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Recovery of Lithium from Seawater by Manganese Oxide Adsorbent

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Abstract

Ion-sieve (microporous) type manganese oxide (HMnO) was prepared by acid treatment of lithium-introduced manganese oxide which was obtained from γ-type manganese oxide and lithium hydroxide. The HMnO showed high selectivity for lithium ions in seawater. The maximum lithium uptake by the HMnO from seawater reached 7.8 mg/g which corresponded to a lithium content of 1.7% as Li_2O. The adsorbed lithium could be easily eluted with 0.01 or 0.05 *M* hydrochloric acid solution. The adsorptive capacity for lithium ion scarcely changed during five repetitions of the adsorption–elution cycle. The column test was carried out by using granulated HMnO which was prepared with polyacrylic hydrazide as a binder.

INTRODUCTION

The requirement of lithium for the blanket region of a controlled thermonuclear fusion reactor has been estimated to be from 200 to 1000 tons per 1 GW generation of electric power (*1*). Present lithium reserves are estimated to be 7.6×10^6 tons (*2*), which will not be sufficient when thermonuclear fusion reactors come into use in the world. One of the future resources of lithium is seawater which contains a total of about 2.5×10^{11} tons of lithium at a low concentration (0.17 ppm).

Various methods have been studied for the recovery of lithium from seawater or brine, such as adsorption (ion-exchange) (*3, 4*), solvent extraction (*5, 6*), and coprecipitation (*7–9*). Because of economic reasons and environmental considerations, the adsorption method is the most

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promising for the recovery of lithium from seawater when a suitable adsorbent is available. Organic ion-exchange resins seem to be unsuitable because of low selectivity for the lithium ion. On the other hand, some of the inorganic ion-exchangers exhibit high selectivity for the lithium ion (*4, 10–12*). Among them, tin(IV) antimonate has been successfully applied for the separation of lithium from seawater (*4*).

An ion-sieve-type manganese oxide has shown high selectivity for the lithium ion among alkali metal ions. The high selectivity of this material for the lithium ion arises from the presence of micropores with a suitable size for fixing the lithium ion. Alkali metal ions other than the lithium ion cannot enter the micropores because their ionic radii is larger than the pore radius. Manganese oxide has been examined as an adsorbent for the recovery of lithium from brine (*13, 14*). Its lithium uptake has reached 13 mg/g from brine with a high lithium concentration (C_{Li} = 241 ppm).

The purpose of this paper is to evaluate the applicability of microporous manganese oxide as an adsorbent for the recovery of lithium from seawater. The rate of lithium adsorption, lithium uptake from seawater, elution of lithium, and stability of the adsorbent against the adsorption-elution cycle were examined.

EXPERIMENTAL

Preparation of Adsorbent

100 g manganese oxide (I.C. 4) was immersed in 2 L of lithium hydroxide solution (1 *M*), stirred for a week at room temperature, and filtered. The lithium ion-containing manganese oxide was heated at 600°C for 4 h. In order to remove the lithium ions, the solid was washed with 0.1 *M* hydrochloric acid solution by decantation until the lithium ion concentration in the supernatant was below 1 ppm. Most of the lithium ions could be removed when the decantation was repeated 7 times; the lithium content of the solid became less than 0.03%. The precipitate was filtered, washed with water, and dried at 70°C. The product was taken as HMnO.

Granulated HMnO was prepared by using polyacrylic hydrazide (PAH) as a binder (*15*). The lithium-introduced manganese oxide (5 g) and 10 mL of an aqueous solution of PAH (5%) were kneaded together and dried at 60°C overnight. The solid was crushed and sieved (42–100 mesh size). The collected samples were washed with 0.1 *M* hydrochloric acid solution in order to remove the lithium ions and then dried.

X-ray and Thermal Analysis

An x-ray diffraction pattern was obtained on a Rigaku Denki Rad II diffractometer using Ni-filtered CuK_α radiation with a graphite monochromater. Thermal analysis was made on a Rigaku Denki Thermoflex 8002 at a heating rate of 10°C/min.

Distribution Coefficients, K_d

The equilibrium K_d values of lithium, sodium, potassium, and calcium ions were determined by the batch technique. The adsorbent (50 mg) was immersed in 15 mL of a 0.2 *M* ammonia water–0.2 *M* ammonium chloride buffer solution (pH 8.1) containing 1 m*M* alkali metal and calcium ions. After equilibrium was reached, the concentrations of metal ions in the solution were determined by atomic absorption spectrometry. The K_d values were calculated by

$$K_d = \frac{\text{amount of metal ions in exchanger}}{\text{amount of metal ions in solution}} \times \frac{\text{mL solution}}{\text{g exchanger}}$$

Adsorption of Lithium from Seawater

The adsorption of lithium from seawater was examined by both the batch and column methods. In the batch method a known weight of the adsorbent was immersed in 2 L seawater and stirred. After stirring for a fixed time, the concentration of the lithium ion in the supernatant was determined by atomic absorption spectrometry. The lithium uptake was calculated from the decrease in the lithium concentration.

In the column method, seawater was passed at a flow rate of 10 mL/min through a small column (0.4 cm i.d.) containing 0.5 g granulated HMnO. After percolation of the seawater for 20 h, the column was washed with 10 mL water and then the adsorbed metal ions were eluted by the HCl solution.

RESULTS AND DISCUSSION

X-ray Diffraction Pattern and DTA-TG Curves

The x-ray diffraction pattern of the product (HMnO) is given in Fig. 1. The strong peaks at $2\theta = 19.1, 37.1$, and $45.1°$, which correspond to those

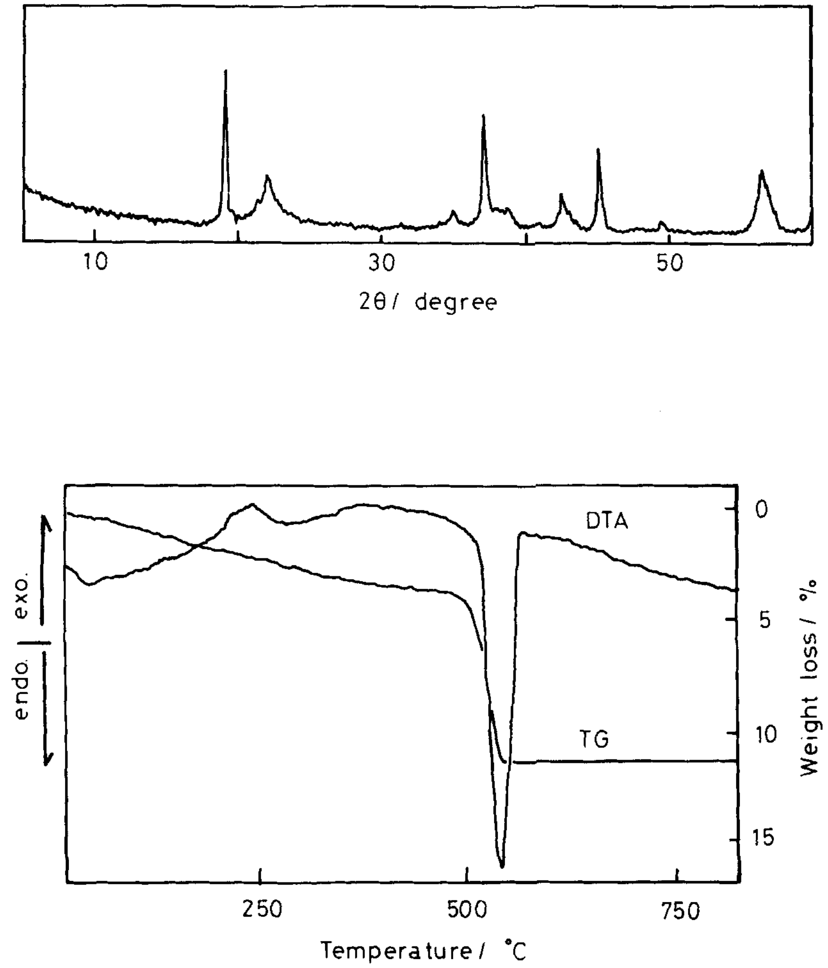

FIG. 1 X-ray diffraction pattern and DTA-TG curves of HMnO.

of $LiMn_2O_4$ (ASTM 18-736), remained after acid treatment with the HCl solution. This indicates that the cubic spinel structure of $LiMn_2O_4$ is scarcely damaged by the removal of lithium ions with the HCl solution. The weak peaks at $2\theta = 22, 43$, and 56° in Fig. 1 suggest the presence of small amounts of unreacted γ-MnO_2. The DTA and TG curves showed a small endothermic peak below 100°C due to dehydration, an exothermic peak at 250°C, and a large endothermic peak at 550°C accompanied by weight loss (Fig. 1). The x-ray analysis revealed the change of the crystal phase as spinel type → γ-MnO_2 (300°C) → β-MnO_2 (500°C) → α-Mn_2O_3 (650°C) by thermal treatment. Thus, the exothermic peak at 250°C corresponds to the transformation from spinel type to γ-MnO_2 and the endothermic peak at 550°C to the transformation from β-MnO_2 to α-Mn_2O_3 accompanied by the loss of oxygen.

Distribution Coefficient

Equilibrium K_d values are given in Table 1 not only for HMnO but also for hydrous tin(IV) oxide (HSnO) (*10*), γ-manganese oxide (γ-MnO_2) (*16*), and hydrous titanium(IV) oxide fiber (HTiO fiber) (*17*). The latter three samples have been developed in our laboratory as adsorbents for the recovery of lithium from geothermal water. However, their lithium uptake from seawater has been very low (0.01, 0.20, and 0.09 mg/g for HSnO, γ-MnO_2, and HTiO fiber, respectively). The selectivity sequence for alkali metal ions is K < Na < Li in all of the samples. The distinctive feature of HMnO was its extremely high selectivity for the lithium ion compared with the other adsorbents. Both the K_d(Li) and the separation factors (α^{Li}_{Na}, α^{Li}_{Ca}) were more than 50 times higher for HMnO than for the other adsorbents.

Adsorption of Lithium from Seawater

Figure 2 illustrates the time course of lithium uptake by HMnO at different temperatures. Lithium adsorption attained equilibrium after 7

TABLE 1
Distribution Coefficients on Adsorbents

Sample	pH	K_d (mL/g) Li	Na	K	Ca	α^{Li}_{Na}[a]	α^{Li}_{Ca}[a]
HMnO	8.1	>50,000	17	14	113	>2,900	>440
HSnO[b]	8.5	43	4	3	1,300	12	0.03
γ-MnO_2[c]	8.5	125	5	1	120	27	1.0
HTiO[d] fiber	8.5	1,300	71	+	300	18	4.3

[a] α^n_m: separation factor = $K_d(n)/K_d(m)$.
[b] Hydrous tin(IV) oxide.
[c] γ-Type manganese oxide.
[d] Hydrous titanium (IV) oxide fiber.

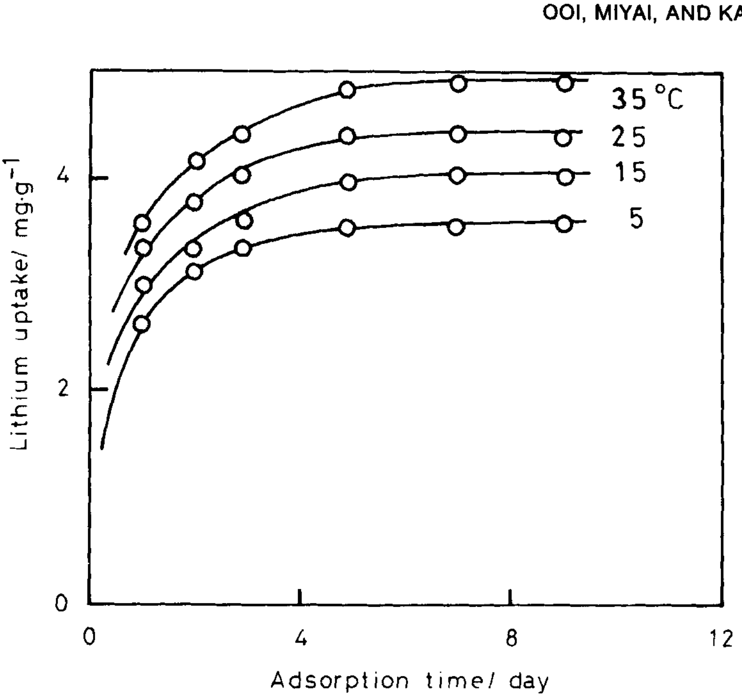

FIG. 2 Time courses of lithium adsorption on HMnO. HMnO, 50 mg; seawater, 2 L.

days of stirring, independent of the adsorption temperature. The equilibrium uptake of lithium increased slightly when the adsorption temperature was increased from 5 to 35°C. The concentration of manganese in the supernatant, which was measured by atomic absorption spectrometry, was below 0.05 ppm (1 ppm = 1 mg/L). Thus, dissolution of the adsorbent was estimated to be less than 0.3%.

Lithium uptake at different ratios of the volume of seawater per gram of adsorbent are given in Table 2. The recovery of lithium (%) decreased with an increase in the seawater/adsorbent ratio while lithium uptake (mg/g) increased with the ratio. The recovery of lithium was 85% at a ratio of 20 L/g, which was about three times higher than that by tin(IV) antimonate (25%) (*4*). The adsorption data in Table 2 follow Freundlich's equation with the slope of 0.5, as shown in Fig. 3. The maximum lithium uptake in seawater can be estimated by extrapolating the adsorption isotherm in Fig. 3 to C_{Li} = 170 μg/L. The extrapolated value was 7.8 mg/g, which corresponds to a lithium content of 1.7% as Li_2O. This value is about 1/3 of the lithium content of such lithium ores as lepidolite (4%), petalite (4%), and spodumene (7%) (*18*).

TABLE 2
Lithium Uptake from Seawater by HMnO

Volume per gram (L/g)[a]	Lithium recovery (%)	Lithium uptake (mg/g)	Lithium concentration (μg/L)
20	85	2.9	25
25	82	3.5	30
40	65	4.4	60
80	44	6.0	95

[a] (L/g): Volume of seawater per gram of HMnO.

Note that the lithium uptake from seawater is about half that from brine (*14*) in spite of the fact that the lithium concentration is 1400 times lower in seawater than in brine. This behavior of HMnO is advantageous for the recovery of lithium from solutions with extremely low lithium concentrations.

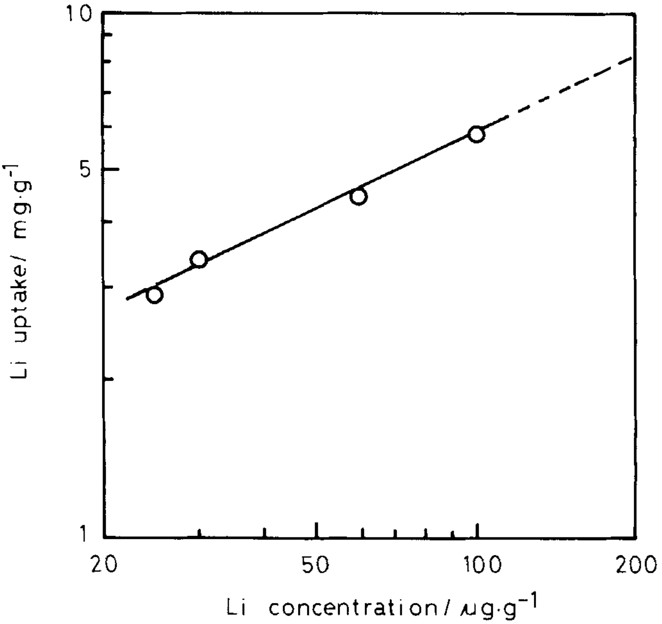

FIG. 3 Adsorption isotherm of lithium on HMnO. Adsorption time, 7 days; temperature, 25°C.

Selectivity for the Elements in Seawater

The adsorption of another metal ions on HMnO was examined by atomic absorption spectrometry after the adsorbent was dissolved in concentrated HCl–HNO_3 solution. The uptake of alkali and alkaline earth metal ions from seawater is given in Table 3. A concentration factor (C.F.) was calculated for each metal ion by using the metal ion concentrations in seawater as follows:

$$\text{C.F. (L/kg)} = \frac{\text{metal ion uptake (mg/kg)}}{\text{metal ion concentration in seawater (mg/L)}}$$

As shown in Table 3, the concentration factor of lithium is extremely high compared with the other metal ions, suggesting that the influence of coexisting ions is comparatively low. The concentration factor of lithium on HMnO is about 500 times higher than that on amorphous aluminum oxide (*7*).

Elution of Lithium

The elution of adsorbed lithium should proceed rapidly and with high yield in order to improve the overall efficiency of the recovery process. The elution of lithium was studied by the batch method. Figure 4 illustrates the time course of lithium elution in 0.01 and 0.05 *M* hydrochloric acid solutions. The rate of the elution is satisfactorily high;

TABLE 3
Enrichment of Elements in Seawater on HMnO

Element	Concentration in seawater (mg/L)	Metal ion uptake (mg/kg)	Concentration factor (L/kg)
Li	0.17	4,400	26,000
Na	10,500	7,000	0.7
K	380	1,000	2.7
Mg	1,350	5,000	3.0
Ca	400	2,100	5.3
Sr	8.0	1,600	200

[a] Adsorption: 2 L of seawater per 50 mg for 7 days.

[b] Concentration factor = metal ion uptake (mg/kg)/concentration in seawater (mg/L).

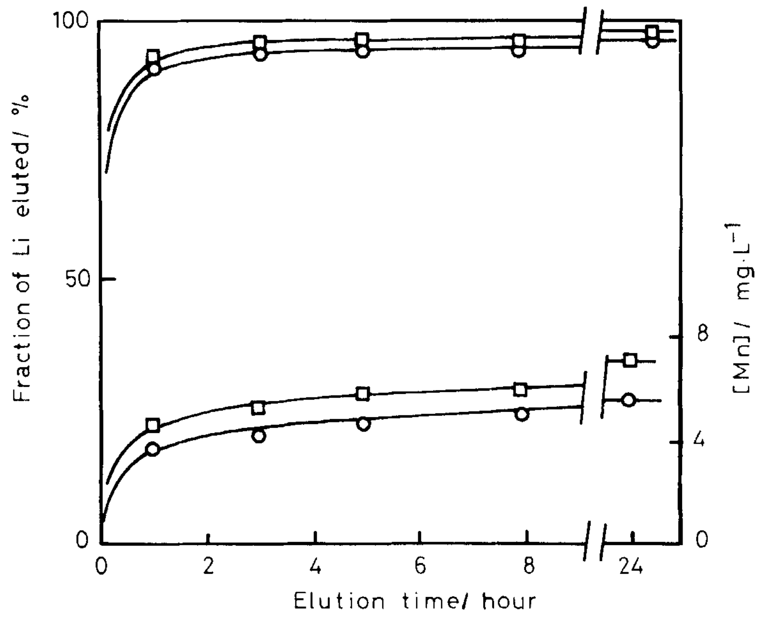

FIG. 4 Time courses of lithium elution in HCl solutions. HMnO, 50 mg; HCl solution, 50 mL; temperature, 25°C. Concentration of HCl: 0.01 *M* (○), 0.05 *M* (□).

the adsorbed lithium can be eluted more than 90% by shaking for 1 h at room temperature. An elution efficiency above 95% is attained by shaking for 24 h. The concentrations of manganese in the supernatant were found to be 5.5 and 7.0 ppm in the 0.01 and 0.05 *M* HCl solutions, respectively, which corresponded to about a 1% loss of the adsorbent. We think that the dissolution of adsorbent can be decreased by using a suitable eluting agent or suitable conditions of elution.

Chemical Stability of HMnO

In order to examine the chemical stability of the adsorbent, five adsorption–elution cycles were carried out using seawater and a 0.05 *M* HCl solution. As shown in Fig. 5, lithium uptake did not decrease during the five recycles and the elution efficiency was always above 95%. Even after 65 cycles of acid treatments with the HCl solution, the adsorbent activity was 60% of the initial activity. These results suggest that the active site in the HMnO is relatively stable for a long-term recycling procedure.

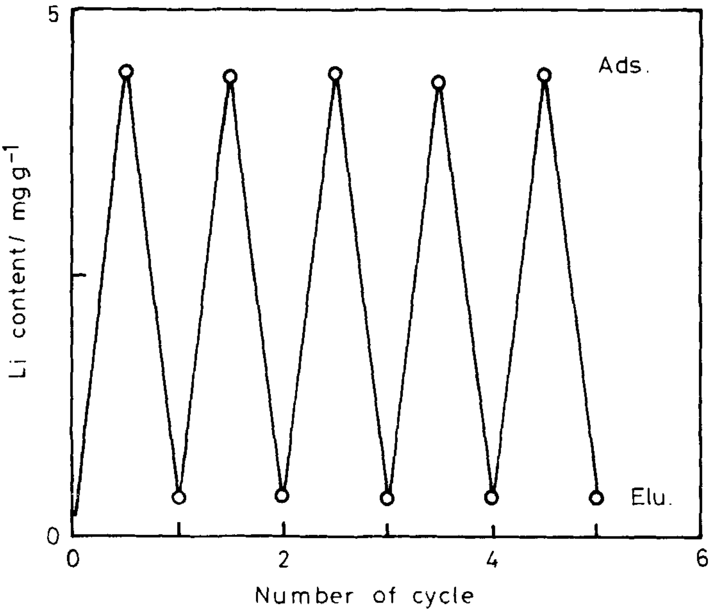

FIG. 5 Lithium adsorption–elution cycles. Adsorption: 50 mg of HMnO in 2 L seawater for 7 days. Elution: 50 mL of 0.05 *M* HCl for 1 day.

Column Experiment

Figure 6 illustates the column elution curves of lithium, sodium, potassium, magnesium, and calcium ions with a 0.1 *M* HCl solution as the eluent. Most of the metal ions were eluted by using 30 mL of the HCl solution. However, separations of the metal ions were not satisfactory because of their low separation factors in acidic solution (*19*). Metal ion uptake values for granulated HMnO, evaluated from the elution curves, were 2.0, 1.7, 0.2, 2.0, and 2.4 mg/g HMnO for lithium, sodium, potassium, magnesium, and calcium ions, respectively. The uptake of each metal ion was smaller than the corresponding value in the batch method (Table 3) except for the case of the calcium ion. Since the particle size of granulated HMnO was much larger than that of HMnO powder (less than 200 mesh), granulated HTiO may not be in adsorption equilibrium with seawater. The large uptake of the calcium ion is probably due to the presence of PAH which contains small amounts of the carboxyl group. Figure 7 illustrates the elution curves of the lithium ion with HCl solutions of different concentrations. The elution peak for lithium

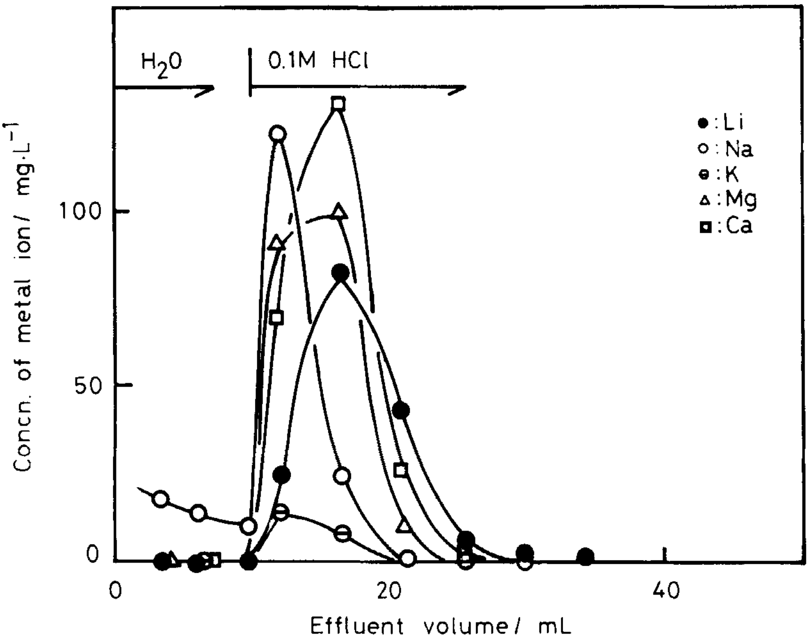

FIG. 6 Elution curves of metal ions with HMnO. Column, 0.4 cm i.d.; 0.5 g of sample. Flow rate: 0.15 mL/min.

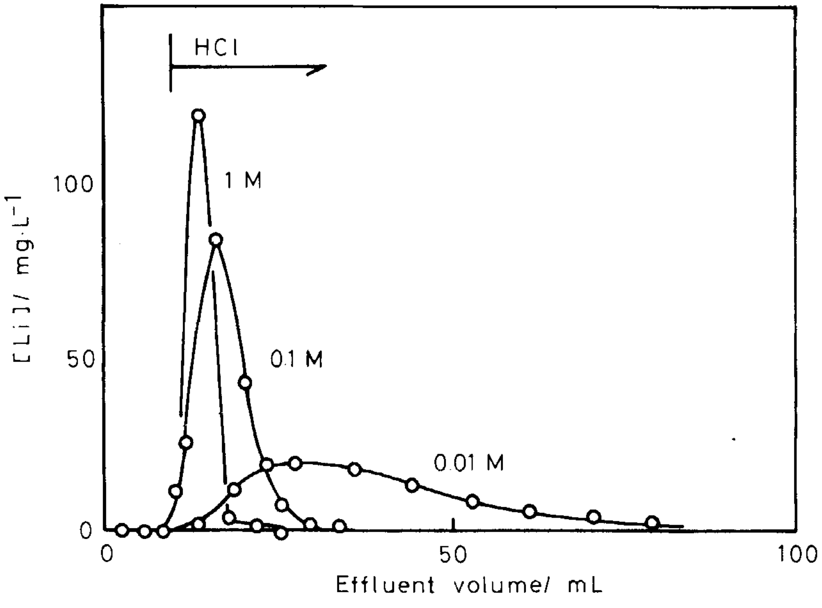

FIG. 7 Elution curves of lithium ions with HMnO. Same conditions as in Fig. 7 except for the HCl concentration.

became sharp and the retention time shortened with increasing HCl concentration.

CONCLUSION

HMnO is one of the most promising adsorbents for the recovery of lithium from seawater because of its high selectivity for the lithium ion in seawater, ease of elution of the lithium ion, and high stability in the adsorption-elution cycle.

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