

# Selective lithium extraction and concentration from diluted alkaline aqueous media by a polymer inclusion membrane and application to seawater

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## Abstract

A method capable of selectively extracting and concentrating lithium from diluted alkaline aqueous media is proposed using a polymer inclusion membrane composed of cellulose triacetate (CTA) and the carriers LIX-54-100 and Cyanex 923 without the addition of plasticizer. Transport conditions were optimized using the modified simplex algorithm. The system can transport lithium against its concentration gradient due to a coupled hydrogen ions countertransport. Under optimized conditions, the membrane can be reused up to 10 times before losing 40% of its initial capacity. Using the proposed system, lithium can be concentrated from diluted aqueous media in presence of high quantities of other metals to get a lithium chloride solution from which it would be easier to get valuable high purity lithium compounds. The membrane was used to extract and concentrate lithium from synthetic and actual seawater and good selectivity and recovery was achieved.

**Keywords:** Lithium recovery, polymer inclusion membranes, synergistic extraction, seawater, valuable metals

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## 1. Introduction

Lithium has become a strategic element since modern lifestyle requires us to have efficient and lightweight ways to store energy [1, 2]. As the lightest solid element having also the higher redox potential and heat capacity, lithium fits perfectly many of our necessities due to its excellent energy storage density besides many other useful properties of its compounds. Lithium natural reserves exist mainly in minerals and brine of salt lakes, geothermal water, groundwater, and seawater. The extraction process from solids involves high cost-demanding and environment-hazardous operations and an increasingly scarce raw material. On the other hand, extracting the lithium that is present in natural liquid sources is usually accomplished by cheaper hydrometallurgy processes which have the advantage of having the element already present in solution. The fast-growing demand for this element is expected to overcome

the predicted availability by the next few decades [3, 4]. The growing lithium demand is greatly influenced by a transport sector shifting to electric propulsion as a low-carbon technologies in a world looking for stop climate change [5]. In these terms, more research is required to find practical ways to extract lithium from resources that are not currently being extracted due to economic constraints that mainly arises from a very low lithium concentration and a high relative concentration of other species.

Oceans compose the biggest known earth's lithium reserves. The water in the oceans has an estimated total volume of  $1.37 \times 10^9$  km<sup>3</sup> and an average lithium concentration of 0.17 - 0.18 mg kg<sup>-1</sup> [2, 6, 7]. Total lithium amount in the oceans (250 million tones) is much bigger than the combined resources of the lithium-rich countries (14 million tones) [8]. Lithium extraction from seawater is not currently possible at the industrial scale for the reasons mentioned above [3].

The predicted shortages of the element may cause inflation in the cost making economically viable its extraction from very diluted media. Several strategies like solvent Extraction (SX) [9–11], combined cation exchange membranes [12, 13], specific adsorption [14], selective electrolysis and electrodialysis [7, 8, 15], nanofiltration [16, 17], supported liquid membranes (SLM) [18–21] and recently, polymer inclusion membranes [22] has been studied to extract lithium from liquid sources. Some of these methods have not been applied to real sample matrices and most of them are far from being implemented at industrial scale. A comprehensive review of membrane technologies for lithium extraction from brines can be found in refer-

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### Abbreviations used:

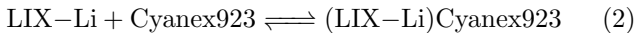
PIM	Polymer Inclusion Membrane
CTA	Cellulose Triacetate
PVC	Poly(vinylchloride)
FAES	Flame Atomic Emission Spectrometry
FAAS	Flame Atomic Absorption Spectrometry
RPM	Revolutions Per Minute
FPS	Frames Per Second
RGB	Red Green Blue

ence [23].

A polymer inclusion membrane (PIM) is a non-porous physical barrier that incorporates extractants (carriers) and a plasticizer into a polymer matrix usually made of cellulose triacetate (CTA) or poly(vinyl chloride) (PVC) [24]. Similar in operation and performance to supported liquid membranes (SLM) which is a porous physical barrier that holds an organic solution of the extractants inside the channels of the membrane [25], PIMs have demonstrated good suitability to extract several valuable metals from seawater overcoming the stability issues commonly related to the use of some SLM systems [26].

Here we present a PIM system capable of selectively extracting and concentrating lithium ions from seawater after two not highly energy-demanding precipitation steps. The synergistic solvent extraction of lithium ions from chloride solutions using LIX-54-100 and Cyanex 923 carriers was firstly reported by Pranolo et. al. [9] and similar approaches have been applied to several SLM lithium extractions [11]. SLM and PIM systems present the advantage over traditional solvent extractions that they use smaller carriers amounts and allow the extraction and stripping steps to be performed simultaneously in processes that can be adapted to work on continuous flow settings [24].

LIX-54-100 (main component 1-phenyldecanone-1,3-dione [27]) is a  $\beta$ -diketone chelating carrier that presents keto-enol tautomerism. In the enolic form, it is capable of reversely exchange the mildly acidic proton by a lithium cation producing a neutral chelate than can be solvated and transported across the membrane by the Cyanex 923 (main component trialkylphosphine oxide, with hexyl and octyl groups [28]). Several  $\beta$ -diketones and solvation extractants have been combined to synergistically extract lithium ions using membranes [11, 22]. Involved reactions are lithium chelation by LIX-54-100 before neutral chelate solvation by Cyanex 923:



The above reactions occur as written in the feed side of the membrane-solution interface and occur in the reverse direction at the strip side of the membrane-solution interface. The driving force is a marked hydronium concentration gradient between the acidic strip solution and the alkaline feed solution. Transport of metal cations can proceed until this proton gradient vanishes but the process may be limited by membrane stability.

In this work lithium recovery and concentration using a PIM system containing the synergic LIX-54-100/Cyanex 923 extractant mixture is optimized and studied in terms of its efficiency factors (permeability, selectivity and stability) with the aim of evaluating its potentiality as a separation method of the metal from diluted alkaline aqueous

media. An application to synthetic and natural seawaters is presented as well.

## 2. Experimental

### 2.1. Reagents and apparatus

All aqueous solutions were prepared using analytical grade reagents and deionized water. Extractants Cyanex 923 and LIX-54-100 were kindly provided by Cytec Canada Inc. and Cognis Corporation, respectively. Cellulose triacetate (CTA, Aldrich. Acetyl content 43.6 wt.%,  $M_w$  72000 to 74000 g mol<sup>-1</sup>), dichloromethane (DCM, J.T. Baker), sodium chloride (Monterey), potassium chloride (Merck), calcium chloride dihydrate (Merck), magnesium sulfate heptahydrate (Merck), hydrochloric acid (Sigma-Aldrich), ammonia hydroxide (Sigma-Aldrich), diammonium hydrogen phosphate (Merk) and sodium hydroxide (Mallinckrodt) were used. Lithium and magnesium chloride solutions were prepared by dissolving the respective carbonates (Aldrich) in stoichiometric diluted hydrochloric acid. All reagents were used without further purification.

Lithium, sodium and potassium ions concentrations were determined by Flame Atomic Emission Spectrometry (FAES, Perkin-Elmer 3100 atomic absorption spectrometer). Calcium and magnesium ion concentration were determined by Flame Atomic Absorption Spectrometry (FAAS, Perkin-Elmer 3100 atomic absorption spectrometer). The analysis were performed under manufacturer recommended conditions. Most determinations were made using external standard calibration with matrix matching. Lithium determination on the seawater matrix was made using a single-point standard addition method [29].

### 2.2. Polymeric inclusion membranes preparation

Membranes were prepared by the casting-evaporation procedure described elsewhere [30]. Weighed amounts of the base polymer and extractants were dissolved in 10 mL DCM by magnetic stirring for at least two hours. The homogeneous solution was quantitatively transferred to a 5 cm diameter Pyrex® glass Petri dish and allowed to slowly evaporate overnight. Transparent homogeneous films were formed. Flooding the glass dish with water facilitated the membrane peeling off from the glass.

Membranes were flexible and had good mechanical strength despite the absence of plasticizer in its formulation. As reported in several studies [22, 31, 32], this is possible due to the double function carrier/plasticizer by one of the extractants. We found that the transport process had better repeatability when the membrane side that was against the glass surface (smoother than the air-exposed side) was facing the source solution. Membrane thickness was measured using a Fowler IP54 digital gauge screw micrometer.

### 2.3. Transport experiments

A 200 mL permeation cell (Figure 1) was used. The membrane exposed area was  $19.6 \text{ cm}^2$  and the initial amount of solution at each side of the cell was 85 mL. After system optimization, the strip solution was  $0.10 \text{ mol kg}^{-1}$  hydrochloric acid while the feed solution was composed of  $0.016 \text{ mol kg}^{-1}$  ammonium hydroxide. Lithium initial concentration in feed phase was kept constant at  $2 \text{ mg kg}^{-1}$ . Solutions were mechanically stirred at  $600 \pm 50 \text{ RPM}$ . The agitation speed was determined using a high-speed camera (240 FPS) and the RGB profile tool of the Open Source Physics video processing software Tracker [33]. Under these hydrodynamic conditions, we found little to no dependency on the agitation speed on transport efficiency. Small aliquots were taken at regular time intervals to monitor metal concentration changes in the solutions.

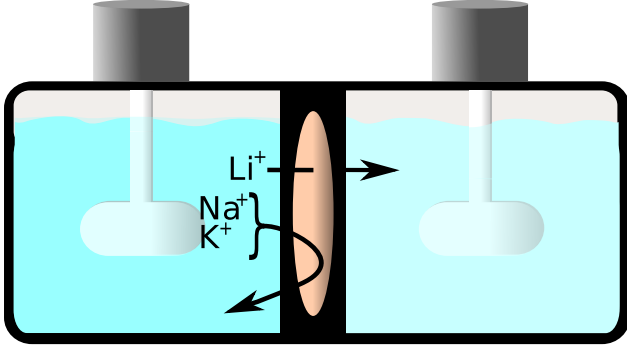


Figure 1: Scheme of permeation cell used.

For the selectivity studies, feed solutions were added with  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  at molar ratios  $\text{M}^{n+}/\text{Li}^+$  1:1, 10:1 and 100:1. Corresponding mass ratios were as high as 331:1, 563:1 and 350:1 for  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ , respectively.

Membrane reuse capabilities were tested by changing feed and strip solutions 10 times each 6 hours. The strip compartment was soaked with deionized water between cycles.

Concentration experiments were made renewing feed solution 5 times every 6 hours while using the same membrane and strip solution.

### 2.4. Artificial and natural seawater experiments

The artificial seawater matrix was made according to the simplified synthetic seawater recipe used to determine thermodynamic properties on seawater [34]. In this recipe, natural occurring concentrations of bromide and fluoride ions are replaced by chloride while strontium is replaced with calcium. Most species having lower concentrations are not considered. The ionic strength of this solution is the same as that of actual seawater [35]. As lithium has a very low concentration in seawater, is not reported in the recipe and then was added to the solution at the average reported concentration of  $0.18 \text{ mg kg}^{-1}$  ( $2.6 \times 10^{-5} \text{ mol kg}^{-1}$ ) [2].

Cations concentrations used are listed in Table 1. Sulfate and chloride concentrations were  $0.028$  and  $0.55 \text{ mol kg}^{-1}$ , respectively.

Cation	Conc. ( $\text{mg kg}^{-1}$ )	Relative molar ratio
$\text{Na}^+$	10780	18000
$\text{Mg}^{2+}$	1280	2030
$\text{Ca}^{2+}$	415	400
$\text{K}^+$	390	390
$\text{Li}^+$	0.18	1

Table 1: Cations present in the simplified synthetic seawater recipe used.

Natural seawater samples were hand-collected along two shores in the Gulf of México and the Caribbean Sea. The samples were filtered to remove large solids and remained refrigerated until use. Both samples were mixed since no significant differences were found regarding pH and lithium, sodium, potassium, calcium and magnesium concentration. The concentration of the those cations in the natural samples were very close to that in the artificial seawater (Table 1).

Transport studies involving both synthetic and natural seawater were performed after magnesium and calcium were almost completely removed by stepwise precipitation/centrifugation using initially sodium hydroxide at a final concentration of  $0.15 \text{ mol kg}^{-1}$  and then diammonium hydrogen phosphate at a final concentration of  $0.005 \text{ mol kg}^{-1}$ . The solution was used without ammonium hydroxide addition as long as excess hydroxide ions that did not precipitate in the first magnesium and calcium removal provided a media alkaline enough to allow lithium transport.

Lithium concentration from natural seawater was made in the same way that the concentration experiments described above but the cycle time shortened to 4.5 hours.

### 2.5. Data treatment and transport optimization

Data analysis and visualization were made in open-source statistical software R [36] mainly using the R-package **transmem** designed to organize and represent data of membrane transport processes. The **transmem** package is available at <https://github.com/Crparedes/transmem>.

To help in the comparison of the experiments, the transport profiles of lithium were adjusted to equations 3 and 4 for the strip and feed phases, respectively.

$$\Phi_{Li_s} = \frac{\alpha_s t^\gamma}{\beta_s + t^\gamma} \quad (3)$$

$$\Phi_{Li_f} = 1 - \frac{\alpha_f t^\gamma}{\beta_f + t^\gamma} \quad (4)$$

where  $t$  is time in hours,  $\alpha$  is an adjustable parameter related to the maximal transported fraction and  $\beta$  is another adjustable parameter that relates the time at which the transported fraction is a given fraction (e.g. the half) it's maximal value. The subscripts  $s$  and  $f$  relates to the

strip or the feed phase, respectively. The model resembles the Michaelis-Menten enzymatic kinetic model [37] with the inclusion of a parameter  $\gamma$  which is used only to enhance fitness and does not need to be changed to compare systems under similar conditions (e.g. along an optimization). If  $\gamma$  is equal to 1 (as in most cases), then  $\beta$  is the time at which the transported fraction is half its maximal value.

The values  $\alpha$  and  $\beta$  and their associated uncertainties can be found by non-linear regression using the Gauss-Newton algorithm [38] but the value of  $\gamma$  must be decided according to the eccentricity of the data under study. The transport process is said to be more efficient for higher values of  $\alpha$  and lower values of  $\beta$ . If no metal is accumulated in the membrane, the parameters are expected to be the same for both phases. This allows their respective unification by weighted averaging considering each estimate quality (i.e. associated error due to lack of fitness). The parameters can be used (individually or combined by a desirability function) to optimize the system using design of experiments. A similar approach was previously reported by our group using factorial and central composite experimental designs to optimize a PIM system for chromium(VI) transport using adjustable parameters of empirical functions that describe the evolution of the system in time [? ].

Lithium permeability coefficient as derived by integrated Fick's law can be obtained by the slope of the linear regression considering lithium concentrations changes in time in the feed solution, the solution's volume  $V$  and the membrane exposed area  $a$  [20].

$$\ln \left( \frac{C_{\text{Li}^+}}{C_{\text{Li}^+}^0} \right) = -\frac{P}{V} a t \quad (5)$$

The separation factor between lithium and other cation is defined as their concentration ratio  $\text{Li}^+/\text{M}^{n+}$  in the strip solution at any given time different from zero divided by the initial value of this ratio in the feed solution [39]. Other definitions referring to the ratio in the feed solution at the same given time [21, 40] are more adequate for continuous membrane systems and will not be used. The separation factor should equal 1 at the beginning of the experiment indicating that no species has been separated yet. Higher separation factors indicate better selectivity for the interest species and separation factors smaller than 1 indicates that the undesired species is transported preferably across the membrane.

$$S_F(AB) = \frac{C_{\text{Li}^+,s}/C_{\text{M}^{n+},s}}{C_{\text{Li}^+,f}^0/C_{\text{M}^{n+},f}^0} \quad (6)$$

where concentrations may be in mole or mass units, subscripts  $s$  and  $f$  indicates strip and feed, respectively. The superscript 0 indicates initial value.

The optimization was performed using the modified (or variable step-size) simplex algorithm from Nelder and Mead [41]. Details of the simplex algorithm optimization

can be found in reference [42]. The algorithm was implemented in R and is available as the R-package `labsimplex` available at <https://github.com/Crparedes/labsimplex>. The optimization objective was to improve the speed of the transport process as long as transport efficiency and selectivity varied slightly with membrane and solutions compositions. As mentioned above, while higher values of  $\alpha$  relates to better final transport efficiency, smaller values of  $\beta$  represented faster transports. For this reason, the simplex optimization consisted on the minimization of the parameter  $\beta$  (or equivalently, the maximization of its inverse).

The separation factor  $\text{Li}^+/\text{Na}^+$  was monitored in all transports during the optimization process to ensure that the selectivity was not sacrificed while improving lithium flux to the strip solution. For this purpose, sodium chloride was added to the feed solution at a molar ratio  $\text{Na}^+:\text{Li}^+$  of 10:1.

### 3. Results and Discussion

#### 3.1. System optimization and uphill lithium transport

A regular initial simplex was constructed using the starting point and step size described in Table 2. The values of the variables (i.e. coordinates) of the experiments (i.e. vertexes) in resulting initial simplex are shown in the same Table. Variables studied were total carriers mass (**X1**, in mg), molar ratio LIX-54-100/Cyanex 923 (**X2**) assuming a molar mass of 246 and 348 g mol<sup>-1</sup> for LIX-54-100 and Cyanex 923, respectively [27, 28]), ammonium hydroxide concentration in feed solution (**X3**, in mol kg<sup>-1</sup>) and hydrochloric acid concentration in strip solution (**X4**, in mol kg<sup>-1</sup>). The mass of base polymer was kept constant at 30 mg as it was determined that smaller amounts did not provided enough mechanical resistance to the membrane and higher values decreased lithium permeability.

	<b>X1</b>	<b>X2</b>	<b>X3</b>	<b>X4</b>	$\beta^{-1}$
Start	70	2.00	0.010	0.07	-
Step size	20	1.00	0.010	-0.06	-
Vertex 1	70.0	2.00	0.010	0.07	0.487
Vertex 2	50.0	2.75	0.010	0.07	0.397
Vertex 3	50.0	1.75	0.016	0.07	0.254
Vertex 4	50.0	1.75	0.007	0.04	0.268
Vertex 5	50.0	2.75	0.007	0.04	0.345

Table 2: Starting simplex coordinates.

Evolution in response against vertex number is shown in Figure 2. Simplex movements are shown in Table 3. The starting point (vertex 1) provided a good response but a better local maxima is found in the ninth experiment.

Vertex	Movement	X1	X2	X3	X4	$\beta^{-1}$
6	R	60.0	2.88	0.000	0.04	0.000
7	Cw	52.5	2.03	0.012	0.06	0.434
8	R	61.2	3.02	0.013	0.08	0.424
9	R	66.8	2.15	0.016	0.10	<b>0.554</b>
10	E	75.3	1.85	0.020	0.13	0.343
11	R	75.3	1.85	0.016	0.09	0.388
12	Cw	56.3	2.52	0.011	0.07	0.422

Table 3: New vertexes evaluated during optimization. Movements R, Cw and E means reflection, contraction on the worst vertex side and expansion of the simplex, respectively. For details see reference [42].

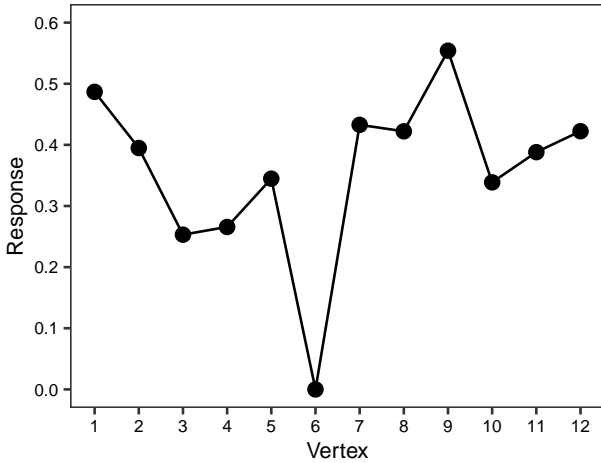


Figure 2: Response against vertex number in simplex optimization. Best results at vertex 9.

Optimized membrane composition was 30 mg CTA as base polymer and 67 mg of the carriers in a molar ratio LIX-54-100/Cyanex 923 of 2.15:1. Final membrane mass and average thicknesses were  $97 \pm 2$  mg and  $14 \pm 4$   $\mu\text{m}$ . The optimal carriers molar ratio is similar to that previously reported in lithium solvent extraction by Pranolo et. al. [9]. Under optimized conditions, lithium ions were completely transported to the strip phase within the first six hours. No appreciable metal transport was observed when membranes containing only LIX-54-100 or Cyanex 923 were used. The transport profile under optimized conditions is shown in Figure 3.

Metal accumulation in the membrane polymeric matrix can be determined by mass balance considering lithium fractions in both solutions. If the sum of the two values is significantly lower than 1, then some of the lithium is being retained in the membrane. No lithium significant accumulation is observed as the sum of feed and strip lithium fractions are between 1.00 and 1.05. Under these conditions, the lithium permeability coefficient is  $2.1 \times 10^{-5}$   $\text{m s}^{-1}$ , similar to that reported in other liquid membranes systems for lithium transport [19, 20, 22].

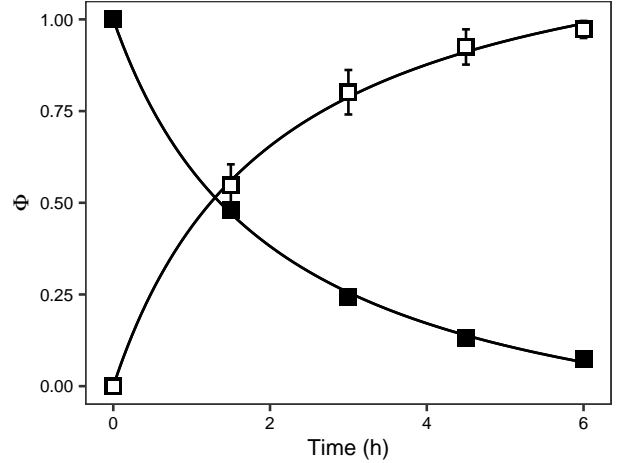


Figure 3: Lithium transport profile for feed (filled squares) and strip (void squares) solutions under optimized conditions.

### 3.2. Selectivity

Transport profiles for systems having lithium and other cations in feed solutions at several molar ratios are shown in Figure 4. Final separation factors are summarized in Table 4. The system does not significantly transport neither sodium nor potassium. Magnesium is transported to the strip solution more efficiently than lithium does, even when magnesium concentration is two orders of magnitude higher than lithium concentration.

Cation	Mole ratio		
	1:1	1:10	1:100
Na <sup>+</sup>	5.4	47	33
K <sup>+</sup>	8.0	36	122
Mg <sup>2+</sup>	0.87	0.55	0.60

Table 4: Separation factors between lithium and other cations at several mole ratios.

Poor selectivity towards magnesium in most lithium extraction systems has been attributed to their almost identical ionic ratio [43] being 69 and 72 pm for lithium and magnesium, respectively. Also, magnesium as a divalent cation will be more strongly solvated by the LIX-54-100 than lithium. The system is then expected to exhibit poor selectivity towards the divalent cation calcium too. The application of the proposed system to a real water sample requires precipitation of magnesium and calcium ions from the solution before being fed to the system.

Permeability coefficients for sodium and potassium are low enough to avoid a significative fraction being transported to the strip solution in short times. However, their fluxes (defined as permeability coefficient multiplied by ion concentration on the feed solution [22]) are not insignificant and led to lithium flux diminution when present.

### 3.3. Membrane reuse and lithium concentration

The membrane had good performance when used several times but transport efficiency gradually decreases af-

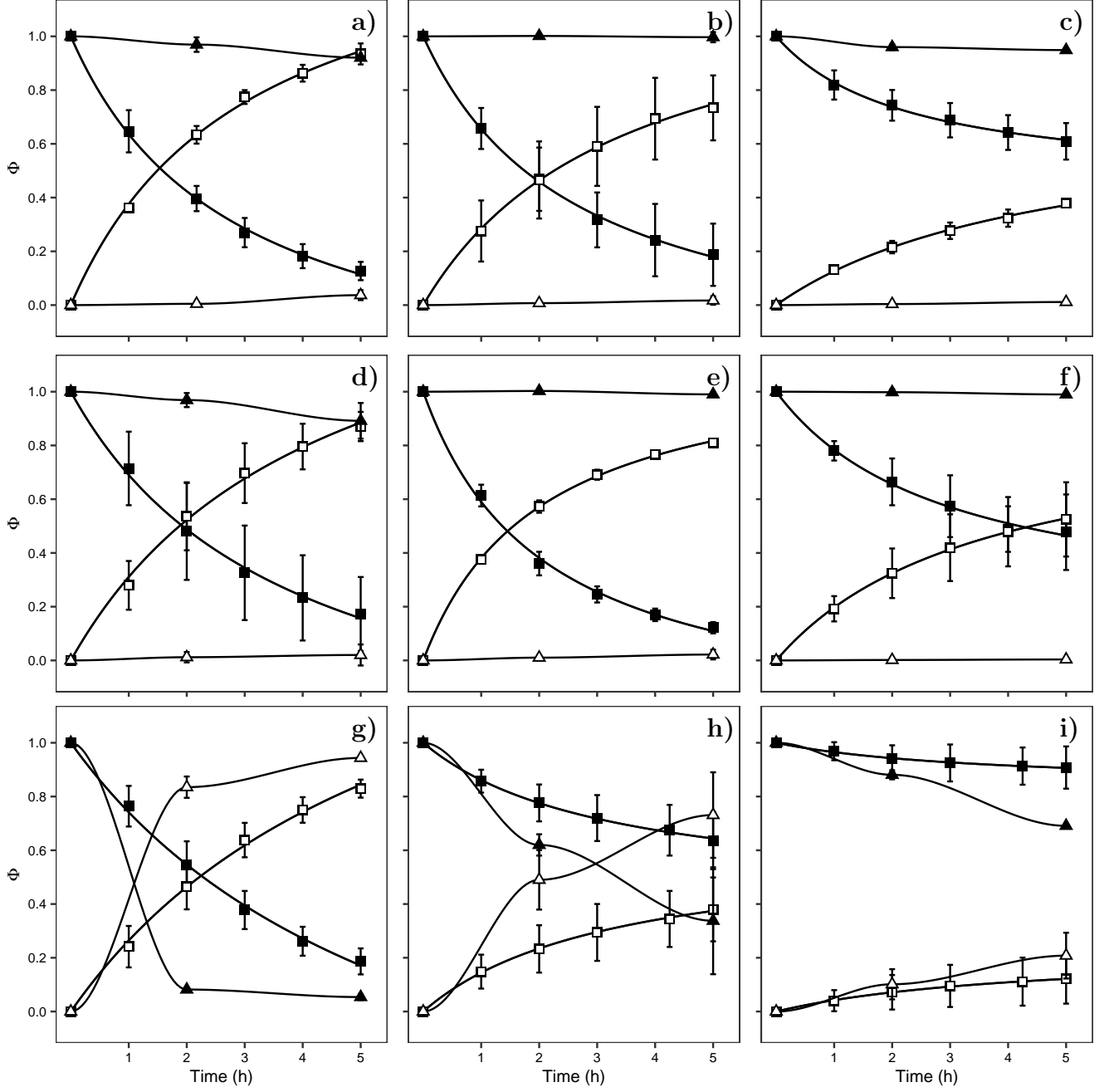


Figure 4: Transport profiles for the systems containing lithium (squares) and other cation (triangles):  $\text{Na}^+$  1:1 (a),  $\text{Na}^+$  1:10 (b),  $\text{Na}^+$  1:100 (c),  $\text{K}^+$  1:1 (d),  $\text{K}^+$  1:10 (e),  $\text{K}^+$  1:100 (f),  $\text{Mg}^{2+}$  1:1 (g),  $\text{Mg}^{2+}$  1:10 (h) and  $\text{Mg}^{2+}$  1:100 (i). Feed fractions are in filled polygons and strip fractions are in void polygons.

ter each cycle. Figure 5 shows the lithium depleted from the feed phase in 10 six-hour cycles. The final transported fraction to the strip phase after each cycle is shown in Figure 6. Membrane instability arises from the fact that LIX-54-100 is lixiviated from the membrane to the feed solution as long as acid  $\beta$ -diketones solubility in aqueous solution increases with pH [44]. Transport efficiency in the tenth cycle is 61% of that in the first cycle meaning a 40% loss of capacity.

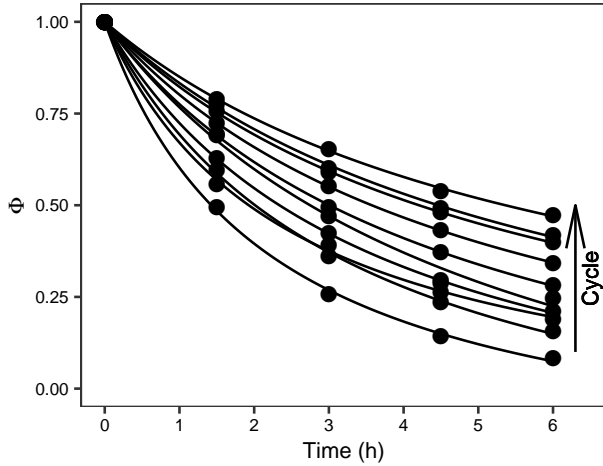


Figure 5: Lithium depletion profiles from feed solution for several cycles using the same membrane.

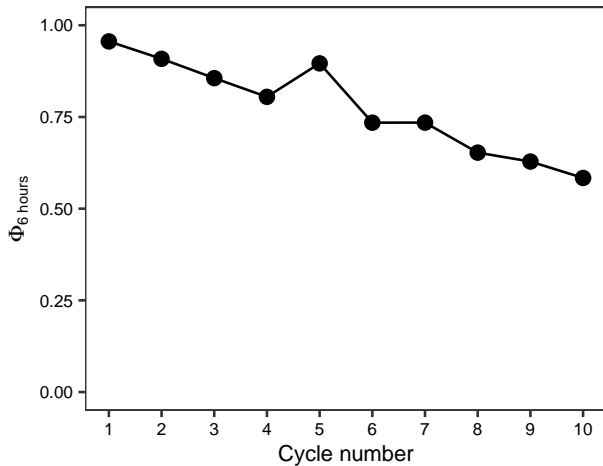


Figure 6: Lithium transported fraction to the strip phase after six hours reusing the same membrane several times.

In lithium concentration experiments, only the feed solution was replaced between cycles. The transported fractions are shown in Figure 7. As mentioned above, lithium transport proceeds against the concentration gradient due to hydronium ions coupled counter-transport. Lithium concentration on strip phase raises to almost three times the initial feed concentration after five six-hour cycles. As seen before, a decrease in the transport efficiency

is observed after each feed solution replacement and longer times will be necessary to deplete the same lithium fraction from the feed solutions.

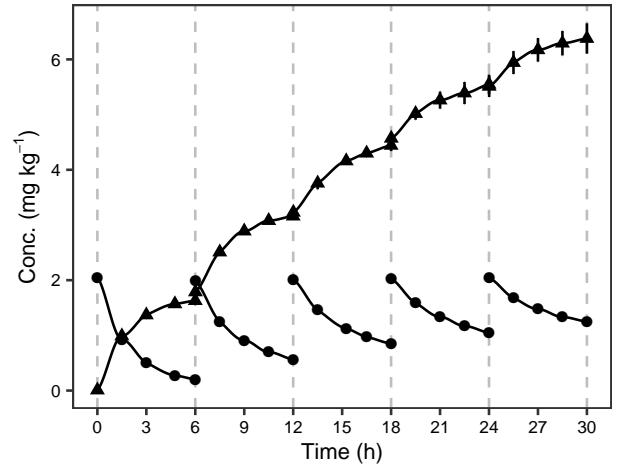


Figure 7: Lithium concentration profile for feed (circles) and strip (triangles) solutions in concentration study. Dashed vertical lines indicate the renewal of feed solution.

### 3.4. Synthetic and natural seawater lithium extraction

Magnesium and most calcium ions were precipitated from both artificial and natural seawater as hydroxides by adding sodium hydroxide to a final concentration of 0.15 mol kg<sup>-1</sup>. Remaining calcium ions were precipitated in a second step by adding diammonium hydrogen phosphate to a final concentration of 0.005 mol kg<sup>-1</sup>. Each precipitation step involved mechanical shaking of solution for 5 minutes and centrifugation at 3000 RPM for 5 minutes. As a consequence of the precipitation process, sodium ion concentration in feed solution increases from 0.47 mol kg<sup>-1</sup> to 0.62 mol kg<sup>-1</sup> and very low residual phosphates remain in solution. Excess hydroxide concentration was then enough to keep the desired hydronium concentration gradient that works as a driving force for the lithium transport to the strip solution.

Transport profiles for lithium, sodium and potassium for the synthetic seawater matrix in extraction studies are shown in Figure 8. There is apparent total lithium transport to the strip solution but in the feed phase at the end of the process, there seems to be a remaining 15% of initial lithium present. This may be attributed to a translational matrix effect in the lithium quantification by FAES. Translational matrix effect can not be compensated by using the standard addition method as long as this method only corrects rotational matrix effects [29].

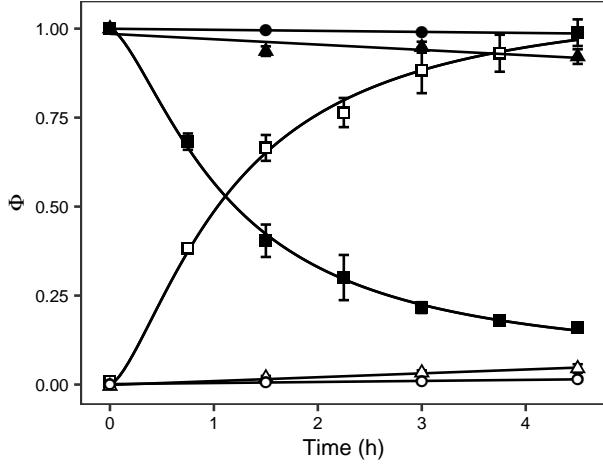


Figure 8: Transport profiles in feed (void shapes) and strip (filled shapes) solutions for lithium (squares), sodium (triangles) and potassium (circles) in synthetic seawater extraction experiments.

Considering the data of strip solution, lithium is transported with an efficiency between 96% and 100% within four hours and a half. Only 5% and 1.5% of sodium and potassium ions are transported to the strip solution, respectively. Separation factors of 130 and 430 are reached for sodium and potassium, respectively.

The lithium extraction from natural seawater raised up the pH of the strip solution due to sodium and potassium ions being transported across the membrane with the respective hydronium ion exchange. If hydronium ions concentration gradient is not high enough, no lithium transport occurs. To achieve lithium concentration, it was necessary to determine hydronium ions concentration in the strip phase at the end of each cycle to reset its value to  $0.1 \text{ mol kg}^{-1}$  using hydrochloric acid  $1 \text{ mol kg}^{-1}$ .

In the feed solution, remaining hydroxide ions concentration after the use of excess sodium hydroxide to precipitate divalent metals was about  $0.04 \text{ mol kg}^{-1}$ . This value is too high for the use of the membrane and despite of accelerating the lithium transport in the first transport cycle, selectivity got deteriorated. A good compromise between selectivity and efficiency was achieved at an initial hydroxide concentration in the feed phase of  $0.02 \text{ mol kg}^{-1}$ . Excess hydroxide ions were neutralized using hydrochloric acid  $0.1 \text{ mol kg}^{-1}$ . Transport profiles for lithium, sodium and potassium in the concentration studies involving natural seawater are shown in Figure 9.

Lithium concentration in strip phase reaches 1.73 times the initial lithium concentration in feed phase after four cycles. The system selectivity towards sodium and specially, potassium, gets lower after each cycle. This may be due to a high membrane degradation rate given the high concentration of monovalent cations susceptible of being transported that are present in the feed solution and produce membrane wear. Final separation factors are 4.9 and 3.4 for sodium and potassium, respectively.

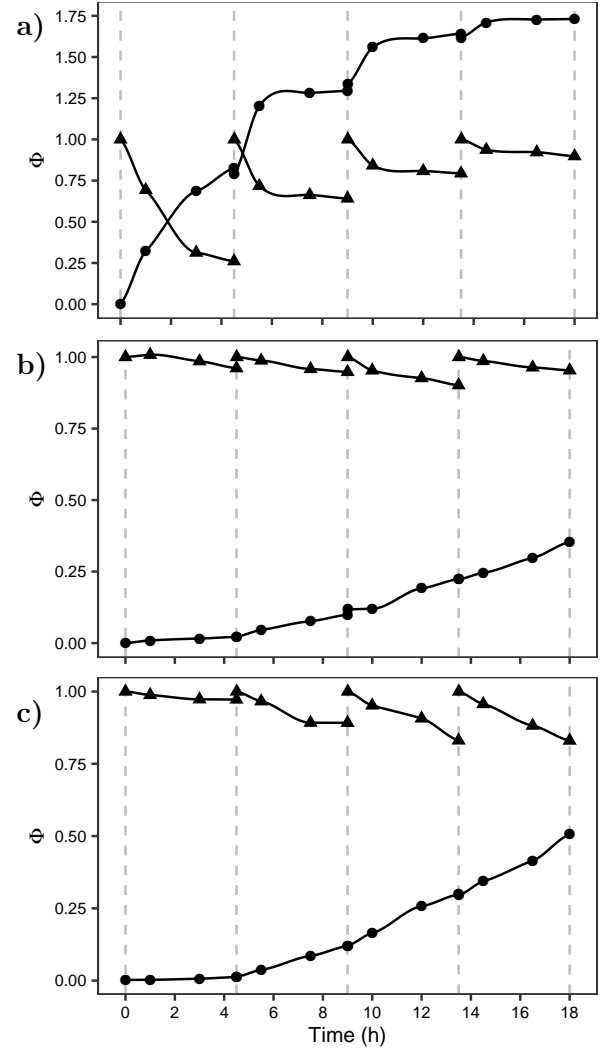


Figure 9: Transport profiles in feed (triangles) and strip (circles) solutions for lithium (a), sodium (b) and potassium (c) in lithium extraction and concentration experiments using natural seawater. Dashed vertical lines indicate the renewal of feed solution.

#### 4. Conclusions

In this study, we firstly report the use of a PIM to selectively extract and concentrate lithium ions from alkaline diluted aqueous solutions. Extraction process finished after 6 hours, time after which no appreciable lithium is transported. Undesired species like sodium and potassium are efficiently excluded in the transport process but a small fraction is transported to the strip solution. The system does not efficiently exclude divalent cations but they may be easily removed by simple precipitation procedures that do not represent an additional energy expenditure since many lithium extraction processes currently employed already need divalent cations pre-removal.

Permeability coefficient for lithium under the optimized conditions is  $2.1 \times 10^{-5} \text{ m s}^{-1}$ . Selectivity of system after divalent cations removal is  $\text{Li}^+ \gg \text{Na}^+ > \text{K}$ . Separation



factors against sodium and potassium on the synthetic seawater matrix is 130 and 430, respectively.

The PIM was used to successfully extract and concentrate lithium from natural seawater samples but hydronium and hydroxide concentrations in strip and feed phases, respectively, must be monitored at least at the beginning of the process. Sodium and potassium selectivity is deteriorated after few extraction cycles due to membrane degradation.

The proposed protocol could be adapted to a bigger scale of continuous operation but the environmental impact of lithium removal from the marine ecosystem must be evaluated. Nonetheless, due to the immense seawater volume on earth, a global average change of just  $1 \mu\text{g L}^{-1}$  would require the lithium extraction of about 1.35 million tones which is bigger than the total lithium consumption in human history [8, 45].

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