Capturing Lithium from Wastewater Using a Fixed Bed Packed with 3-D MnO₂ Ion Cages

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S Supporting Information

INTRODUCTION

Lithium (Li) is a critical material for energy-related technologies.¹ Accordingly, there has been increasing demand for lithium and Li compounds, particularly in the rapid expansion of rechargeable lithium ion batteries (LIBs).^{2,3} We are now facing a contraction the of the Li supply and increasing demand. Currently, approximately 200–500 MT of spent LIBs are produced each year.⁴ The Li content in spent LIBs is 2–7 wt %, which is an important resource of lithium. Effective and efficient recovery of Li could become very important because it not only can relieve Li shortages but also can resolve environmental pollution problems caused by spent LIBs. Additionally, research on lithium recovery from LIBs has attracted considerable interest in recent years.^{5–7} Conventional technological approaches, including nanofiltration and electrolysis, have been used to remove lithium from wastewater.⁸ According to Tsuruta, the biological recovery of Li(I) can also be achieved using various microorganisms.⁹ However, precip-

itation is the most common technology used for lithium recovery. However, precipitation is difficult to use on lithium wastewater with high Mg/Li contents because Li₂CO₃ is highly soluble (approximately 1.3 g/100 mL H₂O).¹⁰ Adsorption is one of the most promising methods for lithium recovery from lithium wastewater because it is one of the most cost-effective and environmentally friendly methods.¹¹

The adsorbent plays a vital role in determining the performance of packed bed adsorption systems; however, the majority of adsorbents have a lower adsorption capacity for smaller cations, such as Li.¹² Moreover, many adsorbents have been used to remove Li(I) but with low capacities. Abe and Chitrakar¹³ synthesized an adsorbent, called the LiSbO₃,

Received: May 5, 2016

Revised: October 21, 2016

Accepted: October 24, 2016

Published: October 24, 2016

precursor, and found that the adsorption capacity is only 1.0–1.4 mg/g. Bauman and Burba¹⁴ prepared a $\text{LiCl} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ -type adsorbent, which exhibited a Li(I) adsorption capacity of 2–3 mg/g. Song et al.¹⁵ investigated the Li(I) adsorption capacity of D751 resin and found that the maximum adsorption capacity was also only 20.82 mg/g and that the Li selectivity was poor as compared to other cations. The waste streams for Li recovery contains large amounts of interfering metal ions such as K, Na, Ca, Mg, Zn, Co, Cr, Cu, Al, Ni, Pb, and Cd, and the process stream is usually alkaline.¹⁶ Therefore, high-capacity and selective adsorbents must be developed to selectively separate Li(I) from wastewater that contains a variety of cations.

Ionic-cage^{17,18} adsorbents possess a “memory effect” and that makes them ideal for extracting target ions with an extremely high selectivity. The specific adsorption sites for 3-D MnO_2 ionic cages (CMO) were prepared by removing target ions from a stable inorganic solid that contain Li in the lattice. The ionic-cage adsorbents have the advantages of low toxicity and high chemical stability,^{19,20} but they have the disadvantage of slow adsorption kinetics. CMO have (1) high selectivity for Li(I) in the presence of competing ions, (2) high adsorption capacity, and (3) a fast adsorption kinetics. These attributes are the result of 8a-16d-8a channels in a three-dimensional interstitial space provided by the $-\text{Mn}-\text{O}-\text{Mn}-\text{O}-$ framework in the $\text{Li}_4\text{Mn}_5\text{O}_{12}$ spine.

The adsorption maximum capacity (Q_0) increases because CMO is endothermic adsorbent. Previous studies have not examined the relationship between Q_0 and T . We explored the relationship between Q_0 and T using the Dubinin-Ashtakhov (DA) Site Energy Distribution model. The increase of the adsorption capacity with temperature adsorption is important for Li(I) removal, because wastewater from southern China can be considerably warmer than wastewater from northern China.

We investigated the performance of a CMO adsorbent for Li(I) removal. To examine the practical applications of the CMO, fixed bed adsorption experiments and a mathematical model were developed.²¹ Some of the classical models include those developed by Thomas,²² Bohart and Adams,²³ Clark,²⁴ and Yoon and Nelson.²⁵ These models typically have simple mathematical solutions. However, they are empirical models, which limits their ability to predict the performance of full-scale adsorption treatment systems. Accordingly, we used the pore diffusion model (PDM)²⁶ to predict and validate small column breakthrough data. Thus, we can use the model to predict lithium breakthrough in full-scale adsorption systems. In brief, our goal is to (1) explore the specific relationship between the Li adsorption capacity (Q_0) and temperature (T), (2) verify a model that can predict the fixed bed performance for removal Li, and (3) provide specific guidance for engineering application.

MATERIALS AND METHODS

Chemicals and Materials. The sources and grades of the chemicals used in this study are provided in Section S1, and the characterization methods are provided in Section S2. Synthetic Li solutions of different concentrations were prepared in DI water for adsorption isotherm, kinetic studies, and shorter column fixed-bed experiments. The solutions with the concentration of 200 $\mu\text{g/L}$ of Li, Na, K, Ca, and Mg, pH = 10, TOC = 48.6 mg/g, were used for competitive adsorption experiments and IX model because Na, K, Ca, and Mg ions have a similar ionic radius. The concentration of all ions was

adjusted to 200 $\mu\text{g/L}$ in order to better study selective adsorption experiments.

Synthesis of 3-D MnO_2 Ion Cages. The process for preparing the 3-D MnO_2 ion cages is described in detail in Section S3. In brief, the 3-D MnO_2 ion cages (CMO) were prepared using a two-step process (Figure 1). First, $\text{Li}_4\text{Mn}_5\text{O}_{12}$

Figure 1. Preparation of the lithium ion cages (CMO).

(LMO) precursor particles were prepared by hydrothermal synthesis via a low-temperature solid-phase reaction. The LMO particles were then washed with aqueous solutions of HCl to remove the Li(I) ions to prepare a selective adsorbent with Li(I) transport channels. These channels consist of interconnected 3-D MnO_2 ion cages within the 3-D lattice of the $\text{Li}_4\text{Mn}_5\text{O}_{12}$ spinels within each adsorbent particle.

Adsorption Isotherm Procedure. Adsorption isotherms were obtained by shaking a mixture containing 20 mg of CMO and 20 mL of the Li(I) solution at pH 10.1 using an incubator shaker at 160 rpm. The adsorption isotherms of Li(I) were obtained at temperatures of 20, 30, and 40 °C. The initial concentrations of Li(I) ranged from 20 to 500 mg/L. After being shaken for 12 h, the resulting mixture was centrifuged at 12 000 rpm (which resulted in 22 550g) to remove the adsorbent. The concentrations of Li(I) in the supernatant before and after adsorption were measured using atomic absorption spectrometry (AAS). The adsorption capacity of the Li(I) ion was calculated using eq 1:

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

where q_e (mg/g) denotes the equilibrium adsorption capacity, C_0 and C_e are the initial and equilibrium concentrations (mg/L) of Li(I), respectively, V is the volume (mL) of adsorption solution, and m is the mass (mg) of the adsorbent.

Adsorption Selectivity. The selectivity of Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} ions with respect to H^+ ions was determined. Fifty milligrams of CMO was mixed with a 50 mL water solution containing competing ions with a concentration of approximately 200 $\mu\text{g/L}$ and pH 10 at 20 °C. The adsorption equilibrium was reached after 12 h of shaking, and the ion concentrations were determined using AAS. In a multi-

component system, separation factors can be converted to different reference ions by using eqs 2 and 3:

$$\alpha_k^i = \alpha_j^i \times \alpha_k^j \quad \left(\alpha_j^i = \frac{q_i C_j}{C_i q_j} = \frac{y_i x_j}{x_j y_i} \right) \quad (2)$$

$$x_i = \frac{C_i}{\sum_{k=1}^m C_k}, \quad x_j = \frac{C_j}{\sum_{k=1}^m C_k}$$

$$y_i = \frac{x_i}{\sum_{k=i}^n (x_i \alpha_i^k)}, \quad y_j = \frac{x_j}{\sum_{k=j}^n (x_j \alpha_j^k)} \quad (3)$$

where α_k^i is separation factor of counterion i with respect to ion k , unitless; q and C represent the equivalent solid phase and liquid phase concentration (mg/L) for ions i and j , respectively; x and y represent the liquid phase and the solid phase equivalent fraction or mole fraction of ions i and j , unitless; i denotes the counterion; j represents the presaturant ion.

Continuous Flow Fixed-Bed Column Adsorption Experiments. A short bed adsorber (SBA) test was conducted to validate the calculated k_f and D_p values.^{27,28} In the SBA test, a column was packed with a CMO. It has a bed depth of 0.9 cm (a mass of 0.65 g) and a diameter of 1.3 cm. The bed had an empty bed approach velocity of 0.09 m/h and had an influent lithium concentration, C_0 , of 200 $\mu\text{g/L}$. The exhausted Li^+ on the CMO column was desorbed using 0.1 mol/L HCl solution and a flow rate of 1.0 mL/min.

Determining the Parameters for Pore Surface Diffusion Modeling. The PSDM assumes that intraparticle mass flux is described by surface and pore diffusion and adsorption equilibrium of individual compounds can be represented by the Freundlich isotherm equation. On the basis of the Gnielinski correlation,²⁹ the external mass transport coefficient (k_f) was estimated using eqs S1–S3 in Section S4. The pore diffusion coefficient (D_p) was estimated using eq 4.³⁰

$$D_p = \frac{\varepsilon_p \times D_1}{\tau} \quad (4)$$

The variable τ was estimated by (eq 5) for electrolyte solutions using the following expression.³¹

$$\tau = \frac{(2 - \varepsilon_p)^2}{\varepsilon_p} \quad (5)$$

where τ is the tortuosity factor and ε_p is the particle porosity ($\varepsilon_p \approx 0.741$). This equation yielded a τ of 2.14 with an estimated D_p of $1.603 \times 10^{-10} \text{ m}^2/\text{s}$. We assumed that the surface diffusion coefficient was equal to zero because the Li ions could not be transported down the surface of the CMO and were transported into the ion channels for removal. Thus, in actuality, we used the pore diffusion model (PDM) to predict the lithium breakthrough curve.^{26,32,33} PDM simulations were conducted using the AdDesignS software (Michigan Technological University).³⁴

The wall effect on mass transfer can be neglected for d_{column}/d_p ratios >20 .^{35,36} The relative importance of the internal (pore) and external (film) mass transport resistances was evaluated using the pore Biot number (B_{ip}) (eq 6) according to Sontheimer et al. as follows:²⁹

$$B_{\text{ip}} = \frac{k_f \times d_p}{2 \times D_p} \quad (6)$$

The calculated value of B_{ip} was 29.8. Accordingly, intraparticle diffusion controls the overall mass transport of the system because $B_{\text{ip}} \geq 20$.³⁷

The maximum number of bed volumes (BV_{MAX}) (eq 7) could be estimated according to Sontheimer et al. as follows:³⁰

$$BV_{\text{max}} = \frac{q_0 \times \rho_{\text{BED}}}{C_0} \quad (7)$$

where ρ_{BED} is the bed density of the media in the packed bed (g/cm^3) and q_0 is the adsorption capacity calculated at C_0 .

RESULTS AND DISCUSSION

As discussed below, we evaluated CMO adsorbent performance for different concentrations, different temperatures, and pH values using isotherm tests, kinetic studies, and fixed bed experiments. With respect to adsorption thermodynamics, we determined the Li site energy distribution using various adsorption isotherm models and data. We verified the PDM by comparing it to batch kinetic and fixed bed experiments. We used the verified model to predict full scale performance and the impact of competing ions on the recovery of Li ion. In addition, we determined the recovery of Li using fixed bed adsorption by conducting adsorption and regeneration experiments.

Adsorbent Characterization. The pore size distribution is shown in Figure S1. The specific surface area (BET) of CMO was approximately $54.1 \text{ m}^2/\text{g}$ (see the figure inset). The XRD patterns of the MO, LMO, and CMO particles are shown in Figure 2. The crystal phases of MO, LMO, and CMO are pure

Figure 2. XRD patterns of MnO_2 oxide (MO), $\text{Li}_4\text{Mn}_5\text{O}_{12}$ trioxide precursor (LMO), and MnO_2 ion cages (CMO).

tetragonal phase (T) $\beta\text{-MnO}_2$ (according to JCPDS 24-0735), pure cubic phase (C) $\text{c-Li}_4\text{Mn}_5\text{O}_{12}$ (according to JCPDS 46-0810), and $\lambda\text{-MnO}_2$ (according to JCPDS 44-0992), respectively. The substitution of H for Li in the lattice causes the crystal cell to shrink, whereas the crystal skeletons of LMO and CMO remain unchanged. As a result, the $-\text{Mn}-\text{O}-\text{Mn}-\text{O}-$ skeleton will be extremely stable during adsorption because the lattice clearance contains vacancies with a high charge density, forming a strong electrostatic field and are the perfect size for Li ions. Thus, the MnO_2 ion cages can adsorb the

lithium ions. Figure 3 shows the SEM micrographs of the obtained samples. Figure 3a,b illustrates that the MO nanorods

Figure 3. (a, b) SEM images of MO; (c, d) SEM images of LMO and CMO, respectively.

are delicate, smooth, and uniform before calcination. In Figure 3c, the resulting LMO particles from the calcined MO are still nanorods. Figure 3d clearly illustrates that CMO maintains a similar morphology as LMO. However, the magnified view shows that the CMO nanorods are partially cracked, and the surface is coarse. The particle surface appears to be partially dissolved during the acid wash that removes Li ions (pickling process). This phenomenon was confirmed by the results of the XRD analysis, shown in Figure 2.

As shown in Figures 3 and S1, the LMO and CMO have a high degree of porosity and large pores between the nanorods, which increases the intraparticle pore diffusion and reduces the impact of counter diffusion. The lack of pore connectivity (nanorods contacting one another as opposed to a solid support that contains pores) and strong electrostatic interaction between ions and the surface eliminates surface diffusion to the intraparticle transport flux. As shown below, liquid-phase pore diffusion is rapid and produces a steep breakthrough curve.

XPS Analyses. The chemical composition of the CMO before and after Li adsorption was measured using X-ray photoelectron spectroscopy (XPS). As shown in Figure 4a,b, the peaks corresponding to Mn 3p, Li 1s, O 1s, and Mn 2p are distinct. The XPS spectrum of Mn 2p is plotted in Figure 4c,d. Two peaks located at 642.1 and 653.8 eV correspond to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively, with a spin energy separation of 11.7 eV, which is consistent with the well-characterized MnO₂ XPS spectra in the literature.³⁸ The ratio of the Mn/O atomic concentration (Mn: 25.89%; O: 51.72%) is 1:2, indicating the dominance of Mn⁴⁺ in the CMO. There was no change in the proportion of O_{ad}/O_{latt} before and after Li adsorption (Figure 4e,f), which was approximately 48.2% on the CMO, after Li adsorption, indicating that the chemical environment is stable and unaffected by the adsorbed Li(I). Figure 4g,h was the XPS spectrum of Li 1s. In Figure 4h, the appearance of the Li 1s peak at the binding energy of 54.9 eV indicates that Li(I) is adsorbed on the CMO. This finding indicates stability of the Mn–O bond, which plays an indispensable role in forming Li cages and has a high charge density. The high charge density forms a strong electrostatic field, which aids in the adsorption of Li(I). Researchers believe that there are three mechanisms that explain the adsorption

Figure 4. XPS characterization of CMO before and after Li(I) adsorption. (a, b) XPS survey spectra of the samples, high-resolution XPS spectra of (c, d) Mn 2p, (e, f) O 1s (O_{latt} (lattice oxygen), O_{ad} (adsorb oxygen), and O_{H₂O} (chemisorbed oxygen species)), and (g, h) Li 1s before and after Li(I) adsorption, respectively.

behavior of Li in ion cages: (i) redox reactions;³⁹ (ii) ion exchange;⁴⁰ (iii) a complexation mechanism from a redox reaction during ion exchange.⁴¹ Our results demonstrate that the Mn valence cannot be reduced when CMO adsorbs Li(I), which was confirmed by XPS (Figure 4c,d). Consequently, the adsorption of Li on the CMO is an ion exchange reaction, which is in good agreement with the results of the analysis using the D-R isotherm model.

Effect of Initial Concentration and Temperature. Figure 5 shows the adsorption isotherms of Li(I) on CMO for three

Figure 5. Adsorption isotherm at different temperatures for Li(I) adsorption on CMO. The initial Li(I) concentration ranged from 20 to 450 mg/L. Adsorbent dose: 1g/L; total solution volume: 20 mL; pH: 10.1; temperature: 20, 30, and 40 °C.

temperatures, i.e., 20, 30, and 40 °C. The adsorption capacity of Li(I) on the CMO increases with increasing concentration and temperature. Moreover, the maximum equilibrium adsorption capacity is approximately 61.32 mg/g at equilibrium concentration of about 300 mg/L at 40 °C, which is higher than those reported for other lithium ion-cage adsorbents. For example, the adsorption capacity is 20.82 mg/g for D751 resins,¹⁵ 17.0 mg/g for $\text{H}_{2.0}\text{Li}_{0.1}\text{Mn}_{4.0}\text{O}_{7.8} \cdot 0.22\text{H}_2\text{O}$,⁴² 31.23 mg/g for LiAlMnO_4 ,⁴³ and 41.36 mg/g for $\text{Li}_4\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_4$.⁴⁴ Hence, the CMO exhibits a significantly higher adsorption capacity than these other adsorbents. Additionally, the maximum Li(I) adsorption capacity on CMO is 15 times greater than on $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-IIP}$ (4.1 mg/g).¹⁶ In addition, the synthesis cost of the CMO adsorbent is much less than $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-IIP}$, which makes industrial lithium recycling more feasible. The adsorption capacity also increased with the increasing temperature, suggesting that the adsorption of lithium is endothermic.

Effect of pH. pH plays an important role in determining the performance of an adsorbent. Figure S2 shows that the adsorption capacity of Li(I) increases with increasing pH. When the pH is below pH 4.0, the adsorption capacity is low due to the protonation of the $-\text{OH}$ group, when the pH is higher than pH 4.0, high adsorption capacity of Li⁺ is observed. The maximum adsorption capacity for Li(I) was obtained at a pH of 12.95. The CMO ion exchange/adsorption site is an $-\text{OH}$ group and can exchange the H^+ for Li(I). At high pH, the $-\text{OH}$ group ionizes and adsorbs Li(I).⁴⁵

Adsorption Selectivity. Competitive adsorption experiments of Li⁺, Na⁺, K⁺, Mg²⁺, and Ca²⁺ were conducted to determine the selectivity of these ions on CMO. The selectivities are summarized in Table 1. As can be seen in Table 1, the CMO exhibit a much higher selectivity separation factor (α_k^i) and affinity of Li(I) as compared with other competitive ions. Hence, the CMO exhibits a higher selectivity toward Li(I) than

Table 1. Selectivity of Various Ions for CMO

metal ions	ionic radius (pm)	α_k^i
Li(I)	76	118.48
Na(I)	102	1.68
K(I)	138	2.35
Mg(II)	72	28.21
Ca(II)	100	49.09

other ions that may be found in wastewater. At approximately 0.7 Å, the three-dimensional (1 × 3) tunnels in the spinel lattice are a suitable size for adsorbing lithium ions in the CMO nanocrystal cubic phase.⁴⁶ In other words, lithium ions can be adsorbed in three-dimensional (1 × 3) tunnels, which have a strong electrostatic field, whereas other larger metallic ions can only be adsorbed to a lesser extent on the surface sites. The ion cages had a higher selectivity for Li⁺ than for Mg²⁺, despite their similar ionic sizes and different valence.

In general, multivalent ions tend to have higher selectivity than monovalent ions. Because the hydration energy of Mg²⁺ is approximately 4 times larger than that of Li⁺ (Mg(II)_{hydration energy} = −455 kcal/mol vs Li(I)_{hydration energy} = −122 kcal/mol),⁴⁷ a higher energy would be required for dehydration to enter the cavity of lithium ion cages. Accordingly, it is easier to remove the water of hydration from Li(I), which results in a higher selectivity for Li(I) ions. Therefore, there are 2 criteria that must be met for adsorption to occur in the three-dimensional tunnels: (1) the ion must fit and (2) the adsorption free energy must be greater than dehydration energy which is required to removal the water of hydration. The dehydration energy causes Li adsorption to be endothermic.

Adsorbent Regeneration in a Batch Reactor. A good adsorbent should have superior desorption and regeneration performance. The regeneration of Li(I) was desorbed using 0.1 mol/L HCl solution; the adsorbent was separated and washed with deionized water and then dried. After that, regenerated CMO was placed into a lithium adsorption solution (the experiment is similar to the isotherm procedure). To assess the CMO's performance, the CMO adsorbent was subjected to six repetitive adsorption–desorption cycles for the removal of Li(I) ions from aqueous solutions. As shown in Figure 6, the adsorption capacity for Li(I) decreased slightly after each regeneration, and the adsorption capacity of the CMO for the sixth adsorption–desorption cycle for Li(I) was only 7.6% less than that for the first cycle. During the adsorbent regeneration, the lost Mn can destroy the 3-D tunnel in the spinel structure,

Figure 6. Regeneration cycles of CMO. Adsorbents mass: 200 mg; initial Li(I) concentration: 300 mg/L; pH: 10.1; temperature: 30 °C.

which can cause a decrease in the adsorption capacity. These results demonstrate that the CMO can be reused for a large number of adsorption–desorption cycles.

Adsorption Isotherm Models. The Langmuir and Freundlich isotherm models, shown here, respectively, were used to fit the CMO isotherm data.

$$q_e = \frac{Q_0 k_L C_e}{1 + k_L C_e} \quad (8)$$

$$q_e = k_F C_e^{\frac{1}{n}} \quad (9)$$

where q_e (mg/g) and C_e (mg/L) are the amount of lithium adsorbed at equilibrium and the equilibrium concentration, respectively. k_L (L/mg) is the equilibrium constant and Q_0 is the maximum adsorption capacity. k_F and $1/n$ are the capacity factor and intensity for the Freundlich isotherm equation.

The isotherm parameters that were determined by fitting the data in Figure 5 are summarized in Table 2. A comparison of

Table 2. Langmuir and Freundlich Parameters for Li(I) Adsorption on CMO

T (°C)	equations					
	Langmuir model			Freundlich model		
	Q_0 (mg/g)	k_L (L/mg)	R^2	$1/n$	k_F ($\text{mg}^{1-(1/n)} \text{L}^{1/n}/\text{g}$)	R^2
20	56.05	0.013	0.9756	0.45	2.854	0.9837
30	71.22	0.011	0.9737	0.51	3.216	0.9879
40	76.80	0.012	0.9798	0.58	3.777	0.9902

the correlation coefficients (R^2) illustrates that the Freundlich equation described the data slightly better than the Langmuir equation, suggesting that the adsorption of Li(I) on CMO occurs on sites that have a distribution of site energies (i.e., heterogeneous site energies). In contrast, the Langmuir equation assumes that all of the site energies are identical.

Adsorption Site Energy Thermodynamics. We used the Dubinin-Radushkevich (D-R) isotherm⁴⁸ to determine whether the adsorption process originated from physical (Van der Waals) or chemical (surface reaction) forces. The D-R isotherm is given by eq 10:

$$\ln q_e = \ln Q_0 - \beta \epsilon^2 \quad (10)$$

where q_e is the amount of metal ions adsorbed on the adsorbent per unit weight (mol/g), Q_0 is the maximum adsorption capacity (mol/g), β_{DR} is the activity coefficient related to the mean free energy of adsorption (mol^2/J^2), and ϵ (J/mol) is the Polanyi potential ($\epsilon = RT \ln(1 + 1/C_e)$). The D-R isotherm model fit the equilibrium data well ($R^2 > 0.99$, Figure S3 and Table S1). The intercept of the plots for 20, 30, and 40 °C yield q_m values of 5.81, 6.21, and 6.91 mol/g, respectively. The mean free energy of adsorption, E (kJ/mol), is determined using eq 11:

$$E = (2\beta_{DR})^{-1/2} \quad (11)$$

The mean free adsorption energy was approximately 8.6 kJ/mol, which is in the energy range of an ion-exchange reaction (i.e., 8–16 kJ/mol).⁴⁹

Thermodynamic calculations were performed to further explain the endothermic nature of the process. The thermodynamic parameters (namely, the Gibbs free energy

(ΔG^0 , kJ/mol), enthalpy (ΔH^0 , kJ/mol), and entropy (ΔS^0 , kJ/mol K)) were estimated by eqs 12 and 13, respectively:⁵⁰

$$\Delta G^0 = -RT \ln K \quad (12)$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \times \frac{1}{T} \quad (13)$$

where R is the universal gas constant (8.314 J/mol K) and T is the temperature (K). K is the thermodynamic equilibrium constant in the adsorption process, which was determined using the method of Khan and Singh⁵¹ by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero q_e .

On the basis of eq 13, the thermodynamic parameters of ΔH^0 and ΔS^0 can be determined from the slope and the intercept, respectively, as shown in Figure S4 and Table S2. The positive value of ΔH^0 (11.34 kJ/mol) proves that the adsorption process is endothermic between 20 and 40 °C. The positive value of ΔS^0 (0.08 kJ/mol K) suggests that the degree of randomness increases during Li(I) adsorption. This may be due to the loss of the water of hydration from the Li. The ΔG^0 was calculated to be −12.20, −13.05, and −13.77 kJ/mol for 20, 30, and 40 °C, respectively, indicating that Li(I) adsorption is thermodynamically favored. A smaller negative ΔG^0 indicates that adsorption is less favored thermodynamically. Moreover, ΔG^0 became more negative (the absolute value of ΔG^0 increased) as temperature increased at the same adsorbate loading, suggesting that the driving force of the adsorption increased with increasing temperature, which is consistent with the adsorption capacity increasing with increasing temperature. This conclusion is in good agreement with the results obtained from the D-R isotherm model.

Dubinin-Ashtakhov (DA) Model-Based Site Energy Distribution. The Polanyi theory⁵² assumes that the adsorption potential is independent of temperature, and application of the theory describes the adsorption process. The nonlinear DA model based on Polanyi theory was used to fit the experimental isotherm data according to eq 14:

$$\log Q_e = \log Q_0 - (\epsilon_{sw}/E_d)^b \quad (14)$$

where Q_e (mg/kg) is the amount of adsorbate compared to adsorbent, Q_0 (mg/kg) is the maximum adsorption capacity, $\epsilon_{sw} = RT \ln(C_s/C_e)$ (J/mol) is the effective adsorption potential, C_s (mg/L) is the water solubility of the adsorbate, C_e (mg/L) is the equilibrium concentration of the adsorbate in the liquid phase, E_d (J/mol) is the “normalized constant”, and b is the empirical isotherm fitting parameter.

The adsorption capacity results from the adsorption onto adsorption sites that have distribution of energies $F(E^*)$ (see Section S5) and is given by eqs S5–S8. Because the resulting site energy distributions are not normalized, the area under the distribution is equal to the maximum adsorption capacity, Q_0 .

Figure S5a and Table S3 illustrate that the experimental data fit the DA model well ($R^2 > 0.99$). The site energy distributions were all unimodal distributions at different temperatures, as shown in Figure S5b. With increasing site energy (E^*), the frequency function $F(E^*)$ increased until it reached the $F(E^*)$ peak apex, after which it decreased to approach zero. Theoretically, the area under the peak represents the number of available adsorption sites in a specific energy range. Increasing the temperature from 20 to 40 °C increased the area under the peak. The affinity of Li for the CMO surface was related to the position of the energy distribution mean on the energy axis.⁵³ A larger value of the mean energy resulted in a

higher adsorption affinity and thus a higher adsorption capacity. The ΔG^0 analysis was consistent with the energy analysis, confirming that the affinity of CMO increased with increasing temperature.

DA Model-Based Average Site Energy and Adsorption Site Heterogeneity. The DA Model-based average site energy distribution was employed to determine the interaction forces between adsorbent and adsorbate, and its width describes the surface energy heterogeneity of the adsorbents. The mean site energy (E_m) and adsorbent site energy heterogeneity index (σ_e^*) were calculated (see Section S6) from eq S10. The adsorbent site energy heterogeneity can be described by determining the standard deviation (σ_e^*) using eqs S11 and S12.

Figure S6 describes the site energy distributions with variations in E_d and b , demonstrating that both the mean and shape of the distribution changed as either E_d or b was varied. This result implies that b could not represent the site energy heterogeneity. E_m increased significantly with increasing temperature (Figure S7 and Table S4), which can be ascribed to the three-dimensional tunnels structure in the CMO, forming additional adsorption sites. The term σ_e^* decreased with increasing temperature, indicating the stronger adsorption affinity for Li on the CMO.

The mean site energy (E_m) was examined to further understand the relationship between the maximum adsorption capacity (Q_0) and adsorption temperature (T). In eq 15, E_m is considered to be a function of T only. In eq 16, Q_0 is determined by E_m by plugging eq 15 into eq 16 and then incorporating the result into eq 17. The adsorption capacity (Q_0) was found to be linearly related to the adsorption temperature (T) based on eqs 15–17:

$$E_m = k_1 \times T + d_1 \quad (15)$$

$$Q_0 = k_2 \times E_m + d_2 \quad (16)$$

$$Q_0 = k_3 \times E_m + d_3 = k_3 \times (a \times T) + d_3 \quad (17)$$

where k_1 (1/K), k_2 , and k_3 ($\mu\text{mol/J}$) are regression coefficients and d_1 , d_2 , and d_3 (mg/kg) are fitting parameters. The terms k_1 , k_2 , and k_3 are dimensionless and represent the contribution fractions of T to E_m , E_m to Q_0 , and T to Q_0 , respectively.

The regression results revealed the contribution of the average site energy (Table S5). The maximum adsorption capacity (Q_0) was found to be linearly related to the adsorption temperature. Furthermore, E_m increased and Q_0 significantly increased with increasing temperature, indicating that the number of adsorption sites also increases with increasing temperature. For endothermic reactions with increasing adsorption temperature, the positive value of ($k_1 \times T$) increased. In contrast, an increasing negative value of ($k_1 \times T$) was observed with increasing temperature for exothermic reactions. The increases in the positive value of ($k_1 \times T$) with increasing temperature are in good agreement with our thermodynamic study.

Using the Pore Diffusion Model (PDM) and the Homogeneous Surface Diffusion Model To Describe Adsorption Kinetics. In the next few sections, we first use batch kinetic tests to determine intraparticle diffusivities. Then, we show that the models can predict Li breakthrough in short fixed bed column tests. Next, we will use the validated models to predict full scale performance, and we evaluated the impact of multiple ions (that are found in a typical wastewater from

LIB recovery operations) on Li breakthrough. We also determine the Li recovery regenerating the fixed bed using acid.

Batch Kinetic Studies. Adsorption kinetics are important in determining the fixed bed performance. A kinetic experiment was performed with CMO. The initial concentration of Li was 300 mg/L, and the CMO dose was 1 g/L. Figure 7 shows that

Figure 7. Adsorption kinetics for Li(I) adsorption on CMO at different temperatures.

the Li(I) adsorption capacity grew rapidly for the first 50 min. Then, the Li(I) uptake gradually reached equilibrium at about 120 min. In addition, the equilibrium adsorption capacity increased with the adsorption temperature, further supporting the notion that the adsorption of Li(I) on CMO is an endothermic process.

To describe the adsorption kinetic data, a simplified version of the homogeneous surface diffusion model (HSDM)⁵⁴ was used to determine the surface diffusion coefficient (see Section S7). The appropriate Freundlich isotherm model parameters for a given temperature were used in the HSDM. The 2 h data obtained from the kinetics test are given in the first two columns of Table S7. The equilibrium concentration was 250 mg/L and $C_e/C_0 = 0.8$. The experimental data and solution to the HSDM were used to fit the dimensionless model concentrations, as illustrated in Figure S8. The best fit values are shown in Table S7. The most appropriate simplified HSDM equation is given in Table S6, and D_s was found to be $4.63 \times 10^{-10} \text{ m}^2/\text{s}$ at 20 °C. We used the simplified HSDM because other researchers could use the simplified HSDM solution that we have provided in the literature.⁵⁴ In addition, we have provided a simplified HSDM for fixed bed calculations that also could be used for fitting short fixed bed experiments and full scale predictions when competing ions are not present.

The most appropriate model to use to fit the kinetic data is the PDM with a D_s value of zero, because as discussed elsewhere, surface diffusion is not possible for CMO. We calculated the D_p using eq 4, and we can calculate a D_s value that would give the same result as the PDM using the surface to pore diffusion flux ratio (SPDFR) equal to 1.0. This gives a D_s value of $2.63 \times 10^{-10} \text{ m}^2/\text{s}$. However, when we fit the data with the simplified HSDM, we found that the SPDFR was 2 (See Section S8). When we ran the PDM with a D_p that was calculated from eq 4, we had an excellent prediction SBA data as discussed below.

Hence, when competing ions are not present, we can use either the HSDM or the PDM because they give similar results. In addition, the two models could be used for preliminary design if there are no competing ions.⁵⁵

Figure 8. (a) The experimental data and the predictions from PDM for Li(I) breakthrough in SBA tests. The initial Li(I) concentration: 200 $\mu\text{g/L}$; pH: 10.1; temperature: 20, 30, and 40 $^{\circ}\text{C}$. (b) Fixed bed column regeneration test using 0.1 mol/L HCl solution at EBCT of 1 min, and PDM prediction for the desorption at EBCTs of 1 and 10 min at 20 $^{\circ}\text{C}$, respectively.

Figure 9. (a) The lithium breakthroughs for Li(I) with the initial concentration of 200 $\mu\text{g/L}$, by using the validated pore surface diffusion model with empty bed contact times (EBCTs) at 2.5, 5, and 10 min, respectively. (b) The same lithium breakthrough predictions in (a), but with liters of treated water per gram dry media at different EBCTs at 20 $^{\circ}\text{C}$. (c) The lithium breakthroughs for Li(I) with the initial concentrations of 20, 50, and 200 $\mu\text{g/L}$, respectively, by using the validated pore surface diffusion model with a fixed EBCT at 10 min. (d) The same lithium breakthrough predictions in (c), but expressed as liters of treated water per gram dry media at different initial Li concentrations at 20 $^{\circ}\text{C}$.

Short Bed Adsorber (SBA) Test and Pore Diffusion Model (PDM). We used the simplified batch HSDM to fit the adsorption kinetic data and determined the surface diffusivity. Next, we used the HSDM to predict SBA data using that surface diffusivity (see Figure S9). The HSDM did not predict the data well ($R^2 \approx 0.86$), because the St for the SBA is smaller than the St_{min} (required to establish a constant pattern). Consequently, the HSDM prediction has an earlier breakthrough. (However, the simplified HSDM could be used for St values (or EBCT values) above those that correspond to St_{min} .) Consequently, we used the PDM to predict Li breakthrough curve and the D_p value that was calculated from eq 4. As shown in Figure 8a, we predicted the SBA data using the PDM and the breakthrough curves for 20, 30, and 40 $^{\circ}\text{C}$ show increasing column capacity with increasing temper-

ature. The Freundlich isotherm values came from fitting the equilibrium data. The pore diffusion coefficient, film transfer coefficient, and sphericity were calculated from eqs 4, S1, and S4 ($D_p = 1.60 \times 10^{-10} \text{ m}^2/\text{s}$, $1.64 \times 10^{-10} \text{ m}^2/\text{s}$, $1.68 \times 10^{-10} \text{ m}^2/\text{s}$, $k_f = 4.79 \times 10^{-5} \text{ m/s}$, $4.91 \times 10^{-5} \text{ m/s}$, $5.03 \times 10^{-5} \text{ m/s}$, and $\Phi = 0.62$ for 20, 30, and 40 $^{\circ}\text{C}$, respectively). The PDM predictions for the SBA were excellent ($R^2 \approx 0.99$). As shown in Figure 8a, in fact, the integrated capacities (areas above the curves as a function of BVs fed) were 1374, 1972, and 2493 BVs, respectively. These are the maximum number of BVs that can be treated, if we had an infinite mass transfer rate (i.e., the breakthrough curve would be a vertical line that occurs when the bed is exhausted).

As shown in Figure 8b, approximately 98.7% of the Li^+ was extracted after approximately 66.41 BVs using a 0.1 mol/L HCl

solution at 20 °C. Additionally, we predict a desorption curve using PDM. The PDM can fit the data well at 1 min of EBCT and predict 10 min of EBCT data. We calculated the enrichment factor using the BV_{max} , which the 10 min EBCT approaches, and the number of bed volumes (using 0.1 mol/L HCl acid) that are required to desorb Li. The number of desorption bed volumes was assumed to be at the point where the Li effluent concentration, C/C_0 , was less than 0.05. This corresponds to 66.42 and 82.41 desorption bed volumes for 1 and 10 min of EBCT, respectively. Using these values, we determined that the enrichment factors were 20 and 15, respectively, by dividing BV_{max} by these desorption volumes. This means that the regenerated solution has a very high concentration of Li and it is easy to recover Li using evaporation.

The above results confirm that a higher temperature is beneficial for increasing the treated number of BVs. Furthermore, reasonable breakthrough and regeneration curves for Li can be predicted using the PDM. As a result, the model can be used to predict full-scale performance, thus reducing the time and cost required as compared to pilot studies.

Predicting Full-Scale Performance Using the Validated PDM. The performance of full-scale fixed bed systems was simulated using PDM with the same operating parameters as the SBA tests. The full-scale operating conditions were as follows: (1) the superficial velocity was the same as in the SBA tests, (2) the empty bed contact times (EBCTs) were 2.5, 5, and 10 min; (3) the influent concentrations were 20, 50, and 200 $\mu\text{g/L}$, which are realistic values for LIB wastewater. The treatment objective was 10 $\mu\text{g/L}$ Li(I). The input data used for the PDM are shown in Table S8.

Figure 9a shows the full-scale breakthrough curves for EBCTs of 2.5, 5, and 10 min and an influent lithium concentration of 200 $\mu\text{g/L}$. For a treatment objective of 10 $\mu\text{g/L}$ Li(I), the number of BVs that can be treated increased with increasing EBCT. The PDM predicted that approximately 740 BVs can be treated at an EBCT of 2.5 min. When EBCT was increased to 5 and 10 min, the number of treated BVs increased to 1051 and 1237, respectively, approaching the BV_{MAX} of 1374 BVs. Figure 9b illustrates the same lithium breakthrough predictions described according to the liters of water treated per gram of dry media. When the EBCT was 2.5, 5, and 10 min, approximately 2.2, 2.9, and 3.2 L of water can be treated when the treatment objective of 10 $\mu\text{g/L}$ is reached.

For an EBCT of 10 min, the lithium breakthroughs for influent lithium concentrations (C_0) of 20, 50, and 200 $\mu\text{g/L}$ were calculated and are presented in Figure 9c. When C_0 increased from 20 to 50 and 200 $\mu\text{g/L}$, the number of BVs that could be treated until reaching 10 $\mu\text{g/L}$ gradually decreased from 1681 to 1414 to 1237 BVs, respectively. Figure 9d presents the same lithium breakthrough predictions based on the liters of treated water per gram dry media at different C_0 values. When C_0 was 20, 50, and 200 $\mu\text{g/L}$, approximately 6.3, 4.5, and 3.2 L of water could be treated per gram of dry media, respectively, until the treatment objective of 10 $\mu\text{g/L}$ was reached.

PDM Predictions for Multiple Ions Breakthrough. The PDM that describes the fate of ions in a fixed bed is also called the IX model when pore diffusion is the only intraparticle transport mechanism and multiple ions are present.⁵⁵ We used the selectivity values that were measured and the multi-component Langmuir equation to description IX equilibria. The PDM can be used for preliminary design and predicts the

breakthrough of all competing ions. Figure 10 shows the predictions for an influent containing Li^+ , Na^+ , K^+ , Mg^{2+} , and

Figure 10. Mathematical model consisting of ion exchange (IX) models for describing the selectivity behavior of the competition ion on the CMO bed. The competition for adsorption of Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} ions with respect to H^+ ions was determined. The initial Li(I) concentration: 200 $\mu\text{g/L}$. The empty bed contact times (EBCT): 10 min; temperature: 20 °C.

Ca^{2+} all at 200 $\mu\text{g/L}$ and pH 10. The other competing ions broke through earlier than Li^+ which is a result of a high selectivity for Li^+ over the other ions. The CMO can treat 420 BVs at EBCT of 10 min for a Li treatment objective of 10 $\mu\text{g/L}$, which is much larger than other competing ions. There were 1237 BVs treated when Li was by itself with 10 min of EBCT and a treatment objective of 10 $\mu\text{g/L}$. This is 150, 93, 34, 4.6 times greater (for Na, K, Mg, and Ca, respectively) than when the other ions are present at concentrations that are typical in LIB wastewater.

Practical Significance. The maximum adsorption capacity (Q_0) increased with increasing temperature, and this relationship was described by using the DA model and its site energy distribution ($F(E^*)$). This increase in the adsorption capacity with temperature is useful because the technology can be used in warm and cold climates. The PDM can be used to predict the lithium ion breakthrough for full-scale processes. The IX model can predict the lithium ion breakthrough when the wastewater contains multiple ions. The predictive power of this model will allow engineers to evaluate the performance of a fixed bed containing CMO when multiple ions are present.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02247.

Chemical and materials; characterization of samples; synthesis of 3-D $\text{Li}_4\text{Mn}_5\text{O}_{12}$ nanorod and MnO_2 ion cages; determining the parameters for pore surface diffusion modeling; DA model-based site energy distribution ($F(E^*)$); DA model-based average site energy (E_m) and adsorption heterogeneity (σ_e^*); using the homogeneous surface diffusion model to determine the surface diffusion coefficient; estimation of the surface diffusion coefficient from the pore diffusion coefficient (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was financially supported by the National Science Foundation of China (51238002, 51272099), the National Science Fund for Excellent Young Scholars (51422807), the Key Project of Science and Technology Department of Jiangxi Province (20143ACG70006), and the Cultivating Project for Academic and Technical Leader of Key Discipline of Jiangxi Province (20153BCB22005). The authors appreciate support from the Brook Byers Institute for Sustainable Systems (BBISS), Hightower Chair, and Georgia Research Alliance at Georgia Institute of Technology.

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