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Separation and Recovery of Lithium from Geothermal Water by Sequential Adsorption Process with λ-MnO_2 and TiO_2

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ABSTRACT

Separation and recovery of lithium from geothermal water have been investigated by adsorption using both λ-MnO_2 and TiO_2 as adsorbents for lithium and arsenic, respectively. The adsorption of lithium in the geothermal water with λ-MnO_2 is suppressed by the coexisting arsenic, and manganese is dissolved during elution of lithium from the loaded λ-MnO_2 in the column, due to the possible redox reaction of manganese by the arsenic adsorbed. TiO_2 adsorbent is therefore applied for the arsenic adsorbent prior to the lithium recovery; that is the TiO_2 and λ-MnO_2 are sequentially applied to the geothermal water. The arsenic in the geothermal water can be effectively removed by the TiO_2 adsorbent, and successive recovery of the lithium with λ-MnO_2 can be achieved.

Keywords: Lithium; Arsenic; Geothermal water; Adsorption

INTRODUCTION

Lithium (Li) is one of the rare elements and is used as the material for large-capacity rechargeable batteries, light aircraft alloys, and nuclear fusion fuel. The present resources of Li are mine and salt lakes, which totally contain about 34 million tons. Although the amount of Li in those resources is sufficient at this moment, alternative resources should be exploited to satisfy the increasing demand in near future[1,2]. Seawater and other unused fluids are considered to be attractive sources of Li[3-5]. Recently, attention for geothermal water as a source of Li has been increasing, due to relatively high concentration of Li and low concentration of coexistent ions[6].

In our group, λ-MnO_2 adsorbent has been developed as an adsorbent for Li and was successfully applied for the recovery of Li from seawater[7]. The λ-MnO_2 adsorbent was then applied for the recovery of Li from geothermal water[8]. Effective adsorption of Li from geothermal water is however not progressed, even though the concentrations of the coexisting components are lower than those in the seawater. Since this was due to the existence of arsenic (As) in the geothermal water, the removal of As is required prior to the adsorption of Li. In the previous work, therefore, adsorption of As with three inorganic adsorbents, magnetite (Fe_3O_4), titania (TiO_2), and alumina (Al_2O_3), was investigated[9]. All adsorbents possess high adsorption ability for As in acidic and neutral pH region, which indicates the all adsorbents are applicable for the As removal from common geothermal waters. Based on the batchwise and chromatographic adsorption experiments, TiO_2 was concluded to be the most suitable adsorbents for the removal of As.

In the present work, therefore, separation and recovery of Li from geothermal water by sequential adsorption process with λ-MnO_2 and TiO_2 were investigated. Effect of temperature and coexisting components in the geothermal water on the adsorption of Li with λ-MnO_2 were firstly investigated. The chromatographic operation was then carried out by the sequential combination of TiO_2 as an As adsorbent and λ-MnO_2 as a Li adsorbent.

EXPERIMENTAL

Materials

Mn_3O_4 was supplied by Soekawa Chemicals Co., Ltd, and $LiOH \cdot H_2O$ were

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supplied by Kanto Chemical Co., Inc. Alumina-based binder (CATALOID AP-1) was supplied by JGC Catalysts and Chemicals Ltd., and all other reagents were supplied by Wako Pure Chemical Industries, Ltd.

Preparation of adsorbents

The adsorbents were prepared by the same manner described in the previous papers[7-9]. In the case of λ-MnO_2 adsorbent, powdery Mn_3O_4 and $LiOH \cdot H_2O$ were mixed at the molar ratio of Li/Mn = 0.75 and ground for 1 h with ball mill. The mixture was sintered at 425 ^oC for 5 h with an electrical oven (Deken KDF-S100G). After cooling to room temperature, it was mixed and ground again for 1 h. The mixture was sintered at 500 ^oC for 5 h with an electrical oven. After slow cooling to room temperature in the electrical oven, powdery spinel type $Li_{1.5}Mn_2O_4$ (Li-type adsorbent) was obtained as an intermediate product. The Li-type adsorbent was treated with 1.0 mol/dm^3 of HCl solution for 12 h five times to obtain the H-type adsorbent (λ-MnO_2).

In the case of titania (TiO_2) adsorbent, aqueous ammonia (1 wt%) is added to $TiCl_4$ solution (1 wt%) until pH = 7 to produce $Ti(OH)_4$, and hydrogen peroxide (H_2O_2) is then added to the suspended solution of $Ti(OH)_4$ to produce amorphous TiO_2. The suspended solution of amorphous TiO_2 was hydrothermally treated at 120 ^oC for 5 h in an autoclave to produce anatase-type TiO_2.

The granulation of the adsorbents was carried out with alumina-based binder to be applied for column experiments. The powdery adsorbent (3 – 6.5 g) and alumina-based binder (3 – 3.5 g) were mixed together with a small amount of deionized water. The kneaded mixture was pressed out from 1 mm hole in diameter by an extruder, and dried at room temperature for overnight. The mixture was then calcined at 550 ^oC for 3 h, and then was cut for 0.5 – 1 mm in length.

Batch Adsorption of Li with λ-MnO_2

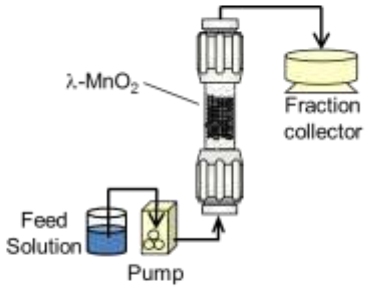
Adsorption isotherms of Li with λ-MnO_2 were obtained under several temperatures at $pH_{eq} = 8.0 \pm 0.1$, which pH was controlled by addition of NaOH solution to HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) solution. The batchwise adsorption of coexisting ions in the geothermal water, As, Ca, Mg, Na, and K, was also conducted at $pH_{eq} = 8.0 \pm 0.1$, which pH was controlled by NH_3-NH_4Cl buffer solution. The metal concentrations were determined by an atomic absorption spectrophotometer (AAS; Shimadzu AA-6800) or an inductively coupled plasma atomic emission spectrometer (ICP-AES; Shimadzu ICPS-7000). The amount of metals on the adsorbent, q_M [mmol/g], was determined by:

$$q_{\mathrm{M}} = \frac{(C_{\mathrm{M0}} - C_{\mathrm{M}}) \cdot L}{W}$$

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

Table 1 *Composition of artificial geothermal water* [6].

element	Concentration [mg/dm^3]
Li	9.83
Na	1501
Mg	0.331
K	229
Ca	16.8
B	33.9
F	3.76
Si	328
S	68
Cl	1914
As	3.23
Br	9.31



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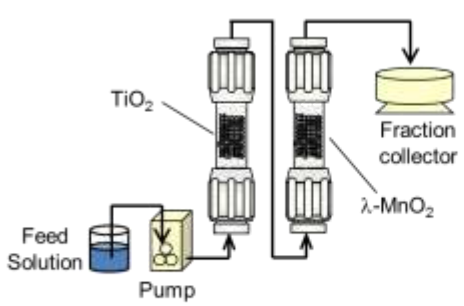

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Figure 1 *Schematic diagram of column operation for the recovery of Li from geothermal water.*

Chromatographic operation for Li recovery from geothermal water

The artificial geothermal water was prepared by dissolving LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, and $AsCl_3$ to deionized water, and then pH was controlled to 8.0 using NH_3, based on the actual geothermal water sampled at Hatchobaru geothermal power plant (Japan)[6]. Composition of the artificial geothermal water is shown in Table 1.

In the present work, two processes, single column process and dual column process, were conducted. Schematic diagram of the processes are shown in Figure 1. The granulated λ-MnO_2 (wet volume 1.5 cm^3) or TiO_2 (wet volume 1.5 cm^3) was packed into glass column together with glass wool to be sandwiched. In the case of λ-MnO_2, the column was treated with 1.0 mol/dm^3 of HCl and deionized water for conditioning.

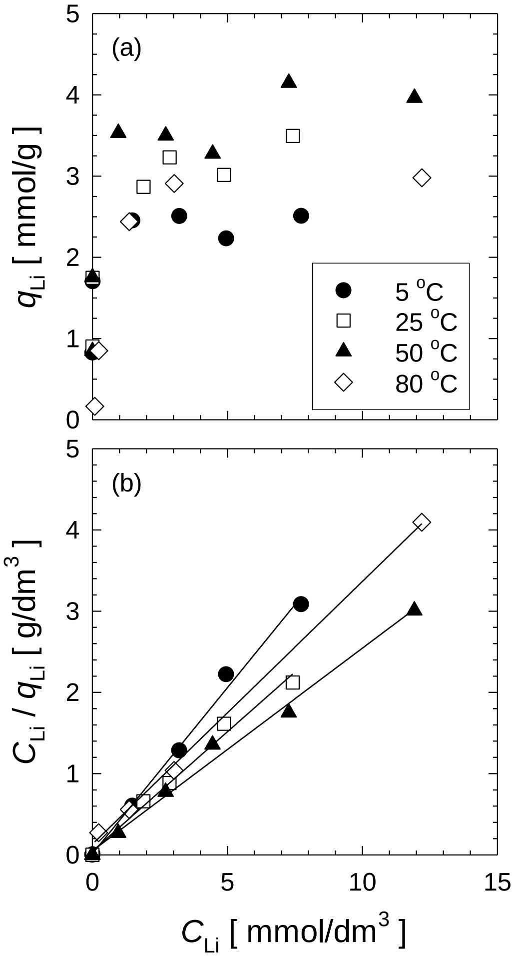

Figure 2 *(a) Adsorption isotherms for Li with λ-MnO_2 at 5, 25, 50 and 80 ^{O}C at equilibrium pH = 8.0 ± 0.1. (b) Linearized Langmuir plots of the adsorption isotherms.*
5 ^{o}C: $y = 0.4909 x + 0.0138$, $r^2 = 0.9943$;
25 ^{o}C: $y = 0.2941 x + 0.0454$, $r^2 = 0.9899$;
50 ^{o}C: $y = 0.2494 x + 0.0505$, $r^2 = 0.9919$;
80 ^{o}C: $y = 0.3753 x + 0.3088$, $r^2 = 0.8746$.

Artificial geothermal was fed upward through the column at a flow rate of 0.2 cm^3/min (S.V. = 8.0 h^{-1} in the cases of λ-MnO_2 and TiO_2, i.e. S.V. is ratio of flow rate to wet volume of adsorbent) using a dual-plunger pump (Flom model KP-11).

The bed volume (B.V.) was calculated by:

$$\text{B.V.} = vt/V$$

where v is the flow rate of the feed solution [cm^3/min], t is the supply time of the feed solution [min], and V is the wet volume of the adsorbent [cm^3]. The metal concentrations were determined by AAS or ICP-AES.

RESULTS AND DISCUSSION

Adsorption behavior of Li with λ-MnO_2

Effect of temperature on the adsorption of Li with λ-MnO_2 was firstly investigated, since the temperature of the geothermal water is generally high within 60 – 100 ^{o}C[6]. Figure 2a shows the adsorption isotherms of Li at several temperatures. The adsorption isotherms fit well

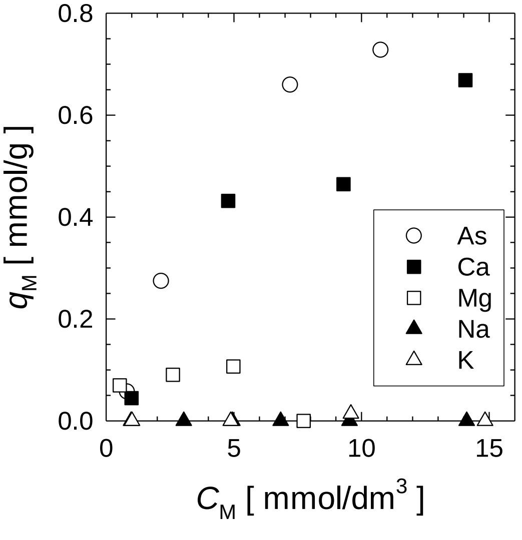

Figure 3 *Adsorption isotherms for As, Ca, Mg, Na, and K with λ-MnO_2 at equilibrium pH = 8.0 ± 0.1.*

Table 2 *Maximum adsorption amount of Li at each temperature*

Temp. [^{o}C]	5	25	50	80
q_{Li0} [mmol/g]	2.13	2.94	4.01	2.66

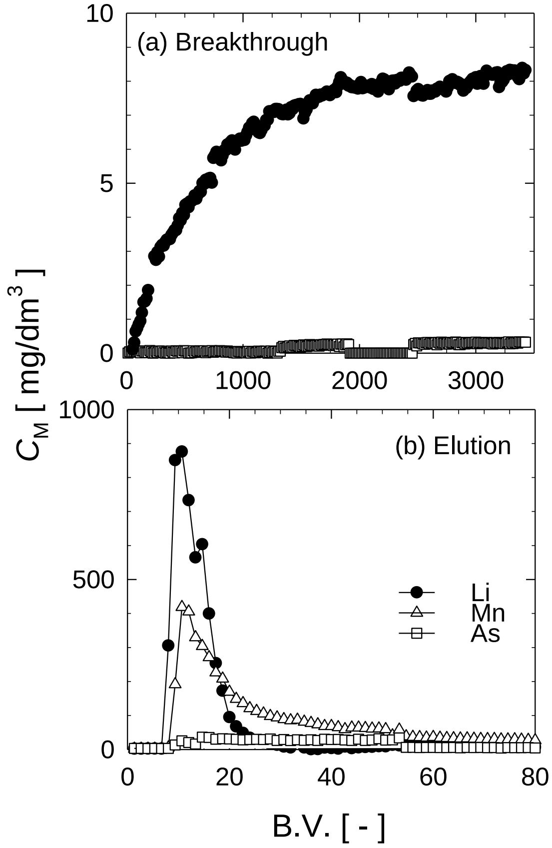

Figure 4 *(a) Breakthrough and (b) elution curves for Li, Mn, and As from geothermal water with single column process.*

with the linear relationship of the Langmuir mechanism, as shown in Figure 2b. Maximum adsorption amounts (q_{Li0}) at each temperature calculated were shown in Table 2. The q_{Li0} was increased with increase in the temperature until 50 ^{o}C, and was then decreased at 80 ^{o}C. The λ-MnO$_2$ is applicable for the geothermal water, since the λ-MnO$_2$ still possesses high adsorption ability for Li even at high temperature.

Figure 3 shows the adsorption isotherms of coexisting ions in the geothermal water. Almost no adsorption is progressed in the cases of Mg, Na, and K, while the adsorption slightly progresses in the cases of Ca and As. Removal of As should be especially conducted prior to the adsorptive recovery of Li.

Chromatographic operation for Li recovery from the geothermal water

Chromatographic operation for the separation and recovery of Li from the geothermal water was then carried out. Firstly, artificial geothermal water was fed to the λ-MnO$_2$ column directly. Figure 4 shows breakthrough and elution curves of Li and As from the single column process. As reported in previous paper[8], effective adsorption of Li is not achieved, and Li is broken thorough immediately in the initial stage. In addition, almost all As is adsorbed by the λ-MnO$_2$. When the column was eluted with 1.0 mol/dm^3 HCl, large amount of Mn was dissolved together with the elution of Li, while no elution of As was observed. Adsorption of As on the λ-MnO$_2$ therefore suppresses adsorption of Li. In addition, As adsorbed is likely to lead redox reaction of Mn in the adsorbents.

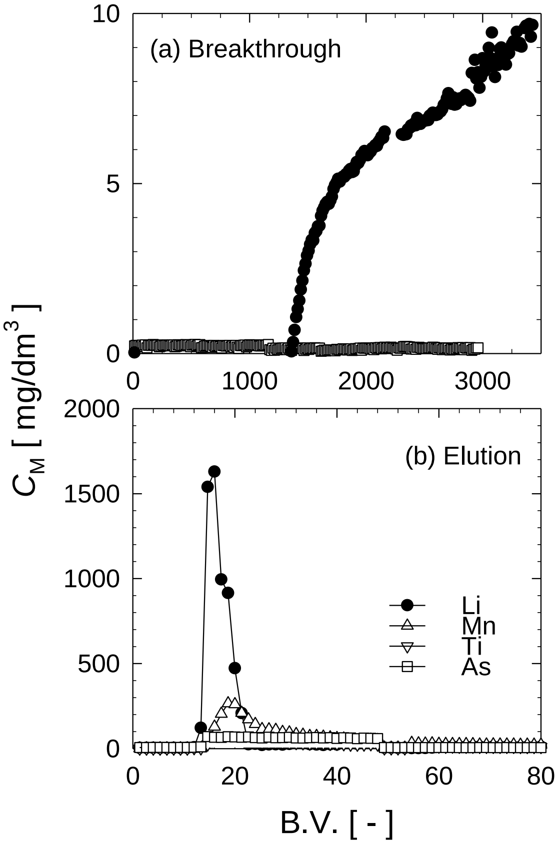

Figure 5 *(a) Breakthrough and (b) elution curves for Li, Mn, and As from geothermal water with dual column process.*

Figure 5 shows the breakthrough and elution curves from the dual column process. As shown in breakthrough curves, Li is successfully adsorbed by the chromatographic operation. TiO$_2$ adsorbent successfully remove As before λ-MnO$_2$ column, and thus the adsorption of Li can be achieved until B.V. = ca. 1400. Elution of Li is also achieved with maximum concentration of ca. 1600 mg/dm^3, although Mn is still slightly eluted from the adsorbent. The sequential chromatographic operation with As-selective TiO_2 and Li-selective λ-MnO_2 is therefore effective for the separation and recovery of Li from the geothermal water.

CONCLUSIONS

The separation and recovery of Li from the geothermal water was investigated with following results.

(1) Adsorption of Li with λ-MnO_2 is effectively conducted even at high temperature of 80 ^oC.

(2) Adsorption of Li in the geothermal water with λ-MnO_2 is suppressed by coexisted As. Mn is dissolved from the adsorbent during the elution step due to possible redox reaction with As adsorbed.

(3) Sequential adsorption process with λ-MnO_2 – TiO_2 was applied for the selective separation of Li in the geothermal water, and the adsorption of Li with the λ-MnO_2 is successfully achieved followed by the adsorption of As with the TiO_2.

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