Lithium recovery from salt-lake brine: Impact of competing cations, pretreatment and preconcentration

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Abstract
© 2020 Elsevier Ltd The global demand of lithium is rising steadily, and many industrially advanced countries may find it hard to secure an uninterrupted supply of lithium for meeting their manufacturing demands. Thus, innovative processes for lithium recovery from a wide range of natural reserves should be explored for meeting the future demands. In this study, a novel integrated approach was investigated by combining nanofiltration (NF), membrane distillation (MD) and precipitation processes for lithium recovery from salt-lake brines. Initially, the brine was filtered with an NF membrane for the separation of lithium ions (Li+) from competing ions such as Na+, K+, Ca2+ and Mg2+. The extent of permeation of metal ions by the NF membrane was governed by their hydrated ionic radii. Rejection by NF membrane was 42% for Li, 48% for Na and 61% for K, while both the divalent cations were effectively rejected (above 90%). Importantly, in the NF-permeate, Mg2+/Li+ mass ratio reduced to less than 6 (suggested for lithium recovery). The result showed that MD can enrich lithium with a concentration of 2.5 for raw brine and 5 for NF-treated brine. Following the enrichment of NF-permeate by the MD membrane, a two-stage precipitation method was used for the recovery of lithium. X-ray diffraction confirmed the precipitation of lithium as well as the formation of lithium carbonate crystals.

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Lithium recovery from salt-lake brine: impact of competing cations, pretreatment and preconcentration

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Abstract
The global demand of lithium is rising steadily, and many industrially advanced countries may find it hard to secure an uninterrupted supply of lithium for meeting their manufacturing demands. Thus, innovative processes for lithium recovery from a wide range of natural reserves should be explored for meeting the future demands. In this study, a novel integrated approach was investigated by combining nanofiltration (NF), membrane distillation (MD) and precipitation processes for lithium recovery from salt-lake brines. Initially, the brine was filtered with an NF membrane for the separation of lithium ions (Li\(^+\)) from competing ions such as Na\(^+\), K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\). The extent of permeation of metal ions by the NF membrane was governed by their hydrated ionic radii. Rejection by NF membrane was 42% for Li, 48% for Na and 61% for K, while both the divalent cations were effectively rejected (above 90%). Importantly, in the NF-permeate, Mg\(^{2+}\)/Li\(^+\) mass ratio reduced to less than 6 (suggested for lithium recovery). The result showed that MD can enrich lithium with a concentration of 2.5 for raw brine and 5 for NF-treated brine. Following the enrichment of NF-permeate by the MD membrane, a two-stage precipitation method was used for the recovery of lithium. X-ray diffraction confirmed the precipitation of lithium as well as the formation of lithium carbonate crystals.

Keywords: Chemical precipitation; Lithium carbonate crystals; Membrane distillation; Nanofiltration; Salt-lake brine
1. Introduction

Lithium, an electrochemically active metal, has been recognised as one of the critical materials for the advancement of modern life due to its superior properties (e.g., redox-potential and specific heat capacity) as compared to other materials. The application of lithium-ion batteries in electric vehicles is a key component of the electric vehicle revolution in the future (Heelan et al., 2016; Swain, 2017). In addition, the application of lithium compounds in a wide range of industries such as pharmaceutical industry, ceramic industry, rocket propellant manufacturing, aluminium manufacturing and nuclear power plants has a favourable effect on its global market (Wang et al., 2015; Terry et al., 2016; Swain, 2017). Given the low concentration of this mineral in natural reserves and other difficulties in its extraction from hard rocks, many industrially advanced countries have found it difficult to secure an uninterrupted supply of lithium for meeting their manufacturing demands. Indeed, this has a significant impact on the price of lithium in the international market. For instance, increase in the price of lithium carbonate from $6400-12,000 per ton was recorded in China (Chen et al., 2018). Therefore, an innovative process should be developed and assessed for the recovery of lithium from alternative sources to satisfy the future demands.

It is important to note that earth’s crust contains approximately 0.007% Li. Although it is found in mineral ores and continental brine, lithium is still considered as a rare metal due to its low concentrations in natural reserves. Hard rocks (e.g., pegmatite and spodumene) and brines are the major sources containing up to 34% and 66% of world’s lithium, respectively (Gruber et al., 2011; Li et al., 2019). Other notable sources include seawater, oil-well brine and geothermal water, but lithium concentration in these sources could be very low, i.e., less than 0.25 mg/L (Grosjean et al., 2012; Vikström et al., 2013; Swain, 2017). Extraction and recovery of lithium from brine is less expensive and entails lower energy consumption as compared to its extraction...
from hard rocks (Li et al., 2016). However, presence of competing elements such as sodium, potassium and magnesium makes the separation of lithium from salt-lake brine challenging (Song et al., 2011; Ushak et al., 2016; Pramanik et al., 2019). Presence of other elements, particularly magnesium, affect the evaporation rate as well as the formation of lithium chloride (LiCl) that is a required step for the production of lithium carbonate. As a result, the yield, purity and separation efficiency of lithium could reduce significantly. A Mg$^{2+}$/Li$^+$ ratio of less than 6 is typically recommended for lithium recovery (Peiro et al., 2013; Vikström et al., 2013; Sun et al., 2015; Pramanik et al., 2019). Thus, an efficient process would be the one that considers effective separation of lithium from brine containing a range of competing elements.

A wealth of studies on lithium extraction from brine solution is available in the literature. The performance of several processes for lithium extraction from brines has been reported. These processes include precipitation (Zhong et al., 2002; An et al., 2012), adsorption (Chitrakar et al., 2014; Zandevakili et al., 2014), ion exchange (Zhang et al., 2007; Özgür, 2010), and solvent extraction (Shu-Ying et al., 2011; Zhou et al., 2012; Yang et al., 2013; Zhou et al., 2013). Among these processes, the lime-soda precipitation process is one of the effective and traditional large-scale industrial production methods for lithium recovery from brines. This process can extract up to 60% of lithium in the form of lithium carbonate (Peiró et al., 2013). However, competing elements at high concentrations (as discussed above) limit the applicability of the lime-soda processes for effective lithium recovery from brines (Kesler et al., 2012). For instance, addition of excess lime is required to reduce magnesium to lithium ratio (less than 6), which would increase the production of toxic sludge as well as the costs associated with its disposal (Trócoli et al., 2014; Sun et al., 2015). Therefore, an efficient and environmentally friendly process of extracting lithium from brines is greatly warranted.
Research on the extraction of lithium from brines using membranes is in its early stages of development. Pressure-driven membrane processes, particularly nanofiltration (NF) technology, has gained momentum in recent times for the separation of lithium from brines (Pramanik et al., 2019; Park et al., 2020). This is because NF has the capability to separate the monovalent cation lithium (Li\(^+\)) from multivalent cations such as magnesium (Mg\(^{2+}\)) and calcium (Ca\(^{2+}\)) (Schäfer et al., 2005; Sun et al., 2015). In a study by Bi et al. (2014), an NF membrane effectively separated Mg from salt-lake brine, reducing the mass ratio of Mg\(^{2+}\)/Li\(^+\) from 40 in feed to 0.9 in permeate. In another study, Quist-Jensen et al. (2016) noted that NF membrane can reject only 26% of Li but can reject above 85% of Mg from seawater, and thereby reducing the Mg\(^{2+}\)/Li\(^+\) ratio in the permeate. The available studies show the effectiveness of the NF process for separating monovalent cations from the and divalent ones (Sun et al., 2015; Park et al., 2020; Zhang et al., 2020). However, to-date, the influence of other competing cations in brine (i.e., Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\)) on Li\(^+\) separation by NF membrane has not been extensively explored and elucidated.

Following Li\(^+\) separation from brine using NF membranes, its concentration may not be high enough, and precipitation in the form of lithium carbonate may not be a viable option (Pramanik et al., 2019). It would be only reasonable to concentrate/enrich Li before the precipitation step. In this context, membrane distillation (MD), another emerging membrane process, could be used for concentrating Li from brines. Previously, the MD processes has been studied for salt recovery from brines (Macedonio et al., 2007; Quist-Jensen et al., 2016; Pramanik et al., 2016), but has rarely been investigated for Li enrichment (Pramanik et al., 2019; Park et al., 2020). Notably, the MD process can concentrate salts up to the supersaturated state to allow crystallization due to its unique mass transfer properties (Ali et al., 2015; Asif et al., 2019a). This process utilizes a partial vapor pressure difference generated by the temperature difference...
on both sides of a hydrophobic microporous membrane to allow the transport of water vapor through the membrane pores. Waste-heat could be utilised for maintaining the temperature of the feed side in MD process, (Alkhudhiri et al., 2012; Pramanik et al., 2017), thereby making it an attractive and potentially cost-effective option for not only desalination but also for mineral recovery. To date, studies related to the investigation of MD process for the recovery of Li along with clean water production are limited. Pramanik et al. (2019) studied a direct contact (DC)-MD process and reported that Li could be concentrated significantly (80%). In another study by Park et al. (2020), DCMD was observed to be effective for Li enrichment. However, following MD concentration step, Li recovery in the form of lithium carbonate remains unexplored.

As compared to conventional resource recovery methods (e.g., solvent extraction, dialysis, and precipitation), the idea of using an integrated membrane separation process can achieve added advantages, particularly clear water production along with resource recovery (Van der Bruggen, 2013; Pramanik et al., 2020). Different combinations of membrane separation processes (e.g., NF-MD and membrane bioreactor-NF/RO) has been assessed for nutrient recovery (Xie et al., 2014), water reclamation (Nghiem et al., 2016) and seawater desalination (Luo et al., 2017). Although an integrated NF-MD process has not been studied extensively for the recovery of metals including lithium, the performance of the MD process for the regeneration of different liquid desiccant solutions such as lithium chloride was reported previously (Duong et al., 2018). During the MD process, in addition to the metal being concentrated, co-existence of dissolved magnesium and calcium salts could cause membrane scaling during long-term operation. This can affect the performance of the process by rapidly reducing the permeate flux (Alkhudhiri et al., 2012). Therefore, an integration of an NF process
with a MD process will not only separate Li\(^+\) but will also reject multi-valent cations that can potentially affect the performance of the MD process during concentration/enrichment step. Studies on the removal of coexisting Mg\(^{2+}\) from salt-lake brine using NF pretreatment as well as Li\(^+\) concentration using MD process are available (Sun et al., 2015; Pramanik et al., 2019; Park et al., 2020). However, importantly, the efficacy of NF pretreatment for the separation of Li\(^+\) from several coexisting competing cations has not been studied, and Li recovery following MD concentration remains untapped. To address these research gaps, this study was conducted with an aim to develop an integrated NF-MD and chemical precipitation process for lithium recovery (as LiCO\(_3\)) from salt-lake brine. Li\(^+\) separation from the coexisting competing cations (Na\(^+\), K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\)) commonly present in brines by the NF membrane was systematically assessed and elucidated in the first step. The MD process was subsequently used to enrich/concentrate the NF-permeate for Li recovery, and salt-lake brine without NF treatment was also fed to the MD to show the efficacy of a pretreatment step on the hydraulic performance of the MD. Finally, efficacy of a two-stage precipitation process is demonstrated to recover lithium in the form of lithium carbonate. A schematic of the different treatment steps investigated in this study is presented in Figure 1.

**Figure 1.** Schematic representation of the integrated NF-MD and chemical precipitation process.
2. Materials and Methods

2.1. Feed solution

A synthetic brine solution was prepared by adding a mixture of sodium, lithium, potassium, calcium and magnesium salts into ultrapure (Milli-Q) water. The concentration of each metal salt was selected based on their reported concentrations in a salt-lake brine of China (Volkov et al., 1997; Sun et al., 2015; Chen et al., 2018). Concentration of each salt in the simulated salt-lake brine solution is shown in Table 1. Analytical grade lithium chloride (LiCl), magnesium chloride (MgCl₂), sodium chloride (NaCl), potassium chloride (KCl) and calcium chloride (CaCl₂) were purchased from Sigma Aldrich (Sydney, Australia) to prepare the simulated feed. The pH of the synthetic brine was not controlled and ranged between 6.5-6.9.

Table 1. Concentration of the selected salts in stimulated brine solution and their mass ratio

<table>
<thead>
<tr>
<th>Salts</th>
<th>Concentration (g/L)</th>
<th>Mass ratio of competing ions</th>
<th>Ionic radii (pm)</th>
<th>Hydrated radii (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>0.141</td>
<td>Not applicable</td>
<td>78</td>
<td>382</td>
</tr>
<tr>
<td>NaCl</td>
<td>117</td>
<td>Na⁺/Li⁺ = 830</td>
<td>117</td>
<td>358</td>
</tr>
<tr>
<td>KCl</td>
<td>3.79</td>
<td>K⁺/Li⁺ = 27</td>
<td>149</td>
<td>331</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.43</td>
<td>Ca²⁺/Li⁺ = 3</td>
<td>100</td>
<td>412</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>5.64</td>
<td>Mg²⁺/Li⁺ = 39</td>
<td>72</td>
<td>428</td>
</tr>
</tbody>
</table>

*‘pm’ = picometer; ionic radii and hydrated radii values are for the cation in each salt*

2.2. Lab-scale NF setup and experimental protocol

A laboratory-scale cross-flow NF system (Supplementary Figure S1) was used to study the separation of Li⁺ from brine solution containing a mixture of coexisting cations such as Na⁺, K⁺, Ca²⁺ and Mg²⁺. A detailed description of the NF setup is available elsewhere (Asif et al., 2018). Briefly, this setup consists of a stainless-steel membrane cell with the capacity to hold a NF membrane, a high pressure pump (HydraCell pump, Wanner Engineering Inc., USA), a digital flow meter (Optiflow 1000, Agilent Technologies, USA) attached to a computer for
measuring the permeate flux, and a rotameter (PSM312, Techfluid, Singapore) for controlling the cross-flow velocity. During the experiments, the temperature of the setup was maintained at 20 °C by using a chiller (Neslab RTE 7, Thermo Scientific, Australia), while cross-flow velocity was kept constant at 40 cm/s. A commercially available NF270 membrane (Dow FilmTec, USA) was used in this study. NF270 is a polyamide thin-film composite (TFC) membrane with a molecular weight cut-off (MWCO) of 300 g/mol.

Before the start of experiment, the NF membrane was operated at a pressure of 8 bar using ultrapure Milli-Q water for at least 2 h. This was done to compact the membrane and to achieve a stable permeate flux. Following compaction at 8 bar, the permeate flux of the NF270 membrane stabilised at around 12 L/m² h. The operating parameters such as applied pressure and pH were optimized in a previous study (Pramanik et al., 2019). The NF system was operated with an initial feed volume of 5 L. To assess the effect of the competing ions on Li⁺ separation from brine, the NF system was first operated for a period 10 h in ‘recirculation mode’ i.e., the simulated brine drawn from the feed tank was passed through the NF membrane, and the NF-permeate was returned to the feed tank. Afterwards, the NF system was run by not returning the membrane permeate to the feed tank. In this way, 1 L of NF-permeate was collected for Li enrichment by the MD process. The description of the MD process is given in the following section. Samples were collected from NF permeate for the quantification of cation concentration, and for determining the change in mass ratio of the elements. Three replicate filtrations were conducted and the average value among three samples were reported in this study.
2.3. Lab-scale MD setup and experimental protocol

A lab-scale direct contact membrane distillation (DCMD) system was used for concentrating NF permeate before recovery in the form of lithium carbonate (Supplementary Figure S2). Compared to other MD configurations (e.g., air gap MD), DCMD was selected due to its better process control and operational simplicity (Alkhudhiri et al., 2012). The DCMD setup consisted of a glass feed tank containing the NF permeate or raw brine, a membrane cell, a distillate/permeate tank, and two gear pumps (Micropump Inc., USA). The acrylic membrane cell consisted of two identical parts, each was engraved with two flow channels (L×W×H = 14.5 cm × 9.5 cm × 0.3 cm). The MD setup was run by maintaining the temperature of the MD feed and permeate tanks at 40 and 20°C, respectively. A heating immersion circulator (Julabo, Germany) and a chiller (Thermo Scientific, USA) were used to maintain the temperature of the MD feed and permeate, respectively.

A hydrophobic polytetrafluoroethylene (PTFE) membrane obtained from Ningbo Porous Membrane Technology (China) was used in this study. This membrane had a thickness of 60 µm, nominal pore size of 0.2 µm, and porosity of 80%. Water from the feed tank (containing NF permeate) and permeate tank (containing ultrapure Milli-Q water) were continuously circulated across the membrane at a flow rate of 1 L/min (corresponding to a cross-flow velocity of 9 cm/s) using two rotameters. The experimental conditions (e.g., temperature and flow rate) for MD were consistent with that reported in previous studies (Duong et al., 2016a; Asif et al., 2019b). The vapor pressure gradient developed due to the difference in temperature allows water to move across the hydrophobic membrane from the hot side (i.e., MD feed) to the cool side (i.e., MD permeate). As a result, the volume of water in the permeate tank increases over time. The change in the volume of the permeate tank was monitored in terms of weight by using a precision balance (Mettler-Toledo, Australia). The change in the weight of
permeate was also recorded in a computer via Balance Link software (Mettler Toledo) for measuring the MD permeate flux.

Before the start of the experiment, mass transfer coefficient ($K_m$) was determined to understand the basic performance of the MD process. A detailed procedure of determining the mass transfer coefficient ($K_m$) has been described previously by Asif et al. (2019b). Briefly, the MD system was operated with Milli-Q water at the MD feed temperature of 35, 40, 45 and 50 ºC and at the distillate temperature of 15, 20, 25 and 30 ºC, respectively for 1 h. Equation 1 can be used to theoretically determine the permeate flux of MD.

$$J = K_m \times (P_{\text{feed}} - P_{\text{distillate}})$$  \hspace{1cm} \text{Eq. (1)}$$

where, $J$, $K_m$, $P_{\text{feed}}$, and $P_{\text{distillate}}$ are the permeate flux ($L/m^2 h$), mass transfer coefficient ($L/m^2 h$ Pa), vapor pressure of water in MD feed, and vapor pressure of water in MD distillate, respectively. In addition, $P_{\text{feed}}$ and $P_{\text{distillate}}$ can be calculated using Equation 2 (Lawson and Lloyd, 1997):

$$P = x_{\text{water}} (1 - 0.5 x_{\text{salt}} - 10 x_{\text{salt}}^2) P_{\text{feed}} - P_{\text{distillate}}$$  \hspace{1cm} \text{Eq. (2)}$$

where, $P$ is the vapor pressure difference between feed and distillate, $x_{\text{water}}$ is the molar fraction of water, and $x_{\text{salt}}$ is the molar fraction of salts. Because MD process was characterized by using Milli-Q water, the values of both $x_{\text{water}}$ and $x_{\text{salt}}$ are taken as 1. Vapor pressure of water either in MD feed or in distillate can be determined by using the Antoine Equation (Lawson and Lloyd, 1997) as given below:

$$P_o = \exp (23.1964 - \frac{3816.44}{T - 46.13})$$  \hspace{1cm} \text{Eq. (3)}$$

where, $T$ is the absolute temperature of water in feed or distillate tanks.
In this study, the MD system was operated with 80% recovery of water, i.e., until 80% of the water from the feed tank was moved to the distillate tank. In addition, the synthetic brine solution without NF treatment (‘control’) was also fed to membrane distillation to assess its impact on the hydraulic performance of MD as well as to understand the significance of pretreatment on the MD performance. At the end of the experiment, samples were collected for analysis. The rejection efficiency of metals by MD membrane was calculated according to Equation (4).

\[ R(\%) = (1 - \frac{C_P}{C_f}) \times 100\% \]  

Eq. (4)

where, \(C_P\) and \(C_f\) are the concentrations of the specific cation in the MD permeate and feed, respectively.

### 2.4. Lithium precipitation process

In this study, a two-stage precipitation process was investigated. In the first stage, sodium hydroxide (NaOH) was added in the MD concentrate, to form precipitates of magnesium and calcium. This stage facilitated the removal of Ca\(^{2+}\) and Mg\(^{2+}\) ions via centrifugation. In the second step, sodium carbonate (Na\(_2\)CO\(_3\)) was added in the supernatant that was obtained from the first stage to recover Li\(^+\) in the form of lithium carbonate. The process was conducted in a 500 mL glass beaker. The MD concentrate was added into the glass beaker and agitated with a mixer impeller. A water bath was used to maintain the temperature of the precipitation process. The precipitation of Ca\(^{2+}\) and Mg\(^{2+}\) was executed at room temperature (20°C) and 400 rpm. Following the precipitation and separation of Ca\(^{2+}\) and Mg\(^{2+}\), a 30% (wt) sodium carbonate solution was added, and the temperature of the solution was increased to 90°C. The final solution was heated to the boiling point and concentrated by evaporation, leading to Li precipitation as lithium carbonate.
2.5. Analytical methods

The concentration of metals was determined using an inductively coupled plasma-optical emission spectroscopy (ICP-OES, 7500CS, Agilent Technologies, USA). Before analysis, each sample was diluted using 5% nitric acid (Suprapur, Sigma-Aldrich, Australia) to ensure their elemental components remain in solution. Before each batch of analysis, detector calibration was performed electronically followed by wavelength calibration using a multi-element wavelength calibration solution. Different dilutions of the standard solutions were prepared to obtain a calibration curve ($R^2 > 0.99$). Solution pH and conductivity were measured using an Orion 4-Star Plus pH/conductivity meter (Thermo Scientific, USA). Change in membrane properties (i.e., membrane hydrophobicity) after filtration was analysed by measuring the contact angle using a goniometer (Rame-Hart, USA).

The recovered crystals of lithium carbonate were characterised using scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) (JSM-6490, JEOL, Japan). The purity of the crystals was verified using X-ray diffraction (XRD) spectrum (GBC MMA, USA) at diffraction angles ($2\theta$) ranging from 5 to 90° with a stepwise increase of 0.02° using Cu-Kα radiation at 40 kV and 150 mA.

3. Results and discussion

3.1. Performance of NF for Li separation

The main objective of treatment with NF system was to separate Li from the brine containing different coexisting cations. These cations, particularly Mg can compete with Li during precipitation, which may affect the yield and purity of lithium (Swain, 2017). In this study, NF membrane achieved above 90% rejection of divalent cations ($Mg^{2+}$ and $Ca^{2+}$), while rejection ranged between 42 and 60% for monovalent cations $i.e.$, $Na^+$, $K^+$ and $Li^+$ (Figure 2). In line
with the findings of previous studies (Zhang et al., 2011; Fang et al., 2013; Sun et al., 2015), extent of rejection by the NF membrane was as follows: \( \text{Mg}^{2+} (94\%) > \text{Ca}^{2+} (91\%) > \text{K}^+ (61\%) > \text{Na}^+ (48\%) > \text{Li}^+ (42\%) \). The NF membranes can reject metals via adsorption/attraction or electrostatic repulsion. However, the extent of rejection may depend on the properties of metal ions (Asif et al., 2019a; Zhang et al., 2020). Indeed, as compared to monovalent cations, multivalent cations such as \( \text{Mg}^{2+} \) are more positively charged, and their rejection by negatively charged membrane via charge repulsion can be expected to be significantly better (Al-Rashdi et al., 2013; Zhang et al., 2020). This is probably the main reason of the better rejection achieved by the NF membrane for \( \text{Mg}^{2+} \) and \( \text{Ca}^{2+} \) as compared to \( \text{Na}^+ \), \( \text{K}^+ \) and \( \text{Li}^+ \) (Figure 2).

**Figure 2:** Rejection of \( \text{Li}^+ \), \( \text{Mg}^{2+} \), \( \text{Ca}^{2+} \), \( \text{N}^+ \) and \( \text{K}^+ \) using NF270 membranes. The error bars represent the standard deviation among three samples.

In addition to the adsorption/charge repulsion, it was observed that the ionic radii (i.e., radius of an ion in a crystal lattice) and hydrated radii (i.e., sum of ionic radii and closely bound water molecules) of metal ions affect their extent of rejection by the NF membrane. The ionic radii of the divalent cations, namely \( \text{Mg}^{2+} \) and \( \text{Ca}^{2+} \) are 72 and 100 picometer (pm), respectively, while \( \text{Li}^+ \), \( \text{Na}^+ \) and \( \text{K}^+ \) have an ionic radii of 78, 117 and 149 pm, respectively (Volkov et al.,...
Theoretically, rejection of metal ions should be in accordance with their ionic radii, i.e., large ionic radii corresponds to low rejection value, but the results of this study suggests no apparent correlation between rejection efficiency and ionic radii. For instance, the extent of Li\(^+\) (ionic radii = 78 pm) rejection was significantly lower (< 45%) than that observed for Ca\(^{2+}\) (ionic radii = 100 pm). Notably, the available literature suggests that ions with small size have greater ionic potential and can attract more water molecules as compared to ions with large size (Volkov et al., 1997; Zhao et al., 2017). Due to the attraction of water molecules, the hydrated radii of small size cations such as Ca\(^{2+}\) and Mg\(^{2+}\) could become larger than the cations with larger ionic radii. In this study, there was a trend between the rejection of metal ions and their hydrated radii (Figure 2). For instance, the lowest rejection was observed for Li\(^+\) with the hydrated radii value of 382 pm, while rejection of Mg\(^{2+}\) with the largest hydrated radii value (i.e., 428 pm) was the highest (94%). This is because the metals with lower hydrated radii can easily pass through the NF membrane as compared to those with higher hydrated radii for maintaining the electroneutrality in the NF feed. Interestingly, for monovalent cations, extent of rejection reduced with the increase in hydrated radii, i.e., K\(^+\) (331 pm, 61%) > Na\(^+\) (358 pm, 48%) > Li\(^+\) (382 pm, 42%). In summary, Figure 2 depicted that the higher the hydrated ionic radii of monovalent ions, the lower the rejection. Conversely, the higher the hydrated ionic radii of divalent ions, the higher the rejection.

As mentioned above, the purpose of the treatment of brine with NF system was to separate Li\(^+\) from competing metal ions, particularly Mg\(^{2+}\) ion. In this study, following NF treatment, mass ratio of other cations to Li\(^+\) reduced significantly (Figure 3). Since Mg\(^{2+}\) ions interfere with the formation of lithium carbonate precipitates (Swain, 2017), separation of Li from Mg is critical for achieving effective recovery and yield of lithium. The Mg\(^{2+}\)/Li\(^+\) mass ratio in brines around the globe varies significantly, and its value could be in the range of 20-50 (Vikström et al., 1997; Chen et al., 2018).
However, for effective lithium recovery, Mg$^{2+}$/Li$^+$ mass ratio of less than 6 has been reported to be suitable (Zhao et al., 2013). Effective separation of Li from Mg by NF has been reported before (Sun et al., 2015; Pramanik et al., 2019). In this study, the NF treatment step reduced the Mg$^{2+}$/Li$^+$ mass ratio from 40 to 4 (Figure 3). This made the NF permeate suitable for Li enrichment and recovery by MD process and precipitation, respectively as demonstrated in next sections.

The hydraulic performance of the NF system in terms of permeate flux was monitored throughout this experiment. Permeate flux of the NF system reduced gradually, and a reduction of 30% in permeate flux was observed. This can be attributed to concentration polarization caused by the accumulation of salts on or near the membrane surface (Sun et al., 2015; Asif et al., 2019a). Aspects of fouling as well as the effect of membrane properties were beyond the scope of this study, and, hence, were not investigated comprehensively.

![Graph showing the mass ratio of metal ions in NF feed and permeate](image)

**Figure 3:** The reduction in the mass ratio of metal ions following treatment with the NF270 membranes. The results suggest a significant reduction in the mass ratio.
3.2. Performance of MD process for Li enrichment

3.2.1. MD mass transfer coefficient

The basic performance of MD processes is often assessed by determining the mass transfer coefficient ($K_m$). Vapor pressure difference induced by temperature is the main driving force for flux in MD, because vapor pressure increases exponentially with the increase in temperature gradient across the membrane surface (Alkhudhiri et al., 2012). Despite that, with the increase in temperature of the MD feed, the permeate flux measured experimentally increased (Figure 4a). Previously, Alklaibi and Lior (2005) also observed that the increase in feed temperature has more favourable effect on permeate flux than the reduction in distillate temperature. Both concentration and temperature polarization can affect the mass transfer coefficient (Alkhudhiri et al., 2012; Duong et al., 2017). Because MD was characterised using Milli-Q water, the effect of concentration polarization can be ignored. Notably, the comparison of the MD characterisation data indicates a slight reduction in mass transfer coefficient values following the increase in feed temperature (Figure 4b). This observation is consistent with that reported previously (Martínez-Diez and Vazquez-Gonzalez, 1999; Khalifa et al., 2017; Asif et al., 2019b). Due to reduction in the mass transfer coefficient with increasing feed temperature, selection of the operating temperature for MD process becomes critical. In this study, for enrichment of Li, the MD system was operated at the feed temperature of 40°C and distillate temperature of 20°C. This is because the mass transfer coefficient did not reduce significantly at 40°C/20°C temperature. Otherwise, the cooling or heating is required to increase or decrease distillate temperature, which is not cost-effective. Under these conditions (i.e., 40°C feed and 20°C distillate), the mass transfer coefficient of the MD with Milli-Q water feed was $2.31 \times 10^{-3}$ L/m² h Pa.
Figure 4. Basic performance of the MD systems at different feed and distillate temperature.

Permeate flux (a) was measured experimentally, while mass transfer coefficient (b) was determined using Equation 1-3.

3.2.2. Concentration of treated and untreated brine by MD

Lithium in the NF-permeate was concentrated by the MD process. The performance of MD was also studied for the concentration of raw brine. This run served as a ‘control’ for understanding the impact of NF pre-treatment on downstream Li concentration and recovery. The MD system in this study was operated at a flow rate of 1 L/min, feed temperature of 40°C and distillate temperature of 20°C. The experiments with raw brine and NF-treated brine were conducted until a water recovery of 80%.

Because water moves across the membrane in vapor form, the MD process can achieve up to 99% rejection of non-volatile metals (Alkhudhiri et al., 2012). In a study by Pramanik et al. (2019), the concentration of Li and Mg in the permeate of the MD system was below the limit of detection. Similarly, Attia et al. (2017) reported above 99% heavy metal rejection by the
MD membrane. In this study, effective rejection of metals, particularly lithium was critical for its recovery. Analysis of the MD-permeate confirmed complete rejection of all the metal ions. In addition, the conductivity of the distillate increased slightly (less than 5%) at the start of MD operation but did not increase further afterwards. The increase in the conductivity of distillate at the start of experiment could be due to the transport of CO\textsubscript{2} from feed to distillate (Duong et al., 2016b). Notably, feed type (raw brine or treated brine) significantly affected the hydraulic performance of the MD process as explained below.

The mass transfer coefficients (Figure 4) measured using Milli-Q water gave understanding about the basic performance of MD process. However, in presence of metal salts, the water flux of the MD process would reduce almost linearly with the increase in salt concentration in MD feed during enrichment (Figure 5). This reduction in permeate flux can be estimated by running the mathematical simulations (Equation 1-3). Since vapor pressure is the driving force of flux in MD, its values calculated using equation (2) reduce with the increase in the concentration of salts. As a result, a decline in the permeate flux of MD is always expected (Duong et al., 2016a). According to the mathematical simulations, the theoretical permeate flux (Figure 5) reduced by 25% for treated brine (NF permeate) and 60% for raw brine at a water recovery of 80% (i.e., at a concentration factor of 5).
Figure 5. Variations in the permeate flux of MD system measured theoretically and experimentally as a function of water recovery. Theoretical flux was calculated using Equation 1-3.

While treating raw brine (without NF treatment), the actual mode of permeate flux reduction (i.e., that measured experimentally) was significantly different than the theoretical flux. For instance, during the concentration of raw brine without NF pre-treatment, permeate flux reduced to almost zero at the water recovery of approximately 60% (Figure 5). This could be attributed to concentration polarization effect (Duong et al., 2016a). When the concentration of salts increases in the feed, the precipitation of salts on membrane surface could occur, which promotes temperature and concentration polarization. This reduces the vapor pressure near membrane surface, and results in flux reduction (Wang et al., 2014; Duong et al., 2016a). The effect of concentration polarization on MD flux following an increase in the concentration of LiCl liquid desiccant has been reported previously (Duong et al., 2017). On the other hand, during the concentration of treated brine (i.e., NF permeate, MD flux reduced gradually (Figure 5), and the variations between theoretical and measured flux were not significant. This is
probably because the concentration of salts in the treated brine (i.e., NF permeate) was significantly lower than that in raw brine.

The concentration of MD feed increases the salt concentration, and this may result in the precipitation of salts on membrane surface (Wang et al., 2014; Duong et al., 2016a). The deposited salt may affect the hydrophobicity of MD membrane. Indeed, a significant reduction in membrane hydrophobicity has been reported during concentration of seawater and liquid desiccant solutions (Duong et al., 2016a; Duong et al., 2018). In this study, the contact angle of the MD membranes was measured using Milli-Q water as a reference. The results indicate that the hydrophobicity of MD membranes reduced from 124° to 58° and 124° to 68° (Figure 6), when raw brine and treated brine (NF permeate) were used as MD feed, respectively. Notably, the reduction in hydrophobicity did not affect the metal rejection by the MD membrane. However, with raw brine, more frequent cleaning of membrane would be required for long term MD operation. Different strategies for scaling prevention and control have been studied previously by Duong et al. (2016a). However, membrane cleaning for scaling mitigation is beyond the scope of this study.

![Figure 6](image.jpg)

**Figure 6.** Hydrophobicity measured as contact angle of the MD membranes. The results are presented as average ± standard deviation (n=5).
3.3. Recovery of Li by precipitation

In this study, the concentration of Li\(^+\) in the enriched brine (*i.e.*, NF permeate concentrated by MD) was about 0.41 g/L and was comparable to that reported in real brines (Sun et al., 2015; Swain, 2017). The precipitates of lithium carbonate were characterised using SEM and XRD. Lithium carbonate crystals has a size of around 30-60 \(\mu\)m (Ooi et al., 2017). However, in this study, as confirmed by the SEM image, 10 \(\mu\)m crystals of lithium carbonate were obtained following the precipitation process (Figure 7). This is because the increase in supersaturation can cause an increase in the number of crystal nuclei. As a result, the size of lithium carbonate crystals can reduce. Similar observations were reported by Ooi et al. (2017) following the direct crystallization of Li\(^+\) in the form of lithium sulphate. The energy dispersive x-ray spectroscopy (EDS) of lithium carbonate crystals (Figure 7) revealed that the crystals did not contain Na\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\), confirming the purity of lithium carbonate crystals.

Figure 7: SEM-EDS of the lithium carbonate crystals recovered by the integrated NF-MD-precipitation process

The lithium chloride crystals were also characterised using XRD to determine the presence of impurities. The peaks in the XRD pattern can largely be connected to lithium carbonate crystals...
Notably, the enriched brine following MD process contained high concentration of Na (300 g/L) and K (8 g/L), but only a small peak corresponding to NaCl was observed in the XRD spectra at 2-theta@30-31 degree (Figure 8). The XRD spectra also showed that the peak intensity of the recovered lithium carbonate almost matched with the standard lithium carbonate (except for the peak intensity at 2-theta@30-34 degree), indicating above 99% purity. The XRD spectra of the lithium carbonate crystals was similar to that reported for lithium carbonate recovered from Uyuni Salar brine in Bolivia (An et al., 2012). The method of lithium precipitation assessed in this study was effective, but more studies are required to compare and optimize different precipitation methods.

**Figure 8.** XRD spectra of the lithium carbonate crystals recovered by the integrated NF-MD-precipitation process

### 3.4. Feasibility and future outlook

Membrane distillation (MD) processes have been predominantly investigated for advanced water and wastewater treatment (Alkhudhiri et al., 2012). According to the available literature, MD has been recognised as a cost-effective technology for desalination as compared to...
pressurized membrane separation processes (e.g., reverse osmosis, RO) mainly possibly due to lower specific energy consumption. Following their integration with solar energy, specific energy consumption could be as high as 4 kWh/m$^3$ for RO and could be as low as 0.13 kWh/m$^3$ (Al-Karaghouli and Kazmerski, 2013). In addition, the operating cost of MD could be further reduced by utilizing low grade waste heat. Indeed, Meindersma et al. (2006) reported that the cost of water production by MD utilizing wastewater heat was only $0.26/m^3$. In a study by Drioli et al. (2002), a comprehensive economic analysis was performed to assess the feasibility of integrated NF/RO process and NF/RO/MD-crystallization process. They found that, at the water recovery rate of 70% and treatment capacity of approximately 18,000 m$^3$/d, the integrated NF/RO/MD-crystallization process recover enough salts to generate a yearly profit of three million dollars.

Literature suggest that the application of the integrated membrane processes has been limited to the lab-scale studies. Nevertheless, techno-economic analysis of NF-MD process for lithium recovery was performed by Park et al. (2020) to assess its feasibility. They estimated both the capital and operating cost of the integrated NF-MD process and compared it with those of conventional solar evaporation technique. They reported that the construction of full-scale solar evaporation ponds accounts for 30% of the total capital cost (i.e., 425 million dollars). On the other hand, at identical treatment capacity, the construction cost of the integrated membrane process was estimated to be 18.6 million dollars, i.e., 14% of the total capital cost of solar evaporation ponds. However, the operating cost of the full-scale integrated membrane process was estimated to be 8% higher that of the solar evaporation ponds (Park et al., 2020). This is due to extensive energy consumption as well as membrane replacement possibly after every five years. As indicated above, thermal energy demand of MD could be reduced by: (i) utilizing waste heat; (ii) recovering the heat energy via a heat exchanger; and/or (iii) implementing
process optimization and automation (Schwantes et al., 2013). However, research on improving the thermal efficiency of is still on-going. Fouling caused by deposition of salts on membrane surface is another concern that could affect the feasibility of the integrated membrane processes. More research is required to address the issues of membrane fouling during long-term operation as well as to compare and optimize different lithium precipitation methods.

4. Conclusions

In this study, an integrated process was developed by combining the nanofiltration (NF), membrane distillation (MD) and precipitation processes for Li recovery from salt-lake brine. Since coexisting metal ions, particularly Mg$^{2+}$ affects Li$^+$ recovery in the form of lithium carbonate, the salt-lake brine was treated with an NF membrane for Li$^+$ separation. The NF membrane achieved effective rejection (>90%) of divalent cations (i.e., Mg$^{2+}$ and Ca$^{2+}$), while rejection of monovalent cations (i.e., Na$^+$, K$^+$ and Li$^+$) ranged between 40 and 60%. Separation of Li$^+$ from the simulated salt-lake brine reduced the mass ratio of Mg$^{2+}$/Li$^+$ and brought it to less than 6 that is recommended for Li recovery. To increase the concentration of lithium, raw brine and treated brine were concentrated using a direct contact – MD process. The results indicate that MD process can effectively concentrate NF-treated brine by five times. High concentration of salts affected the hydraulic performance of the MD membrane while treating raw brine. Following concentration by MD, Li was recovered in the form of lithium carbonate using a two-stage precipitation process. Characterisation of recovered lithium was carried out using SEM-EDS and XRD to confirm the formation of lithium carbonate crystals. This is the first study demonstrating the efficacy of NF-MD and precipitation process for lithium recovery.
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