SELECTIVE RECOVERY OF LITHIUM FROM SEAWATER USING A NOVEL MnO₂ TYPE ADSORBENT II – ENHANCEMENT OF LITHIUM ION SELECTIVITY OF THE ADSORBENT

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ABSTRACT

A novel spinel-type manganese dioxide adsorbent has been developed for the selective recovery of Li^+ from seawater. The adsorbent can be prepared from a lithium-rich component of spinel-type lithium dimanganese tetraoxide $Li_{1.5}Mn_2O_4$, followed by ion exchange of Li^+ by H^+ with diluted hydrochloric acid. The X-ray analysis of the adsorbent suggests the adsorption-elution cycle of Li^+ progresses under γ expansion-shrinking mechanism of the adsorbent. The adsorption of Li^+ progresses via cation exchange, and the selective recovery of Li^+ can be carried out, even when the large amount of Na^+ coexists in seawater. The chromatographic selective recovery of Li^+ from the artificial seawater shows that Li^+ can be selectively adsorbed with remaining most of Na^+ in the feed solution in the break through step, while Li^+ of high purity can recover and concentrate into the elutant in the elution step.

Keywords: Adsorption; Recovery of lithium; Seawater; Manganese dioxide

INTRODUCTION

The demand for lithium has increased in recent decades, due to its application as raw material for large-capacity rechargeable batteries, light

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aircraft alloys, and nuclear fusion fuel. Li is now recovered from the mines and from salt lakes which contains about 14 million tons of Li. Although the amount of Li in those resources is quite insufficient at this point, alternative resources should be found to satisfy the increasing demand in the near future [1,2]. Seawater, which contains 2300 hundred million tons of Li in total, has thus recently become an attractive source of this element and the separation and recovery of Li from seawater by co-precipitation, solvent extraction, and adsorption have been investigated [3-6]. Among these three techniques, the adsorption is most suitable to apply for recovery of metals from the diluted solutions.

In the previous work [7], novel λ-type, manganese dioxide has been developed as the adsorbent for lithium recovery from seawater, and the separation and recovery of Li was carried out. The adsorbent could be prepared from the spinel-type $LiMn_2O_4$ (molar ratio of Li/Mn = 0.5) with the ion exchange between Li^+ and H^+. The batch and chromatographic procedures for the recovery of Li^+ from its aqueous solution containing both Li^+ and Na^+ showed that the effective recovery of Li^+, with majority of Na^+ remaining in the aqueous solution, could be achieved. This adsorption process is based on the ion exchange between Li^+ in the aqueous phase and H^+ in the adsorbent. A more effective adsorbent with higher adsorption ability is thus expected to be developed by increasing the molar ratio of Li/Mn in the adsorbent.

In the present work, the novel λ-type manganese dioxide adsorbent is developed by lithium-rich spinel-type lithium dimanganese tetraoxide $Li_{1.5}Mn_2O_4$ (molar ratio of Li/Mn = 0.75), in order to enhance the adsorption ability and selectivity towards Li^+. The prepared adsorbent was at first characterized with a scanning electron microscope and an X-ray diffractometer. The batch adsorption of Li^+ on the adsorbent was then carried out in the binary Li^+ and Na^+ system. The adsorbent was finally applied for the chromatographic separation of Li^+ from the artificial seawater.

EXPERIMENTAL
Reagent

Mn_3O_4 powder (more than 99.9 %) was obtained from Soekawa Chemicals, chitin was obtained from Tokyo Kasei, and the other reagents were obtained from Kanto Chemicals as analytical-grade reagents. In the case of the batch experiment, aqueous feed solution was prepared by dissolving LiCl and NaCl in deionized water to the concentration 5 $mmol/dm^3$. The pH value was adjusted with NH_4Cl-NH_4OH buffer solution at 8.1. In the case of column operation, the aqueous solution (pH=8.1) containing 40 ppm of both Li^+ and Na^+, or artificial seawater, was used as the feed solution. Artificial seawater was prepared by adding 10 ppm Li^+ into the aqueous solution of Aquamarin[TR] (Yashima Pure Chemicals), which

contains ca. 10000 ppm Na^+ and other components, pH value of which was 8.1.

Preparation of λ-MnO₂ absorbent

Powdered Mn_3O_4 (10.00 g, 0.044 mol) and $LiOH \cdot H_2O$ (4.125 g, 0.098 mol) were mixed (molar ratio of Li/Mn = 0.75) and ground for 15 min. The mixture was sintered at 698 K for 5 h in an electric oven. The sintered mixture was mixed and ground again for 15 min, and then cooled for 1.5 h at room temperature. The mixture obtained was again sintered at 773 K for 5 h with the electric oven. After slow cooling in the electric oven for 12 h, spinel type $Li_{1.5}Mn_2O_4$ powder (Li-type adsorbent) was obtained as an intermediate product. Reaction scheme is as follows:

$$9LiOH + 4Mn_3O_4 + [O_2] \rightleftharpoons 6Li_{1.5}Mn_2O_4 + \frac{9}{2}H_2O \qquad (1)$$
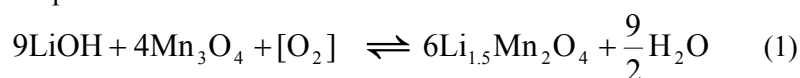
The Li-type adsorbent was treated with 1.0 mol/dm³ HCl solution (overnight, 5-times), for the exchange between Li^+ in the adsorbent and H^+ in HCl solution. The volume of HCl solution was set as that the molar ratio of H^+ in the solution to Li^+ in the adsorbent was more than 40. The composition of the Li-type adsorbent was determined by means of an inductively coupled plasma emission spectrophotometer (ICP-AES, Perkin Elmer OPTIMA4300DV CYCLON), following the powder dissolving in the mixture of 30 wt% H_2O_2 and 1 mol/dm³ HCl. The characteristics of the crystal structure of the H-type and the Li-type adsorbents were recognized using a scanning electron microscope (SEM, Hitachi S-300N) and a powder X-ray diffractometer (XRD, 40 kV and 30 mA, CuK_α, Rigaku XRD-DSC-X II).

In the case of chromatographic separation, the adsorbent with large particles is preferred to prevent the high pressure drop in the column. For chromatographic operation purposes, therefore, Li-type powder adsorbent was additionally granulated with the use of chitin binder. LiCl (2.5 g) was put into the mixed solution of chitin (0.5 g) and *N*-methyl 2-pyrrolidinone (50 dm³), and the obtained solution was stirred for 48 h (chitin binder). The Li-type powder adsorbent (5 g), the chitin binder (5 g), and *N*-methyl 2-pyrrolidinone (20.49 g) were mixed, and then, the mixture was dropped into 2-propanol with a pipet. The granules obtained were then dried in the electric oven at 343 K.

Batch adsorption of lithium

The H-type powder adsorbent (20 mg) and aqueous feed solution (10 dm³) were contacted and shaken vigorously at 303 K for 5 h. The concentration of Li^+ was analyzed by an atomic adsorption spectrophotometer (AAS, Shimadzu AA-6800), and the corresponding adsorption amounts (q_{Li} [mmol/g]) were determined from the material balance, as follows.

$$q_{Li} = \frac{(C_{Li0} - C_{Li}) \cdot L}{w} \qquad (2)$$

where C_{Li0} and C_{Li} are initial and equilibrium concentrations of Li^+ in the aqueous phase [mmol/dm^3], L is volume of aqueous solution [dm^3], and w is weight of adsorbent [g]. The pH of aqueous phase was measured with a pH-meter (Horiba F-23).

Chromatographic separation and concentration of lithium

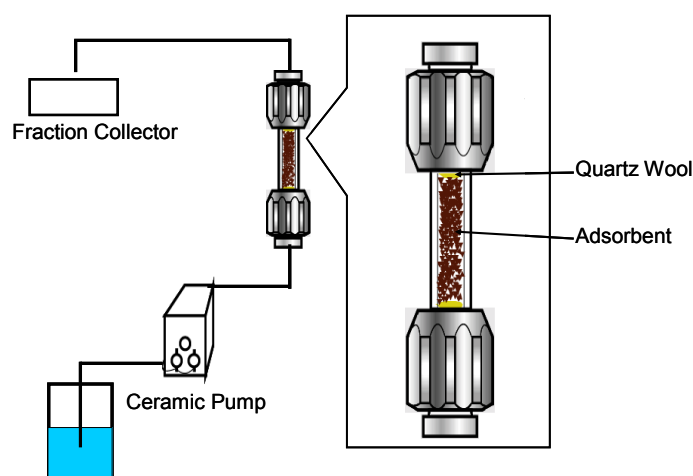The chromatographic operation was carried out in a column apparatus setup, as shown in Fig. 1.

Fig. 1. Schematic flowsheet for the column adsorption apparatus setup.

The granulated Li-type adsorbent was packed into the column tube of 10 cm (volume of the wet adsorbent was 2.6 cm^3) or 20 cm (volume of the wet adsorbent was 8.0 cm^3) together with quartz wool to be sandwiched, and was treated with 1.0 mol/dm^3 HCl solution to obtain the H-type adsorbent. The aqueous feed solution (flow rate: 0.393 cm^3/min for the 10 cm column and 0.325 cm^3/min for the 20 cm column) was then fed upward to the column by a ceramic pump (EYELA VSP3050). The 10 cm column was used in the case of aqueous solution containing both Li^+ and Na^+ of 40 ppm, and the 20 cm column was used for Li^+ separation from artificial seawater. After the break thorough of the metal ions, deionized water was fed into the column to wash out the feed aqueous solution remaining in the column. The metals adsorbed were then eluted with 1.0 mol/dm^3 HCl solution. The effluent was collected with a fraction collector (Advantec CHF122SA), to measure the concentrations of Li and Na by the AAS and ICP, respectively. Bed volume of the effluent solution, BV, was calculated by:

$$BV = v \cdot t / V \tag{3}$$

where v is flow rate of solution [cm^3/min], t is supplying time of feed solution [min], and V is the volume of wet adsorbent [cm^3].

RESULTS AND DISCUSSION
Characterization of the Adsorbent

The crystal structure of the adsorbent was characterized with XRD. Fig. 2 shows the XRD patterns of the present (Li-rich $Li_{1.5}Mn_2O_4$) and previous ($LiMn_2O_4$) powder adsorbent. The XRD patterns indicate that the both adsorbents are of triclinic crystal structure($Li_{1.5}Mn_2O_4$: a = 8.04 Å, b = 7.64 Å, c = 8.38 Å, α = 87.1°, β = 88.7°, γ = 89.1°, and unit cell volume = 514.63 $Å^3$, $LiMn_2O_4$: a = 8.03 Å, b = 8.14 Å, c = 8.24 Å, α = 89.5°, β = 90.5°, γ = 88.4°, and unit cell volume = 538.23 $Å^3$). The molar ratios of Li/Mn of the adsorbent powder, which were determined with ICP-AES, are 0.56 ($LiMn_2O_4$) and 0.86 ($Li_{1.5}Mn_2O_4$), respectively. These results indicate that the b axis of the Li-type adsorbent crystal shrinks with an increase in the amount of Li, and thus the unit cell volume decreases.
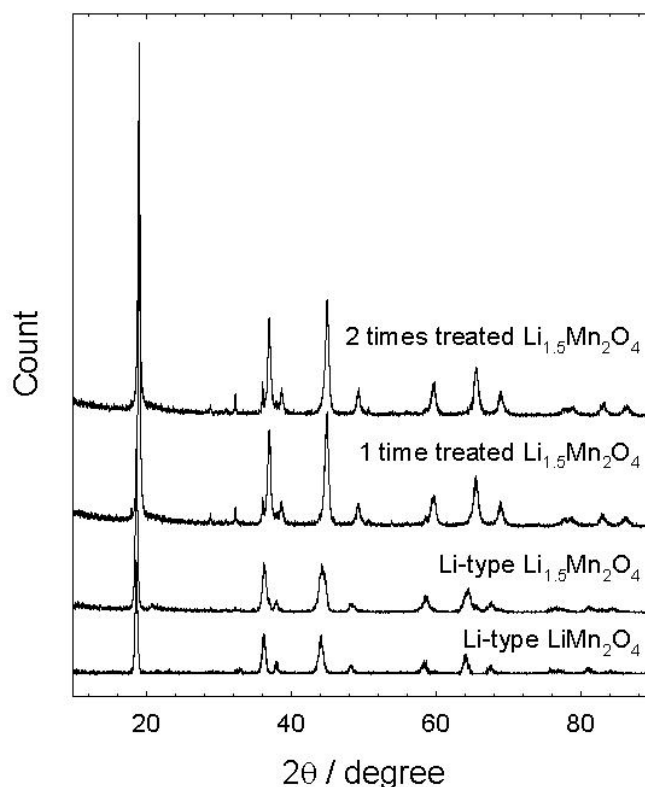

Fig. 2. X-Ray diffraction patterns for the present and previous powder,
before and after HCl treatment with indicated times.

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The effect of acid treatment on the XRD patterns, for the exchange from the Li-type adsorbent to the H-type one is also shown in Fig. 2. All peaks of the adsorbent powder can be seen to shift to wider-angle after single treatment with acid, while changes in the patterns are hardly seen after 2 – 5 times acid treatment (The XRD patterns of the powder corresponding with 3 – 5-times treatment with acid are omitted in Fig. 2). The exchange, between Li^+ on the adsorbent and H^+ in the HCl solution thus occurs with 1 – 2 -times acid treatment. The lattice constants of the H-type adsorbent are $a = 8.15$ Å, $b = 7.62$ Å, $c = 8.06$ Å, $\alpha = 89.4°$, $\beta = 89.5°$, and $\gamma = 92.7°$ in the case of $Li_{1.5}Mn_2O_4$, and $a = 7.99$ Å, $b = 8.04$ Å, $c = 8.03$ Å, $\alpha = 89.9°$, $\beta = 89.7°$, $\gamma = 89.9°$ in the case of $LiMn_2O_4$ [7]. The γ value increases dramatically during treatment with acid in the case of the present adsorbent ($Li_{1.5}Mn_2O_4$) system, while lower expansion of γ is observed in the previous adsorbent ($LiMn_2O_4$) system. These results suggest that the adsorption-elution efficiency of Li^+ is related to shrinkage of b axis and expansion-shrinkage of γ, and thus, the present adsorbent is expected to have larger adsorption ability for Li^+.

The granulation of the adsorbent was also characterized by means of scanning electron microscopy (SEM). The typical SEM images of the granulated adsorbent are shown in Fig. 3. The granulated adsorbent with the surface of high density was prepared as shown in Fig.3(a). The large adsorbent with the particle size of ca. 1-2 mm was obtained as shown in Fig. 3(b).
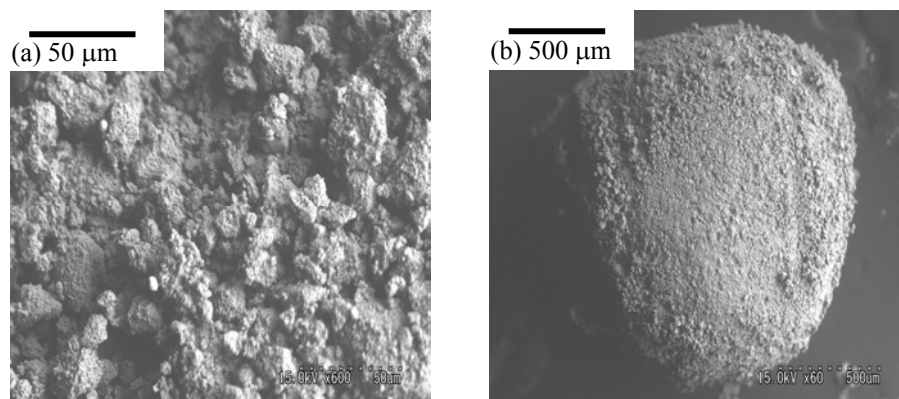

Fig. 3. Scanning electron micrographs for the adsorbent obtained.

Batch Adsorption of Lithium

The batch adsorption of Li^+ was carried out using the H-type adsorbent powder. The effect of equilibrium pH value of the aqueous solution on the adsorption amount of Li^+, q_{Li}, with $Li_{1.5}Mn_2O_4$ is shown in

Fig. 4, together with the data concerning $LiMn_2O_4$. The q_{Li} increases with increasing pH value. This indicated that the adsorption processes via cation exchange between H^+ in the adsorbent and Li^+ in the aqueous solution and therefore the high adsorption can be achieved at high pH region. In addition, the present adsorbent has higher adsorption ability than the previous one especially within high pH region, which could be expected from the X-ray analysis of the adsorbent. The effective recovery of Li^+ should be carried out at around pH = 8.1, corresponding with seawater value of pH.
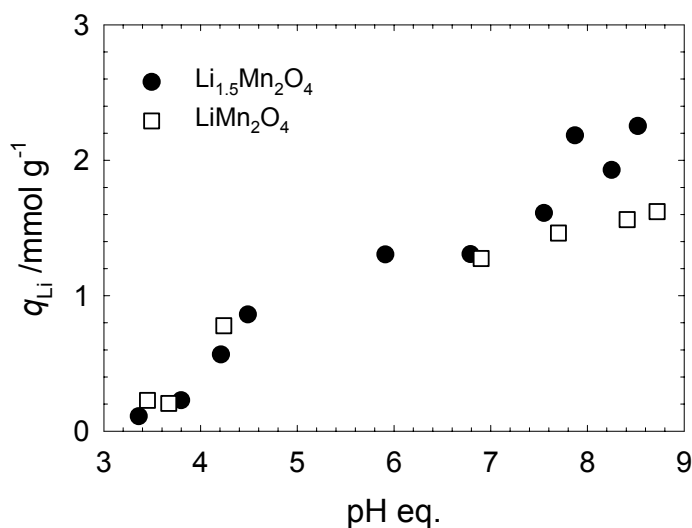

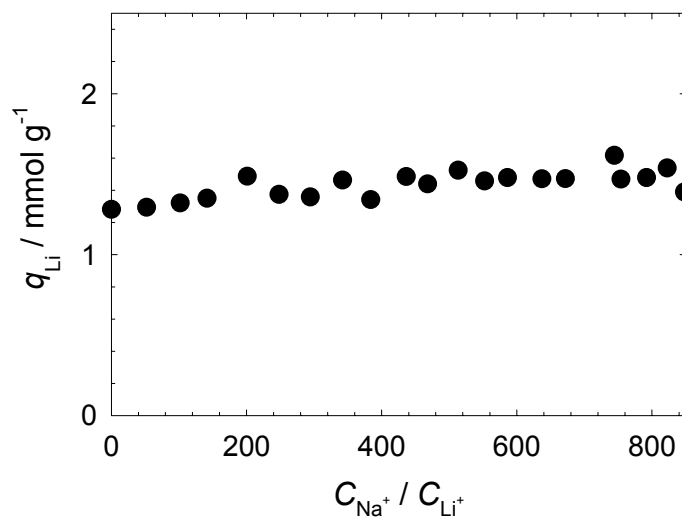Fig. 4. Effect of aqueous pH value on the adsorption amount of lithium, q_{Li}.

Fig. 5. Effect of Na^+ in the aqueous solution on the adsorption of lithium, q_{Li}.
The initial pH of the aqueous solution is adjusted at 8.1 with the buffer solution.

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Fig. 5 shows the effect of coexisting Na^+ on the q_{Li}. In this case, the concentration of Li^+ in the aqueous feed solution was kept at 5 mmol/dm^3, and the concentration of Na^+ was changed from 0 mmol/dm^3 to 4000 mmol/dm^3. There is no influence of the Na^+ on the adsorption of Li^+, and thus the selective recovery of Li^+ is expected to be achieved from seawater, which contains large amount of Na^+, with the adsorbent prepared.

Chromatographic Separation and Concentration of Lithium

Based on the above study, a chromatographic operation was carried out. Firstly, the buffered aqueous solution (pH=8.1) which contained 40 ppm of both Li^+ and Na^+ was used as the feed solution.
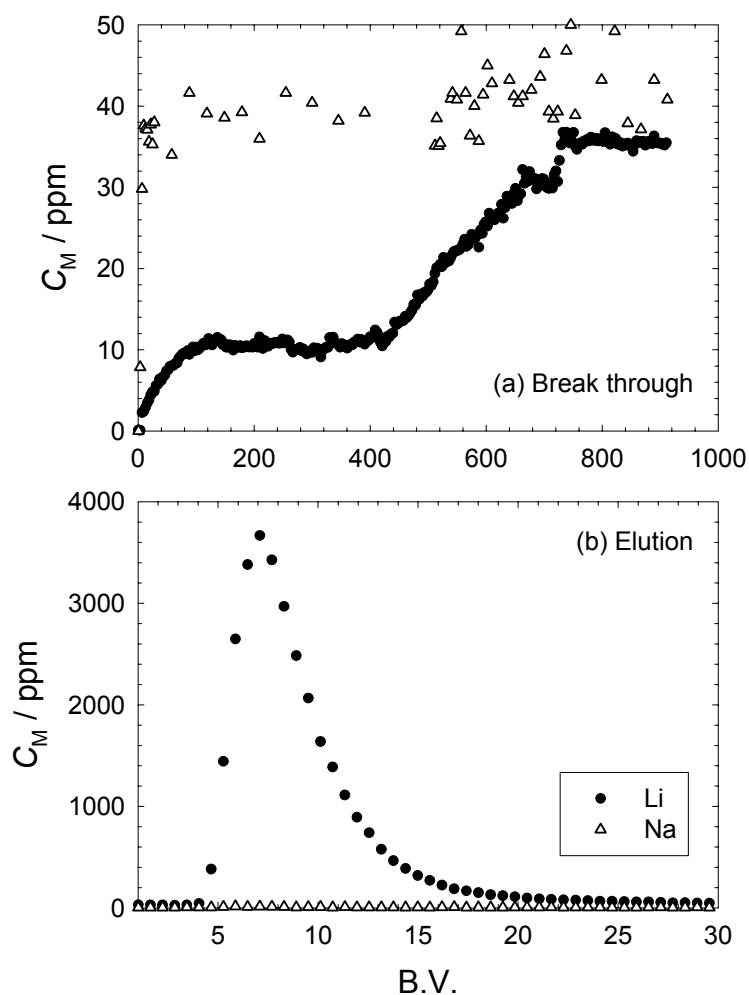

Fig. 6. (a) Break through and (b) elution profiles of Li^+ and Na^+ from the aqueous solution of buffer solution (pH = 8.1) containing $Li^+ = Na^+ = 40$ ppm.

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Fig.6(a) shows the break through profile of Li^+ and Na^+. Break through Li^+ may be adsorbed under a two-step adsorption mechanism since Li^+ is adsorbed by two-step diffusion from the outside (surface) to the inside of the adsorbent. In addition, Na^+ is scarcely adsorbed, and thus, most of Na^+ in aqueous solution was flown out into effluent solution. The elution profile of metal ions from the adsorbent with 1.0 mol/dm^3 is shown in Fig.6(b). The results indicate that Li^+ is easily eluted from the adsorbent, while Na^+ is eluted in negligible amount.

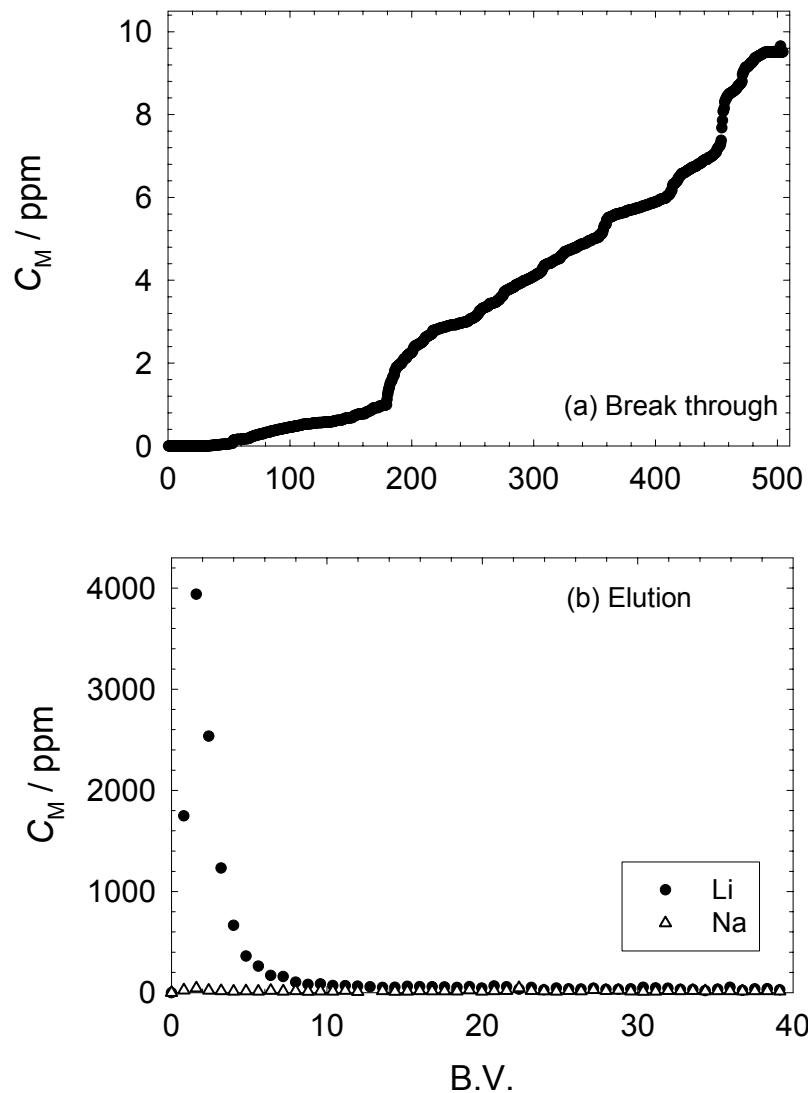Fig. 7. (a) Break through and (b) elution profiles of Li^+ and Na^+ from the artificial seawater containing 10 ppm of Li^+ and 10000 ppm of Na^+.

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The adsorbent was then applied for artificial seawater. The break through and elution profiles are shown in Fig. 7(a) and (b), respectively. The effect of large amount of Na^+ in seawater is scarcely observed, and a similar break through profile in Fig. 6(a) is obtained. In the elution step, Li^+ of high purity is to be recovered at the very early time (B.V.<10), and the concentration in eluted solution achieves ca. 4000 ppm, i.e. the concentration 400 times higher than in seawater.

CONCLUSION

The selective recovery of Li^+ with a novel spinel type manganese dioxide adsorbent was investigated with the following results.

(1)   The spinel-type manganese dioxide adsorbent can be prepared from $Li_{1.5}Mn_2O_4$, after ion exchange between Li^+ and H^+ from diluted hydrochloric acid.

(2)   The adsorbent shows the effective separation and recovery ability for Li^+ from a large amount of Na^+, and the selectivity of Na^+/Li^+ in the aqueous feed solution achieves more than 800 (in molar ratio).

(3)   The selective recovery of Li^+ from artificial seawater can be carried out by chromatographic separation, and 400 times higher concentration of Li^+ can be achieved while most of Na^+ remains in seawater.

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