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Recovery of Lithium from Seawater Using a New Type of Ion-Sieve Adsorbent Based on $MgMn_2O_4$

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Abstract

A new type of ion-sieve manganese oxide, HMnO(Mg), was prepared by an acid treatment of $MgMn_2O_4$. The HMnO(Mg) showed a remarkably high selectivity for lithium ions among alkali metal and alkaline earth metal ions. The selectivity sequences were Na $\doteqdot$ K $\ll$ Li for alkali metal ions and Mg < Ca < Sr < Ba for alkaline earth metal ions at pH 8. The HMnO(Mg) showed a high selectivity for lithium ions in seawater. The lithium uptake increased with increasing solution pH and adsorption temperature. The maximum lithium uptake from native seawater reached 8.5 mg/g, corresponding to a lithium content of 1.8% in the form of Li_2O. The adsorbed lithium could easily be eluted with a dilute acid solution. The adsorptive capacity for lithium ions gradually decreased through repeated adsorption/elution cycles. The HMnO(Mg) after 4 cycles showed a lithium adsorptivity which was about 60% of the initial value.

INTRODUCTION

Future requirements for lithium as an energy source for such applications as a lithium battery and the blanket region of controlled thermonuclear fusion reactors may exceed the current availability of that mineral as well as brine reserves (*1, 2*). One of the possible future sources of lithium is seawater; the world supply contains a total amount of about 2.5×10^{11} tons at a low concentration (170 ppb).

Various methods have been studied for the recovery of lithium from seawater, brine, and geothermal water. These can be classified into three groups: adsorption (ion-exchange) (*3–14*), solvent extraction (*2, 15, 16*), and coprecipitation (*17–22*). Since the concentration of lithium is very low in seawater compared to that in brine or geothermal water, the adsorption method is the most promising for a seawater system owing to economic and environmental considerations. Organic ion-exchange resins are unsuitable owing to their low selectivity for lithium ions. On the other hand, some inorganic adsorbents show high selectivities for lithium ions. The lithium uptakes from seawater are 0.31 mg/g by hydrous magnesium–aluminum oxide (*7*), 0.50 mg/g by hydrous aluminum–iron oxide (*8*), 1.4 mg/g by tin(IV) antimonate (*4*), and 7.8 mg/g by ion-sieve manganese oxide (*14*).

Ion-sieve manganese oxides were first synthesized by Vol'khin et al. (*12*, *23*, *24*). They are obtained by thermal crystallization of metal ion-saturated manganese hydroxides followed by the extraction of the metal ions with an acid solution. Therefore, their adsorptive properties are dependent on the kind of metal ions introduced into the manganese hydroxide precursors. When lithium ions are used as the introducing ions, the adsorbent obtained (HMnO(Li)) shows a remarkably high selectivity for lithium ions (*12*, *14*). The selectivity sequence is Na < Cs < K < Rb < Li for alkali metal ions at pH 3.5 (*25*). When sodium and potassium ions are used, the adsorbents obtained (HMnO(Na), HMnO(K)) show remarkably high selectivities for potassium and rubidium ions; the selectivity sequence is Li $\doteqdot$ Na < Cs $\ll$ K $\doteqdot$ Rb for alkali metal ions (*25*). The difference in the selectivity could well be explained in terms of the difference in the size of micropores or tunnels formed by an introduction/extraction reaction involving metal ions.

We have developed a new type of ion-sieve manganese oxide, HMnO(Mg), by using magnesium ions as the introducing ions (*26*). A preliminary adsorption study showed that it has a high selectivity for lithium ions among alkali metals and alkaline earth metal ions. The high selectivity for lithium ions could be ascribed to the presence of micropores which are suitable in size for fixing the lithium ions, since the ionic radius of magnesium (0.72 Å) is nearly equal to that of lithium (0.74 Å) (*27*). From a practical point of view, HMnO(Mg) has an advantage in that one of the raw materials, $Mg(OH)_2$, can be easily obtained from seawater. Therefore, its cost should be much lower than that of HMnO(Li).

The purpose of this paper is to evaluate the applicability of HMnO(Mg) for the recovery of lithium from seawater. Lithium adsorptive properties, the elution of lithium, and its stability in the adsorption/elution cycle were examined.

EXPERIMENTAL

Preparation of Adsorbent

$MgMn_2O_4$ was prepared by heating a mixture of γ-MnOOH and $Mg(OH)_2$ in a molar ratio of 2:1 at 950°C for 1 h. The x-ray diffraction pattern of the $MgMn_2O_4$ agreed well with that in an ASTM card (No. 23-392). The $MgMn_2O_4$ (10 g) was immersed in a 0.1 *M* HCl solution (5 L) and stirred for 10 days at 25°C. The acid-treated sample was then washed with water, dried at 60°C, and sieved (less than 200 mesh size). The product was designated HMnO(Mg).

X-Ray Diffraction, X-Ray Fluorescence, and Thermal Analyses

A powdered x-ray diffraction analysis was made on a Rigaku Denki x-ray diffractometor (Model RAD II) using Ni-filtered CuK_α radiation with a graphite monochrometer. An x-ray fluorescence analysis was made on a Rigaku Denki x-ray fluorescence spectrometer (Model KG-X). A 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 alkali metal and alkaline earth metal ions on HMnO(Mg) were determined by a batch technique. HMnO(Mg) (100 mg) was immersed in 25 mL of a 0.2 *M* ammonia water–0.2 *M* ammonium chloride buffer solution (pH 8) containing 10^{-3} *M* alkali metal and alkaline earth metal ions. After equilibrium was reached, the concentrations of the metal ions in the solution were determined by atomic absorption spectrometry. The amounts of metal ions adsorbed on HMnO(Mg) were determined from the concentrations relative to the initial concentrations in the solution. The K_d values were calculated using

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

Adsorption from Seawater

Seawater samples were taken a few kilometers offshore of Sakaide, Kagawa, Japan and filtered through a membrane filter (0.45 μm size).

The lithium concentration was 170 ppb (1 ppb = 1 μg/L). A known weight of HMnO(Mg) was immersed in 2 L seawater and stirred for a fixed time; then the HMnO(Mg) was collected by filtration and dried at 70°C. The collected sample was dissolved in a mixed solution of concentrated HNO_3 and HCl. Finally, the concentration of metal ions was determined by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Characterization of HMnO(Mg)

The magnesium and manganese contents of HMnO(Mg) were determined by atomic absorption spectrometry after HMnO(Mg) was dissolved in a mixed solution of concentrated HNO_3 and HCl. They were 0.6 and 58.0%, respectively, indicating that more than 90% of the magnesium was extracted from the $MgMn_2O_4$ by acid treatment.

The x-ray diffraction pattern of HMnO(Mg) is given in Fig. 1. The diffraction pattern of HMnO(Mg) was similar to that of HMnO(Li) in terms of the relative line position, but the diffraction lines were slightly broader. This indicates that acid treatment of $MgMn_2O_4$ leads to the formation of a manganese oxide with the same "spinel structure" found in HMnO(Li) (*14*). The spinel-type manganese oxide has vacant tetrahedral sites with a cubic close-packed oxygen framework (*28*). The broader diffraction lines indicate that the crystallite size of HMnO(Mg) is smaller than that of HMnO(Li).

Thermogravimetric (TG) and differential thermal analysis (DTA) curves are given in Fig. 1. The first weight loss corresponds to a loss of water with a maximum at 120°C. The water content of HMnO(Mg), which was calculated from the weight loss by heating at 400°C, was 12%; this value is larger than that of HMnO(Li) (4%). The broad exothermic peak around 250°C corresponds to a transformation from spinel type to γ-MnO_2, and the two endothermic peaks at 550 and 600°C correspond to a transformation from β-MnO_2 to α-Mn_2O_3 accompanied by an oxygen loss.

Distribution Coefficient

The equilibrium K_d values of alkali metal and alkaline earth metal ions at pH 8 are given in Table 1 for HMnO(Mg) as well as for HMnO(Ca),

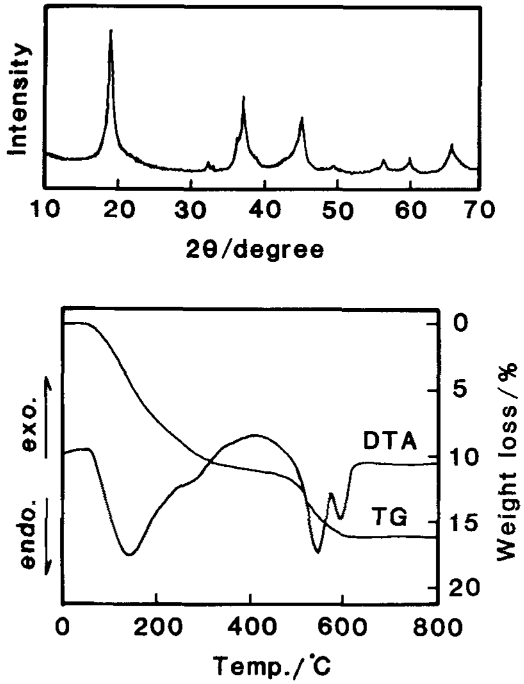

FIG. 1. X-ray diffraction pattern and DTA-TG curves of HMnO(Mg).

HMnO(Sr), and HMnO(Ba). The latter three samples were prepared by the same procedure as for HMnO(Mg) by using $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$, respectively, as doping agents. The selectivity sequence of alkali metal ions was $K \doteqdot Na < Li$ for all samples. However, HMnO(Mg) showed an extremely high selectivity for lithium ions; K_d(Li) was more than 400 times higher on HMnO(Mg) than on the other samples. The selectivity sequence of alkaline earth metal ions is $Mg < Ca < Sr < Ba$ for all samples. This is a "normal" sequence that is usually found for a strong acid ion-exchange resin (*29*).

The above results show that only HMnO(Mg) has an unusually high selectivity for lithium ions. It is interesting that HMnO(Mg) has a higher selectivity for lithium ions than magnesium ions, in spite of the fact that it is prepared with magnesium ions as the introducing ions. Since magnesium ions have a free energy of hydration that is about four times higher than for lithium ions (*30*), they may require larger energies in order to be dehydrated and to enter the micropores of HMnO(Mg).

TABLE 1
Distribution Coefficients on Different Types of Ion-Sieve Manganese Oxides at pH 8[a]

Sample	Distribution coefficients of metal ion (mL/g)						
	Li	Na	K	Mg	Ca	Sr	Ba
HMnO(Mg)	10,000	<1	<1	<1	130	200	280
HMnO(Ca)	5	<1	<1	<1	<1	3	70
HMnO(Sr)	25	<1	<1	11	35	43	207
HMnO(Ba)	25	14	<1	11	27	39	127

[a] HMnO, 100 mg; total volume, 25 mL; initial concentration of metal ions, 1 × 10^{-3} M in NH_4Cl-NH_4OH buffer.

Adsorption of Lithium from Seawater

We first examined the rate of lithium adsorption on HMnO(Mg) from seawater. Figure 2 illustrates the time course of lithium adsorption at 25°C.

Figure 3 illustrates the effect of the adsorption temperature on equilibrium lithium uptake from seawater. The lithium uptake increased slightly with increasing adsorption temperature between 5 and 35°C. The same tendency has been observed for lithium adsorption on HMnO(Li). The concentration of manganese ions in the supernatant was measured

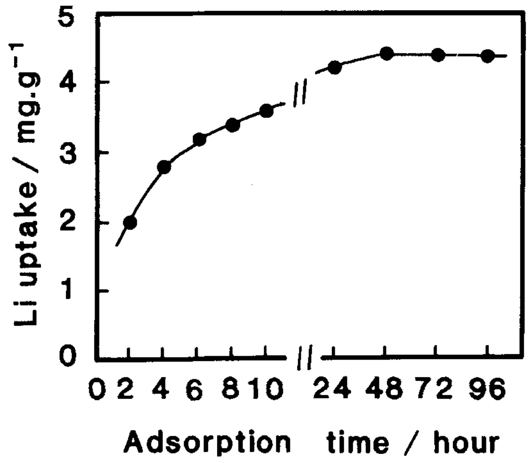

FIG. 2. Rate of lithium adsorption on HMnO(Mg) from seawater. HMnO(Mg), 50 mg; seawater, 2 L; 25°C.

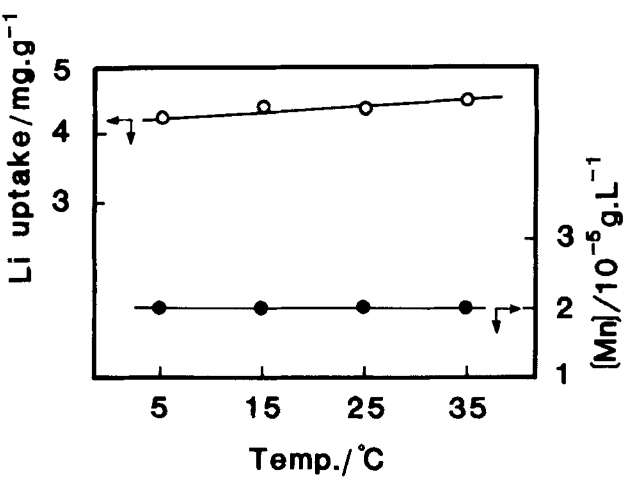

FIG. 3. Temperature dependence of lithium uptake by HMnO(Mg). HMnO(Mg), 50 mg; seawater, 2 L; adsorption time, 4 d.

by atomic absorption spectrometry. It was below 0.02 ppm between 5 and 35°C, indicating that the dissolution of HMnO(Mg) was less than 0.2%.

The pH dependence of lithium uptake was examined by adjusting the pH of seawater with a 0.1 *M* HCl or 0.1 *M* NaOH solution (Fig. 4).

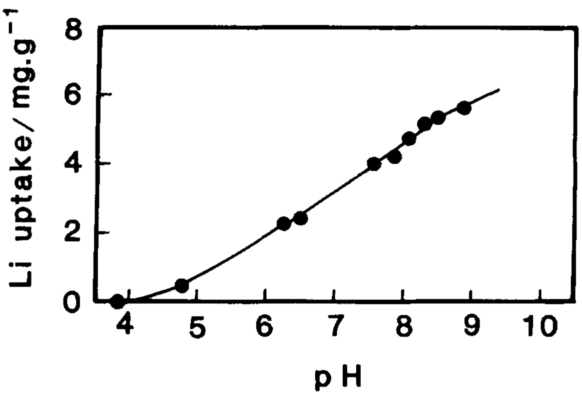

FIG. 4. The pH dependence of lithium uptake by HMnO(Mg). HMnO(Mg), 50 mg; seawater, 2 L; 25°C; adsorption time, 4 d.

HMnO(Mg) did not adsorb lithium ions at a solution pH below 3.8. Above pH 3.8, the lithium uptake increased with increasing solution pH and reached 5.6 mg/g at pH 8.9.

An adsorption isotherm of lithium on HMnO(Mg) was obtained by determining the lithium uptake at different ratios of the volume of seawater per gram of adsorbent at 25°C. The adsorption data followed Freundlich's equation with a slope of 0.7 (Fig. 5). The maximum lithium uptake in seawater can be estimated by extrapolating the adsorption isotherm to C_{Li} = 170 ppb. This is 8.5 mg/g, slightly higher than that by HMnO(Li) (7.8 mg/g). Up to the present, this value is the highest observed in a seawater system. The lithium content (1.8% as Li_2O) is about half that of such lithium ores as lepidolite (4%) and petalite (4%) (*31*).

Selectivity of the Elements in Seawater

The uptakes of alkali metal ions and alkaline earth metal ions by HMnO(Mg) and HMnO(Li) are given in Table 2. The uptakes of rubidium, cesium, and barium ions were found to be less than 0.1 mg/g. Concentration factors (C.F.'s) of metal ions were calculated by using the metal ion concentrations in seawater as follows:

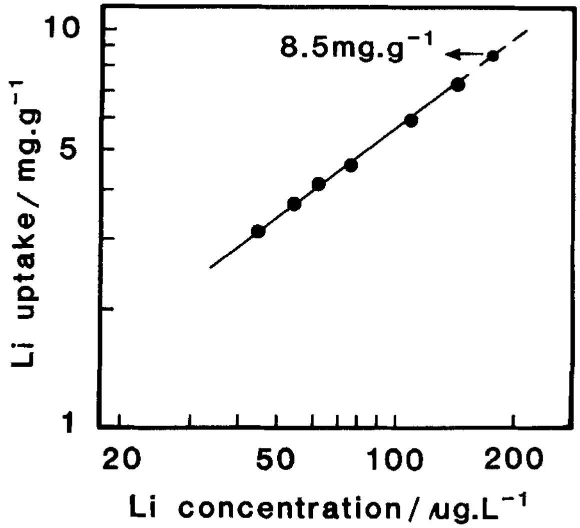

FIG. 5. Adsorption isotherm of lithium on HMnO(Mg). HMnO(Mg), 10–80 mg. The other conditions are the same as in Fig. 4.

TABLE 2
Metal-Ion Uptakes from Seawater[a]

Adsorbent		Metal ion					
		Li	Na	K	Mg	Ca	Sr
HMnO(Mg):	Metal-ion uptake (mg/g)	4.5	4.4	3.3	3.3	12.5	2.8
	Concentration factor (L/kg)	26,000	0.4	8.7	2.4	31.3	350
HMnO(Li):	Metal-ion uptake (mg/g)	4.4	7.0	1.0	5.0	2.1	2.5
	Concentration factor (L/kg)	26,000	0.7	2.6	3.7	5.2	310

[a] Adsorption: 2 L seawater/50 mg. Concentration factor (L/kg) = metal-ion uptake (mg/kg)/metal-ion concentration in seawater (mg/L).

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

Similarly to HMnO(Li), HMnO(Mg) had a remarkably high C.F. value of lithium ions compared with those of other metal ions. This indicates that the influence of major metal ions in seawater on lithium uptake is not very great. HMnO(Mg) showed a relatively high selectivity for calcium ions compared to HMnO(Li).

The x-ray fluorescence spectra of HMnO(Mg)'s before and after adsorption are given in Fig. 6. The spectra show that HMnO(Mg) adsorbs zinc, copper, nickel, and iron from seawater in addition to alkali metal and alkaline earth metal ions. The uptakes of these heavy metal ions were estimated by atomic absorption spectrometry to be less than 2 mg/g in total.

Elution of Lithium

The elution of lithium was studied by a batch method with HCl solutions of different concentrations. Figure 7 shows the time courses of lithium elution at 25°C. The rate of lithium elution was satisfactorily high; near equilibrium was obtained after shaking for only 8 h. The elution efficiency increased from 66 to 91% with an increase in HCl concentration from 0.002 to 0.25 *M*. However, there was a disadvantage in that the solubility of HMnO(Mg) increased with increasing HCl concentration. Losses of HMnO(Mg) were 0.7 and 6.9% at HCl concentrations of 0.002 and 0.25 *M*, respectively (the loss was estimated from the concentration of manganese ions in the supernatant). We think that the

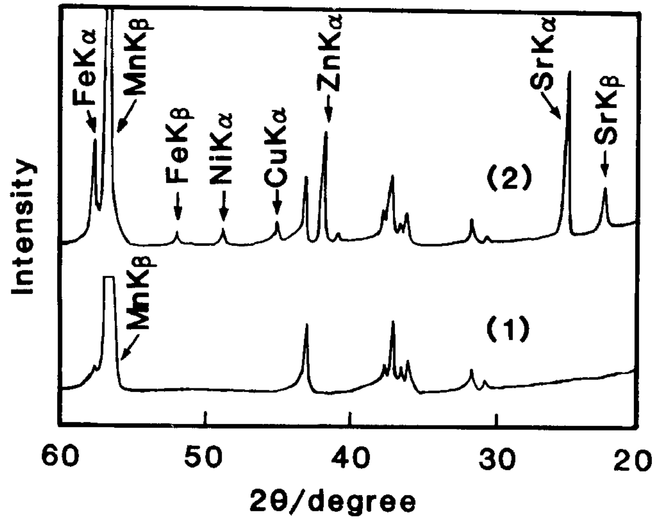

FIG. 6. X-ray fluorescence spectra of HMnO(Mg)'s: (1) original; (2) after adsorption. X-ray tube, W-target (50 kV, 40 mA); crystal, LiF; detector, S.C.

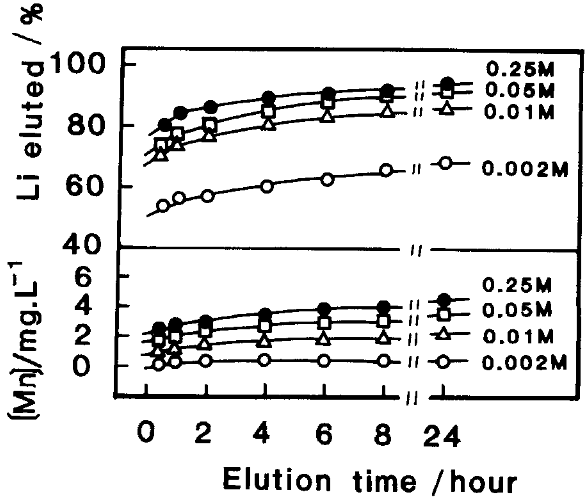

FIG. 7. Rate of lithium elution from HMnO(Mg). HMnO(Mg), 50 mg (lithium uptake 4.6 mg/g); HCl, 50 mL; 25°C.

dissolution of HMnO(Mg) can be decreased by using a suitable eluting agent or suitable elution conditions.

Adsorption/Elution Cycle

Five adsorption/elution cycles were carried out using seawater and a 0.01 *M* HCl solution. As shown in Table 3, the lithium uptake gradually decreased with repetitions of adsorption/elution cycles; the HMnO(Mg) after 4 cycles showed a lithium uptake that was about 60% that of the initial value. An x-ray diffraction analysis showed that the intensities of the diffraction peaks were weakened after 5 repetitions of adsorption/elution (Fig. 8). Therefore, the decrease in the lithium adsorptivity could be ascribed to the destruction of the spinel structure of HMnO(Mg). Since the destruction of the spinel structure may occur during an elution step due to the dissolution of HMnO(Mg), it may be depressed by adopting more suitable eluting conditions. The elution efficiency was always above 88% during 5 cycles.

CONCLUSION

A new type of ion-sieve manganese oxide, HMnO(Mg), is one of the most promising adsorbents for the recovery of lithium from seawater owing to its high selectivity for lithium in seawater and the ease of elution of lithium ions. Compared with HMnO(Li), HMnO(Mg) has an additional advantage in that one of the raw materials, $Mg(OH)_2$, can easily be obtained from seawater. A future problem is to develop a HMnO(Mg) with a higher chemical stability against adsorption/elution treatments.

TABLE 3
Changes of Lithium Uptake and Elution Efficiency during Repeated Adsorption/Elution Cycle[a]

	Number of cycle				
	1	2	3	4	5
Lithium uptake (mg/g)	4.5	4.1	3.7	3.3	2.7
Efficiency of lithium elution (%)	88	91	89	89	90

[a] Adsorption: 50 mg sample in 2 L seawater for 4 days. Elution: 50 mL of 0.01 *M* HCl for 6 h.

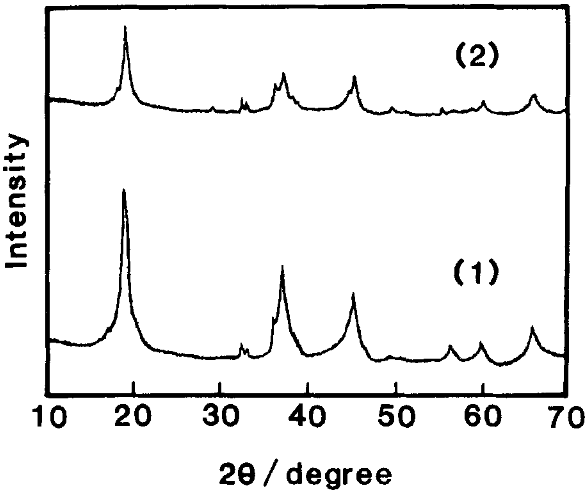

FIG. 8. Change in the x-ray diffraction pattern through repetitions of adsorption/elution: (1) original; (2) after 5 cycles of adsorption/elution.

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