



## Continuous lithium mining from aqueous resources by an adsorbent filter with a 3D polymeric nanofiber network infused with ion sieves



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### HIGHLIGHTS

- Adsorbent filter with 3D nanofiber (NF) network was fabricated via electrospinning.
- NF contained hydrophilic polyacrylonitrile matrix infused with lithium ion sieves.
- NF adsorbent filter exhibited high water flux, low pressure requirement, and effective Li<sup>+</sup> capture.
- Breakthrough studies fitted with nine well-known models reveal the suitability of Bohart-Adams.
- Feed can be continuously fed through the NF to collect and concentrate Li<sup>+</sup> from aqueous resources.

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### ABSTRACT

Electrospun composite nanofiber (NF) was fabricated and employed as an adsorbent membrane filter in a continuous Li<sup>+</sup> mining process from seawater. The filter was composed of a hydrophilic polyacrylonitrile (PAN) matrix infused with lithium ion sieves (LIS) H<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>. Characterization of the LIS/PAN NF confirmed its favorable structural and surface properties for effective Li<sup>+</sup> adsorption. The LIS/PAN NF was mechanically suitable as a microfiltration membrane with high water flux and low pressure requirement. Breakthrough experiments at varied feed concentrations ( $C_f$ ), seawater flowrates ( $F$ ), and NF thicknesses ( $Z$ ) revealed the dynamic adsorption behavior of the filter. The seawater residence time was most critical and must be kept  $\geq 0.12$  min at any given  $C_f$  and  $Z$  to maximize the Li<sup>+</sup> capacity of the filter. This can be conveniently achieved by adjusting the  $F$  of the process. Analogous to a packed bed system, the predictive power of nine breakthrough models were determined through non-linear regression analyses. Results reveal that bed-depth-space-time, Bohart-Adams (BA) and Thomas models adequately predicted the performance of the filter albeit BA exhibited the best agreement. Meanwhile, Wolborska failed to converge with any of the experimental results while Yoon-Nelson, Wang, Clark, dose-response, and modified dose-response were too simple to provide any meaningful information. Cycled Li<sup>+</sup> adsorption-desorption runs successfully collected and concentrated Li<sup>+</sup> in a mild acid stripping solution. After ten cycles, Li<sup>+</sup> was separated 155–1552 times more efficiently than Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>. Overall results demonstrate the potential of LIS/PAN NF as an adsorbent membrane filter for continuous Li<sup>+</sup> mining from aqueous resources.

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### 1. Introduction

As an important energy storage component in portable electronic devices and electric vehicles, Lithium (Li) has become one of the most valuable alkali metals in technological industries [1,2]. The increasing popularity of Li indicates a possible challenge

on its supply in the future. While Li has been typically mined from ores and brine pools, these resources may not be able to meet the expected demands [3]. Thus, its collection from secondary aqueous resources like the industrial wastewater and seawater (i.e. 230 GT Li<sup>+</sup>) has become an attractive option [1,4].

Adsorption is an effective strategy to capture diluted Li<sup>+</sup> in the presence of more abundant cations like Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> in seawater [5]. Specifically, H<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>, H<sub>1.33</sub>Mn<sub>1.67</sub>O<sub>4</sub>, MnO<sub>2</sub> and H<sub>2</sub>TiO<sub>3</sub> have been used as lithium ion sieves (LIS) to selectively adsorb Li<sup>+</sup> from aqueous streams [5–10]. These inorganic powdery LIS are typically processed into composites to ensure their convenient handling and reuse. A mild acid stripping solution is used to simultaneously collect the captured Li<sup>+</sup> and regenerate the composite adsorbents.

General preparation of LIS composites requires LIS dispersion in polymers like polyvinyl chloride, chitosan, polysulfone, polyurethane, polyvinyl alcohol and polyacrylonitrile (PAN) [5,11–16]. The LIS-infused polymer mixture can be granulated, membranized, molded into foams or fabricated as nanofibers to obtain the composites [7,11–20]. However, majority of these fabrication methods substantially reduce the Li<sup>+</sup> adsorption capacity and kinetics of the LIS [11,14,17,19,21]. Some of the cited reasons include mass transport limitation, polymer blockage of LIS adsorption sites and reduced feed affinity due to the hydrophobicity of the polymer matrix [17–20].

An earlier study demonstrated that a composite with a nanofiber (NF) structure resolved these challenges [16]. The three-dimensional (3D) open network of NF eliminated the dead-end pores typically found in foams, granules and phase inversion membranes thereby maximizing the adsorbent accessibility to the feed. The nano-scale fiber diameter of the NFs facilitated LIS exposure on the matrix surface, which alleviated polymer blockage and minimized the adsorption capacity loss of the LIS. Appropriate selection of a hydrophilic matrix such as PAN was also beneficial as it improved the aqueous feed affinity to the NF [12,16,19].

Composite LIS have been routinely tested in batch Li<sup>+</sup> adsorption systems [14–16,18,20]. However, continuous Li<sup>+</sup> collection would be more beneficial as it can alleviate the pH decline which occurs in a confined volume of feed in a batch system [9]. The gradual accumulation of concomitantly released H<sup>+</sup> with Li<sup>+</sup> capture eventually limits further Li<sup>+</sup> adsorption [13]. Furthermore, continuous operation could significantly increase the throughput of the process, and simplify the operation [3,22–24]. Thus far, continuous Li<sup>+</sup> recovery has been intensively reported using granulated LIS in packed bed systems [3,5,11,21,25]. Meanwhile, the NF can also be employed in a continuous system as an adsorbent filter, through which the feed can be conveniently permeated. As adsorbent filters, the back pressure would be minimal due to their lower compressibility than the packed bed columns. The convective feed delivery through the NF would enhance Li<sup>+</sup> transport to the LIS surface and alleviate the internal pore diffusion limitation encountered in conventional packed bed systems [26–29].

However, appropriate NF filter design and operation conditions must be known to maximize the continuous Li<sup>+</sup> production rate. As a filter, the NF with a 3D network is analogous to a packed bed system, only with a significantly higher aspect ratio (i.e. filter area/thickness) [30]. Thus, recruitment of existing breakthrough models used in packed bed systems could be an effective strategy to predict the dynamic Li<sup>+</sup> adsorption behavior of the NF adsorbent filter.

Herein, infused LIS in PAN matrix (LIS/PAN) was fabricated as a 3D network of NF via electrospinning. Particularly, H<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub> was selected as one of the LIS with the highest Li<sup>+</sup> adsorption capacity and selectivity [7]. Furthermore, the benefits of adapting the 3D NF network can be easily known since majority of the reported LIS composites have used H<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub> [15,16,18,19,21].

The LIS/PAN NF was thoroughly characterized to confirm its surface and structural favorability towards Li<sup>+</sup> adsorption. Its applicability for continuous Li<sup>+</sup> mining from seawater was investigated by employing it as an adsorbent filter. Breakthrough studies were performed at different Li<sup>+</sup> feed concentrations, flow rates, and NF thicknesses. Well-known models derived from mass transport phenomena and adsorption isotherms were recruited to elucidate and predict the dynamic Li<sup>+</sup> adsorption behavior of the NF. Cycled adsorption-desorption runs were carried out to demonstrate the performance consistency of the LIS/PAN NF for long-term application as an adsorbent filter. The collected product, in the form of an enriched Li<sup>+</sup> stripping solution, was analyzed to evaluate the separation efficiency of Li<sup>+</sup> from other cations in seawater.

## 2. Materials and methods

### 2.1. Materials

Lithium manganese dioxide particles (LiMnO<sub>2</sub>, >99% trace metal basis, size <1 μm), lithium hydroxide (≥98% LiOH) and PAN polymer (MW = 150,000 g mole<sup>-1</sup>) were purchased from Sigma-Aldrich (MO, USA). Lithium chloride (LiCl, ≥98%) was purchased from Fluka (Switzerland) whereas dimethylformamide (>99.5% DMF), heavy metal-free hydrochloric acid (35–37% HCl) and nitric acid (60% HNO<sub>3</sub>) were supplied by Junsei Chemical Co., Ltd. (Japan). All chemicals were used without further purification.

Real seawater was collected and used as feed for breakthrough experiments and continuous Li<sup>+</sup> recovery operations. The seawater was allowed to settle and the suspended solids were removed before it was used as feed. Characterization of the seawater feed was provided as [Supplementary Table S1](#), including those of competing ions, Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>.

### 2.2. Preparation of the 3D NF adsorbent filter

The ion sieves were synthesized via calcination of LiMnO<sub>2</sub> as described in detail elsewhere [7,16]. The powder was placed in a furnace (10 °C min<sup>-1</sup>), under air at 450 °C for 4 h. The produced Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub> particles were sieved (Standard Testing Sieve No. 200 Aperture = 75 μm, Chung Gye Sang, Seoul Korea) and then dried in an oven at 60 °C for 24 h. The product was examined and confirmed via X-ray diffraction (XRD) analysis, which was consistent with those in literature ([Supplementary Fig. S1](#)) [8,16].

A solution of PAN (10 wt%) dissolved in DMF was prepared and dispersed with 90 wt% Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub> (w.r.t. PAN amount). After 8 h of agitation at 60 °C, the slurry was cooled then placed in a plastic syringe and extruded by a syringe pump (4 mL h<sup>-1</sup>) to form the nanofibers using an electrospinning apparatus (Model: ESP200D/ESP100D, NanoNC Co., Ltd., South Korea). The electrospinning was controlled between 20 and 23 V while the needle/collector distance was fixed at 100 mm to minimize bead formation. The collector was rotated at 500 rpm to achieve uniform thickness. The mesh with a 3D NF network was retrieved and vacuum-dried at 60 °C for one day and then kept in a sealed dry environment when not in use.

To activate the infused Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub> into LIS (H<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>), the NFs were cut in squares (approx. 85 mg) and then soaked in 100 mL 0.5 M HCl solution for 24 h at 25 °C to facilitate the Li<sup>+</sup> exchange with H<sup>+</sup> [31]. The delithiation efficiency was around 91%, which suggests the presence of residual Li<sup>+</sup> in LIS/PAN NFs. The delithiated NFs were washed with deionized (DI) water until neutral pH was achieved. The LIS/PAN NFs were dried at 60 °C for 24 h and stored when not in use.

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