



## **SELECTIVE RECOVERY OF LITHIUM FROM SEAWATER USING A NOVEL $\text{MnO}_2$ TYPE ADSORBENT**

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### **ABSTRACT**

A novel  $\gamma$ -type manganese dioxide ( $\gamma$ - $\text{MnO}_2$ ) adsorbent has been developed for selectively recovering  $\text{Li}^+$  from seawater. This adsorbent can be prepared from spinel-type lithium di manganese tetra-oxide ( $\text{LiMn}_2\text{O}_4$ ) using ion exchange of  $\text{Li}^+$  by hydrogen ion. In batch adsorption,  $\gamma$ - $\text{MnO}_2$  adsorbent can effectively adsorb  $\text{Li}^+$  at elevated pH (like seawater; pH=8.1) with quite high selectivity for  $\text{Li}^+$  vs.  $\text{Na}^+$  (molar ratio of  $\text{Li}^+/\text{Na}^+$  exceeding 800). In chromatographic separation,  $\text{Li}^+$  can be effectively adsorbed on the adsorbent packed into column, while  $\text{Na}^+$  is only scarcely adsorbed. In elution stage,  $\text{Li}^+$  can be concentrated more than 75 times compared to its initial concentration in the feed solution of adsorption stage, while little  $\text{Na}^+$  was eluted. The molar selectivity coefficient of  $\text{Li}^+/\text{Na}^+$  to 2300 can be achieved.

Keywords: adsorption, recovering lithium, seawater, manganese dioxide

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### **INTRODUCTION**

Since many valuable components are dissolved in seawater such as gold, uranium, lithium etc., the recovery of such components has been noticed from viewpoint of their absolute contents [1]. The concentrations of these elements in seawater are in general quite low, except for potassium, bromine, magnesium and sodium chloride. Since the concentration of lithium in seawater, a target element in this study, is quite high (0.18 ppm in average [1]), the recovering of lithium from seawater may secure resources for production of large-capacity rechargeable batteries, light aircraft alloy,

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nuclear fusion fuel etc. In order to develop an effective process of recovering of lithium by adsorption, it is important to develop adsorbents with high selectivity for  $\text{Li}^+$  vs.  $\text{Na}^+$  ( $> 10000\text{ppm}$ ).

In this study,  $\gamma$ -type manganese dioxide ( $\gamma\text{-MnO}_2$ ) has been studied as a novel type adsorbent for lithium recovering from seawater. This adsorbent can be prepared by elution of lithium from spinel type lithium di-manganese-tetra-oxide ( $\text{LiMn}_2\text{O}_4$ ) with aqueous hydrochloric acid. Fig. 1 shows the schematic diagram of adsorption and elution of lithium in  $\gamma\text{-MnO}_2$  adsorbent. Since  $\gamma\text{-MnO}_2$  consists of both ion-exchangeable pillared-manganese layer and structural  $\text{MnO}_2$  layer,  $\text{H}^+$  can be exchanged by  $\text{Li}^+$  without breaking the crystal structure because pillared-manganese can support  $\text{MnO}_2$  layer[2-4].

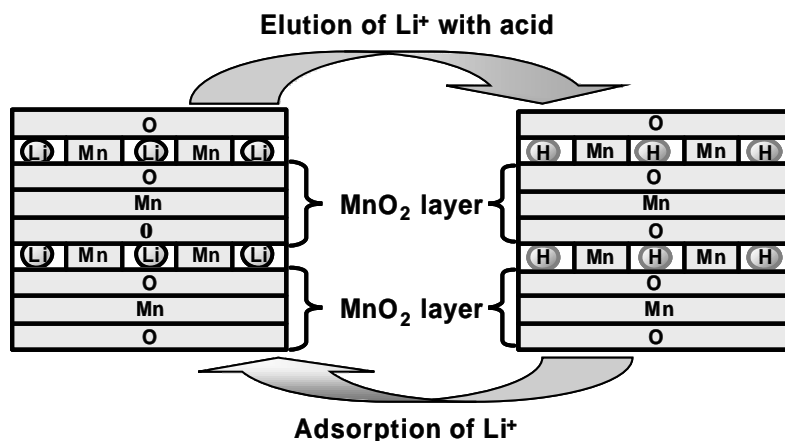


Fig. 1. Schematic diagram of adsorption and elution mechanism of  $\text{Li}^+$  in  $\gamma\text{-MnO}_2$  adsorbent.

We have investigated the adsorption of  $\text{Li}^+$  from the aqueous solution containing high concentration  $\text{Na}^+$  at elevated pH. Moreover, the performance of column separation and concentration of  $\text{Li}^+$  from model seawater was investigated.

## EXPERIMENTAL

### Preparation of $\gamma\text{-MnO}_2$ adsorbent

Powders of  $\text{Mn}_3\text{O}_4$  (5.00 g, 0.022 mol) and  $\text{LiOH}\cdot\text{H}_2\text{O}$  (1.403 g, 0.033 mol) were mixed and ground for 15 min. Here, we set the mixing ratio of powders to molar ratio of  $\text{Mn}/\text{Li} = 2$ . The mixture was sintered at  $425^\circ\text{C}$  for 5 h with an electric oven. After slow cooling at room temperature for 1.5 h, the sintered mixture was mixed and ground again for 15 min. The mixture was also sintered at  $500^\circ\text{C}$  for 5 h with an electric oven. After slow cooling

in an electric oven for 12 h, spinel type  $\text{LiMn}_2\text{O}_4$  was obtained as an intermediate product. Reaction scheme is as follows:



This product was sieved within 300  $\mu\text{m}$  to 150  $\mu\text{m}$  using standard sieve. The product was treated 5 times for overnight with 1.0  $\text{mol}/\text{dm}^3$  HCl solution to obtain  $\gamma$ - $\text{MnO}_2$  adsorbent. To keep the spinel type of crystal structure, we treated the powder of  $\text{LiMn}_2\text{O}_4$  with aqueous HCl solution. Here, we set the volume of HCl solution to keep more than 40 of molar ratio of  $\text{H}^+$  to  $\text{Li}^+$ . We observed the crystal structure of  $\gamma$ - $\text{MnO}_2$  after each acid treatment with X-ray powder diffractometer (Rigaku XRD-DSC-X II). The content of  $\text{Li}^+$  in  $\gamma$ - $\text{MnO}_2$  was calculated by the summation of the concentration of  $\text{Li}^+$  in each HCl solution treated, which concentration was measured by an atomic absorption spectrophotometer (Perkin-Elmer AA100)

#### Batch adsorption of lithium

The adsorbent (20 mg) was shaken with 0.1  $\text{mol}/\text{dm}^3$   $\text{NH}_4\text{Cl}$  - 0.1  $\text{mol}/\text{dm}^3$   $\text{NH}_4\text{OH}$  aqueous buffer solution (10  $\text{cm}^3$ ) of various pH containing different concentrations of  $\text{Li}^+$  and  $\text{Na}^+$ . All batch experiments were carried out at 30  $^\circ\text{C}$  for 2 h.  $\text{Li}^+$  and  $\text{Na}^+$  concentrations before and after equilibria were measured by AAS.

Adsorption amount of metals on adsorbent,  $q_M$  [mmol/g], is calculated by:

$$q_M = (C_{M0} - C_M) \cdot L / w \quad (M = \text{Li}^+, \text{Na}^+) \quad (2)$$

where  $C_{M0}$  and  $C_M$  are initial and equilibrium concentrations of M ions in the aqueous phase [ $\text{mmol}/\text{dm}^3$ ],  $L$  is volume of aqueous solution [ $\text{dm}^3$ ], and  $w$  is weight of adsorbent [g].

#### Chromatographic separation and concentration of lithium

Fig. 2 shows the column apparatus setup in this experiment. The adsorbent (500 mg) was packed into the column tube (10 cm), together with cotton and glass beads (1 mm diameter) to be sandwiched. Wet volume of the adsorbent in the column was 1.2  $\text{cm}^3$ . The aqueous solution was flow upward to the column with micro tube pump (EYELA VSP-3050W). Flow rate of the feed solution was 0.33  $\text{cm}^3/\text{min}$ . In the column adsorption stage, feed solution was 0.1  $\text{mol}/\text{dm}^3$   $\text{NH}_4\text{Cl}$  - 0.1  $\text{mol}/\text{dm}^3$   $\text{NH}_4\text{OH}$  aqueous buffer solution (pH = 8.1) containing both 40 ppm of  $\text{Li}^+$  and  $\text{Na}^+$  ( $[\text{Li}^+] = 5.7$   $\text{mmol}/\text{dm}^3$ , and  $[\text{Na}^+] = 1.7$   $\text{mmol}/\text{dm}^3$ , respectively). In the column elution stage, feed eluting solution was 1.0  $\text{mol}/\text{dm}^3$  HCl solution. After break through of metal ions from the column in the adsorption stage, deionized water was fed owing to wash out the feed solution from the column. Then eluting solution was fed into the column of the adsorbent loaded  $\text{Li}^+$  and  $\text{Na}^+$  in the adsorption stage. The effluent was collected with a fraction collector (EYELA DC-1500), to measure the concentrations of metals by AAS.

Bed volume, B.V., is calculated by:

$$B.V. = v \cdot t / V \quad (3)$$

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

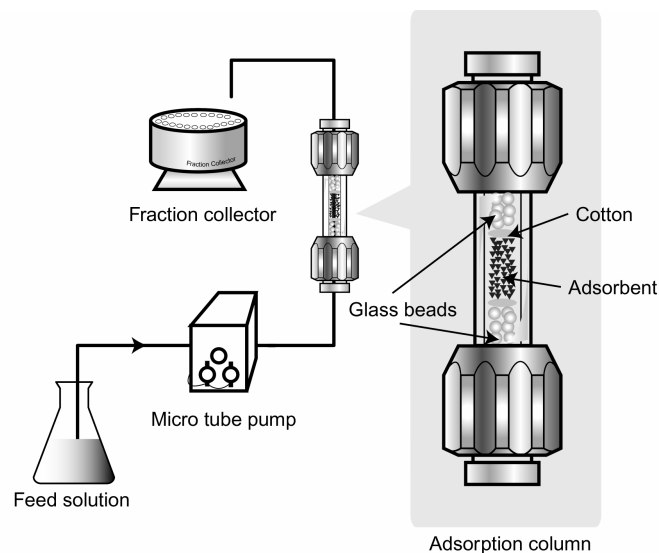


Fig. 2. Column adsorption apparatus.

## RESULTS AND DISCUSSION

### Characteristics of $\gamma\text{-MnO}_2$ adsorbent

Fig. 3 shows XRD patterns of  $\text{LiMn}_2\text{O}_4$  and 5 kinds of the intermediate  $\gamma\text{-MnO}_2$  after each acid treatment with  $1.0 \text{ mol/dm}^3$  HCl solution. The closed circles in the figure indicate the peaks of spinel structure. Since the XRD pattern of each treated  $\gamma\text{-MnO}_2$  is quite good agreement with spinel type  $\text{LiMn}_2\text{O}_4$ , the spinel crystal structure of  $\gamma\text{-MnO}_2$  can be completely kept until 5 times treatment[5, 6]. The lattice constants of  $\gamma\text{-MnO}_2$  are  $a = 7.99 \text{ \AA}$ ,  $b = 8.04 \text{ \AA}$ ,  $c = 8.03 \text{ \AA}$ ,  $\alpha = 89.9^\circ$ ,  $\beta = 89.7^\circ$  and  $\gamma = 89.9^\circ$ , respectively. The crystal structure of  $\gamma\text{-MnO}_2$  is almost cubic system in which b and c axes expand a little.

96.4 % of  $\text{Li}^+$  was eluted from the  $\text{LiMn}_2\text{O}_4$  by 5 times acid treatment, that is, the product of  $\gamma\text{-MnO}_2$  is  $\text{Li}_{0.036}\text{Mn}_2\text{O}_4$ .

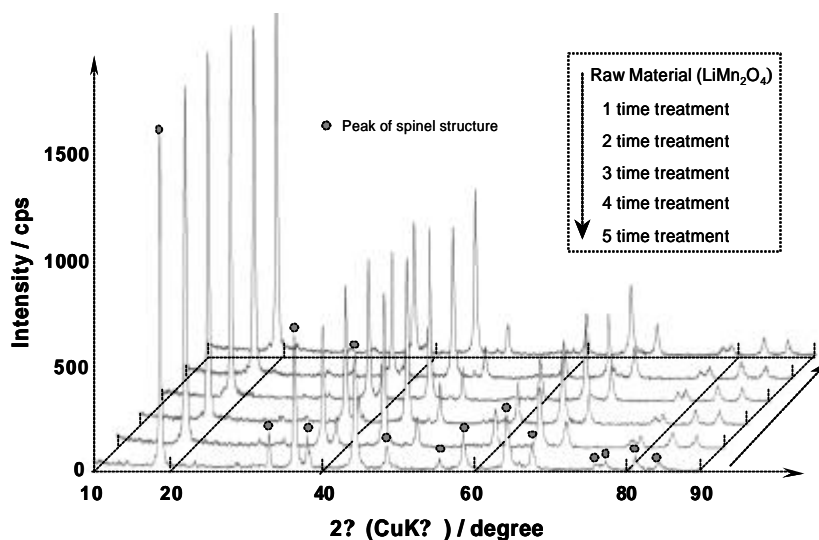


Fig. 3. XRD patterns of  $\text{LiMn}_2\text{O}_4$  and the intermediates  $\gamma\text{-MnO}_2$  during the acid treatment.

### Batch adsorption of lithium

Fig. 4 shows  $q_{\text{Li}}$  vs. acid treatment time of adsorbent. Progressing 4 times acid treatment of adsorbent,  $q_{\text{Li}}$  approaches toward the constant level, 1.5 mmol/g. This level of  $q_{\text{Li}}$  corresponds to commercial ion exchange resins of some alkali metals such as sodium ion.

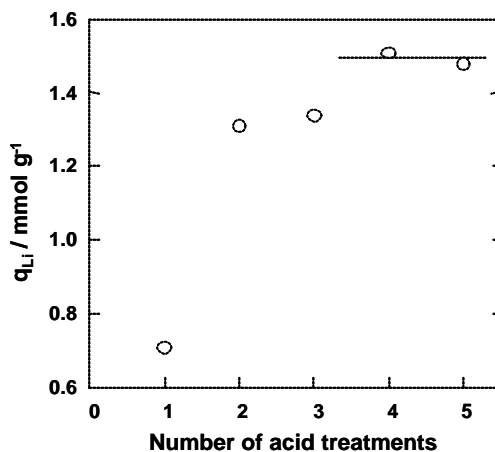


Fig. 4. Adsorption amount of lithium on adsorbent,  $q_{\text{Li}}$ , vs. number of acid treatments of adsorbent; Metal conc.:  $\text{Li}^+$  ( $5 \text{ mmol/dm}^3$ ),  $\text{Na}^+$  ( $5 \text{ mmol/dm}^3$ ).

Fig. 5 shows  $q_{\text{Li}}$  vs. pH of aqueous solution at equilibrium. This adsorbent has high adsorption ability of  $\text{Li}^+$  in high pH region. In particular,

since the pH of seawater is 8.1, this adsorbent can effectively adsorb  $\text{Li}^+$  from seawater.

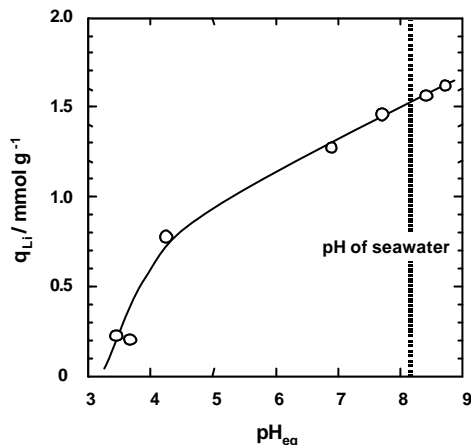


Fig. 5. Adsorption amount of lithium on adsorbent,  $q_{\text{Li}}$ , vs. pH of aqueous solution at equilibrium; Metal conc.:  $\text{Li}^+$  (5 mmol/dm<sup>3</sup>),  $\text{Na}^+$  (5 mmol/dm<sup>3</sup>).

Fig. 6 shows  $q_{\text{Li}}$  vs. molar ratio of  $\text{Na}^+/\text{Li}^+$  in aqueous solution. Here, we cannot set the molar ratio of  $\text{Na}^+/\text{Li}^+$  exceeding 800, because the solubility of sodium chloride in 0.1 mol/dm<sup>3</sup>  $\text{NH}_4\text{Cl}$  - 0.1 mol/dm<sup>3</sup>  $\text{NH}_4\text{OH}$  aqueous buffer solution is limited to 4000 mmol/dm<sup>3</sup>. Since no influence on  $\text{Li}^+$  adsorption was observed until 800 times higher concentration of  $\text{Na}^+$ , it is elucidated that quite high selectivity for  $\text{Li}^+$  vs.  $\text{Na}^+$  (molar ratio of  $\text{Li}^+/\text{Na}^+$  exceeding 800) can be achieved using this  $\gamma\text{-MnO}_2$  adsorbent.

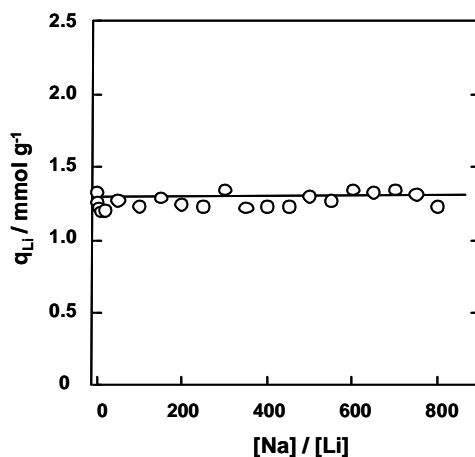


Fig. 6. Adsorption amount of lithium on adsorbent,  $q_{\text{Li}}$ , vs. molar ratio of  $\text{Li}^+/\text{Na}^+$  in feed aqueous solution; Metal conc.:  $\text{Li}^+$  (5 mmol/dm<sup>3</sup>),  $\text{Na}^+$  (5-4000 mmol/dm<sup>3</sup>).

### Chromatographic separation and concentration of lithium

Fig. 7 shows the break through profile of  $\text{Li}^+$  and  $\text{Na}^+$  (metal concentration vs. B.V.). Breakthrough times of  $\text{Li}^+$  and  $\text{Na}^+$  are 4.8 h and 4 min, respectively.  $\text{Li}^+$  can effectively adsorbed on the adsorbent packed into column, while  $\text{Na}^+$  is scarcely adsorbed.

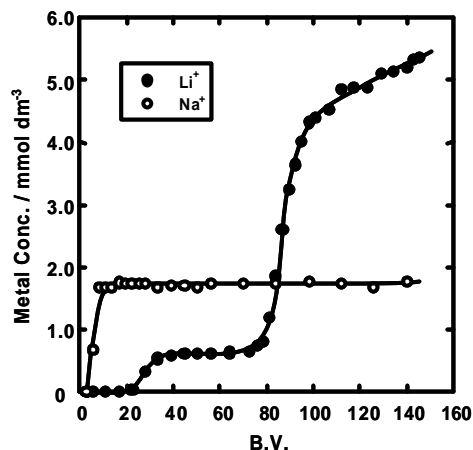


Fig. 7. Break through profile of  $\text{Li}^+$  and  $\text{Na}^+$ .

Fig. 8 shows the elution profile of  $\text{Li}^+$  and  $\text{Na}^+$  from the metal-loaded adsorbent in the column adsorption stage.  $\text{Li}^+$  can be concentrated up to 2980 ppm (429 mmol/dm<sup>3</sup>), while only 4.3 ppm (0.187 mmol/dm<sup>3</sup>) of  $\text{Na}^+$  was eluted. From these results, it can be calculated that the molar selectivity of  $\text{Li}^+$  vs.  $\text{Na}^+$  can be achieved to 2300 times.

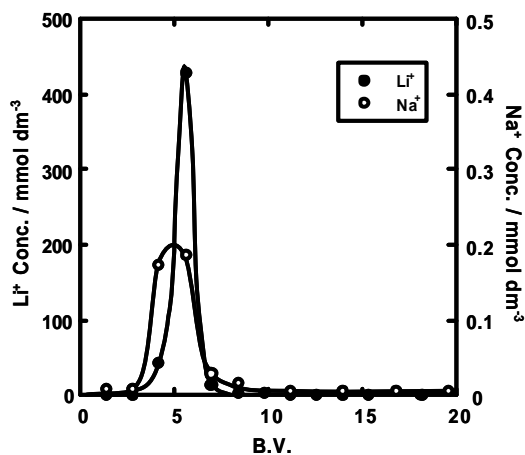


Fig. 8. Elution profile of  $\text{Li}^+$  and  $\text{Na}^+$ .

### CONCLUSION

In order to selective recovery of lithium from seawater, we have studied the adsorption equilibria and chromatographic separation of lithium using a novel  $\gamma$ - $\text{MnO}_2$  adsorbent. The following results can be concluded:

- (1)  $\gamma$ - $\text{MnO}_2$  can be prepared from spinel type  $\text{LiMn}_2\text{O}_4$  using ion exchange of  $\text{Li}^+$  by  $\text{H}^+$ .
- (2) In batchwise adsorption,  $\gamma$ - $\text{MnO}_2$  adsorbent can effectively adsorb  $\text{Li}^+$  at elevated pH with quite high selectivity of  $\text{Li}^+/\text{Na}^+$  over 800 molar ratio.
- (3) In chromatographic separation, the molar selectivity of  $\text{Li}^+/\text{Na}^+$  to 2280 can be achieved.

Therefore, high and efficient separation and concentration of lithium from seawater can be achieved with studied  $\gamma$ - $\text{MnO}_2$  adsorbent.

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### REFERENCES

- [1] E. Kunugita, J. H. Kim, I. Komasaawa, *Kagaku Kogaku Ronbunshu* 1990, 16, 1045-1051.
- [2] K. Ooi, Y. Miyai, S. Katoh, H. Maeda, M. Abe, *Chem. Lett.* 1988, 989-992.
- [3] K. Ooi, Y. Miyai, S. Katoh, H. Maeda, M. Abe, *Langmuir* 1989, 5, 150-157.
- [4] K. Ooi, Y. Miyai, J. Sakakihara, *Langmuir* 1991, 7, 1167-1171.
- [5] W. Tang, H. Kanoh, K. Ooi, *J. Solid State Chem.* 1999, 142, 19-28.
- [6] A. Tanaka, H. Tamura, R. Furuichi, *Electrochem.* 1999, 67, 974-977.