

Selective Recovery of Lithium from Brines

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ABSTRACT

Expansion of geothermal energy production over the entire U.S. will involve exploitation of low-to-medium temperature thermal waters. Creating value streams from the recovery of metals, such as lithium, will encourage geothermal expansion. We describe a lithium solid-phase extraction process based on a new, highly selective, low-cost, and reusable nanocomposite sorbent comprised of lithium ion sieve nanoparticles and a lithium-imprinted polymer. The sorbent is processed in the form of beads and tested in flow-through columns. When the brine contacts the sorbent, Li ions are selectively captured and concentrated in the sorbent. The sorbent was tested in a packed bed flow-through column for its ability to extract lithium in the presence of high concentrations of alkali and alkaline earth metals. The kinetics of lithium uptake were found to be fast with lithium capacity up to 16.2 mg Li/g sorbent. High selectivity for Li uptake in synthetic brines with high concentrations of Na⁺, K⁺, and Mg²⁺, and Ca²⁺ ions was determined.

1. INTRODUCTION

Expansion of geothermal energy production in California will greatly benefit from the creation of a value stream produced by the recovery of critical metals from geothermal fluids. The efficient separation of metals, such as lithium, from geothermal brines promises to make the production of geothermal power economically favorable, even from low-temperature geothermal fluids. Revenue will be produced from the sale of the marketable metals, and the scaling and re-injection issues associated with high-solid-content brines will be minimized.

Lithium is a high-value metal used in the production of lithium rechargeable batteries, and it is found in low but significant concentrations in geothermal waters (i.e., a few hundred ppm). Because of the very large volume of brine processed in a geothermal power plant (>6000 gal per min), even low-lithium brines represent a valuable resource. To support the rapid market growth of lithium rechargeable batteries, there is a strong demand for new lithium recovery methods.

Extraction of Li from brines is currently the dominant method of Li production because of the higher cost efficiency of extraction compared to processing of mineral deposits. High-grade Li compounds are mostly processed from salar brines in Argentina, Chile, and Bolivia due to low operation costs. However, Li separation from salar brines is typically slow (i.e., a few months), since it is based on solar evaporation of the brines in ponds and requires multiple purification steps. Solvent extraction processes and solid-phase extraction processes are currently being evaluated for lithium recovery from brines (Neupane and Wendt, 2017).

Geothermal brines present unique opportunities and challenges for mineral recovery and therefore require development of new low-cost extraction processes. Our proposed approach addresses selective recovery of lithium from brines that are rich in dissolved solids and relatively low in lithium and promises to enable the economic recovery of lithium from geothermal brines.

2. APPROACH

Low-cost recovery of lithium from brines demands the use of selective high-capacity reusable sorbents. We have prepared a new hybrid sorbent consisting of nanostructured manganese oxide (HMO) embedded within a Li-imprinted polymer in the form of porous beads that has demonstrated selective lithium extraction in a continuous solid-phase extraction process.

2.1 Hydrous Manganese Oxide Ion Sieve

Inorganic sorbents, such as aluminum hydroxide, manganese oxide, or titanium oxide are relatively inexpensive, stable over a high temperature range, and have shown promising properties for the selective adsorption of lithium. Hydrous manganese oxide (HMO) such as Li_{1.35}Mn_{1.61}O₄, is of great interest because of its high lithium capacity (up to 62 mg/g depending on pH) and selectivity for the removal of lithium in the presence of very large concentrations of Na, K, Ca, Mg and other metal ions (e.g., Zandevakili et al., 2014; Sun et al., 2014; Chitrakar et al., 2001; Shi et al., 2011).

The HMO Li ion sieves are prepared with a two-step method. First, spinel-type lithium manganese oxide, such as Li_{1.35}Mn_{1.61}O₄ or others (i.e., Li₄Mn₅O₁₂, Li_{1.6}Mn_{1.6}O₄, or LiMn₂O₄), is prepared using the Li⁺ template ion. Next, Li⁺ is extracted by treatment with an acidic aqueous solution such as HCl_(aq) to obtain HMO. The Li ions are replaced by H⁺ and the correspondent HMO is formed. The HMO retains the framework of the parent compound and is characterized by pore structures and vacant sites in the spinel phase that are uniquely suited for the insertion and de-insertion of lithium ions (Shi et al, 2011). The mechanism for the Li ion sieve adsorption of Li⁺ can therefore be explained by an ion-exchange process as follows:



where the bars refer to the ion species in the adsorbent.

2.2 Lithium-imprinted Polymer

We have prepared Li-imprinted polymers in the presence of Li-ion templates that, once desorbed, leave behind “imprints” with the size, shape, and arrangement of binding sites that are specific for binding Li. Metal ion selectivity is imparted by: (1) the affinity of the ligand for the imprinted metal ion; and (2) the size and shape of the generated cavities (Branger, C. et al., 2013). As recognition sites are generated from the self-assembly of some ligand(s) around the template metal ion (M) and subsequent crosslinking, this arrangement enables the binding sites to match the charge, size, and coordination number of the metal ion. Furthermore, the binding sites’ geometries are preserved through the crosslinking and leaching steps, thus generating a favorable environment for the template ion rebinding (Figure 1).

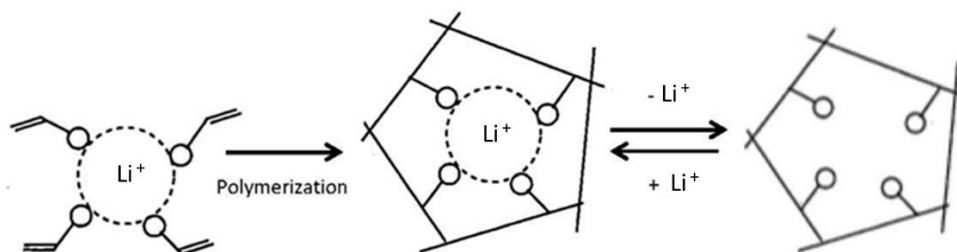


Figure 1. Schematic illustration of the synthesis of metal-imprinted polymers.

As inorganic ion sieves, lithium-imprinted polymers are prepared in their lithiated form and activated by treatment with an acidic aqueous solution such as $\text{HCl}_{(aq)}$ to extract Li^+ with formation of the Li-imprinted polymer.

The Li-imprinted polymers have shown to have lithium uptake capacity as high as 2.6 mg of Li/g sorbent and good selectivity in the presence of competing concentrations Na^+ and K^+ ions (Ventura. S. et al., 2016) (Figure 2).

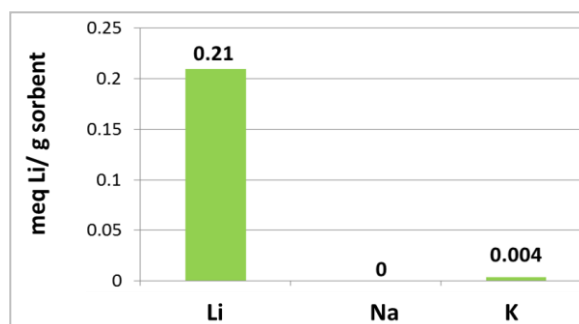


Figure 2. Batch metal uptake of Li-imprinted polymer at $T = 45^\circ\text{C}$ from a synthetic brine containing 412 mg Li/L brine, 405 mg Na/L brine, and 435 mg K/L brine.

2.3 Hybrid Nanocomposite Sorbent

It is highly desirable to prepare HMO nanoparticles to enhance Li sorption kinetics, but sorbents in the form of nanopowders are not suited for the flow-through separation processes because of large pressure drops in column operations and high-energy consumption. A hybrid nanocomposite sorbent consisting of nanoparticles of an ion sieve embedded into a porous polymer support provides a solution to this problem. Polymers, such as polyvinylchloride (PVC), polyacrylonitrile (PAN), or polyacrylamide (PAM), have been used as binders of micron or sub-micron size ion sieves (Xiao, G. et al, 2012; Xiao, J.-L. et al., 2015)). However, these polymers do not have any lithium ion transport properties and may end up blocking access to the inorganic lithium adsorbent.

We have chosen to prepare a nanocomposite sorbent that combines the advantages of both ion sieve nanoparticles and polymers by using an inorganic ion sieve such as HMO and a selective ion-exchange Li-imprinted polymer. Inorganic ion sieves, such as HMO, have well-known high lithium uptake capacity, while the Li-imprinted polymer binds Li^+ and enhances its concentration at the HMO-polymer interface, improving the Li uptake kinetics.

3. RESULTS AND DISCUSSION

3.1 Preparation and Characterization of Nanostructured LMO

Nanostructured lithium manganese oxide (LMO) is prepared via hydrothermal synthesis as previously reported (Zandevakili et al., 2014). First, MnO_2 is prepared from equimolar amounts of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_8$ dissolved in deionized water. The aqueous solution is transferred into a stainless-steel autoclave, and heated for 12 hours at 120°C . The resulting black solid is filtered, washed thoroughly with deionized water and dried overnight at 100°C . Next, the manganese oxide powder is thoroughly mixed with a suitable amount of 0.5M LiNO_3 (aq) in the desired Li/Mn molar ratio. This mixture is then heated in the oven for 12 hours at 100°C to remove water. Finally, the resulting mixture is calcined in a furnace at 450°C for 6 hours to obtain the LMO nanopowder. The nanostructure of the resulting LMO powder is confirmed by scanning electron microscope (SEM) analysis. The photographs in Figure 3 show the needle-like nanostructure of the lithium manganese oxide that has a width of 100 nm and length less than 1 micron. The X-ray phase analysis of the powder shows the spinel phase of $\text{Li}_{1.35}\text{Mn}_{1.61}\text{O}_4$.

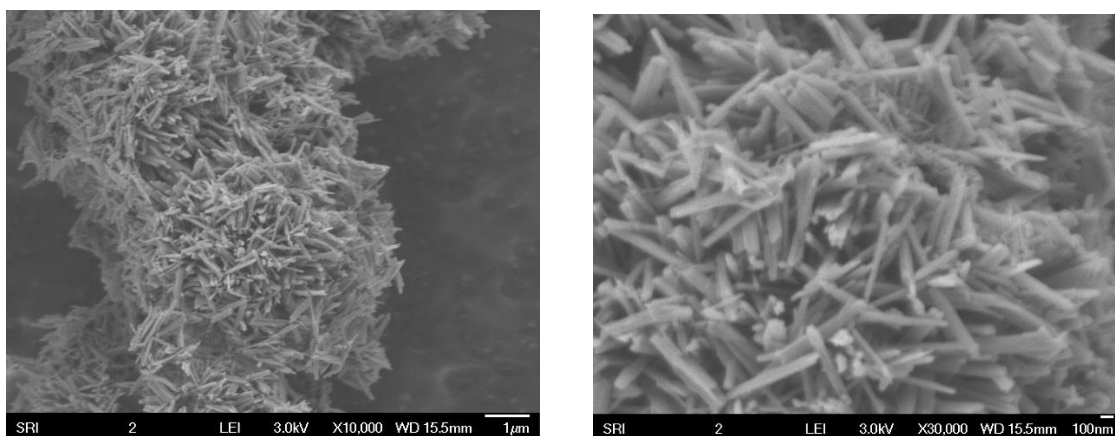


Figure 3. Scanning electron microscope (SEM) photographs of the synthesized LMO.

3.2 Synthesis of the Hybrid Nanocomposite Sorbent

Hybrid nanocomposite sorbent beads are prepared by suspension polymerization of a polymerizable lithiated monomer with a crosslinking agent in the presence of LMO nanopowder. The LMO nanopowder is suspended in the monomer mixture, and the resulting dispersion is suspended in oil under vigorous stirring. The radical polymerization is initiated by azobis(isobutyronitrile) (AIBN) when the suspended mixture is heated at 70°C over several hours. After cooling, the nanocomposite beads are collected by filtration and thoroughly washed with an organic solvent and water.

We prepared sorbent beads with a minimum size of 150 micron and variable LMO:polymer ratio. After removing lithium by treatment with an acidic solution, the sorbent beads were tested for their lithium extraction properties.

Sorbents were tested in a fixed bed configuration to determine their capacity and selectivity. In these experiments, a lithium containing brine is fed into a column of sorbent, and the composition of the exiting brine is measured as a function of time, until the exit composition matches the feed composition. Taking into consideration the fact that the composition of geothermal brines can vary widely depending on the source reservoir, we have tested the sorbent performance at various temperatures, pH values, and concentrations of competing metals using synthetic brines. Synthetic brines were prepared using the specified metal chlorides. The pH values of the brines were controlled using buffer solutions from pH 5 up to pH 7.

3.3 Brine Adsorption/Regeneration Procedure

The sorbent beads were suspended in water and loaded into a jacketed column with diameter of 1-cm and height of 30-cm. The actual height of the packed bed depended on the amount of sorbent loaded. The column temperature was controlled by circulating water at a constant temperature through the column jacket. The brine flow rate was controlled by a constant-displacement pump.

The outlet solution was collected in consecutive fractions, and each fraction was analyzed for its lithium concentration using ion exchange chromatography. After the adsorption was completed, the sorbent was regenerated using 0.5M HCl. The regeneration solution was collected and analyzed for total lithium content to provide a measurement of lithium capacity.

The lithium separation coefficients were calculated as follows:

$$\alpha_{\text{Li}/\text{Me}} = Q_{\text{Li}}/C_{\text{Li}} * C_{\text{Me}}/Q_{\text{Me}}$$

where Q_{Li} and Q_{Me} are the adsorption capacities of Li and a generic metal ion Me in the polymer (mg Li or Me/g sorbent), and while C_{Li} and C_{Me} are the concentrations of Li and metal ion Me in the brine (mg Li or Me/L brine) tested.

The concentration of lithium ion and other metal ions were tested by ion exchange chromatography.

3.4 Lithium Adsorption Tests

The hybrid sorbent generation was tested for its lithium adsorption and selectivity under variable conditions, including pH, composition and temperature.

In a typical experiment, the hybrid nanocomposite fixed bed was tested for its adsorption of Li^+ from a synthetic brine containing 255 ppm Li, 10570 ppm Na and 10400 ppm of K in a pH 6 0.4M sodium phosphate buffer solution. The brine was passed through the column at a flow rate of 27 BV/hr (where BV is the bed volume defined as $\text{BV} = L\pi r^2$ with L equal to the length of the sorbent packed bed and r is the radius of the column) and the exiting brine was collected in small fractions. The lithium content of each fraction was measured, and the adsorption experiment was continued until the sorbent was saturated and the exiting brine had the same lithium content as the feed. The sharp breakthrough adsorption curve (Figure 4) indicates that the lithium uptake is fast.

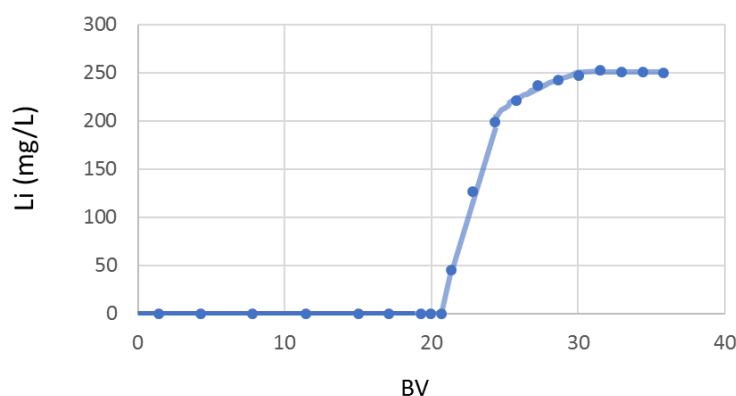


Figure 4. Breakthrough curve of Li^+ from a fixed-column packed with the hybrid nanocomposite sorbent. The brine's tested composition was: 255 ppm Li, 10570 ppm Na and 10400 ppm of K in a pH 6 0.4M sodium phosphate buffer solution. $T = 70^\circ\text{C}$, flow rate 27 BV/hr.

The lithium capacity and selectivity in the presence of high concentrations of Na and K ion are shown in Table 1. It should be noted that, the lithium capacity is calculated from the amount of the lithium released by treatment with 0.5 M HCl, after the sorbent was saturated with Li.

Table 1. Sorbent Li capacity and selectivity in synthetic brines at variable pH

pH	Li brine conc. (mg/L)	Na brine conc. (mg/L)	K brine conc. (mg/L)	Mg brine conc. (mg/L)	Ca brine conc. (mg/L)	Li capacity (mg Li/g sorbent)	Sep. coeff. $\alpha_{\text{Li}/\text{Na}}$	Sep. coeff. $\alpha_{\text{Li}/\text{K}}$	Sep. coeff. $\alpha_{\text{Li}/\text{Mg}}$	Sep. coeff. $\alpha_{\text{Li}/\text{Ca}}$
7.2	250	17134	10749	-	-	16.2	323	107	-	-
6	255	10570	10400	-	-	14.2	211	77	-	-
5	242	10059	-	964	9250	10.8	198	-	High *	71

Experimental conditions: flow rate 27BV/hr, temperature 70°C . (*) no Mg uptake was detected.

The binding capacity of Mg from synthetic brines containing 964 mg/L of Mg^{2+} was found to be negligible, with no detected Mg uptake under the experimental conditions summarized in Table 1, therefore, we could not calculate an actual separation coefficient.

The three synthetic brines in Table 1 were prepared from buffer solutions to simulate the pH of geothermal brines. The 0.4 M sodium phosphate solutions were used for the pH 7.2 and 6 buffer, while a 0.1 M acetic acid/sodium acetate solution was used for the pH 5 buffer. The sorbent Li capacity for all the three brines was greater than 10 mg Li/g sorbent, and as high as 16.2 mg Li/ for the brine at pH 7.2.

Additional adsorption tests were performed by varying the adsorption temperature and using synthetic brine at pH 5 that contained concentrations of Li, Na, K and Ca comparable to those found in California's Salton Sea geothermal brines (Table 2). Thus, the brine tested contained 377 mg/L of Li, 57777 mg/L of Na, 14448 mg/L of K and 26766 mg/L of Ca. Even in the presence of high concentration of other metal ions, the sorbent Li capacity was greater than 11 mg Li /g sorbent at 70°C with a Li separation coefficient of 3855 compared to Na, 211 compared to K and 119 compared to Ca. When the adsorption process was conducted at 50°C and 30°C, the lithium capacity of the sorbent was still greater than 10 mg Li/g sorbent with high selectivity.

Table 2: Sorbent lithium capacity and separation coefficient in complex brine

T (°C)	Li capacity (mg Li/g sorbent)	Li Separation	Li Separation	Li Separation
		Coefficient	Coefficient	Coefficient
		$\alpha_{Li/Na}$	$\alpha_{Li/K}$	$\alpha_{Li/Ca}$
70	11.25	3855	211	119
50	10.12	3876	185	109
30	10.16	1351	164	136

Brine composition: Li 377 mg/L, Na 57777 mg/L, K 14448 mg/L, Ca 26766 mg/L. Experimental conditions: flow rate 30 BV/hr, pH 5

The sorbent is currently being evaluated for its ability to extract lithium from actual brines and undergo multiple cycles of sorption and regeneration without degradation.

4. CONCLUSIONS

We have developed a new hybrid nanocomposite sorbent based on nanostructured hydrous manganese oxide and a Li-imprinted polymer. The sorbent was tested in a flow-through system for its ability to extract lithium in the presence of high concentration of alkali and alkaline earth metals. The kinetics of lithium uptake were found to be fast and lithium sorption was demonstrated in a packed bed column with brine flowing at rates up to 30 BV/hr. The sorbent showed excellent lithium capacity (up to 16.2 mg Li/g sorbent) and high selectivity for Li⁺ in the presence of high concentrations of Na⁺, K⁺, and Mg²⁺ and Ca²⁺ ions. Future work will include adsorption/desorption tests using geothermal and other brines to evaluate the sorbent durability over multiple cycles.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- Branger, C., Meouche, W., Margailan, A.: Recent Advances on Ion-imprinted Polymers, *Reactive and Functional Polymer*, **73**, (2013), 859-879.
- Chitrakar, R., Kanoh H., Miyai, Y., and Ooi, K., Recovery of lithium from sea water using manganese oxide adsorbent (H_{1.6}Mn_{1.6}O₄) derived from Li_{1.6}Mn_{1.6}O₄, *Ind. Eng. Chem. Res.*, **40** (2001), 2054.
- Neupane, G., and Wendt, D.S.: Assessment of Mineral Resources in Geothermal Brines in the US, *Proceedings*, 42th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA (2017).
- Shi, X., Zhao, D., Zhang, Z., Yu, L., Xu, H., Chen, B., and Yang, X.: Synthesis and Properties of Li_{1.6}Mn_{1.6}O₄ and its adsorption application, *Hydrometallurgy*, **110**, (2011), 99-106.
- Sun, S.-Y., Xiao, J.-L., Wang, J. Song X. and Yu, J.-G.: Synthesis and Adsorption Properties of Li_{1.6}Mn_{1.6}O₄ by a Combination of Redox precipitation and Solid-Phase, *Ind. Eng. Chem. Res.*, **29**, (2014), 15517-15521.
- Ventura, S., Bhamidi, S., Hornbostel, M., Nagar, A., and Perea, E.: Selective Recovery of Metals from Geothermal Brines, (2016), Final Report, SRI International (EERE/GTO Contract No. DE-EE0006747).
- Xiao, G., Tong, K., Zhao, L., Xiao, J., Sun, S., Li, P., and Yu J.: Adsorption and Desorption Behavior of Lithium Spherical PVC-MnO₂ Ion Sieve, *Ind. Eng. Chem. Res.*, **51**, (2012), 10921-10929.
- Xiao, J.-L., Sun, S.-Y., Zhao, L., Song, X., Li, P., and Yu J.: Lithium Ion Recovery from Brines using Granulated Polyacrylamide-MnO₂ sieve, *Chem. Eng. J.*, **279**, (2015), 659-666.
- Zandevakili, S., Ranjibar, M. and Ehteshamzadeh, M.: Recovery of lithium from Urmia Lake by nanostructured MnO₂ sieve, *Hydrometallurgy*, 149 (2014) 148-152.