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Preparation and Adsorption Properties of λ-MnO_2-Cellulose Hybrid-Type Ion-Exchanger for Lithium Ion. Application to the Enrichment of Lithium Ion from Seawater

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Abstract

Spherical beads of a hybrid-type ion-exchanger (HIE) have been prepared by dispersing microcrystalline λ-MnO_2 in macroporous cellulose gel beads. The beads were 0.1 to 0.3 mm in diameter and contained 0.71 g λ-MnO_2/g dry HIE. The ion-exchange behaviors of HIE for lithium and sodium ions were investigated by batch and column methods. The uptakes for lithium and sodium ions were 2.8 and 0.1 mmol/g dry HIE, respectively, at pH 12.3 by the batch method and 1.0 and 0.1 mmol/g dry HIE at pH 11.6-11.8, respectively, by the column method. When 1.52 L seawater was passed through a column containing 0.05 g wet HIE at a flow rate of 0.3 mL/min, 2.0 mg lithium/g dry HIE was recovered, indicating that the enrichment ratio for lithium ion was 1.3×10^4 mL/g and the enrichment factors for lithium ion to sodium, potassium, calcium, and magnesium ions were 7.1×10^4, 1.7×10^3, 1.0×10^3, and 6.9×10^3, respectively.

INTRODUCTION

Lithium is an important element for ceramic materials, alloys, and nuclear fusion materials. In recent years, several kinds of synthetic

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inorganic ion-exchanger have been studied for the separation (*1*) and recovery of lithium ion from brine, hydrothermal, and seawater (*2–5*). One of the excellent materials for this purpose is so-called "λ-MnO_2" (*5*, *6*) which is easy to prepare and exhibits extremely high selectivity for the lithium ion due to its ion sieving effect (*5*).

Since most of the inorganic ion-exchanger are amorphous materials or microcrystals, they are not suitable for column operation. During the past several years we have been successful in preparing the hybrid-type ion-exchanger (HIE) by dispersing a microcrystalline inorganic ion-exchanger in spherical hydrophilic organic polymer beads. HIE has high metal ion selectivity due to the dispersed inorganic ion-exchanger, and has high performance properties for column operation due to the spherical bead form. For example, polyacrylamide beads, in which microcrystalline stannic phosphate or titanium phosphate was dispersed, were found to show high ion-selectivity for sodium and lithium ions, as well as to exhibit high column performance properties (*7*).

In this paper the ion-exchange properties of HIE, which was prepared by dispersing microcrystalline λ-MnO_2 in spherical beads of macroporous cellulose gel, are reported. It showed high ion-exchange selectivity for lithium over sodium ion, and has been successfully applied for the enrichment of lithium ions from seawater by column operation.

EXPERIMENTAL

Materials

Preparation of So-Called Crystalline "λ-MnO_2"

Microcrystalline λ-MnO_2 was preapred as described by Hunter (*6*) by heating a 2:1 (molar ratio) mixture of Mn_2O_3 (commercial product, Mitsuwa Chemical, >99.9%, or prepared from manganese nitrate) and Li_2CO_3 (Wako, Analytical grade) at 850°C overnight, followed by treatment of the resulting intermediate $LiMn_2O_4$ with 0.5 *M* nitric acid until the pH was stabilized at 1 and the lithium ion in the supernatant could not be detected by the flame test. The product was washed with water and dried at 80°C. The structure was checked by powder x-ray diffraction analysis with a Rigaku Denki RAD IIIB X-Ray diffractometer (CuK_α radiation with a nickel filter).

Preparation of λ-MnO_2 Hybrid-Type Ion-Exchanger (HIE)

Cellulose triacetate was dissolved in a 95:5 (v/v) mixture of dichloromethane and isooctane by occasional shaking until the solution became clear. The fine powder of λ-MnO_2 was added to this solution and dispersed well in the medium by mechanical stirring and sonication for 20–30 min. The suspension was dropped into a 0.1% polyvinyl alcohol aqueous solution under vigorous stirring at room temperature overnight, then continued stirring at 30°C for 9 h, and finally at 45°C for 1 h to evaporate the dichloromethane. The resulting spherical beads were filtered and washed with water.

The cellulose triacetate beads thus obtained were treated with 0.1 *M* methanolic sodium hydroxide solution to regenerate hydrophilic cellulose gel beads. The gel beads were filtered through a glass filter and washed with water until no sodium ion could be detected by the flame test. HIE was treated with 0.25 *M* nitric acid and washed to pH 6 with water before use.

Uptake Curves and Distribution Coefficients (K_d) by Batch Method

For the measurement of uptake curves, 0.3 g HIE containing about 0.1 g λ-MnO_2 was shaken with 10 mL of 0.1 *M* lithium ion solution (mixture of LiCl and LiOH) or 0.1 *M* sodium ion solution (mixture of NaCl and NaOH) at 25 ± 1°C for 3 days. Then the concentration of lithium (or sodium) ion and the pH were measured on the supernatant.

For the determination of K_d, 0.65 g HIE was shaken with 25 mL of 0.1 *M* alkali metal ion solution.

The K_d values were calculated by the following equation:

$$K_d = \frac{\text{amount of } Li^+ \text{ (or } Na^+\text{) on HIE (mmol/g dry HIE)}}{\text{amount of } Li^+ \text{ (or } Na^+\text{) in solution (mmol/mL)}}$$

Analytical Procedures

The metal ion concentration was measured by atomic absorption spectrophotometry in 0.1 *M* hydrochloric acid solution with a Hitachi 180-30 Atomic Absorption Spectrophotometer.

The concentration of lithium ion in seawater was determined by the

standard addition method, while the rest of the metal ions were determined by the direct method.

The manganese content in HIE was determined by decomposing the sample with a 1:1 mixture of sulfuric acid and hydrogen peroxide, followed by EDTA titration (*8*).

Column Experiments

The sample solution was passed through a microcolumn using a peristaltic pump, and the effluents were collected in 1 mL fractions with a fraction collecter (TOYO SF-160).

RESULTS AND DISCUSSION

Preparation and Some Chemical Behaviors of $LiMn_2O_4$ and So-Called "λ-MnO_2"

Results of powder x-ray diffraction analysis on these two samples indicated that the *d* values and the lattice constants (8.22 Å for $LiMn_2O_4$ and 8.04 Å for λ-MnO_2) were almost identical with those reported by Hunter (*6*) as shown in Table 1.

In order to prepare HIE, the cellulose triacetate beads containing microcrystalline λ-MnO_2 had to be treated in methanolic sodium hydroxide solution to regenerate cellulose gel beads by hydrolysis. Accordingly, some chemical behaviors of $LiMn_2O_4$ and λ-MnO_2 were investigated under the following conditions.

A. $LiMn_2O_4$ was dipped in 2 *M* methanolic sodium hydroxide solution at room temperature for 50 h.
B. λ-MnO_2 was shaken with 0.1 *M* lithium ion solution (LiCl + LiOH, pH 7.2–8.0) at 25°C for 3 days.
C. λ-MnO_2 was shaken with 0.1 *M* lithium ion solution (LiCl + LiOH, pH 11.2–12.5) at 25°C for 3 days.
D. λ-MnO_2 was shaken with 0.1 *M* sodium hydroxide solution (pH 12.3) at 25°C for 3 days.
E. λ-MnO_2 was dipped in methanol at room temperature for 50 h.
F. λ-MnO_2 was dipped in 2 *M* methanolic sodium hydroxide solution at room temperature for 50 h.

TABLE 1
Chemical Stability of λ-MnO_2 and $LiMn_2O_4$ in Alkaline Solution and Methanol

Sample[d]	*d* values of x-ray diffraction							
$LiMn_2O_4$	[a]4.77	2.49	2.39	2.07	1.89	1.59	1.46	1.39
	[b]4.72	2.47	2.39	2.05	1.88	1.58	1.45	1.39
A	4.78	2.49	2.39	2.07	1.89	1.59	1.46	1.39
B	4.72	2.46	2.36	2.04	1.87	1.57	1.44	1.38
C	4.79	2.49	2.38	2.07	1.90	1.59	1.46	1.39
λ-MnO_2	[a]4.65	2.42	2.32	2.01	1.85	1.55	1.42	1.36
	[c]4.66	2.42	2.31	2.01	1.84	1.55	1.42	1.35
D	4.62	2.42	2.32	2.01	1.84	1.55	1.42	1.36
E	4.65	2.43	2.32	2.01	1.84	1.55	1.42	1.36
F	7.14	4.76	3.58	2.67	2.44	—	—	—

[a]Products prepared in this work.
[b]ASTM 18-736.
[c]Values reported by Hunter (*6*).
[d]Sample A, B, C, D, E, and F correspond to the conditions of treatment of manganese compounds described in the text.

The resulting materials were analyzed with a powder x-ray diffractometer as summarized in Table 1. The following conclusions are derived from these results.

(1) The spinel structure of $LiMn_2O_4$ did not change when it was dipped in 2 *M* methanolic sodium hydroxide solution, but that of λ-MnO_2 changed seriously under the same condition, giving a somewhat amorphous material.
(2) λ-MnO_2 was converted to $LiMn_2O_4$ after being shaken with lithium ion solution (pH 7.2–8.0 or 11.2–12.5), but it did not change after being shaken with 0.1 *M* sodium hydroxide solution.
(3) The crystal structure of λ-MnO_2 did not change when it was dipped in methanol.

As to the reaction between λ-MnO_2 and lithium ion, Clearfield and his group proposed an ion-exchange reaction between HMn_2O_4 and lithium ion (*9*):

$$HMn_2O_4 + Li^+ \rightleftharpoons LiMn_2O_4 + H^+$$

whereas Ooi and his group proposed an ion insertion redox reaction (*10*):

$$MnO_2 + xLiOH \rightarrow Li_xMnO_2 + \frac{x}{2}H_2O + \frac{x}{4}O_2 \qquad (0 < x < 0.5)$$

However, it is rather difficult to answer the question as to whether so-called "λ-MnO_2" is HMn_2O_4 or spinel-type manganese oxide, because differentiation by chemical analysis is not easily accomplished and their x-ray diffraction patterns are very similar.

Conditions for the Preparation of HIE

Our purpose was to prepare spherical hydrophilic gel beads in which microcrystalline inorganic ion-exchanger particles are dispersed. In our previous work, crosslinked polyacrylamide gel was chosen as a hydrophilic gel matrix. However, it has a drawback in that the polymer tends to hydrolyze in strongly acidic or alkaline conditions. Therefore, in this work the regenerated cellulose gel, which was obtained by the hydrolysis of cellulose triacetate, was chosen as a hydrophilic gel matrics.

As stated in the experimental section, λ-MnO_2 was dispersed in a solution of cellulose triacetate which was dissolved in a mixture of dichloromethane–isooctane. Isooctane is a poor solvent for cellulose triacetate and behaves as an auxiliary solvent in obtaining macroporous gel beads. The mixture was sonicated to obtain a finely dispersed suspension before it was dropped into water containing 0.1% polyvinyl alcohol as an emulsion stabilizer. Uniform cellulose triacetate beads were obtained as the solvent evaporated. The bead size and the uniformity of the beads were strongly dependent upon the cellulose triacetate concentration, the mixing ratio of λ-MnO_2 to cellulose triacetate, the stirring speed of the suspension, and the rate of solvent evaporation which was controlled by the heating conditions of the suspension.

A typical example of conditions for the preparation of cellulose triacetate beads is as follows. Six grams of λ-MnO_2 was sonicated in 200 mL of a 95:5 (v/v) mixture of dichloromethane and isooctane which contained 4 g cellulose triacetate, and the dispersion was dropped into 1400 mL of a 0.1% polyvinyl alcohol aqueous solution at a stirring speed of 900 rpm. The mixture was processed as described in the experimental section to obtain black beads 0.1–0.3 mm in diameter. The black beads were hydrolyzed by shaking them with 100 mL of 0.1 *M* methanolic

sodium hydroxide solution at room temperature for 30 min, then dipping them in another 100 mL of methanolic sodium hydroxide solution for 50 h to obtain macroporous cellulose gel particles. Yield: 16.7 g (wet). The extent of hydrolysis was followed by observing the infrared absorption spectra of powdered gel particles at 1700–1800 cm^{-1} ($\nu_{C=O}$). Although the rate of hydrolysis was higher with a more concentrated sodium hydroxide solution, the crystal structure of λ-MnO_2 changed considerably, resulting in a lower exchange capacity. Figures 1(a) and (b) are microscopic pictures of microcrystalline λ-MnO_2 and the HIE gel particles, respectively.

Properties of HIE

HIE was stored in a wet condition in a closed container. The water content of wet HIE was determined to be 54.7% by drying a 1 g sample in a vacuum drying oven at 40°C to constant weight.

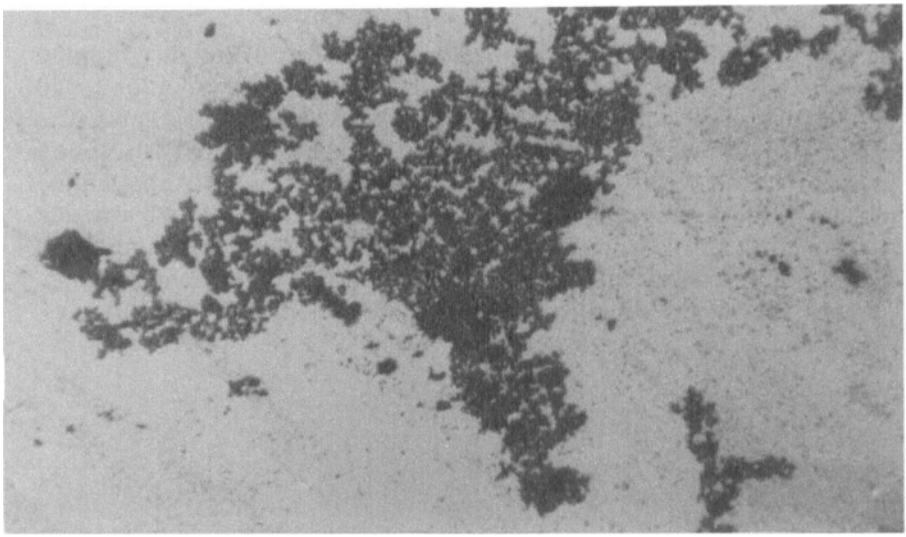
The manganese content of HIE was determined to be 0.32 g MnO_2/g wet HIE, or 0.71 g MnO_2/g dry HIE.

Ion-Exchange Behaviors of HIE

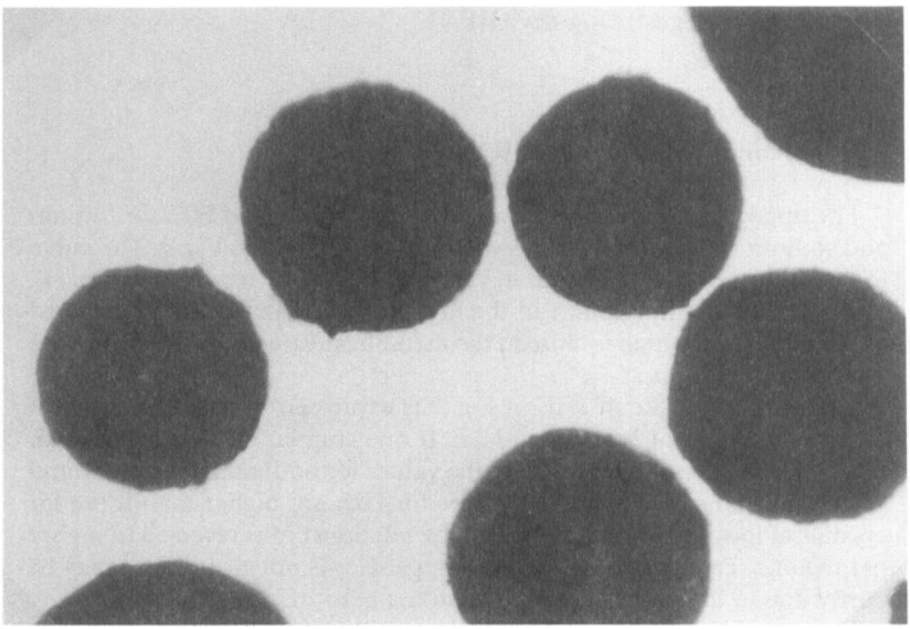
The uptake behaviors of microcrystalline λ-MnO_2 and HIE for lithium and sodium ions at different pH values are illustrated in Fig. 2. The curve for λ-MnO_2 is slightly different in shape from the one reported by Ooi (*4*). However, the lithium uptake in the higher pH region (pH > 11) reached about 5 mmol/g, which is close to the theoretical value estimated from the formula of $LiMn_2O_4$.

The lithium uptake of HIE in Fig. 2 is expressed in terms of mmol of lithium ion per g of λ-MnO_2 in HIE. If one compares these values with those of microcrystalline λ-MnO_2, the values for both materials at around pH 8 are similar. However, the values for HIE are higher than those for crystals at lower pH region, whereas the relationship is reversed in higher pH regions. The reason for these discrepancies is not clear, but it may be partly due to the matrix effect of cellulose gel.

The separation factor of HIE between lithium and sodium ions was determined at around the pH value of seawater (pH 8) by observing the distribution coefficient of HIE for the respective metal ion separately:



(a)



(b)

FIG. 1. Microscopic photograph of λ-MnO_2 (a) and HIE (b) (×150).

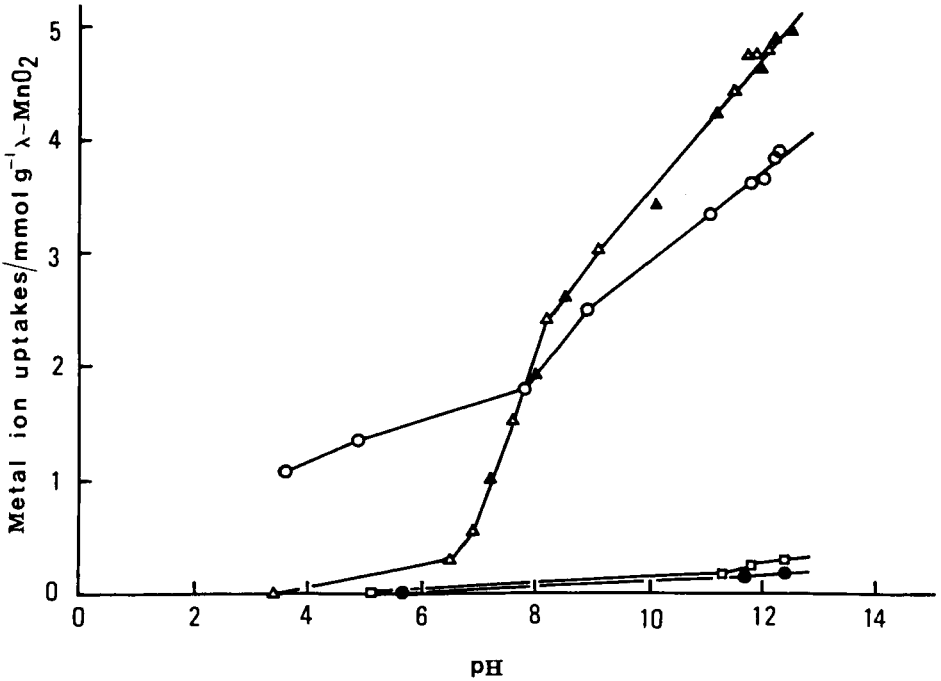


FIG. 2. The pH dependence of metal ion uptakes on λ-MnO_2 and HIE in the batch method. (△): Li^+ on λ-MnO_2 prepared from Mn_2O_3 as the starting material. (▲): Li^+ on λ-MnO_2 prepared from $Mn(NO_3)_2 \cdot 6H_2O$ as the starting material. (○): Li^+ on HIE. (□): Na^+ on λ-MnO_2. (●): Na^+ on HIE.

$$K_d^{Li} = 21.9 \text{ mL/g dry HIE (equilibrated at pH 8.2)}$$

$$K_d^{Na} = 1.1 \text{ mL/g dry HIE (equilibrated at pH 8.6)}$$

$$\text{Separation factor} = K_d^{Li}/K_d^{Na} = 19.9$$

Ion-Exchange Behavior of HIE under Column Operation

A sample solution containing 0.18 *M* lithium ion (LiCl + LiOH, pH 11.8) or a sample solution containing 0.18 *M* sodium ion (NaCl + NaOH, pH 11.6) was passed through the column (90 × 6 mm i.d.) containing 2 g wet HIE at a flow rate of 0.2 mL/min. Then the column was washed with water, and finally the column was eluted with 0.1 *M* nitric acid. The breakthrough curves and elution curves for lithium and sodium ions are

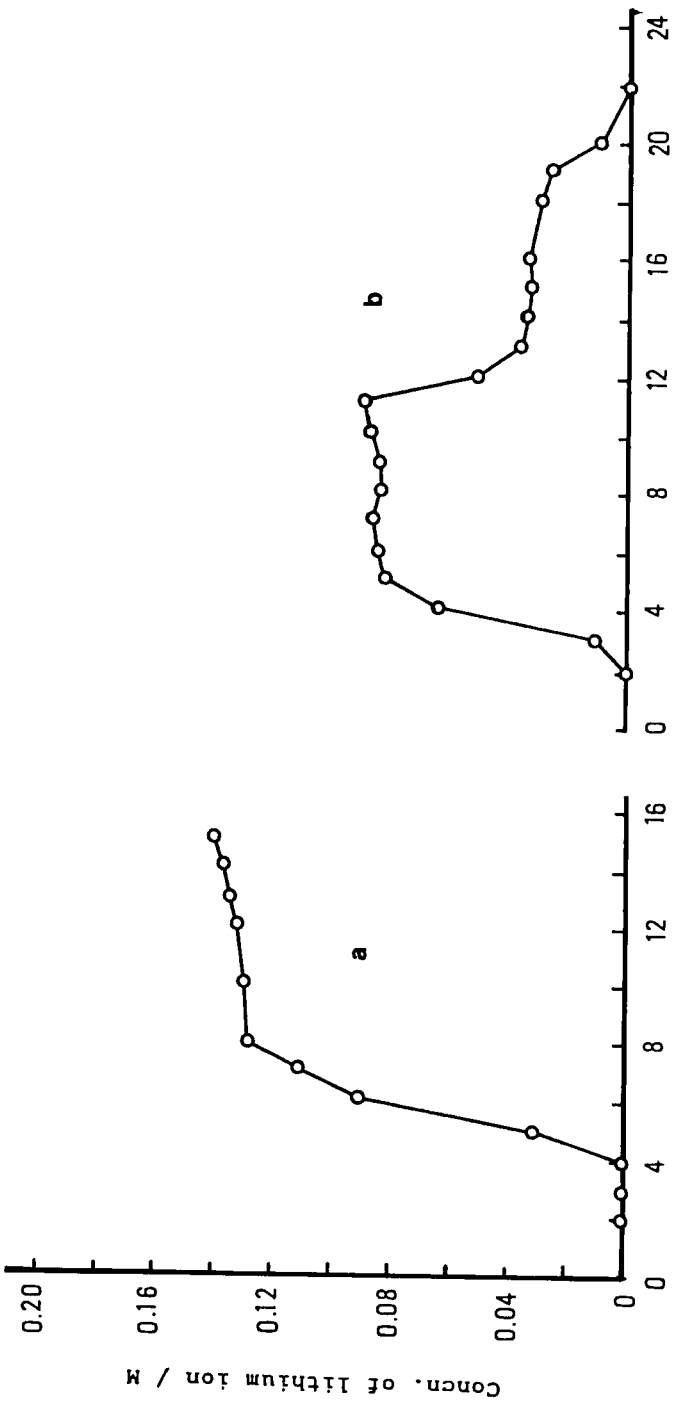


FIG. 3. The breakthrough and elution curves of lithium ion on HIE in column operation. (a) Breakthrough curve. (b) Elution curve. The left-hand scale refers to both curves. Column: 6 mm i.d. HIE: 2.0 g. Flow rate: 0.2 mL/min. Eluent: 0.1 *M* HNO_3.

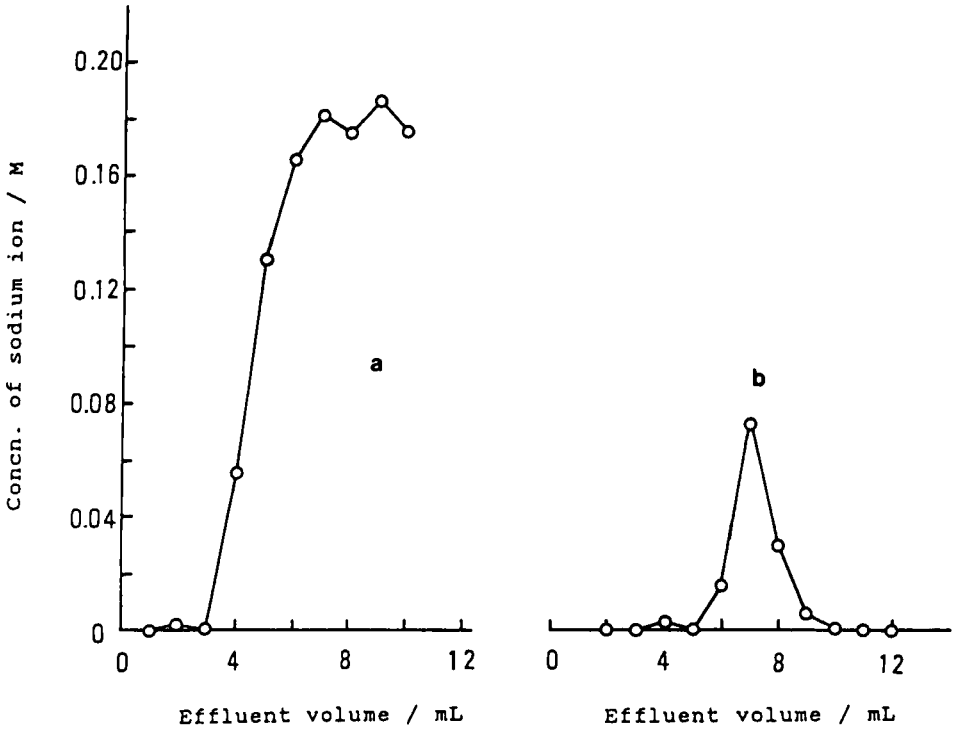


FIG. 4. The breakthrough and elution curves of sodium ion on HIE in column operation. (a) Breakthrough curve. (b) Elution curve. The left-hand scale refers to both curves. Experimental conditions are the same as in Fig. 3.

shown in Figs. 3 and 4, respectively. The uptakes of lithium and sodium ions by HIE were evaluated from the elution curves, giving 1.0 and 0.13 mmol/g dry HIE, respectively.

A similar experiment was carried out by using a mixed solution of lithium (0.088 *M*) and sodium (0.085 *M*) ions at pH 11.9 on a column (70 × 3 mm i.d.) containing 0.5 g wet HIE, followed by washing with water, then by eluting with 0.01 *M* nitric acid. The breakthrough curves and elution curves for lithium and sodium ions are illustrated in Figs. 5 and 6, respectively. It is noticed from Fig. 5 that the breakthrough behavior of HIE is slightly different for lithium and sodium ions. The breakthrough curve for sodium ion rapidly reached the initial concentration after taking four 1-mL fractions, whereas that for lithium ion reached 0.07 *M* after taking four 1-mL fractions, then increased slowly to the initial concentration and reached ful saturation after taking 32 1-mL fractions. The uptakes for lithium and sodium ions, in this case, were found to be

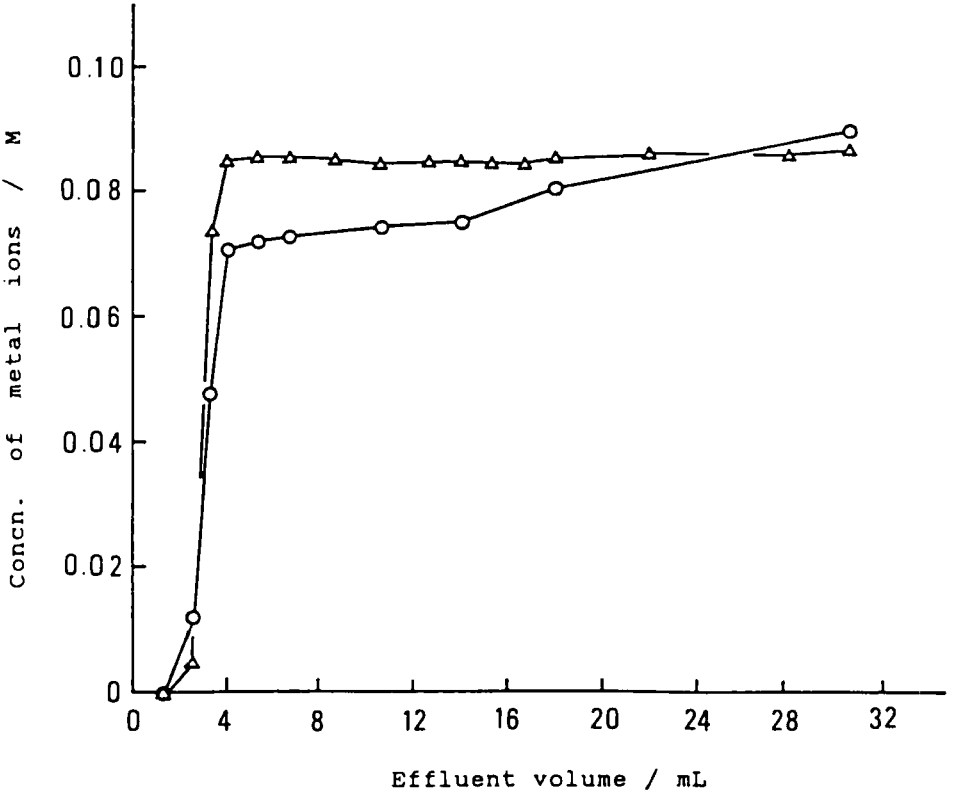


FIG. 5. The breakthrough curves of a mixed solution of lithium and sodium ions on HIE in column operation. Column: 3 mm i.d. HIE: 0.5 g. Flow rate: 0.3 mL/min. (○): Li^+. (△): Na^+.

0.9 and 0.3 mmol/g dry HIE, respectively. The experiments were repeated three times, but no indication of a decrease of uptake was observed.

Enrichment of Lithium Ion from Seawater

The results obtained in the above experiments encouraged us to apply HIE to the enrichment of lithium ion from seawater.

Seawater from Ariake Bay of Kyushu Island was passed through a membrane filter (0.45 μm), and a 1.52-L aliquot was passed through a column (8 × 3 mm i.d.) containing 0.05 g wet HIE at a flow rate of 0.3 mL/min. Following the sorption cycle, which took three and a half days, the

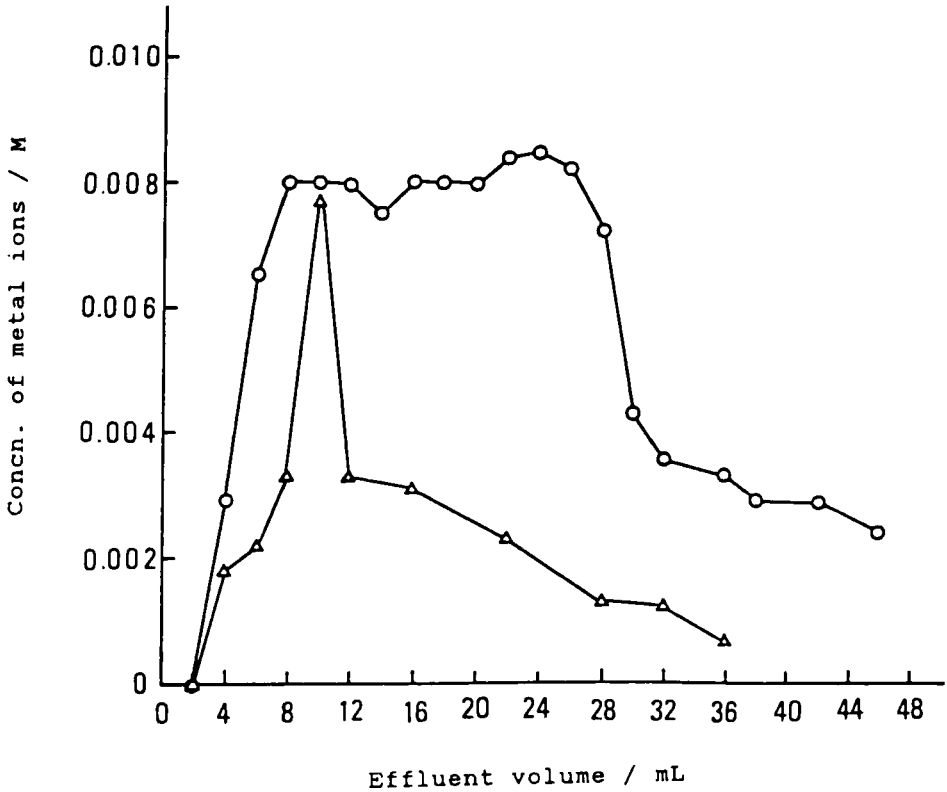


FIG. 6. The elution curves of a mixed solution of lithium and sodium ions on HIE in column operation. (O): Li^+. (△): Na^+.

column was washed with 30 mL water, then eluted with 0.1 *M* nitric acid.

The breakthrough curve and elution curves are illustrated in Figs. 7 and 8, respectively. It is seen from Fig. 7 that no lithium ion could be found in the first 60 mL fractions, and the lithium ion concentration increased fairly rapidly to the 1.5×10^{-5} *M* level after 200 mL fractions, then increased slowly to reach the seawater level after 1200 mL fractions. This characteristic behavior of lithium ion was also observed in a column experiment using a model mixture of lithium and sodium ions, as discussed in the previous section. It seems that there are two steps in lithium uptake by HIE, a fast and a slow one, although the mechanisms corresponding to each step are not clear.

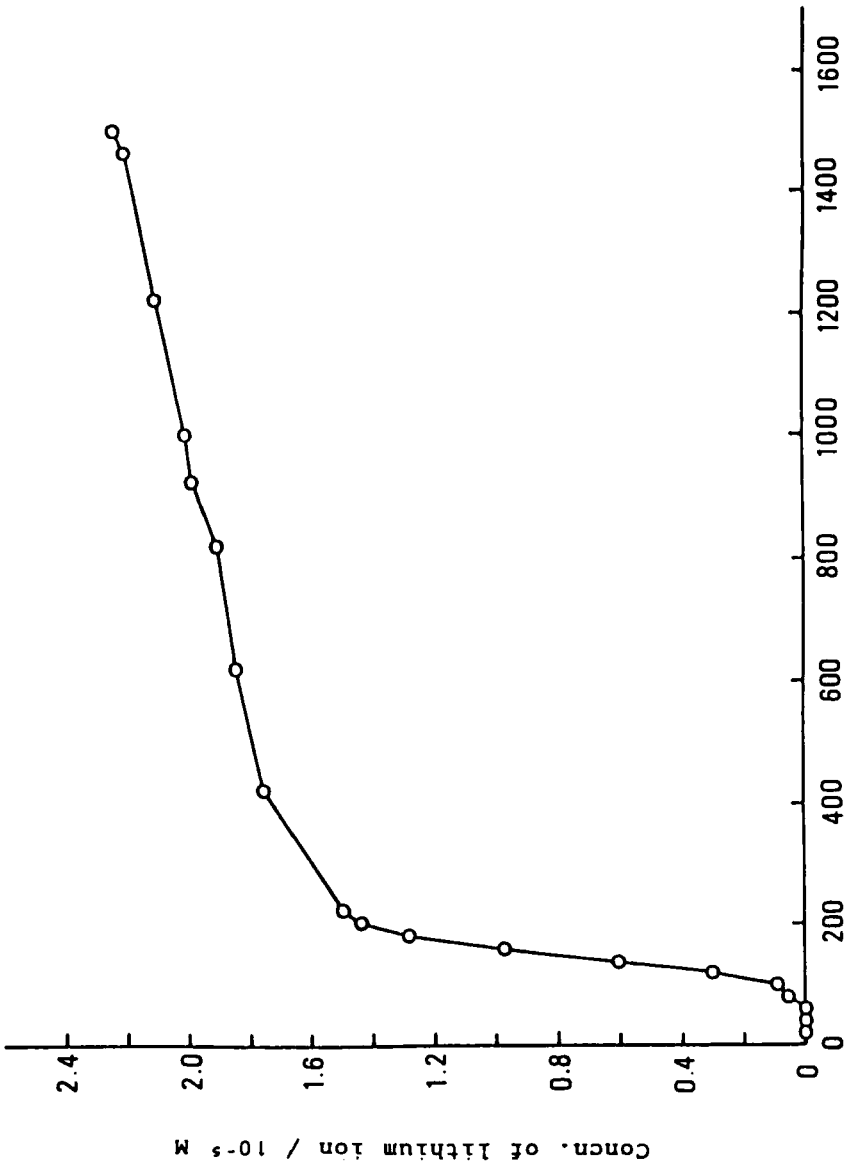


FIG. 7. The breakthrough curve of lithium ion in the column experiment with seawater. Column: 3 mm i.d. HIE: 0.05 g. Flow rate: 0.3 mL/min.

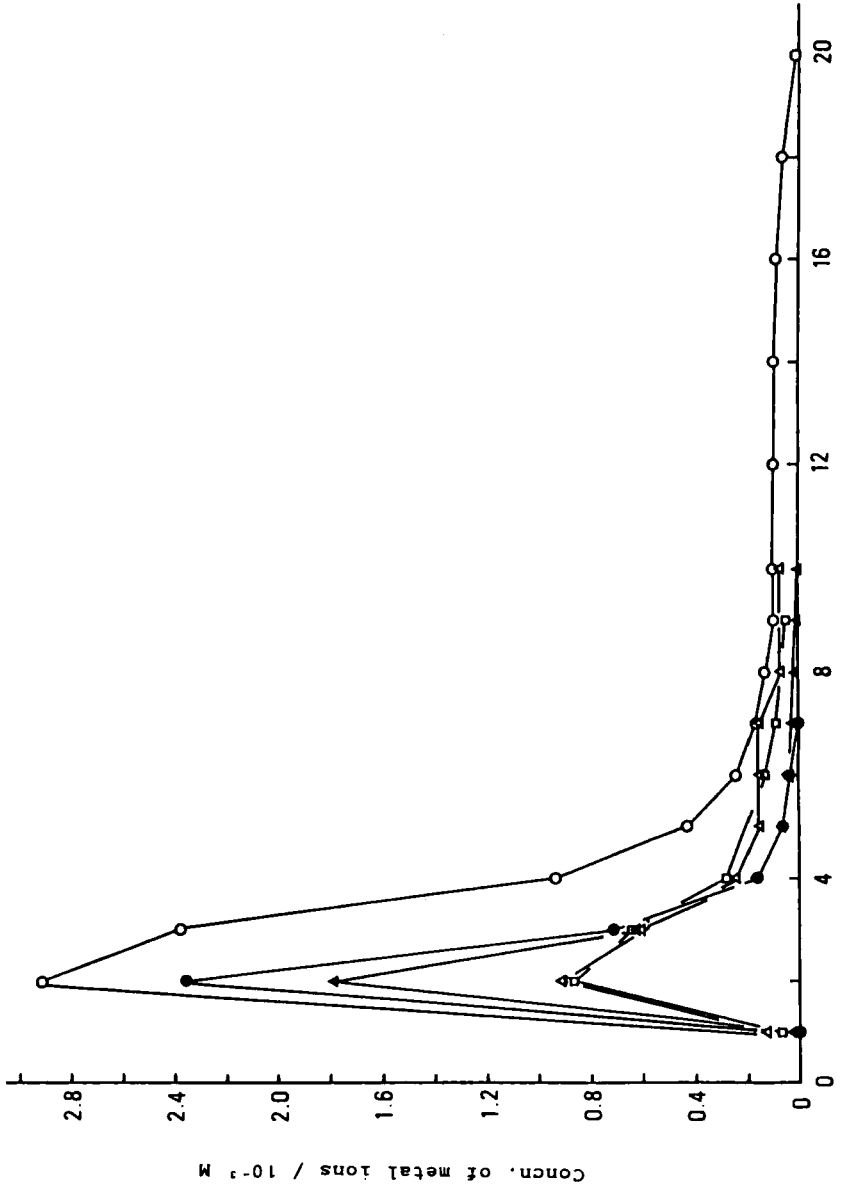


FIG. 8. The elution curves of metal ions after sorption of seawater. (○): Li^+. (△): Na^+. (□): K^+. (▲): Mg^{2+}. (●): Ca^{2+}.

The uptake of lithium, sodium, potasium, calcium, and magnesium ions were calculated from the elution curves (Fig. 8), and the enrichment ratios and the enrichment factors for these metal ions were derived from these results, as summarized in Table 2. The enrichment ratio and enrichment factor for lithium ion are much higher than those of the other ions, indicating that HIE is a very promising material for the selective sorption of lithium ion in the presence of a large excess of other metal ions such as in the case of seawater.

Under our experimental conditions the uptake of lithium ions from seawater is 0.29 mmol/g dry HIE. This value is considerably lower than that obtained by the batch method (1.4 m mol/g dry HIE at pH 8.0) using a lithium ion solution of relatively higher concentration. However, if it is remembered that the contact time of seawater in the HIE column is only 0.19 min, which was calculated from the volume of HIE in the column and the flow rate of seawater, and the extremely low concentration of lithium ions in seawater, it is reasonable to realize that HIE did not reach saturation under this experimental condition, resulting in the rather low recovery (23%) of lithium ions from seawater. Nevertheless, this value is higher than those reported for SnSbA or TiSbA (0.15–0.20 mmol/g), which are known as highly selective inorganic ion-exchangers for lithium (*2*, *3*), and is on the same level as the value (2.0 mg or 0.29 mmol/g) reported on the granulated HMnO (*11*).

TABLE 2
Enrichment of Metal ion from Seawater on HIE by Column Operation

Ion	Concentration in seawater (μg/mL)	Metal ion uptake		Enrichment ratio[b] (mL/g)	Enrichment factor[c]
		mg/g[a]	mmol/g[a]		
Li^+	0.16	2.0	0.29	1.3×10^4	—
Na^+	11.7×10^3	2.08	0.0905	0.2	7.1×10^4
K^+	420	3.22	0.0824	7.7	1.7×10^3
Mg^{2+}	13.3×10^2	2.40	0.0987	1.8	6.9×10^3
Ca^{2+}	390	4.76	0.119	12.2	1.0×10^3

[a]Values per grain of dry HIE.

[b]Enrichment ratio = amount of metal ion in HIE (mg/g)/amount of metal ion in seawater (mg/mL).

[c]Enrichment factor = ratio of lithium ion to metal ion in HIE/ratio of lithium ion to metal ion in seawater.

The spherical form of HIE beads and the high selectivity of HIE for lithium ions make HIE an ideal material for the enrichment of lithium ions from seawater.

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