Study on the recovery of lithium from high Mg$^{2+}$/Li$^+$ ratio brine by nanofiltration

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ABSTRACT

An experiment to recover lithium from high Mg$^{2+}$/Li$^+$ ratio brine by nanofiltration (NF) was carried out. The combination of Donnan exclusion, dielectric exclusion and steric hindrance governed the mass transport inside the NF membrane. Experimental results showed that NF is an efficient technique to recycle Li$^+$ and reduce Mg$^{2+}$/Li$^+$ ratio from high Mg$^{2+}$/Li$^+$ ratio brine. When content reached 6.0 g/L, operating pressure reached 0.8 MPa and Mg$^{2+}$/Li$^+$ ratio in feed was 40, the rejection of magnesium ($R$(Mg$^{2+}$)) and the separation factor (SF) were 0.96 and 42, respectively. The Mg$^{2+}$/Li$^+$ ratio in permeate could be reduced to 0.9, and Li$^+$ recovery ratio was 85%. Adding potassium (K$^+$) or sodium (Na$^+$) to solution can reduce $R$(Mg$^{2+}$) and SF.

Key words | high Mg$^{2+}$/Li$^+$ ratio, nanofiltration, recovery of lithium, rejection rate, separation factor

INTRODUCTION

The nanofiltration (NF) process, as a pressure-driven separation process, has been widely used in the pharmaceutical industry, food industry and water treatment industry. A NF membrane has two prominent features (Rautenbach & Groschl 1990): firstly its molecular weight cut-off is between reverse osmosis membranes and ultrafiltration membranes; secondly it can be used to remove inorganic salts from salt solution, especially extracting monovalent ions from systems containing multivalent ions. Therefore, NF should be feasible for separation of monovalent ions and bivalent ions.

Lithium is known as the most important energy metal and a significant element that is pushing the world forward in the 21st century. Consumption of lithium and its compounds is growing a lot in many fields, including aerospace, nuclear power, battery power and ultra-high strength lithium-aluminum alloy (Shen & Dai 2009). From the beginning of the 1980s, development and utilization of lithium from salt lake brine has gradually become the primary source for the lithium industry. However, it is difficult to separate lithium and magnesium, since they have similar properties. At present, several methods are employed in the separation of lithium from salt lake brine, such as precipitation (Zhong et al. 2002), extraction (Liang et al. 2009), adsorption (Lee 1980) and electro dialysis method (Wen et al. 2006). Zhong et al. (2002) used hydroxide and sodium carbonate as precipitant to form boron and magnesium co-precipitants, to separate them from lithium. It is a simple process, but a large amount of precipitating agent will be used, and loss rate of lithium is high. Lee (1980) prepared an aluminate adsorbent (LiCl·2 Al(OH)$_3$·nH$_2$O) to adsorb lithium from brine. Wen et al. (2006) found electrodialysis is an effective method to recover lithium chloride from lithium-containing waters, but it requires that monovalent ion content is not less than 50 mmol/L. In spite of this, the recovery of lithium from high Mg$^{2+}$/Li$^+$ ratio salt lake brine is still an arduous task. Many researchers have focused on the separation of lithium from salt lake brine by NF (Yang et al. 2011); however, some factors on the separation of lithium are not considered in those studies. It is necessary to do further research on recovery of lithium from brine.

In this work, lithium chloride was recovered from high Mg$^{2+}$/Li$^+$ ratio brine. The effects of salt concentration, pressure and the existence of K$^+$ or Na$^+$ with different Mg$^{2+}$/Li$^+$ molar ratio in feed ($\left(\frac{\text{Mg}^{2+}}{\text{Li}^+}\right)_i$) on the performance of NF membrane were investigated.

EXPERIMENTAL

Experimental set-up

The experimental set-up is shown in Figure 1. The NF element was a spiral-wound DK-1812 model (the membrane core model is 3B02S-DAC8-1812, hereafter referred to as 3B02S) supplied by Suntar Membrane Technology (Xiamen) Co., Ltd, which is...
of a composite type having an active area of 0.24 m². The storage tank jacket was circulated with cooling water to stabilize the feed temperature at (20 ± 0.5) °C. A pump allowed circulation of the solution from a feed tank of 7 L to the membrane module where it flowed over the active layer of the membrane. The permeate solution was collected at various transmembrane pressures when a constant filtration regime was achieved. Then the permeate and retentate flowed back to the feed tank to maintain a constant feed concentration.

Materials and preparation of feed solution

Magnesium chloride hexahydrate (MgCl₂·6H₂O), lithium chloride (LiCl), potassium chloride (KCl) and sodium chloride (NaCl) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (Beijing, China).

The feed solutions were prepared using the above reagents. Aqueous solutions were prepared with pure water obtained by means of a reverse osmosis membrane system (UPT-1-5T, China). The molar ratios of magnesium to lithium (Mg²⁺/Li⁺ ratios) ranged from 20 to 40. The concentrations of solutions (C_i) were 2.0, 4.0, 6.0 and 8.0 g L⁻¹, respectively. Table 1 lists the bulk diffusion coefficient and radius of the solutes.

Measurement and analysis

Inductively coupled plasma (ICP; ICAP6500 spectrometer, USA) was used to investigate the cation concentrations (Mg²⁺, Li⁺) of samples. The operating conditions set on the ICP spectrometer during the measurements were as follows: forward power 1150 W, observation height 12 mm, Ar gas partial pressure 0.6 MPa, auxiliary gas flow rate 0.5 L min⁻¹, nebulization flow rate 0.35 L min⁻¹. The most prominent analytical lines of the studied metals were selected for investigation, i.e. Mg ~ 279.0 nm, Li ~ 670.7 nm.

The pure water flux (J_v, m²·m⁻²·h⁻¹) was used to express the rate at which water permeated the membrane and was defined as the permeate water volume per area per unit of time

\[ J_v = \frac{V}{A \times \Delta t} \]  

where V, A, and \( \Delta t \) are the permeate water volume (m³), active surface area of membrane (m²), and permeation time (h), respectively.

The rejection rate of Mg²⁺ (R(Mg²⁺), unitless) was calculated by Formula (2)

\[ R(Mg^{2+}) = 1 - \frac{(C_{Mg^{2+}})_p}{(C_{Mg^{2+}})_f} \]  

where \((C_{Mg^{2+}})_p\) and \((C_{Mg^{2+}})_f\) are the concentrations of Mg²⁺ in permeate (g L⁻¹) and feed (g L⁻¹), respectively.

The membrane separation factor (SF, unitless) was used to express the separation efficiency of systems

\[ SF = \frac{(C_{Li^+}/C_{Mg^{2+}})_p}{(C_{Li^+}/C_{Mg^{2+}})_f} \]  

where \((C_{Li^+})_p\) and \((C_{Li^+})_f\) are the concentrations of Li⁺ in permeate (g L⁻¹) and feed (g L⁻¹), respectively.

**RESULTS AND DISCUSSION**

The separation performance of the membrane usually can be characterized by water flux, rejection rate and SF etc. Rejection rate (Formula (2)) reflects the membrane separation
selectivity of solutes. The bigger the rejection difference of the composition, the better the separation performance of the membrane. The SF of membrane (Formula (3)) is used to express the separation efficiency of systems. Mainly rejection rate and SF are discussed in this paper.

**Effect of feed concentration on rejection and SF**

The mass transport inside the NF membrane is governed by the combination of steric hindrance, Donnan exclusion and dielectric exclusion (DE) (Szymczyk & Fievet 2005). The Donnan exclusion on rejection is based on ion valance – an increase as the co-ion valance increases, and a decrease as the counter-ion valance increases. The DE is partly due to ions with different dielectric constants at the interface of external solution and pore solution of membrane. The exclusion energy is proportional to the square of ion charge including cations and anions.

Figure 2 illustrates the variation of rejection rate of Mg$^{2+}$ ($R$(Mg$^{2+}$)) and SF versus feed concentration. The results exhibit a high rejection rate of Mg$^{2+}$, which increases and then tends to be stable as the feed concentration increases. This phenomenon is consistent with the results reported by other researchers (Labbez et al. 2002; Tsuru et al. 2002; Van Gestel et al. 2002). The rejection could reach 0.96 when $(Mg^{2+}/Li^+)_f$ is 40. The $R$(Mg$^{2+}$) is higher when $(Mg^{2+}/Li^+)_f$ is 20 rather than 30. This is partly due to the DE of NF. DE makes the Donnan exclusion stronger whereas the presence of fixed charges on the pore walls of the NF membrane as well as the ionic atmosphere surrounding an ion weakens the DE effects by screening the image charge forces. Thus, the increase of fixed charge density in the NF membrane will strengthen Donnan exclusion, whereas the DE will be screened and declined in strength. Due to the large amount of chloride ion through the membrane, an electric potential is formed at the separation interface. Mg$^{2+}$ is a divalent ion which does not easily pass through the membrane. In order to maintain electroneutrality conditions, Li$^+$ is driven through the membrane because of the existence of electric potentials. However, DE can also be weakened as the concentration increases, leading to a decrease of $R$(Mg$^{2+}$) at the feed concentration of 8.0 g/L. SF, with the increase of the solution concentration, increased and then decreased, as the increase of Mg$^{2+}$/Li$^+$ ratio increased, except the $(Mg^{2+}/Li^+)_f$ is 20. Therefore, the suitable feed concentration is 6.0 g/L.

**Effect of operating pressure on rejection and SF**

Figure 3 demonstrates the variation of $R$(Mg$^{2+}$) and SF against operating pressure. The trend of Figure 3(a) is same as that of Figure 2(a). Mg$^{2+}$ exhibits higher rejection, which, with the increase of the operating pressure, increases and then tends to be stable. The highest rejection could reach 0.95 when $(Mg^{2+}/Li^+)_f$ is 40. When $(Mg^{2+}/Li^+)_f$ are 30 and 20, $R$(Mg$^{2+}$) is similar and less than 0.95. This is mainly because of the DE of NF. With the increase of the operating pressure SF increases and then decreases after 0.6 MPa, and is enhanced with the increase of $(Mg^{2+}/Li^+)_f$, which indicates that, to separate lithium and magnesium efficiently, the operating pressure should not be too high.

**The variation Mg$^{2+}$/Li$^+$ ratio between feed and permeate solution and recovery of Li$^+$**

The Mg$^{2+}$/Li$^+$ ratio and concentration of Li$^+$ in feed and permeate solutions, and Li$^+$ recovery ratio ($C_f=6.0$ g/L, $P=0.8$ MPa, $T=20^\circ C$).
The Mg\(^{2+}\)/Li\(^{+}\) ratio in solution decreased rapidly, from 40 to 0.9, by the NF process. The (Mg\(^{2+}\)/Li\(^{+}\))\(_{p}\) remained little changed with the increase of (Mg\(^{2+}\)/Li\(^{+}\))\(_{f}\). The recovery ratio of Li\(^{+}\) can reach 85%. Therefore, NF is feasible to reduce the Mg\(^{2+}\)/Li\(^{+}\) ratio, to separate lithium from high Mg\(^{2+}\)/Li\(^{+}\) ratio brine.

Effect of the existence of K\(^{+}\) or Na\(^{+}\) on rejection and SF

The effect of potassium (K\(^{+}\)) and sodium (Na\(^{+}\)) on R(Mg\(^{2+}\)) and SF are clearly shown in Figures 4 and 5. It can be observed that adding K\(^{+}\) or Na\(^{+}\) can reduce R(Mg\(^{2+}\)) and SF. Compared to Na\(^{+}\), K\(^{+}\) shows more effects on R(Mg\(^{2+}\)) and SF. This result is consistent with the literature (Bandini & Vezzani 2005). This phenomenon can be explained by the presence of DE. Owing to the sequence of Stokes radius (Na\(^{+}\) < K\(^{+}\) < Li\(^{+}\)) and diffusion coefficient (Na\(^{+}\) > K\(^{+}\) > Li\(^{+}\)), Na\(^{+}\) and K\(^{+}\) will precede the Li\(^{+}\) through the membrane. More Li\(^{+}\) stays at the retentate, so the SF reduces.

![Figure 4](https://iwaponline.com/wst/article-pdf/70/10/1690/470020/1690.pdf)

**Table 2** The Mg\(^{2+}\)/Li\(^{+}\) ratio and concentration of Li\(^{+}\) in feed and permeate solution, and Li\(^{+}\) recovery ratio (C\(_{f}\) = 6.0 g/L, P = 0.8 MPa, T = 20°C)

<table>
<thead>
<tr>
<th>Mg(^{2+})/Li(^{+}) ratio [mol mol(^{-1})]</th>
<th>Feed</th>
<th>Permeate</th>
<th>(C(<em>{Li^{+}}))(</em>{f}) [g L(^{-1})]</th>
<th>(C(<em>{Li^{+}}))(</em>{p}) [g L(^{-1})]</th>
<th>Li(^{+}) recovery ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.1</td>
<td>0.0217</td>
<td>0.0317</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1.1</td>
<td>0.0145</td>
<td>0.0357</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.9</td>
<td>0.0109</td>
<td>0.0195</td>
<td>85</td>
<td></td>
</tr>
</tbody>
</table>
largely. Therefore, the presence of Na⁺ or K⁺ is not conducive to separation and recovery of Li⁺ from lithium-containing waters.

CONCLUSION

In this study, NF has been proved to be an efficient technique to recover Li⁺ and reduce Mg²⁺/Li⁺ ratio from high Mg²⁺/Li⁺ ratio brine. The combination of Donnan exclusion, DE and steric hindrance governed the mass transport inside the NF membrane. The results showed that the 3B02S NF membrane exhibited satisfactory rejection of Mg²⁺. The \( R(\text{Mg}^{2+}) \) and SF with 6.0 g/L of feed concentration, 0.8 MPa of operating pressure and 40 of \( (\text{Mg}^{2+}/\text{Li}^+) \), reached 0.96 and 42, respectively. Adding K⁺ to solution can reduce \( R(\text{Mg}^{2+}) \) and SF. The Mg²⁺/Li⁺ ratio could be reduced from 40 to 0.9. However, Li⁺ recovery ratio was only 85%; it remains to be increased through adding a filtration stage or improving the performance of NF membrane.

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REFERENCES


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