Encapsulation of a powdery spinel-type Li⁺ ion sieve derived from biogenic manganese oxide in alginate beads

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Abstract

A powdery lithium ion sieve (HMO) derived from biogenic birnessite was homogeneously integrated in sodium alginate (AL) beads. The composite beads were then characterized and their Li^+ adsorption properties were investigated. Scanning electron microscopy–energy dispersive spectroscopy analysis showed that the HMO particles were homogeneously dispersed in the AL beads even after drying. The adsorption isotherm of Li^+ adsorption to HMO encapsulated in AL beads (HMO–AL) was well fitted by the linear Langmuir model, and the beads showed a maximum adsorption capacity of 3.61 mmol/g based on HMO, which is comparable with the value of the original powdery HMO. Kinetic studies revealed that adsorption of Li^+ follows a pseudo-second-order model with rate constant $k_2 = 2.8\text{--}11.9 \times 10^{-3} \text{ g}/(\text{mmol min})$ for the initial Li^+ concentration range 2.56–4.23 mM. Diffusion of Li^+ from aqueous solution to the HMO particle through the Ca–AL network is the rate-limiting step for Li^+ adsorption to HMO–AL beads. **The HMO-AL beads enhanced the handling efficiency for Li^+ adsorption and reused without significant reduction of Li^+ adsorption efficacy.**

Keywords: lithium ion sieve; lithium manganese oxide; alginate; biogenic birnessite; encapsulation.

1. Introduction

The increased use of the lithium ions (Li^+) for energy storage applications demands Li^+ ion recovery. Lithium-rich natural sources such as seawater and geothermal brine are future sources of lithium [1, 2]. Efficient and selective removal of Li^+ from aqueous solution has been achieved using delithiated lithium manganese oxide (LMO) spinels [3, 4]. Li^+ can be topotactically ion exchanged with H^+ in delithiated manganese oxides (HMOs) without changing their structure [5]. LMO spinels are usually synthesized by solid-state reactions using Mn salts, MnO_2 or MnOOH , manganese acetate as a precursor, and hydrothermal or detonation synthesis methods [3, 6–10].

Biogenic birnessite is a naturally occurring layered MnO_2 -type mineral produced through bio-oxidation of Mn(II) to Mn(III, IV) by bacteria or fungi [11–13]. Biogenic birnessite usually appears in diverse morphologies depending on the physicochemical properties of the culture and biological species [12, 14]. We have previously demonstrated synthesis of lithium-imprinted manganese oxide spinel using biogenic birnessite and applied its delithiated form (i.e., HMO) to the removal of Li^+ from aqueous solution. This method produced biotemplated HMO on fungal hyphae in a novel microtube-like shape, which maintained excellent performance as a Li^+ ion sieve even in the presence of 1000 mg/L Na^+ [14–17]. Li^+ ion sieves should be designed to enable their reuse, so separation must be facilitated after adsorption. The engineering aspects of modification of the sorbent need to be considered to overcome such practical difficulties.

Alginates (ALs) are biomolecules in algae that consist of polysugars containing β -(1→4)-linked D-mannuronic acid and α -(1→4)-linked L-guluronic acid residues [18]. ALs form hydrogels by networking with cations. AL beads containing silica–AL–fungi biocomposites [19], lanthanum carbonate [20], layered double hydroxides [21], hydroxyapatite [22] and iron nanoparticles [23] have been produced and used for remediation of a diverse range of

aqueous pollutants. However, Li^+ adsorption to AL composite beads has been scarcely reported in the literature. Recently, Song *et al.* investigated Li^+ adsorption to pure Ca–AL beads, and they found that these beads have a very low Li^+ adsorption capacity (1.2 mg/g) [24]. Integrated HMO in polyurethane has been successfully fabricated and the adsorption capacity of Li^+ is around 7.9 mg/g at pH 12 [25]. Fabrication of HMO in polyvinyl chloride has also been successfully performed, and the adsorption capacity of Li^+ is around 26.2 mg/g at pH 12 [26]. In these cases, the adsorption capacities for Li^+ always decreased after integration.

Herein, we report integration of biotemplated HMO in AL beads (HMO–AL). The HMO–AL beads were characterized by different physicochemical methods. The composite was investigated for removal of Li^+ from aqueous solution and the removal efficiency is compared with the precursor materials. The adsorption kinetics for the removal of Li^+ to HMO–AL were also investigated.

2. Experimental Methods

2.1 Preparation of powdery biogenic manganese oxide

Biogenic birnessite was prepared by fungal oxidation of Mn^{2+} by *Paraconiothyrium* sp. WL-2 strain [27]. In brief, 3 g of pregrown wet fungal tissue was inoculated in 1 L of a medium containing 0.6 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.07 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.65 g/L $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, 0.05 g/L peptone, 0.05 g/L yeast extract, and 4.5 g/L piperazine-*N,N'*-bis(2-ethane sulfonic acid) at pH 6.6 and 25 °C. After 7 days incubation, the dark brown solid mass obtained was collected by filtration, washed with ultrapure water to remove excess medium contents, and lyophilized. A sample of the powdery product (0.33 g) was resuspended in a specific amount of 20 mM LiCl to maintain a Li/Mn molar ratio of 1. The mixture was agitated at 200 rpm for 12 h, and then dried at 100 °C until complete evaporation of the liquid. The obtained Li^+ -

sorbed solid residue was calcined at 500 °C for 4 h. The calcined product was mixed with 0.1 M HCl at a solid to liquid ratio of 2 g/L and agitated for 12 h. After acid washing, the solid was separated by vacuum filtration using a membrane filter with a pore diameter of 0.2 µm and then freeze-dried to obtain powdery HMO.

2.2 Preparation of biogenic HMO–AL beads

About 0.4 g of biogenic HMO was suspended in 20 mL of water and continuously stirred for 1 h. Sodium alginate (0.3 g, 1.5 w/v %) was then added to the mixture under vigorous stirring at 60 °C for another 1 h. The homogeneous suspension was dropped in 200 mL of 0.2 M CaCl₂ solution using a disposable syringe needle with an inner diameter of 0.8 mm. The beads were aged in the same solution for 12 h, washed three times with decarbonized water, and stored in water prior to use. Similarly, blank AL beads were also prepared without HMO particles.

2.3 Li⁺ adsorption

Li⁺ adsorption isotherms were determined using a specific amount of wet blank AL beads (~0.56 g) or biogenic HMO–AL beads (~0.56 g containing approximately 20 mg HMO) in 20 mL of 4.23 mM LiCl at pH 8.5 buffered by NH₄Cl/NH₃. For comparison, Li⁺ adsorption to powdery HMO was also investigated under the same experimental conditions. The mixture was agitated at 100 rpm for 24 h at 25 °C, and the supernatant was separated and the remaining Li concentration was determined by atomic adsorption spectrometry (AAS, Thermo iCE 3400, Yokohama, Japan).

The Li⁺ adsorption kinetics were investigated using ~0.56 g of wet biogenic HMO–AL beads (approximately 20 mg HMO) mixed with 20 mL of solutions containing 2.56–4.23 mM LiCl at pH 8.5. The mixtures were agitated at 100 rpm for 0.5–96 h at 25 °C. The supernatant

was removed at different time intervals to determine Li^+ concentration by AAS. The adsorption isotherms were determined under the same conditions.

2.4 Reusability of biogenic HMO–AL beads on Li^+ adsorption

The cyclic-adsorption and desorption of Li^+ was performed on encapsulated HMO-AL beads to access the reusability. The Li^+ adsorption was performed using a specific amount of wet biogenic HMO–AL beads (~0.56 g containing approximately 20 mg HMO) in 20 mL of 4.23 mM LiCl along with 0.1 M CaCl_2 at pH 8.5 buffered by $\text{NH}_4\text{Cl}/\text{NH}_3$ for 24 h. The Li^+ adsorbed on HMO-AL beads was extracted using 40 ml mixture of 0.1 M HCl and 0.1 M CaCl_2 solution (to keep solid HMO to liquid ratio of 2 g/L) and agitated for 12 h. The cyclic Li^+ adsorption and desorption process was repeated up to five cycle.

2.5 Material characterization

Powder X-ray diffraction (PXRD) patterns of the synthesized materials were collected using a Rigaku Ultima IV diffractometer (Akishima, Japan) with $\text{CuK}\alpha$ radiation (40 kV, 40 mA) at a scanning speed of 2° min^{-1} with a 0.02° step size. Scanning electron microscopy (SEM) analysis of the wet HMO–AL beads was performed using a desktop Miniscope TM3030 Plus, (Hitachi, Tokyo, Japan). SEM elemental mapping analyses were performed by field-emission SEM–energy dispersive spectroscopy with micro calorimeter detector (SEM–EDS, Zeiss ULTRA55 + SII TES) using preheated HMO–AL beads stabilized in resin at 60°C overnight and then microtome cut with a diamond knife. Transmission electron microscopy (TEM) observation of the cross-sectional specimens was performed using a FEI TECNAI-20 transmission electron microscope (JEOL, Tokyo, Japan).

3. Results and Discussion

3.1 Characterization of HMO–AL beads

PXRD patterns of powdery HMO, HMO–AL, and AL are shown in **Fig. 1**. The powdery HMO shows a single phase proton-exchanged manganese oxide spinel structure without any impurity phases. The phase of HMO is fitted well by spinel type $\text{Li}_{0.48}\text{Mn}_2\text{O}_4$ (PDF Card No. 057-0720) because exchange of Li^+ by H^+ does not influence the crystal structure. The AL beads show a broad reflection at $2\theta = 41^\circ$ corresponding to the presence of amorphous biopolymer. The HMO–AL composite beads show only the HMO phase and amorphous AL is hidden behind the higher crystallinity of HMO.

Photographs of both the wet and dry forms of AL and HMO–AL beads are shown in **Fig. 2**. Encapsulation of HMO gave the AL beads a blackish color (**Fig. 2(c) and (d)**). The diameter of the wet beads was around 3 mm on average (**Fig. 2(a) and (c)**) and the beads shrank to 1 mm in diameter after drying for 24 h in air (**Fig. 2(b) and (d)**).

SEM images of the surface and cross-section of wet HMO–AL beads show that the distribution of HMO particles on the beads is homogeneous on both the surface and in the bulk (**Fig. 3**). The thin gel-like substances similar to folded sheets correspond to the Ca–AL network in which the HMO particles are entrapped (**Fig. 3(c) and (f)**). Powdery HMO formed octahedral crystals with clear edges on specific fungal hyphae, which can be called biotemplated HMO after calcination of biogenic birnessite (**Fig. 4(a)**). The biotemplated HMO microtubes have a wall thickness of ~ 300 nm and an inner diameter of ~ 1.5 μm . SEM images of the cross-section of dried beads show that HMO is almost homogeneously dispersed in the HMO–AL beads (**Fig. 4(b)–(h)**). However, the microtube morphology is not observed after HMO encapsulation in the AL beads and then drying. Encapsulation of HMO in AL was performed under continuous magnetic stirring of HMO particles in water, which may have destroyed the tube-like morphology. Secondary electron imaging shows that the

beads contain holes in the HMO part, which may be voids between HMO crystals. The homogeneous distribution of HMO particles on the AL beads offers high accessibility for Li^+ . Elemental mapping analysis of Mn on HMO–AL beads indicates that HMO is entrapped in the Ca–AL network. The overlapping elemental distributions of C and Ca in the dried beads suggest formation of a Ca–AL network by coordination of Ca to carboxyl groups of AL. The distribution of Mn also suggests that HMO is entrapped in the network. In addition, the oxygen distribution is similar to the superimposed elemental distributions of C and Mn because of the presence of oxygen in both AL and HMO.

EDS analysis shows that the Mn content in the composite is ~ 37.0 wt%, which is very close to the calculated value based on 57 wt% $\text{H}_4\text{Mn}_5\text{O}_{12}$ in the composite. This further confirms that $\text{H}_4\text{Mn}_5\text{O}_{12}$ particles are homogeneously distributed throughout the composite (**Fig. 4(h)**). In addition, the O content in the composite is ~ 44.7 wt%, which is in good agreement with the calculated value of 44.4 wt% based on a mixture of 57 wt% $\text{H}_4\text{Mn}_5\text{O}_{12}$ and 43 wt% calcium AL ($\text{C}_{10}\text{H}_{14}\text{O}_8(\text{COO})_2\text{Ca}$). The Ca content of 7.8 wt% is slightly higher than the calculated value of 4.4 wt%. All of the weight percentages were calculated by omitting H atoms, which were also excluded in EDS observations.

The TEM image of powdery HMO shows 20–40 nm rhombic particles (**Fig. 5(a)**). After encapsulation of HMO in AL, the TEM image of the cross-section of the composite beads of HMO shows that HMO particles seem to be homogeneously distributed (**Fig. 5(b)**). By enlarging the square red region in **Fig. 5(b)**, the particles are very similar to the original particles (**Fig. 5(a) and (c)**). Each HMO nanoisland is greatly spread in the Ca–AL network. It should be noted that the TEM images were observed using dried beads at 60 °C, which are about 1/3 of their original size. The reason why preheating of HMO–AL beads is necessary is to prevent separation of HMO–AL and the resin. To solidify the specimen in resin it must be

heated at 60 °C overnight. Therefore, in the original beads without heating, HMO nanoislands will be more spread than those in the dried beads.

3.2 Li^+ adsorption studies

Adsorption of 4.23 mM Li^+ to biogenic HMO–AL beads was performed by the batch method with a HMO to liquid ratio of 1.0 g/L. Adsorption of Li^+ to powdery HMO and AL are compared with HMO–AL in **Fig. 6**. Powdery HMO shows a maximum Li^+ adsorption capacity of 3.67 mmol/g. The HMO–AL beads optimized for HMO content show a Li^+ adsorption capacity of 3.59 mmol/g, corresponding to 2.06 mmol/g of dried HMO–AL composite bead. Therefore, the adsorption capacity is mostly maintained even after encapsulation of HMO in AL beads. Formation of AL beads involves coordination of Ca^{2+} ions to carboxylic groups of AL. The Ca^{2+} ions in the network structure can be ion-exchanged with other cations [28]. To understand the effect of the matrix on Li^+ uptake (blank test), Li^+ adsorption to AL beads was investigated. The AL beads show a very small amount of Li^+ adsorption of 0.17 mmol/g, which is comparable with Li^+ adsorption values reported in the literature [24]. These results suggest that adsorption of Li^+ to the HMO–AL composite mainly occurs by ion exchange of protons present in the HMO spinel. Using beads for Li^+ adsorption offers easier separation of spent sorbent from the adsorption medium than using powdery nanosized HMO particles.

3.3 Adsorption isotherm of Li^+

To determine the maximum adsorption capacity of HMO–AL composite materials, the adsorption isotherm was determined at 25 °C, as shown in **Fig. 7**. Normalizing the adsorbed amount of Li^+ to the HMO mass, the results of HMO–AL and powdery HMO are similar. The experimental data were fitted to the linear Langmuir equation [29]:

$$C_e/q_e = 1/(K_L q_m) + 1/q_m C_e \quad (1)$$

where q_e is the adsorbed amount of Li^+ mass per unit mass of adsorbent (mmol/g), q_m is the maximum adsorption capacity (mmol/g), C_e is the equilibrium Li^+ concentration (mmol/L), and K_L is the Langmuir constant (L/mmol). The results indicate that the adsorption isotherm is fitted well by the Langmuir model because of the high correlation coefficient (**Table 1**). The maximum Li^+ adsorption capacities according to Eq. (1) are 3.61 and 3.68 mmol/g for HMO–AL composite beads and powdery HMO, respectively. These values are also consistent with our previous results [14].

3.4 Kinetics of Li^+ adsorption

The kinetics of Li^+ adsorption to HMO–AL beads reveals that equilibrium adsorption of Li^+ is reached within 6 h at an initial Li^+ concentration of 2.56 mM (Fig. 8). However, the equilibrium time increases with increasing initial Li^+ concentration, and it takes 48 h to reach equilibrium at an initial Li^+ concentration of 4.23 mM. Our earlier observation showed that the kinetics of Li^+ adsorption to powdery HMO was very rapid and reached equilibrium within 1 h. The slower kinetics of Li^+ adsorption to HMO–AL compared with powdery HMO can be attributed to diffusion of Li^+ ions from the solution to HMO through the Ca–AL matrix. Diffusion of Li^+ through the Ca–AL network is the rate-limiting step for Li^+ adsorption to HMO–AL beads. The kinetic data were fitted with the pseudo-second-order model to understand the adsorption mechanism and the equilibrium time. The linear form of the pseudo-second-order equation is [30]

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t \quad (2)$$

A plot of t/q_t versus t gives a straight line, and the values of the kinetic constant k_2 (g/mmol min) and the equilibrium adsorption capacity q_e (mmol/g) are obtained from the observed intercept and slope of the curve. The results show that Li^+ adsorption to HMO–AL composite

beads is well fitted by the pseudo-second-order model because of the high correlation coefficient values (**Table 2**). The values of the apparent rate constants at different initial Li^+ concentrations are listed in **Table 2**. They show that the adsorption rate is higher for lower Li^+ concentration [31].

3.5 Reuse of biogenic HMO-AL beads for Li^+ adsorption

The change in the Li^+ adsorption sorption density with reuse time are shown in Fig. 9. The Li^+ adsorption capacity was decreased slightly with increase in the number of cycle. Which may be due to the slight dissolution of Mn^{2+} during the extraction of Li^+ using HCl solution. The Li^+ adsorption efficiency during reuse of HMO-AL beads is almost maintained and showed at above 90 % in the fifth cycle similar to the powdery HMO reported earlier [15]. It promising the use of alginate biopolymer for the encapsulation of HMO particles for Li recovery. It should be noted here, that the HMO-AL beads was exceptionally stable with the addition of CaCl_2 . The intension to the addition of CaCl_2 was to avoid the breakage of beads with the high concentration of NH_4^+ and H^+ present in the medium. In the absence of CaCl_2 the HMO-AL beads swelled and broken after second successive Li^+ adsorption-desorption cycles due to the formation of water soluble NH_4^+ - or H^+ - alginate complex by ion-exchange. The independent Li^+ adsorption experiments revealed that the addition of Ca^{2+} in the medium has little influence on Li^+ adsorption capacity. The Li^+ recovery from the real seawater may not need to be conditioned with CaCl_2 as it contains higher amount of Ca^{2+} in its composition. To conclude the HMO-AL beads enhances the handling efficiency and facilitate the reuse without compromising its adsorption capacity up to five cycles.

4. Conclusions

Biogenically derived HMO nanoparticles were successfully encapsulated in AL biopolymer. The fabricated HMO-AL composite beads were characterized by PXRD, SEM-

EDS, and TEM, and their Li^+ removal efficiency from aqueous solution was evaluated. SEM-EDS and TEM analyses of the sample showed that the HMO nanoparticles are homogeneously distributed at the nanoscale. Adsorption isotherm studies indicated that the HMO–AL composite beads have a maximum adsorption capacity for Li^+ of 3.61 mmol/g-HMO, which is comparable with the original powdery HMO. The kinetics of Li^+ adsorption follows the pseudo-second-order model. The equilibration time of the HMO–AL beads is slightly higher than that of powdery HMO. The rate-limiting step for Li^+ adsorption to the HMO–AL beads is diffusion of Li^+ ions from aqueous solution to the HMO particle through the Ca–AL matrix network. The composite beads will greatly facilitate to reuse by separation and handling after adsorption and desorption of Li^+ , compared with powdery HMO without significant reduction in the adsorption capacity.

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Figure captions

Fig. 1. PXRD patterns of the HMO–AL composite and the precursors. The inset is the pattern of AL beads in a narrow intensity range.

Fig. 2. Photographs of (a) wet and (b) dry AL beads, and (c) wet and (d) dry HMO–AL beads.

Fig. 3. SEM images of the surface (a)–(c) and cross-section (d)–(f) of wet HMO–AL beads at different magnification.

Fig. 4. SEM image of (a) powdery HMO and SEM-EDS image of cross-sectioned HMO–AL dried beads. (b) Energy selective backscattered electron image. (c) Secondary electron image. (d) SEM image for elemental mapping. Elemental mapping of (e) C, (f) O, (g) Ca, and (h) Mn.

Fig. 5. TEM images of (a) powdery HMO and (b) the cross-section of dried HMO–AL beads. The red square in (b) is magnified in (c).

Fig. 6. Comparison of the adsorption capacity of Li^+ to different materials. Initial Li^+ concentration 4.23 mM, volume 20 mL, mass of HMO 20 mg, mass of wet HMO–AL beads 0.56 g (corresponding to 20 mg HMO), pH 8.5, and time 24 h.

Fig. 7. Adsorption isotherms of adsorption of Li^+ to powdery HMO and HMO–AL beads. Mass of wet HMO–AL beads 0.56 g (corresponding to 20 mg of HMO), pH 8.5, and time 48 h.

Fig. 8. Kinetics of Li^+ adsorption to HMO–AL beads with initial Li^+ concentrations of 2.56–4.23 mM. Inset: pseudo-second-order kinetics model linear plot.

Fig. 9. Change in the Li^+ adsorption capacity to HMO-AL beads with reuse time. For adsorption: Initial Li^+ concentration 4.23 mM in 0.1 M CaCl_2 , volume 20 mL, mass of wet HMO–Al beads 0.56 g (corresponding to 20 mg HMO), pH 8.5, and time 24 h. For desorption: 40 ml mixture of 0.1 M HCl and 0.1 M CaCl_2 for 12 h.

Table 1 Langmuir parameters of lithium adsorption to powdery HMO and HMO–AL beads.

Adsorbents	q_{obs} (mmol/g)	q_{max} (mmol/g)	K_L (L/mmol)	R^2
Powdery HMO	3.67	3.68	151.0	0.9999
AL-HMO beads	3.59	3.61	73.5	0.9954

Table 2 Kinetics parameters of Li^+ adsorption to HMO–AL beads for different initial Li^+ concentrations.

Initial $[\text{Li}^+]$ (mM)	q_e (mmol/g)	k_2 (g/mmol min)	R^2
2.56	2.61	0.0062	0.9998
3.43	3.10	0.0028	0.9960
4.23	3.88	0.0119	0.9982

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Graphical Abstract

Alginate encapsulated Li^+ ion sieve