National Institute for Fusion Science, 322-6, Oroshi-cho, 509-5292 Toki-shi, Gifu, Japan*

[c]*Department of Electric and Electronic Engineering, Kindai University, 3-4-1, Kowakae, 577-8502 Higashiosaka-shi, Osaka, Japan*

Abstract

The syntheses of crown ether-type organic composite adsorbents embedded in high-porous silica beads for simultaneous recovery of lithium and uranium in seawater have been achieved and the adsorption behavior of lithium and uranium on the composite adsorbents has been examined in several types of original seawater in the wide temperature and pH ranges. As a result, the composite adsorbents composed of benzo-15-crown-5 (BC15) and benzo-18-crown-6 (BC18) showed the top-class maximum adsorption capacities for lithium [6.5 mg / g (BC15), 11 mg / g (BC18)] and uranium [12 mg / g (BC15), 4.2 mg / g (BC18)].

Keywords: Crown ether-type organic composite adsorbent; high-porous silica beads; Lithium; Uranium; Seawater; Simultaneous recovery

1. Introduction

Lithium (Li) can be distinguished as one of specific minerals in the world because the extraction of Li from the environment is very difficult due to technical and economic issues. On the other hand, Li is one of elements essential for our modern lives. Now, there is a large magnitude of industrial demand for Li and Li also has the potential to be more extensively available element for a variety of industrial fields in the near future. Concretely, a lot of industrial applications including Li ion batteries [1], Li lubricating greases [2], Li additive agents for glass production [2], Li glazes for ceramic and enamel

coatings [2], Li-7 salt (LiOH) used as pH controller in pressurized water reactors [3], and Li-6 as a raw material of tritium (T) production in nuclear fusion reactors using ^{6}Li (n, α) T reaction [3] lead to the rise in demand of Li. Especially, a large amount of Li-6 will be surely required to operate nuclear fusion reactors in near future. Unfortunately, absolute amount of Li will decrease due to the tritium breeding using Li-6. Also, the recycle of Li from spent products has not yet been performed in Japan. As long as such a condition persists, the demand may overwhelm supply in the near future. As a result, we may run out of Li resources in a short time. Therefore, it will be required to secure other resources of Li supply and / or to develop a new Li recycling technology based on economics.

Li is produced from Hombre Muerto Salt Lake in Argentina and Atacama Salt Lake in Chile located in South America. The production accounted for 70 % of the world's Li production until several years ago [4]. Other Li production plants from Olaroz Salt Lake, Rincon Salt Lake, and Uyuni Salt Lake have been recently operated.

Apropos, it has been generally accepted that an enormous amount of Li is contained in seawater. The total amount of Li in seawater reaches approximately 2.3 hundred billion tons [5]. The average concentration in seawater has been reported as 26 μM (M = mol / L, L = dm^3) [6]. But, these Li resources dissolved in seawater are not counted as the amount of Li reserves because there is not any economical technology selectively to recover Li from a huge amount of impurities such as sodium, potassium, magnesium, etc. in seawater. Therefore, if innovative Li recovery technology is acquired, the maldistribution and the rapid depletion of Li resources would ideally be relaxed [7, 8]. It is very interesting for chemists to develop selective recovery adsorbents, etc. for Li ion in seawater [5, 7-10]. The foregoing Li recovery processes using ion exchange and complexation reactions are very simple but the Li adsorption capacities of them are not so high or some adsorbents may dissolve into seawater by long immersion time. Seawater contains other alkali metals whose chemical behavior is similar to that of Li and their order of concentration is Na (0.48 M), K (10 mM), (Li (26 μM)), Rb (1.4 μM), Cs (2.3 nM) [6]. Thus, the higher selectivity and stability properties have been required.

Crown ethers with many kinds of cavity sizes are widely regarded as extractants for specific elements recovery and their cavity sizes and ionic diameters have been already reported [11-13]. Recently, we have successfully synthesized seven kinds of crown ether resins embedded in high-porous silica beads, benzo-12-crown-4 (Abbreviated as BC12), dibenzo-14-crown-4 (DBC14), benzo-15-crown-5 (BC15), benzo-18-crown-6 (BC18), dibenzo-18-crown-6 (DBC18), dibenzo-21-crown-7 (DBC21), and dibenzo-22-crown-6 (DBC22) resins to evaluate the Li adsorption behavior in seawater (see Fig. 1). As a result, it was found that the BC15 and BC18 resins

have comparatively higher adsorption ability for Li ion in seawater and their adsorption behavior strongly depends on the cavity size and the degree of hydrophobicity of these crown ethers [7].

Uranium (U) which is largely concentrated in several regions such as Canada, Kazakhstan, Niger, etc. exists mainly as uraninite. U reserves for nuclear power generation are predicted to be approximately 80 - 120 years at the current rates of consumption [14]. However, present global energy requirements will be associated with a twofold increase in high annual growth of emerging economics and high world population growth rate by 2050 [14]. Hence, it is projected to supply some of the increased world's energy using nuclear power generation [14]. U can be regarded to be low-carbon source of base load power generation. U exists in seawater at a concentration of 14 nM [5] and U reserves from seawater amount to about 4.5 billion tons which is more than 1,000 times larger than those from terrestrial ores and are sufficient to power the world's reactor fleet for 13,000 years [15]. The possible chemical species of U in seawater are estimated to be $Ca_2[UO_2(CO_3)_3]$, $Ca[UO_2(CO_3)_3]^{2-}$, $Mg_2[UO_2(CO_3)_3]$, $UO_2(CO_3)_3^{4-}$, $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$, and $(UO_2)_2CO_3(OH)_3^{-}$ [5,14,16,17]. This tendency implies that U can exist as neutral and anionic species in seawater. Inorganic adsorbents (IAs) [18], polymer adsorbents (PAs) [19], radiation-induced graft polymerization prepared adsorbents (RIGPAs) [20, 21], atom transfer radical polymerization prepared adsorbents (ATRPAs) [22], and nanostructured carbons (NCs) [23], metal - organic frameworks (MOFs) which are one of porous materials formed by the reaction of organic ligand struts with metal cluster nodes to form infinite 1-, 2-, or 3-D networks [24], mesoporous silica adsorbents (MSAs) [25], high affinity genetically-engineered proteins and their related materials (HAGEPs) [26], are available for extraction of U from seawater. The performances per unit weight of many adsorbents for recovery of U from water and seawater (mg / g) are 6×10^{-3} - 8.50×10^2 and 7×10^{-3} for IAs, 1.7×10^{-2} - 5.50×10^2 and 4.2×10^{-3} - 2.81×10^1 for PAs, 3×10^{-3} - 9.24×10^2 and 6×10^{-4} - 5 for RIGPAs, 2 - 1.79×10^2 and 6×10^{-1} - 5.2 for ATRPAs, 6×10^{-3} - 1.932×10^3 and 2×10^{-3} - 3.4 for NCs, 0 - 8.40×10^2 for MOFs in water, 8×10^{-3} - 2.77×10^2 and 1×10^{-2} - 1×10^{-1} for MSAs, and 1 and 9.2×10^{-3} for HAGEPs, respectively [14]. These results indicate that U adsorption reactions using these adsorbents are strongly influenced by some elements in seawater. Thus, the higher selectivity and stability properties of adsorbents for U recovery have been required to lead to a dramatic cost reduction as well as the adsorbents for Li recovery. However, it seems to be so difficult to surmount the economical challenge because of extremely low concentration of U in seawater.

As one of solutions of these matters, we have suggested to simultaneously extract Li and U from seawater using some simple organic adsorbents. This new U recovery process equipped with Li recovery ability has high added value and may contribute to the success of the development of the relevant industrial application. For simultaneous recovery of Li and U in seawater, we have successfully synthesized the crown ether-type organic composite adsorbents embedded in high-porous silica beads having two functional groups composed of ether oxygen in crown ether to bind Li and hydroxyl group in bisphenol A to bind U in seawater (see Fig. 1). In our previous works, it was found that phenol type resins such as bisphenol A type and tannic acid type resins have high adsorption ability for U in seawater [16, 27, 28]. We have also identified that the swelling and shrinking behavior which affects separation performance in varying degree is one of important parameters in a chromatographic process. Hence, the composite adsorbents embedded in high-porous silica beads were used because the silica beads can suppress the swelling and shrining behavior of the composite adsorbents. In addition, use of silica beads can generally enhance mechanical strength of adsorbents. This factor seems to be very important for industrial application.

Based on these backgrounds, the adsorption behavior of Li and U on these crown ether-type adsorbents has been examined in many kinds of seawater in the wide temperature range, compared with those of other adsorbents.

2. Experimental
2.1. Materials

HCl (Purity: 35.0 wt%) and NaOH (Purity: 93.0 wt%) were obtained from Nacalai Tesque, Inc. The aqueous solution of U ion containing Be, Mg, Co, Ni, In, Pb, Bi, and Ce ions was supplied by AccuStandard, Inc. The mixed solution was used without removal of the elements such as Be, Bi, Ce, etc. as a source of U ion because seawater originally contains these elements at somewhat lower concentrations [6]. This U ion dissolved in 2 wt% nitric acid solvent was used as U salt after evaporation of the solvent by using a combination of a hotplate kept constant at ca. 373 K and an infrared heating and drying lamp (375 W). LiCl whose purity was more than 99.0 wt% was purchased from Wako Pure Chemical Ind., Ltd. The above chemicals were used without further purification in this study. The chemicals with special pure grade were used for analyses. These salts were added into the stock solutions for the adsorption experiments of Li and U species using concentrated and diluted seawater. On the other hand, the Li and U species containing originally in the original seawater were used with no addition of Li and U salts under most experimental conditions. We sampled the original seawater from the Sea of Japan

around Gokahama in Nishikan-ku, Niigata, Japan. Its sampling date was on September 29, 2017. The total volume of seawater was approximately 40 L. Anion exchange resins (WA10 (OH form), WA20 (OH form), WA30 (OH form), PA308 (Cl form), PA312 (Cl form), and PA316 (Cl form)), cation exchange resins (WK10 (H form), WK40L (H form), PK208 (Na form), PK216 (Na form), PK220 (Na form), PK228 (Na form), PK228L (Na form), SK112L (Na form)), and chelating resin (CR10 (Na form)) were obtained from Mitsubishi Chemical, Co., Ltd. and their structural details and chemical properties have been reported elsewhere [29]. BT - AG®1-X8-type anion-exchange resin (OH form, 200 - 400 mesh) was produced from Bio-Rad Laboratories, lnc. BC15 and BC18 adsorbents were synthesized and the detailed explanation was mentioned in our pervious paper [7]. On the other hand, BC12, DBC14, DBC18, DBC21, and DBC22 adsorbents which were previously synthesized were used. In short, MST-8C silica beads were mainly used in our previous paper [7]. In the syntheses of BC15 and BC18 adsorbents, MST-2 type silica beads instead of MST-8C silica beads as a supporter were used to compare the adsorption behavior between specific metal ions and crown ether-type organic composite adsorbents on different kinds of silica beads. These silica beads were provided from Mizusawa Industrial Chemicals, Ltd. as trial products.

2.2. Sample preparation

The fine particles contained in the seawater sampled from the Sea of Japan, were removed using MF-Millipore glass fiber filter (Pore size: 2.0 μm, diameter: 47 mm, thickness: 1.2 mm) before all adsorption experiments. The initial Li concentration of filtered seawater was found to be 1.6×10^{-5} M. This concentration was somewhat lower than that from the literature [6]. This may be caused by the rainfall on the previous day of the sampling. We made an attempt to adjust the concentrations of Li and U ions in the seawater to about 1.0×10^{-4} M for Li ion and about 1.7×10^{-6} M for U ion, respectively using an UC-0515 type ultrasonic apparatus made by Tocho in the adsorption experiments of Li and U species in concentrated and diluted seawater. However, the final concentrations of both metal ions were lower than the expected concentrations. Hence, the stock solutions were also filtered using the same glass fiber filter once again because these results may be caused by their fine precipitation. The diluted seawater was prepared by mixing with ultrapure water and its concentration factor (Abbreviated as CF) was 1 / 10, 1 / 5, 1 / 3, 1 / 2, and 1, respectively. To the contrary, the concentrated seawater of CF = 1.5 was obtained by the mild evaporation of the seawater using a hotplate heated at ca. 373 K and an infrared heating and drying lamp (375 W). The time taken to reach dryness was two days. The initial pH values of seawater were adjusted using NaOH and HCl and

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the finally adjusted pH values were confirmed using a pH tester with 0.1 pH resolution (HI98103S, Hanna). All sample solutions were prepared by mixing with ultrapure water produced from Milli-Q Integral 3 type ultrapure water system made by Merck Millipore. It was confirmed that the values of specific electrical resistance and concentration of total organic carbon of the ultrapure water were $\geq$ 18.2 MΩcm and $\leq$ 3 ppb (ppb = ng/g), respectively. The similar method has been shown elsewhere [7].

2.3. Adsorption experiments

The batch-wise technique was applied for the adsorption experiments of Li and U ions using the crown ether-type adsorbents embedded in high-porous silica beads in order to evaluate the distribution coefficients (K_d) and the thermodynamic parameters (ΔG, ΔH, and ΔS) in various seawater and in a wide temperature range. The crown ether-type adsorbents of 250 or 500 mg were individually added into the various types of seawater (10.0 mL) in the tubes. The level of confidence in all experiments was in the range of $\pm 1\sigma$. The initial chemical form of counter cation of functional groups in the crown ether-type adsorbents was exchanged with H. Two types of vials made of borosilicate glass and polypropylene have been prepared and then the concentrations of Li and U ions before and after adsorption tests under the condition; Temp. = 278-333 K, no adsorbents have been preliminarily checked to evaluate their adsorption degree against the surface of these vials. In short, the seawater with Li and U ions, 1 wt% HNO_3, and / or MeOH were added into those vials to intercept the adsorption by the ion-exchange reaction and the hydrophobic interaction between the materials and Li or U ions. As a result, we found that little difference of Li and U concentrations before and after these adsorption tests is observed. In conclusion, the adsorption behavior between these materials and Li or U ions can be negligible under all experimental conditions. The sample solutions were constantly stirred in a shaking water bath kept constant at 278 - 333 K. This shaking procedure was continued for 24 hours. Each concentration of Li and U ions was measured using a 7700x type ICP/MS analyzer made by Agilent and / or an AA-6200 type AAS analyzer made by Shimadzu. The sample solutions were filtered using the regenerated cellulose fiber filter made by Sartorious Stedim (Pore size: 0.45 μm) to remove the adsorbents in the sample solutions and / or the adsorbents and the sample solutions were physically separated by using a H-36α type centrifuge separator made by Kokusan. The operating time was 30 min at 3500 rpm. Some of these procedures have been shown in ref. [7]. The surface structure and chemical structure of the synthesized crown ether-type adsorbents were evaluated by a VE-8800 type SEM made by Keyence and an IRAffinity-1S type FT-IR spectrometer made by Shimadzu, respectively. The classical KBr pellet method was used

for FT-IR measurements. All pellets were prepared by grinding the mixture of adsorbents and granular KBr on the agate mortar, where the weight ratio of each adsorbent and KBr is 1 : 500. All FT-IR data and most of SEM images were abbreviated in this manuscript because the similar data have already shown in our previous work [7].

2.4. Chromatography experiments

The glass and plastic columns were used to calculate the maximum adsorption capacities of Li and U ions on the BC15 and BC18 adsorbents using a typical chromatographic technique, respectively. The glass column was equipped with the water jacket made of glass and this jacket was used to keep the constant temperature in the column. On the other hand, the inside temperature of plastic column was controlled using the air conditioner. The glass and Mini-column S type plastic columns were purchased from Nihon Seimitsu Kagaku, Co., Ltd and Muromachi Chemicals Inc. The length of glass column was 10 cm and its inner diameter (ID) was 10 mm. The specification of plastic column was the length of 5 cm and ID = 5.0 - 5.5 mm. The respective apparatuses were connected in series with the polytetrafluoroethylene tubes having ID = 2 mm and 3 mm outer diameter (OD) or silicone rubber tube (ID = 3 mm, OD = 5 mm) and PharMed BPT tube (ID = 0.8 mm, OD = 4 mm). The above-mentioned adsorbents were packed into the columns. The total weight of those adsorbents embedded into the columns was 5.97 $\times$ 10^{-1} g for Li / BC15 and 6.26 $\times$ 10^{-1} g Li / BC18 systems, respectively. For U / BC15 and U / BC18 systems, each weight of adsorbents was 2.50 $\times$ 10^{-2} g and 2.62 $\times$ 10^{-2} g, respectively. The weight of high-porous silica beads in the adsorbents was excluded from the total weight of adsorbents. By using the air conditioner and the circulator, the reaction temperature was kept constant at 298 K. The initial chemical form of Na of the crown ether-type adsorbents was preliminarily conditioned to H form by using 1.0 M HCl solution, then the crown ether-type adsorbents were rinsed using ultrapure water to remove free H^+ until the pH of effluent became neutral. Then, the column chromatography experiments using seawater which contained Li ion of 4.8 $\times$ 10^{-3} M and U ion of 1.4 $\times$ 10^{-6} M or 2.2 $\times$ 10^{-6} M, respectively were carried out under the constant flow rate of approximately 1.0 mL / min. The maximum pressure in the flow path was set below 2.0 MPa. Each effluent volume of seawater was adjusted to around 200 - 220 mL for Li tests and around 105 - 111 mL for U tests, respectively. The flow rate was controlled by a NP-KX-210 type high-pressure pump equipped with an analogue pressure gauge made by Nihon Seimitsu Kagaku for Li adsorption test and a standard peristaltic tube pump (SJ-1211-II-H, Atto) for U adsorption test. A CHF100AA type fraction collector made by Advantech was used finally to collect 100 fractions including approximately 1

mL or 2 mL eluent in each tube. The pH of each collected sample solution was measured using the same pH tester. The Li and U concentrations were measured by using the ICP/MS and / or AAS analyzers. The aqueous solution of 1 wt% HNO_3 was used as a diluent for all ICP/MS and AAS measurements. This procedure has been constructed by reference to the literature [8].

These adsorbents do not adsorb Cl^- ion which exists in seawater as anion species. If these adsorbents have somewhat adsorption ability for Cl^- ion, the concentration of Cl^- ion in seawater is large excess, compared with that adsorbed on the adsorbents. As a result, the adsorption effect for the dead volume can be vanishingly small. Hence, the dead volume was estimated by measuring the concentration of Cl^- ion in the eluents. The ion chromatograph (IC) made by Tosoh (IC-2001), was used to analyze dissolved chloride ion in the sample solutions qualitatively and quantitatively at room temperature. A mixture of 6.0 mM $Na_2B_4O_7$, 15 mM H_3BO_3, and 0.2 mM $NaHCO_3$ as a mobile phase was supplied at 0.8 mL/min. TSKgel SuperIC-Anion type column made by Tosoh (ID = 4.6 mm, 150 mm length) packed with 5 μm spherical particles with a quaternary ammonium group was used. The column temperature was kept constant at 313 K by using a column oven. The IC with an electrical conductivity detector was used.

3. Results and Discussion

3.1. Adsorption behavior of Li and U ions on crown ether-type adsorbents in seawater

The adsorption experiments of Li and U ions using BC12, DBC14, BC15, BC18, DBC18, DBC21, and DBC22 adsorbents embedded in high-porous silica beads were performed by well-known batch-wise techniques in order to evaluate the K_d values of Li and U ions in seawater at room temperature. The calculation of K_d values was performed by using the following Eq. (1).

$$K_d = (C_r / C_s) \times (V_s / V_r) = \{(C_0 - C_s) / C_s\} \times (V_s / V_r) \tag{1}$$

where C_r, C_s, C_0, V_s, and V_r are concentrations of Li and U ions on adsorbent after adsorption equilibrium, concentrations of Li and U ions in seawater after adsorption equilibrium, initial concentrations of Li and U ions in seawater, volume of solution, and volume of adsorbent, respectively. As shown in our previous work [7], the ascending order of the K_d values of Li ion using the seven crown ether-type adsorbents was found to be DBC14 < BC12 ≒ DBC21 ≒ DBC18 < DBC22 < BC18 ≤ BC15 and it was found that the BC15 and BC 18 adsorbents have comparatively higher adsorption ability

for Li ion (see Fig. 2). This result is reasonable because each cavity size of BC15 and BC18 adsorbents is close to the Stokes radius of Li ion. On the other hand, the K_d value of BC18 adsorbent was different from that of DBC18 adsorbent in spite of the same cavity size (see Fig. 2). Hence, we have estimated the values of hydrophobicity (C Log P) of seven kinds of crown ethers. Each C Log P was calculated by using a software (ChemBioOffice Ultra 14.0, Cambridge Soft Corporation). We attributes the difference of this adsorption behavior to the hydrophobicity of crown ether-type adsorbents because the hydrated Li ion can be more accessible to BC18 (C Log P = 1.15) adsorbent rather than DBC18 adsorbent (C Log P = 3.49), as shown in Fig. 1. These results and the similar discussion were also mentioned in the reference [7]. Moreover, these adsorption abilities of BC15 and BC18 adsorbents were compared with those of typical commercial resins. We found that PK208, PK216, PK220, PK228, PK228L, and SK112L resins with a sulfo group, WK10 and WK40L resins with a carboxylic group, and CR10 type chelating resin with two carboxylic groups have little adsorption ability for Li ion in seawater although the porous-type sulfonated styrene-divinylbenzene resins are often used in the Li isotope separation research (see Fig. 3) [3, 8, 30]. These results imply that the Li adsorption reactions are interfered by other elements in seawater. It has been known that the selectivity of sulfo group in PK and SK-type resins is K > Na > Li in water as well as the selectivity of WK-type resins [8]. Seawater contains plenty of K ions. The adsorption ability of CR-type resin depends strongly upon the valence state of metal ions and this resin has high adsorption ability for the trivalent metal ions such as Cr^{3+}, In^{3+}, and Fe^{3+} [29]. Hence, we can estimate that this resin has comparatively lower adsorption ability for Li ion. BC15 and BC18 adsorbents have the highest adsorption ability for Li ion in seawater among them.

Moreover, we confirmed that the seven crown ether-type adsorbents have much higher adsorption ability for U ion in seawater (see Fig. 2). The range of K_d values were from $(4.52 \pm 0.20) \times 10^2$ to $(3.83 \pm 0.52) \times 10^3$. It can also be confirmed that bisphenol A type and tannic acid type resins have also much higher adsorption ability for U ion in seawater and these phenomena are caused by the complexation reactions between U ion and hydroxyl group in bisphenol A and hydrolyzed tannic acid [16]. These results were compared with those using the previously described commercial resins. As a result, it was found that the commercial resins (WA10, WA20, WA30, WK10, WK40L, BT-AG, and CR-10) as well as the synthesized adsorbents have much higher adsorption ability for U ion in seawater (see Fig. 3). Ohta, A. has reported that the ionic strength (I) of seawater is 0.7 [31]. Therefore, we predicted some chemical forms of U ions in the seawater by using the reliable stability constants between U ion and OH^-, Cl^-, CO_3^{2-}, and $CO_2(g)$ (I =

0.5 at 298 K) [17] in order to examine the possibility of the proposed adsorption mechanisms in sample solutions. The previously reported diagram of U species was updated [16] and this result is shown in Fig. 4. In case of the adsorption behavior of U ion with WA10 resin which is an acrylic polymer with a tertiary amine group, WA20 resin composed of a styrene polymer with a primary and secondary amine group, and WA30 resin (A styrene polymer with a tertiary amine functionality), it was estimated that $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$ is a main chemical form of U ion in our seawater because before and after pH values of seawater were found to be 8.0 and 8.0 - 8.1, respectively. In brief, the anion exchange reaction between the U species and the amine group proceeded in the seawater. This reaction mechanism may also be similar to that of BT-AG anion exchange resin. On the other hand, after the adsorption experiments of U ion using WK10 resin (Methacrylic-type) having carboxylic acid functionality and WK40L resin whose functionality is carboxylic acid on acrylic polymer, the pH value decreased at pH = 2.4 and 3.4, respectively. The main chemical form of U ion was found to be UO_2^{2+} in the pH ranges. Hence, the cation exchange reaction between the U species and the carboxylic group occurred in the seawater as well as the reaction mechanism of CR-10 resin (Styrene-type) with two carboxylic groups.

Additionally, we have examined the adsorption behavior of Li and U ions on BC15 and BC18 adsorbents in order to understand the adsorption mechanisms between metal ions (Li and U ions) and the adsorbents (BC15 and BC18) in various seawater under the following conditions: CF = 1 / 10, 1 / 5, 1 / 3, 1 / 2, 1, and 1.5, initial pH = 1.2 - 9.7, Temp. = room temperature. Fig. 5 shows plots of K_d values of Li ion with BC15 and BC18 adsorbents in the acidic pH range in seawater at room temperature. It was found that the K_d values of Li ion increase slightly with an increase in the pH of seawater up to pH = 3.1 for BC15 system and pH = 1.8 for BC18 system while the K_d values of U ion between pH = 3.3 - 5.2 increase sharply with increasing pH of seawater. The desorption reactions of Li ion on BC15 and BC18 adsorbents are available by the decrease of pH values of seawater using HCl. The behavior of Li adsorption in seawater was found to be similar to that of our previous work [7]. It has been known that Li ion exists as an aqua complex such as $[Li(H_2O)_n]^+$ (n = 3 - 4) in a wide pH range [13]. Concretely, this phenomenon suggests that the cation-exchange reaction proceeds in seawater by the following chemical reaction.

$$BC15(BC18)\cdot H^+ + Li^+ \rightleftharpoons BC15(BC18)\cdot Li^+ + H^+$$
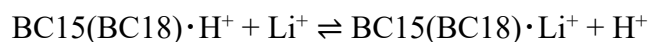
Apropos, it can be estimated that BC15 and BC18 adsorbents have much higher adsorption ability for $(UO_2)_{11}(CO_3)_6(OH)_{12}{}^{2-}$. In this condition, the chemical forms were not the cationic species such as $UO_2{}^{2+}$ and $(UO_2)_2(OH)_2{}^{2+}$ (see Fig. 4). Recently, Choi et al. and Zhang et al. have reported the adsorption mechanisms between U ion and the functional adsorbents modified with amidoxime and carboxyl groups [32, 33]. According to their reports, the suggested adsorption mechanism is the complexation reaction between U ion and the carbonyl group of adsorbents or the associated (-OH) and dissociated hydroxyl group (-O-) of adsorbents. However, the chemical surroundings of U ion are excluded in their suggesting mechanisms. In addition, the estimated chemical form is $(UO_2)_{11}(CO_3)_6(OH)_{12}{}^{2-}$ in seawater in the pH range. Hence, we predicted that the estimated reasonable mechanism is the electrostatic interaction between $(UO_2)_{11}(CO_3)_6(OH)_{12}{}^{2-}$ and the single chemical bond between the oxygen and carbon atom with higher positive charge caused by the electronegativity in hydroxyl groups in bisphenol A. Similarly, the desorption reactions of U ion on BC15 and BC18 adsorbents proceed easily using HCl. The equilibrium reaction can be expressed as follows.

$$BC15(BC18) + (UO_2)_{11}(CO_3)_6(OH)_{12}{}^{2-} \rightleftharpoons BC15(BC18) \cdot (UO_2)_{11}(CO_3)_6(OH)_{12}{}^{2-}$$
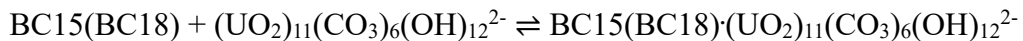
By reference to these results, the adsorption behavior of Li and U ions in diluted and concentrated seawater was also examined at room temperature. The concentration of Li and U ions in the diluted and concentrated seawater was adjusted to the constant one by addition of Li and U salts in this paper whereas the concentration control of Li ion was not performed in our previous work [7]. It is revealed that the K_d values of Li ion decrease gradually with increasing CF of seawater in order of 0.10, 0.20, 0.33, 0.50, 1.0, and 1.5, as seen from Fig. 6. This phenomenon implies the Li adsorption selectivity is clearly influenced by other elements which can prevent the adsorption of Li ion in seawater. However, the adsorption tendency of U ion was very different from that of Li ion. We confirmed that BC15 and BC18 adsorbents have enormously higher adsorption ability for U ion even in case of CF = 1.5.

3.2. Thermodynamics of Li and U ions on BC15 and BC18 adsorbents in seawater

As mentioned in a previous paper, the equilibrium constant, K variable must be dimensionless [34]. The recalculation of K as dimensionless by multiplying the K by 55.5 (number of moles per liter of H₂O solution) is available [35]. As a result, the *Gibbs* equation can take the following form; $\Delta G = - R \cdot T \cdot \ln (55.5 \cdot K)$ [36]. In addition, if the K has the unit of L / g, the conversion of the unit can be done by multiplying the K with

1   1000 in case of 1 g / mL H_2O. However, if the K is originally dimensionless, the K_d can

2   be directly used instead of K [37, 38].

3   Based on this theory, we have checked the chemical surroundings of BC15 and

4   BC18 adsorbents and Li and U ions in seawater to evaluate experimentally the validity of

5   aforesaid adsorption mechanisms. We calculated the apparent thermodynamic parameters

6   (ΔH, ΔS, and ΔG values) for the adsorption of Li and U ions on BC15 and BC18

7   adsorbents from the linear plots of ln K against (1 / T) using the following equation (2)

8   which is frequently used in many papers [7, 8, 28, 34, 37] under the following condition

9   of Temp. = 278-333 K and initial pH = 8.0 (see Fig. 7).

10

11   ln K_d = - ΔG / $R \cdot T$ = - ΔH / $R \cdot T$ + ΔS / R (2)

12   (K_d is converted into K)

13

14   where R and T represent gas constant and absolute temperature.

15   As mentioned in our previous works, we observed one straight line in case of Li /

16   BC15 system, suggesting that the surface of MST-8C silica beads is evenly covered by

17   crown ether-type organic composite adsorbents [7]. Additionally, it was found that the K_d

18   values of Li ion for composite adsorbents using MST-2 type silica beads are smaller than

19   those using MST-8C type silica beads. The difference of previous and present works for

20   Li / BC15 and Li / BC18 systems is kinds of high-porous silica beads, that is, MST-8C

21   and MST-2 type silica beads have the different pore size. This tendency come from the

22   different coverage of crown ether-type organic composite adsorbents against MST-8C

23   and MST-2 type silica beads. In brief, we estimated that the surface of silica beads was

24   partially exposed in case of MST-2 type silica beads system. The plots of ln K $vs.$ (1 / T)

25   should be a straight line if our assumption that one reaction proceeds is reasonable.

26   However, we observed two bent straight lines only in Li / BC15 and Li / BC18 systems

27   but did not observed U / BC15 and U / BC18 systems as shown in Fig. 7. This

28   phenomenon represents that two kinds of adsorption mechanisms between Li ion and

29   BC15 and BC18 adsorbents exist in the aqueous solution ranging in temperature from

30   278 - 298 K and 308 - 333 K for Li / BC15 system and Li / BC18 system. The final pH

31   values in the seawater was 4.7 - 5.2. The hydroxyl group on SiO_2 beads in seawater is

32   charged with negative electricity since the pH range of its isoelectric point is from 1.0 to

33   2.0 [39]. Basically, the dissociated hydroxyl group on the SiO_2 beads has somewhat

34   adsorption ability for Li ion in seawater. Moreover, another cation exchange mechanism

35   can proceed through the reaction between Li ion and the protonated ether oxygen in BC15

36   and BC18 adsorbents. For U / BC15 and U / BC18 systems, the electrostatic interaction

between U ion and the single chemical bond between the oxygen and more positively charged carbon atom combined with hydroxyl group in bisphenol A is reasonable, judging from the linearity of the plots.

The values of ΔH, ΔS, and ΔG values were summarized in Table 1. The values from Li / BC15 system are different from our previous ones because of the difference of pH value after equilibrium, initial concentration of Li ion, and kinds of silica beads [7]. The negative ΔG values indicate the spontaneous processes between BC15 and BC18 adsorbents and Li and U ions in the seawater.

The positive and negative ΔH values show the endothermic and exothermic processes of Li ion using BC15 and BC18 adsorbents in the temperature range from 278 to 333 K. The exothermic reactions are corresponding to 278 - 298 K for Li / BC15 and Li / BC18 systems. In contrast to these results, the endothermic reactions were also confirmed in Li / BC15 and Li / BC18 systems and their temperature ranges were from 308 to 333 K. In addition, the adsorption processes of U ion using these adsorbents were found to be slightly exothermic in seawater with 278 - 333 K. It can be considered that Li ion is surrounded by plenty of water in seawater. On the other hand, the ether oxygen atom in crown ether ring in BC15 and BC18 adsorbents and a large polynuclear complex such as $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$ which may have a lower solubility, can be seen as a higher hydrophobic functionality, compared with that of hydroxyl group in bisphenol A. Before the cation exchange reaction between Li ion and the ether oxygen atoms occurs in seawater, the hydration shell of Li ion and the ether oxygen atom in crown ether ring in BC15 and BC18 adsorbents must be broken. This implies that these dehydration processes require somewhat energy. Besides, the comparatively larger energy to stabilize the conformation between Li ion and ether oxygen atoms in crown ether rings has been emitted in the adsorption processes. This emitted energy must be larger than that to be used for the destruction of hydration shell of Li ion and the ether oxygen atom in crown ether ring in BC15 and BC18 adsorbents because of a less number of hydrated water of the ether oxygen atom in crown ether ring. The obtained ΔH values must be negative in these mechanisms. The SiO_2 beads partially covered with bisphenol A, has comparatively higher hydrophilicity. Therefore, the comparatively larger energy to break the hydration shell among them will be needed, compared with that emitted to stabilize the adsorption conformation between the dissociated hydroxyl group with SiO_2 beads and Li ion in seawater. The estimated logic is based on the weak chemical bond between the dissociated hydroxyl group in SiO_2 beads and Li ion in seawater. As a result, it was found that the obtained ΔH values must be slightly positive. The slight negative ΔH values indicate that the energy emitted by the stabilization of a large polynuclear complex like

14

1    $(UO_2)_{11}(CO_3)_6(OH)_{12}{}^{2-}$ is larger than that to be used for the destruction of hydration shell

2   of hydroxyl group in bisphenol A and U ion in seawater.

3   The positive ΔS values indicate that the randomness produces because of the

4   destruction behavior of hydration shell of U ion and the corresponding functional group

5   far superior to the adsorption behavior of U ion on the surface of the two kinds of

6   adsorbents. On the other hand, we can confirm that the adsorption reactions between Li

7   ion and the oxygen atom in crown ether rings in BC15 or BC18 adsorbents have negative

8   ΔS values because of catching free Li ion in seawater. The dehydration processes between

9   Li ion and SiO_2 beads is dominant in the higher temperature range. Accordingly, it was

10   found that the cation exchange reaction between Li ion and the ether oxygen atom in

11   crown ether ring in BC15 and BC18 adsorbents proceeds predominantly in case of

12   comparatively lower temperature range.

13

14   **3.3. Chromatography of Li and U ions on BC15 and BC18 adsorbents in seawater**

15   The Li and U chromatographic concentration curves were given in Fig. 8. The

16   saturated concentrations of Li and U ions were compatible with the initial ones. Each

17   concentration of Li and U ions was gradually saturated and their effluent volumes of

18   saturated points were 43 and 65 mL for Li / BC15 and BC18 systems and 33 and 28 mL

19   for U / BC15 and BC18 systems, respectively. The dead volumes were also shown in the

20   figure and their volumes were individually 14 mL for Li / BC15 and BC18 systems and

21   3 mL for U / BC15 and BC18 systems. When the effluent volume reached 9 mL, a steep

22   decrease in concentration of U ion using BC15 and BC18 adsorbents was observed. We

23   can realize that the concentration of U ion increase with an increase of pH values in

24   respective effluent volume. The chemical forms of U ion appear in our structural

25   estimation of U ion (see Fig. 4) as completely mutable in the pH range. This phenomenon

26   is caused by many complexation reactions between various types of U ions and BC15 and

27   BC18 adsorbents. On the other hand, the chemical structure of Li ion is very stable in the

28   wide pH range and the stability constants between Li ion and other elements from

29   seawater are very low.

30   Based on the relationship between these concentration curves and the initial

31   concentrations of feed solutions of Li and U ions, the maximum adsorption capacities of

32   Li and U ions for BC15 and BC18 adsorbents were calculated. These data were

33   summarized in Table 2 and compared with those reported previously. The calculated

34   maximum adsorption capacities for Li were 1.4×10^{-3} mol / g - BC15, - BC18 and the

35   capacities obtained for the experimental results were found to be 9.3×10^{-4} mol / g - BC15

36   and 1.8×10^{-3} mol / g - BC18. The calculation of maximum adsorption capacities was

carried out by dividing the moles of benzo-15-crown 5-ether and benzo-18-crown 6-ether on BC15 and BC18 adsorbents by the weight of the BC15 and BC18 resins on BC15 and BC18 adsorbents. This calculation is also based on the assumption that the 1 : 1 cation-exchange reaction is proceeded. It seems that the capacity from U / BC18 system is overestimated. However, this result is reasonable because the crown ether ring of BC18 adsorbent has larger cavity size than the Stokes radius of Li (2.4 Å) (see Fig. 1). This implies that the crown ether in BC18 adsorbent can take in more than one Li ion. On the other hand, the maximum adsorption capacities of U ion using BC15 and BC18 adsorbents were obtained as 4.8×10^{-5} mol / g - BC15 (Experiment), 3.8×10^{-2} mol / g - BC15 (Calculation), 1.8×10^{-5} mol / g - BC18 (Experiment), and 3.6×10^{-2} mol / g - BC18 (Calculation), respectively. These results mean that the part of adsorption points of BC15 and BC18 adsorbents is occupied by other elements from seawater. These calculated adsorption capacities were prepared by dividing twice moles of bisphenol A on BC15 and BC18 adsorbents by the weight of the BC15 and BC18 resins on BC15 and BC18 adsorbents, based on the assumption that the 1 : 2 reaction is proceeded. As shown in Table 2, BC15 and BC18 adsorbents have higher adsorption capacities for Li ion than that of λ-MnO$_2$ provided from K. Yoshizuka's work by 12 and 23 times, respectively [5]. As opposed to the above comparative result, it was found that BC15 and BC18 adsorbents have about one-third the capacity of Li ion of the adsorbent developed by Chitrakar et al. [41]. In addition, the maximum U adsorption capacities using BC15 and BC18 adsorbents were compared with those reported previously. As a result, it was found that BC15 adsorbent has third highest adsorption capacity among them. After these chromatography experiments, the BC15 and BC18 adsorbents attached with Li and U ions were collected. The collected adsorbents were washed using ultrapure water three times and were dried for a day in a vacuum dry oven at 60ºC. Then, we tried to find the chemical bonds between metal ions (Li and U ions) and adsorbents (BC15 and BC18) using a FT-IR analyzer. As a result, we found that the C-O-C stretching vibrations (1140 - 1070 cm^{-1}) in the crown ether rings and C-C-OH stretching vibrations (ca. 1050 cm^{-1}) in the bisphenol A structure overlapped widely the Si-O-Si stretching vibrations (1080 - 1050 cm^{-1}) derived from silica with the ring structure (data not shown). The particle shapes of BC15 and BC18 adsorbents did not change entirely after experiments (see Fig. 9).

Judging from the degree of the obtained adsorption capacities, our data will be positive for industrial application to recover Li and U ions simultaneously from seawater.

4. Conclusion

1   Specific crown ether-type adsorbents embedded in high-porous silica beads, that is,
2   seven kinds of crown ether-type adsorbents have been prepared using a previously
3   reported synthetic method and the adsorption behavior of Li and U ions on these
4   adsorbents has been studied in seawater at room temperature. As a result, it was found
5   that BC15 and BC18 adsorbents have much higher adsorption abilities to recover
6   simultaneously Li and U ions from seawater. Therefore, the adsorption mechanisms of Li
7   and U ions for BC15 and BC18 adsorbents have been examined in the wide pH range and
8   in seawater of different CF. Due to the slight dependence of H^+ for Li adsorption reactions,
9   we have suggested that the cation-exchange reactions between aqua Li ion and ether
10   oxygens of crown ether rings of BC15 and BC18 adsorbents proceed in seawater. It can
11   also be seen that the estimated reasonable mechanism is the adsorption path through the
12   electrostatic interaction between $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$ and the single chemical bond
13   between the oxygen and carbon atom with higher positive charge caused by the
14   electronegativity in hydroxyl groups in BC15 and BC18 adsorbents. Besides, it was
15   revealed that the K_d values of Li ion decrease gradually with increasing CF of seawater
16   in order of 0.10 - 1.5. This phenomenon implies the Li adsorption selectivity is clearly
17   influenced by other elements which can prevent the adsorption of Li ion in seawater. On
18   the other hand, we confirmed that BC15 and BC18 adsorbents have enormously higher
19   adsorption ability for U ion even in case of CF = 1.5.

20   In addition, the chemical surroundings of BC15 and BC18 adsorbents and Li and
21   U ions in seawater have been examined in further detail, namely, the apparent
22   thermodynamic parameters (ΔH, ΔS, and ΔG values) for the adsorption of Li and U ions
23   on BC15 and BC18 adsorbents, ranging in the wide temperature, were calculated using
24   the widely accepted equation. The negative ΔG values indicated that the spontaneous
25   processes between BC15 and BC18 adsorbents and Li and U ions occur in seawater. The
26   negative and positive ΔH values showed the exothermic and endothermic processes of Li
27   ion for BC15 and BC18 adsorbents in the temperature range from 278 to 333 K. In
28   addition, the processes of U ion using these adsorbents were found to be exothermic in
29   seawater with 278 - 333 K.

30   Furthermore, the chromatography experiments to calculate the maximum
31   adsorption capacities of Li and U ions on BC15 and BC18 adsorbents were carried out in
32   seawater at 298 K. BC15 and BC18 adsorbents have larger adsorption capacities for Li
33   ion than that of λ-MnO_2 provided from the leading work by 12 and 23 times, respectively.
34   In addition, the maximum U adsorption capacities for BC15 and BC18 adsorbents were
35   compared with those reported previously. We found that BC15 and BC18 adsorbents have
36   third and fourth largest adsorption capacities among them.

In conclusion, the degree of the obtained adsorption capacities indicates that our data will be positive for industrial application to recover simultaneously Li and U ions from seawater.

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