Article

Selective Recovery of Lithium Ion in Saline Water Using A Novel λ -MnO₂ Adsorbent

Kazuharu YOSHIKAZU and Takuya SUZUKI

Department of Chemical Processes and Environments, The University of Kitakyushu, Hibikino 1-1, Kitakyushu 808-0135, Japan

Katsutoshi INOUE

Department of Applied Chemistry, Saga University, Honjo 1, Saga 840-8502, Japan

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Abstract

A novel λ -type manganese dioxide (λ -MnO₂) adsorbent has been developed for selectively recovering Li⁺ from seawater. This adsorbent can be prepared from spinel-type lithium di manganese tetra oxide (LiMn₂O₄) using ion exchange of Li⁺ by hydrogen ion. In batchwise adsorption, λ -MnO₂ adsorbent can effectively adsorb Li⁺ in high pH region like seawater (pH = 8.1) with quite high selectivity more than 800 molar ratio of Li⁺/Na⁺. In chromatographic separation, Li⁺ can effectively adsorbed on the adsorbent packed into column, while Na⁺ is scarcely adsorbed in adsorption stage. In elution stage, Li⁺ can be concentrated more than 50 times compared with initial lithium concentration in feed solution of adsorption stage, while little Na⁺ was eluted. The selectivity of Li⁺/Na⁺ can be achieved to 1500 times in molar base.

1 Introduction

Since there are many components dissolved in the saline water, and the recovery of the components have been noticed from viewpoint of the size of the absolute contents. However, though the element concentrations in saline water are generally very low, it is few available industrial scale recovery except for potassium, bromine, magnesium, sodium chloride. Since the concentration of lithium, a target ion this study, in the saline water is quite high (0.18 ppm in average[1]) compared with uranium, the recovery of lithium from the saline water is promising application for securing of resources of large-capacity battery and material of the light alloy for the aircraft or nuclear fusion fuel etc. In order to develop the effective recovery process of lithium, the adsorbents having selectivity for lithium ion from high-dense coexistence sodium ion (> 10000 ppm) should be necessary.

Fig. 1. Schematic diagram of adsorption and elution mechanism of Li⁺ in λ -MnO₂ adsorbent

In this study, λ -type manganese dioxide (λ - MnO_2) has been studied as a novel type adsorbent for lithium recovering from saline water. This adsorbent can be prepared by elution of lithium from spinel type lithium di-manganese-tetra-oxide (LiMn_2O_4) with aqueous hydrochloric acid. Figure 1 shows the schematic diagram of adsorption and elution of lithium in λ - MnO_2 adsorbent. Since λ - MnO_2 consists of both ion-exchangeable pillared-manganese layer and structural MnO_2 layer, H^+ can be exchanged by Li^+ without breaking the crystal structure because pillared-manganese can support MnO_2 layer.[2-4]

We investigated the adsorption of lithium ion in the solution coexisting high concentration sodium ion. We also investigated the column selective concentration of lithium ion from model saline water.

2 Experimental

2.1 Preparation of λ - MnO_2 adsorbent

Powders of Mn_3O_4 (20.0 g, 0.088 mol) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (5.61 g, 0.132 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°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°C for 5 h with an electric oven. After slow cooling in electric oven for 12 h, spinel type LiMn_2O_4 was obtained as an intermediate product.

The product was treated 5 times for overnight with 1.0 mol/dm^3 HCl solution to obtain λ - MnO_2 adsorbent. To keep the spinel type of crystal structure, we treated the powder of LiMn_2O_4 with aqueous HCl solution. Here, we set the volume of HCl solution to keep more than 40 of molar ration of H^+ to Li^+ . We observed the crystal structure of λ - MnO_2 after each acid treatment with X-ray powder diffractometer. The content of Li^+ in λ - MnO_2 was calculated by the summation of the concentration of Li^+ in each HCl solution treated, which concentration was measured by an atomic absorption spectrophotometer (AAS).

2.2 Batch adsorption of metal ion

The adsorbent (20 mg) was shaken with 0.1 mol/dm^3 NH_4Cl - 0.1 mol/dm^3 NH_4OH aqueous buffer solution (10 cm^3) of various pH containing different concentrations of Li^+ and Na^+ . All batch experiments were carried out at 30°C for 2 h. Li^+ and Na^+ concentrations before and after equilibria were measured by AAS.

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

$$q_M = (C_{M0} - C_M) \cdot L / w \quad (M = \text{Li}^+, \text{Na}^+) \quad (1)$$

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

2.3 Chromatographic separation and concentration of lithium ion

The adsorbent (3.0 g) 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 6.0 cm^3 . The aqueous solution was flow upward to the column with micro tube pump. Flow rate of the feed solution was $0.8 \text{ cm}^3/\text{min}$. In the column adsorption stage, feed solution was 0.1 mol/dm^3 NH_4Cl - 0.1 mol/dm^3 NH_4OH aqueous buffer solution ($\text{pH} = 8.1$) containing both 40 ppm of Li^+ and Na^+ ($[\text{Li}^+] = 5.7 \text{ mmol/dm}^3$, and $[\text{Na}^+] = 1.7 \text{ mmol/dm}^3$, respectively). In the column elution stage, feed eluting solution was 1.0 and 0.1 mol/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 Li^+ and Na^+ in the adsorption stage. The effluent was collected with fraction collector, to measure the concentrations of metals by AAS.

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

$$\text{B.V.} = v \cdot t / V \quad (2)$$

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

3 Results and Discussion

3.1 Characteristics of $\lambda\text{-MnO}_2$ adsorbent

Figure 2 shows XRD patterns of LiMn_2O_4 and 5 kinds of the intermediate $\lambda\text{-MnO}_2$ after each acid treatment with 1.0 mol/dm^3 HCl solution. The closed circles in the figure indicate the peaks of spinel structure. Since the XRD pattern of each treated $\lambda\text{-MnO}_2$ is quite good agreement with spinel type LiMn_2O_4 , the spinel crystal structure of $\lambda\text{-MnO}_2$ can be completely kept until 5 times treatment.[5, 6] The lattice constants of $\lambda\text{-MnO}_2$ are $a = 0.799 \text{ nm}$, $b = 0.804 \text{ nm}$, $c = 0.803 \text{ nm}$, $\alpha = 89.9^\circ$, $\beta = 89.7^\circ$ and $\gamma = 89.9^\circ$, respectively. The crystal structure of $\lambda\text{-MnO}_2$ is almost cubic system in which b and c axes expand a little.

96.4 % of Li^+ was eluted from the LiMn_2O_4 by 5 times acid treatment, that is, the product of $\lambda\text{-MnO}_2$ is $\text{Li}_{0.036}\text{Mn}_2\text{O}_4$.

3.2 Batch adsorption of metal ion

Figure 3 shows q_{Li} vs. pH of aqueous solution at equilibrium. This adsorbent has high adsorption ability of Li^+ in high pH region. In particular, since the pH of seawater is 8.1, this adsorbent can effectively adsorb Li^+ from seawater.

Figure 4 shows q_{Li} vs. molar ratio of Na^+/Li^+ in aqueous solution. Here, we cannot set the molar ratio of Na^+/Li^+ exceeding 800, because the solubility of sodium chloride in $0.1 \text{ mol/dm}^3 \text{ NH}_4\text{Cl}$ - $0.1 \text{ mol/dm}^3 \text{ NH}_4\text{OH}$

Fig.2. XRD patterns of LiMn_2O_4 and the intermediates $\lambda\text{-MnO}_2$ during the acid treatment

Fig.3. Adsorption amount of lithium on adsorbent, q_{Li} , vs. pH of aqueous solution at equilibrium, $c_{\text{Li}0} = 0.029 \text{ mmol/dm}^3$ ($=0.2 \text{ ppm}$)

Fig.4. Adsorption amount of lithium on adsorbent, q_{Li} , vs. molar ratio of Na^+/Li^+ in aqueous solution, $c_{\text{Li}0} = 0.029 \text{ mmol/dm}^3$ ($=0.2 \text{ ppm}$)

aqueous buffer solution is limited to 4.0 mol/dm^3 . Since no influence on Li^+ adsorption was observed until 800 times higher concentration of Na^+ , it is elucidated that quite high selectivity for Li^+ vs. Na^+ (molar ratio of Li^+/Na^+ exceeding 800) can be achieved using this $\lambda\text{-MnO}_2$ adsorbent. This separation coefficient is 1.5 times greater than the same kinds of MnO_2 adsorbents in the previous papers by Ooi *et al.* [2-4]

3.3 Chromatographic separation and concentration of Lithium ion

Figure 5 (a) and (b) shows the break through profile of Li^+ and Na^+ and the elution profile of Li^+ and Na^+ from the metal-loaded adsorbent in the column adsorption stage (metal concentration vs. B.V.), respectively. Breakthrough times of Li^+ and Na^+ are 43 h and 5 min, respectively. Li^+ can effectively adsorb on the adsorbent packed into column, while Na^+ is scarcely adsorbed. Li^+ can be concentrated up to 2680 ppm (386 mmol/dm^3), while only 5.9 ppm (0.257 mmol/dm^3) of Na^+ was eluted, without dissolving manganese in the adsorbent. From these results, it can be calculated that the molar selectivity of Li^+ vs. Na^+ can be achieved to 1500 times. This separation coefficient is the best in the previous published works.

Fig.5. Break through profile (a) and Elution profile (b) of Li^+ , Na^+ and Mn

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