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Towards lithium recovery from desalination brines via an integrated scheme

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ABSTRACT

Lithium salts are significant for numerous commercial and industrial applications. This paper proposes a simulated integrated scheme for salt recovery from seawater. The developed scheme targets the separation of Lithium from brine as an end product. It comprises chemical treatment, membrane separation, thermal separation and ion exchange processes. The selected integrated scheme is designed according to screened and analyzed reported data on separation technologies as well as equilibrium/kinetics of lithium adsorption using selective adsorbents. The developed 20,000 m^3/d seawater desalination/salt recovery scheme is estimated to produce recovered salts of 113, 186 and 1,670 ton/d of raw calcium, magnesium and sodium, respectively. The separated mixed potassium and lithium chloride salts amounted to about 575 ton/d and 47 kg/d (including 62% lithium chloride), respectively. For lithium adsorption, the required amount of selected manganese oxide adsorbent was estimated to be 0.5 ton/column bed based on the equilibrium exchange capacity of the selected lithium adsorbent. The estimated overall lithium recovery was 72%. These results confirm the promising features of the developed desalination/salt recovery process.

Keywords: Desalination; Salt recovery; Lithium; Seawater; Ion exchange; Integrated separation scheme

1. Introduction

There has been recently a growing demand for Li recovery due to its myriad applications in rechargeable batteries, light aircraft alloys and next generation of nuclear fusion fuel; as well as in different industries such as rubber synthesis, pharmaceuticals, ceramics, refrigerants, aluminum, grease and lubricants [1–3]. There are various lithium resources in land and in water. The former contributes to a total of about 14 million tons that are found in mine ores and salt lake brines. The major salt lakes that produce lithium are Atacama in Chile, Hombre Muerto in Argentina and the Great Salt Lake. The first two lakes produce about 70% of the total global lithium [4,5].

Seawater and desalination brines are becoming attractive alternative resources for Li production. Seawater contains approximately 230 billion tons of Li but with very low average concentration of about 0.1–0.2 ppm. The quantity of brine discharged from desalination plants has been sensibly increasing in the last 15 years and this trend is expected to be maintained in the near future. The average concentration of lithium in desalination brines is about 0.27 ppm [3, 6]. Lithium was recovered from seawater and brines using magnesium precipitation [4], mixed solvent extractant system to recover Fe, Cu, Al, Co, Ni and Li [7], membrane separation using nanofiltration (NF) and reverse osmosis (RO) [2,5,8,9].

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Adsorption could be a promising technique if the appropriate adsorbent was selected [10,11]. Lithium selective inorganic adsorbents were prepared and used by a number of workers; many of them have focused on lithium selective manganese oxide adsorbents [1,3,12–18]. A combined system comprising adsorption followed by multistage electrodialysis was employed to enrich lithium in brine by up to 1,500 and 1,800 ppm, respectively. The adsorbent was granulated manganese oxide powder that contained lithium. Effluent Lithium concentrate was then passed to a precipitator to separate lithium in the form of lithium carbonate [19]. In another study, a granular adsorbent comprising lithium manganese oxide and a polymeric binder was used to recover lithium from aqueous solutions. About 25 mg/g adsorption capacity was obtained at 200 mg/L of lithium [20].

Numerous technical and economic challenges mandate development of an innovative cost effective process for lithium recovery as part of an integrated scheme for salt recovery from marine resources and desalination brines. The proposed scheme aims at treating seawater with a typical capacity of 20,000 m^3/d by firstly recovering Ca and Mg via precipitation, concentrating the effluent solution using RO, then removing monovalent ions (other than Li) from the RO concentrate via engineered solar ponds and finally recovering Li by means of ion-exchange. To our knowledge, this is the first reported process proposed for the recovery of Li from softened RO brines (RO concentrates) generated from softened seawater. It is also the first to recover Li after prior removal of other monovalent ions. Thus although this process targets Li recovery, it offers the added advantage of recovering other monovalent ions along with Ca and Mg.

2. Approach and methodology

A medium-scale integrated seawater desalination/salt recovery scheme having water production capacity of 20,000 m^3/d has been developed. Focus was given to the process of lithium recovery incorporated in this scheme. Li is accompanied by other salts (e.g., KCl, NaCl) that were also estimated to be recovered. The scheme comprises units for chemical treatment, reverse osmosis (RO) membrane separation, solar pond and ion exchange system (IX).

2.1. Process description

Mediterranean Seawater was employed as the feed and its typical composition is given in Table 1. As shown in the process flow diagram in Fig. 1, Ca and Mg ions in feed water are first removed via a two-stage precipitation system. Afterwards, the softened water stream is desalinated through an RO plant. Monovalent ions in the RO concentrate are then removed via solar pond evaporation and finally Li, in the concentrated stream, is removed via an ion-exchange process.

2.2. Overall process design

The developed process design is based on extensive screening and analysis of the reported experience of direct relevance to the proposed scheme pertinent to salt recovery from seawater and desalination brines in general and lithium in particular [2,4,10,12,14,15,18,19,21–24], in addition to the author's previous work [25,26] [2].

2.2.1. Overall mass balance calculations

Amounts of salts produced from the developed desalination/salt recovery facility were determined by overall mass balance calculations, from which the amounts of adsorbents were determined. Basis for calculations were 20,000 m^3/d of fresh water with average total dissolved solids (TDS) as indicated by WHO guidelines.

The mass balance calculations were based on performance indicators and main technical specifications for the proposed processes as depicted from previous endeavors and investigations done by authors. In addition, some of the membrane technical parameters were evaluated using WT-Cost II© software developed by the Bureau of Reclamation and Moch Associates. Such indicators include, for example, precipitation efficiencies using different precipitants (for the chemical precipitation units), membrane recovery and rejection (for the RO unit), solubility limits at different degrees of salinity (for the solar pond), equilibrium and kinetic parameters for the selected adsorbents (for ion exchange and elution units). These indicators are shown in Table 2 and explained thoroughly in section 3. The results of mass balance, given as elemental composition of each stream are presented in Fig. 1.

2.3. Unit process design calculations

2.3.1. Precipitation processes

Ca and Mg ions were separated via a two-stage precipitation process using sodium carbonate, followed by sodium hydroxide. Precipitation calculations were based on the authors' previous experimental and theoretical results regarding precipitation of Ca and Mg from saline solutions [25,26].

2.3.2. RO desalination process

Softened water produced from the precipitation units was desalinated via an RO system. Recovery and rejection for the RO system were estimated to be 35% and 99.6%, respectively [2,22,23,25] according to the following equations:

$$\text{Salt Rejection} = (1 - C_p/C_f) \times 100 \tag{1}$$

Table 1
Typical composition of Mediterranean feed seawater [25,26]

Element	Ca^{2+}	Mg^{2+}	Na^+	K^+	Li^+	Cl^-	SO_4^{2-}	TDS
Concentration (mg/L)	440	1,460	11,000	500	0.1	20,000	27,000	36,320

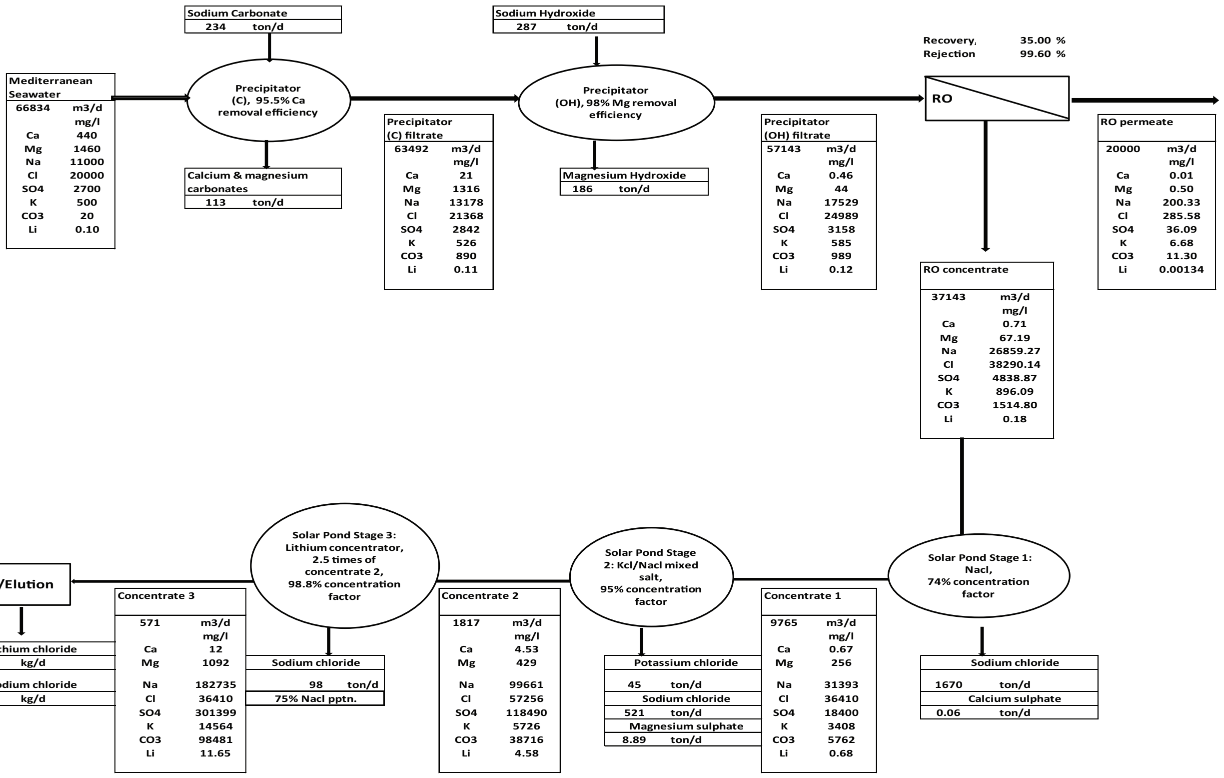


Fig. 1. Schematic flow diagram of the proposed integrated desalination/salt recovery scheme.

Table 2
Typical performance indicators for the main processes/units adopted in the proposed desalination/salt recovery scheme

Process	Element removal efficiency (%)						Water recovery*/ Concentration factor (%)
	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Li^{+}	Cl–	
Precipitation [21,25,26]	95.5 (C) 14 (OH)	98 (C) 97 (OH)	–	–	–	–	–
RO membrane system [2,22,23,25, 27–32]	96–99.6	95.5–99.6	95–99.6	94–99.6	94–99.6	95–99.6	35/–
Solar pond [24,31–37]							
Stage (I)	–	–	70–74	–	–	75	–/74
Stage (II)	–	75	70–74	75	–	75	–/95
Stage (III)	–	–	70–74	–	–	75	–/98.5
IX [12,18,38]	–	–	–	–	(11 mg/g)		(95–100)/–

*From seawater and RO brine.

$$Recovery\,\% = (Q_p / Q_f) \times 100 \quad (2)$$

where C_p and C_f are the concentrations of permeate and feed, respectively; while Q_p and Q_f are the flow rates of permeate and feed, respectively. Mass balance equation for the RO unit is:

$$Q_f \times C_f = (Q_p \times C_p) + (Q_c \times C_c) \quad (3)$$

where Q_c is the concentrate flow rate.

2.3.3. Solar pond evaporation

Three-stage solar pond evaporation was performed on the RO concentrate in order to remove monovalent ions. Solar pond concentration factor is estimated to be 74% – 98.5% (as will be discussed in section 3.2).

2.3.4. Ion-exchange adsorption

Li is finally concentrated in a two-stage ion exchange system. Selection of adsorbent was based on reported equilibrium and kinetic parameters for selected lithium adsorbents, as well as, the authors previous work [12,18,20, 39–42]. Equilibrium and kinetic parameters for selected lithium adsorbents are compiled in Tables 3 and 4, respectively.

3. Results and Discussion

3.1. Seawater softening and RO desalination

As shown in Fig. 1, feed water stream is subjected to calcium precipitation (removal efficiency 95.5%) using sodium carbonate at pH 9.2 (Precipitator C). The choice of pH value is based on previous experimental and theoretical studies of the authors [25,26], as well as other international endeavors [21]. The formed precipitate is expected to contain mainly calcium ions accompanied with some magnesium ions, as well as other trace water contaminants such as barium, strontium, silica, … etc. The first precipitator overflow is then directed to a second precipitator for magnesium precipitation using sodium hydroxide at pH 12 (Precipitator OH) with about 98% removal efficiency, as previously reported by Irving [21]. The precipitate should contain mainly magnesium hydroxide. It was revealed that seawater softening using sodium carbonate resulted in maximum Ca concentration reduction from 440 to 21 mg/L. Further, the corresponding Mg concentration reduction was from 1,460 to 1,316 mg/L. Overall Ca and Mg separation process efficiencies were 99.9% and 97% which agrees with the authors' previously published work [26]. Fig. 1 presents the flowrate and TDS content of each stream, as well as, amounts of salts recovered from different units. The developed scheme enabled overall water recovery of about 30%. Raw $CaCO_3$ generated after the first chemical precipitation amounted to about 113 ton/d, while magnesium hydroxide $Mg(OH)_2$ obtained from the second precipitator was about 186 ton/d.

Afterwards, the supernatant of the second precipitator is directed to an RO membrane unit with 35% recovery and an average overall rejection of 99.6% as calculated using "WT Cost II" software, along with ion specific rejection values. These values depend on feed water content, operating conditions including adjusted pH, temperature, feed pressure, recovery and specific water quality requirements [22,23,27–30]. It is worth mentioning that pH was adjusted

Table 3
Equilibrium parameters for the state-of-the-art adsorption studies

Adsorbent	Feed solution	Equilibrium model	Maximum sorption capacity (mg/g)	Sorption constant	pH/ temperature (°C)	Ref.
Manganese oxide based adsorbents						
MnO_2 nano crystals ion sieve	Synthetic	Langmuir	16.77	27 L/mg	9.2/20	[16]
MnO_2 nanorod	Synthetic	–	20.36	–	10.1/30	[14]
$LiMn_2O_4$ or Li_2MnO_3	Synthetic (LiCl)	–	25	–	11/25	[20]
Nano-sieve $H_{1.51}Li_{0.08}Mg_{0.24}Mn_{1.49}O_4$	Synthetic	Competitive adsorption	33.7	K_{Li} = 9.73 mg/L K_H = 0.03 mg/L	12/20	[18]
Sieve1: $H_{1.36}Li_{0.07}Mn_{1.65}O_4$	Synthetic	Langmuir	34.07	3.957 L/mg	12/25	[39]
Sieve2: $H_{1.41}Li_{0.07}Mn_{1.65}O_4$		Langmuir	40.98	1.957 L/mg		
MnO_2 nanorod	Synthetic	Freundlich	45.68	K_f = 35.76 n = 1.2	10.1/30	[17]
Manganese oxide –polymer modified based adsorbents						
PVC-$H_{1.6}Mn_{1.6}O_4$ Li ion sieve membrane	Synthetic	Langmuir	36.77	4.97 L/mg	12/25	[43]
PAN (20%)–$H_{1.6}Mn_{1.6}O_4$ Li ion sieves	Simulated seawater desalination retentate	Langmuir	10.7	0.99 L/mg	11/25	[40]
Non-manganese oxide based adsorbents						
Titania ion sieves	Synthetic	Freundlich	25.46	K_f = 3.47 n = 12.56	9.2/30	[15]
Amberlite IR 120 Na-H	Synthetic (LiCl)	proposed ion exchange model	2.2–20	0.4–0.65	7/–	[41]
Molecular sieve 13X			25	0.3	7/-	

Table 4
Kinetic parameters for the state-of-the-art adsorption studies

Adsorbent	Feed solution	Kinetic model	Sorption capacity (mg/g)	Rate constant	pH/temperature (oC)/time (h)	C_o (mg/L)	Ref.
Manganese oxide based adsorbents							
MnO_2 nanocrystals ion sieve	Synthetic	Pseudo- first order	11.73	$2.16*10^{-6}\,s^{-1}$	9.19/20/120	68.38	[16]
MnO_2nanorod	Synthetic	Pseudo-first order	38	$3.29*10^{-4}\,s^{-1}$	10.1/30/25	69	[17]
Nano-sieve $H_{1.51}Li_{0.08}Mg_{0.24}$ $Mn_{1.49}O_4$	Synthetic	Pseudo-second order	25 31.2–33.2	0.0078–0.0092 0.012 g/mg.h	12/20/24	10 50 100	[18]
Sieve1: $H_{1.36}Li_{0.07}Mn_{1.65}O_4$	Synthetic		35		12/25/20	50	[39]
Sieve2: $H_{1.41}Li_{0.07}Mn_{1.65}O_4$			40		12/25/20	50	
MnO_2 nanorod	Synthetic		16.56		10.1/30/30	69	[14]
Manganese oxide –polymer modified based adsorbents							
PVC-$H_{1.6}Mn_{1.6}O_4$ Li ion sieve membrane	Synthetic	Pseudo-second order	33.41	27.154 m^2/mg.h	12/25/8	150	[44]
Chitosan (19%) Li Mn oxide granules	Synthetic (LiCl)	Pseudo-second order	10	0.04 g/mg/day	7–10.2/–/	30	[45]

in compliance with specifications given by membrane manufacturers as well as the type of membrane used. "WT Cost II" software estimated that the RO seawater membranes requires seven elements per vessel with a total of about 1,300 elements and 185 pressure vessels. The estimated specifications of the used membranes are given in Table 5.

Table 5
The estimated specifications of the membrane used

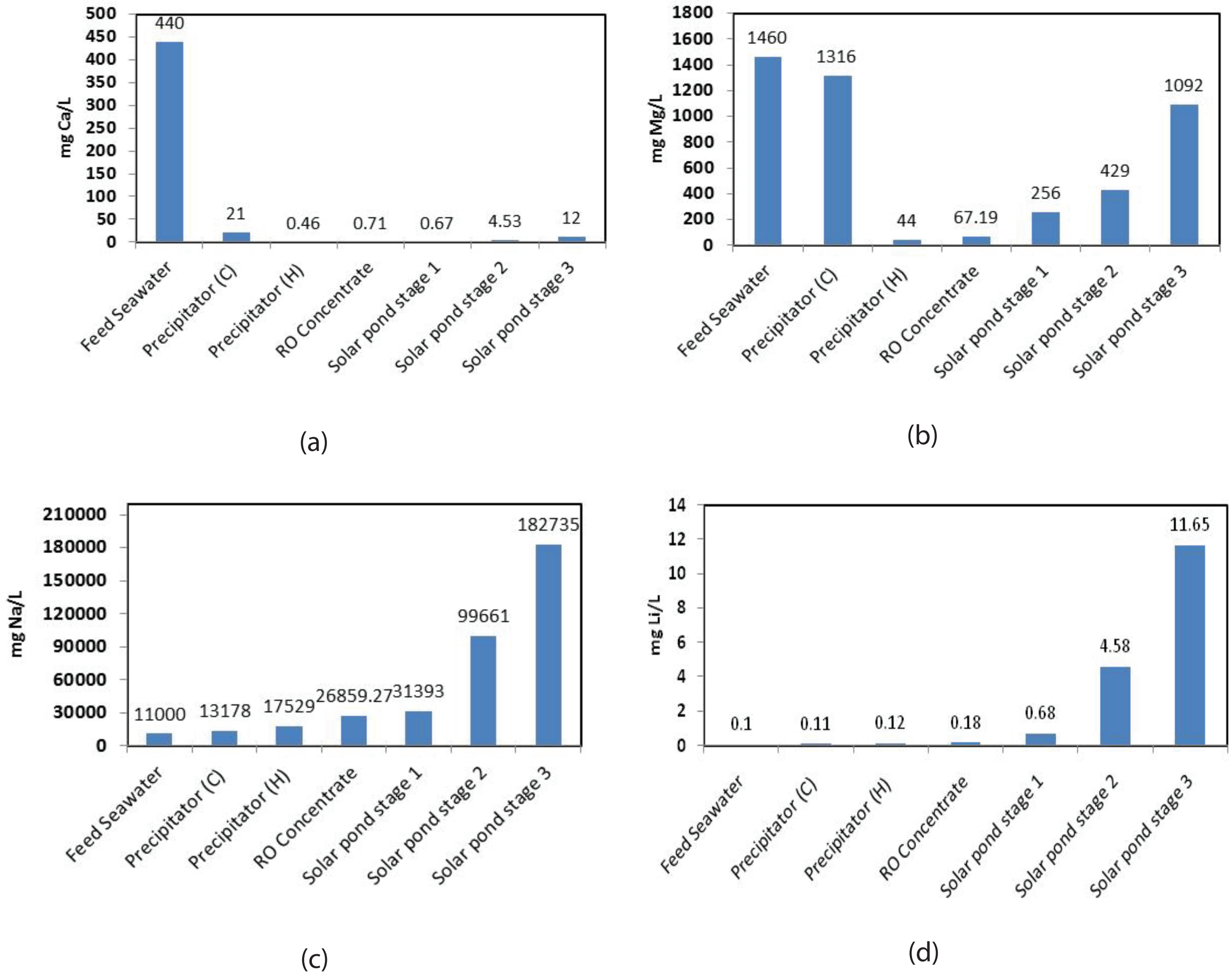
Parameter	Value
Element flow, gpd (m^3/d)	4,000–9,000 (15.1–34.1)
Fouling factor	0.8–1.0
Feed pressure, psig (bar)	700–1,200 (47.6–81.5)
Pressure drop, psi (bar)	25–60 (1.7–4)
Elements per vessel	6–8
Chloride rejection, %	99.0–99.8
Sulfate rejection, %	99.5–99.9

3.2. Solar pond concentration

The RO reject stream, with calculated TDS approaching 72,500 mg/L, is then fed to a multistage solar pond for sequential salt precipitation [24,33,34]. The precipitation sequence in the solar evaporation pond tends to precipitate almost pure sodium chloride salt since the steps preceding solar evaporation decreased the concentration of possible carbonate salts (Ca and Mg) [34]. According to the solubility limits at different degrees of salinity, concentration factors and precipitation efficiencies, sodium chloride is estimated to precipitate first, followed by potassium chloride/sodium chloride mixed salt and finally more sodium chloride is precipitated in the final lithium concentration step [33–35]. The overall concentration factor is initially 74% in the first stage where the TDS approaches about 72,826 mg/L, and reaches 95% in the second stage where the TDS approaches about 96,994 mg/L then finally reaches 98.5% [36] in the last stage where the TDS approaches about 329,448 mg/L. Accordingly, the average salts precipitation efficiency approaches 75% [33,37]. Sodium chloride separated from the solar pond in the first stage was 1,670 ton/d. While, the amounts of separated mixed potassium chloride, sodium chloride and magnesium sulfate salts were estimated to be about 45, 521 and 9 ton/d, respectively from the second stage.

In the third precipitation stage, lithium is concentrated by about 2.5 times relative to its concentration in the effluent of the second stage [33–35] such that it finally approaches 11.7 mg/L, as calculated from the overall mass balance.

Concentrations of the major investigated ions (Ca, Mg, Na and Li) that exist in the effluent streams of the different process units preceding ion exchange are shown in Fig. 2. It is clear that calcium and magnesium ions concentrations significantly decrease after their precipitation, then the concentrations start to increase gradually after concentrating the solution in the different stages of the solar pond. As for lithium and sodium, their concentrations increase gradually as they pass across the different units of the developed scheme. The amount of this increase depend on



(a) (b) (c) (d)

Fig. 2. Concentrations of the major investigated cations [(a) Calcium, (b) Magnesium, (c) Sodium, (d) Lithium] present in the effluent streams of the different process units preceding ion exchange.

the concentration factors and the separation (precipitation) efficiencies pertinent to each process, as was shown earlier.

3.3. Lithium recovery via adsorption

The final solar pond Li concentrated effluent stream is directed to an ion exchange (IX) adsorption and elution (regeneration) columns for the recovery of lithium as will be discussed in section 3.2.4. Selection of the Li selective adsorbent depends mainly on the analysis of reported equilibrium and adsorption kinetics data for selected lithium adsorbents Reported equilibrium and kinetic parameters for selected lithium adsorbents were compiled, screened and analyzed; values thereof are given in Tables 3 and 4, respectively. More detailed discussion on the ion exchange step will be dealt with in the following sections.

3.3.1. Adsorption equilibrium

Table 3 summarizes the results of the equilibrium studies conducted for lithium adsorption onto various adsorbents. The equilibrium parameters and the conditions at which they were measured are given. Clearly, most of the reported studies employed manganese oxide based adsorbents and these showed higher maximum sorption capacities than titania based adsorbents as well as the commercial polymeric adsorbents of Amberlite and Molecular Sieve. Furthermore, MnO_2 nano-rod exhibited the highest sorption capacity among the reported adsorbents and this amounts to about 46 mg/g obtained at pH 10.1 and 30°C.

3.3.2. Adsorption kinetics

The studies reported on the kinetics of lithium adsorption were also summarized in Table 4 which compiles the kinetic parameters and the conditions at which they were determined. The highest sorption capacities (40 mg/g) were exhibited by ion sieve $H_{1.41}Li_{0.07}Mn_{1.65}O_4$ within 20 h and at an initial concentration of 50 mg/L. The adsorbent PVC-$H_{1.6}Mn_{1.6}O_4$ Li ion sieve membrane achieved a slightly lower sorption capacity in a much lower time of 8 h but at a much higher initial concentration of 150 mg/L [39]. Given that the concentration of lithium in brine and seawater is very low, the former adsorbent is more appropriate for lithium recovery under saline conditions.

3.3.3. Ion exchange features

A dual-column system is proposed for adsorption. The system comprises two columns working in parallel either for adsorption or regeneration mode. Li selective Manganese oxide based adsorbents were selected for this study based on the fact that they exhibited higher adsorption capacities relative to their counterparts as shown in Table 4. The lithium concentration before being fed to the adsorption column is (11.7 mg/L) as depicted in Fig. 1. Ion exchange adsorption will be conducted after adjusting the pH to 8 [18]. About 85%–90% of the final volume of the concentrated effluent from the pond evaporation process will be fed to the IX column. Considering the working parameters adopted in this study (pH 8,11.7 mg/L initial concentration and 571 m^3/d feeding rate), and according to reported work by Tian et al. [18], the static sorption capacity was estimated to be 11 mg/g for the adsorbent ion Sieve $H_{1.51}Li_{0.08}Mg_{0.24}\ Mn_{1.49}O_4$ [18] at the pre -mentioned conditions. This value for the capacity was employed as the dynamic sorption capacity for the proposed column. The efficiencies of column adsorption and elution are assumed to be 85% and 90%, respectively [38]. Thus, the corresponding amount of adsorbent required for each column bed will therefore be 0.5 ton in order to produce 29.4 kg/day lithium chloride accompanied with 17.8 kg/day sodium chloride, where the LiCl/NaCl weight ratio approaches 1.67 according to Yoshizuka et al. [12].

The dynamic sorption capacity, which in case of symmetrical breakthrough curves, corresponds to a $t_{1/2}$ value (the time corresponding to half the maximum concentration ($0.5 \times C_f$)) is determined from the following equation [46]:

$$q \cdot \mathrm{m} = \mathrm{C}_f \times t_{1/2} \times F \tag{4}$$

where q is the dynamic sorption capacity (mg/g), m is the mass of adsorbent (g), C_f is the feed bulk concentration (mg/m^3), and F is the flow rate (m^3/d). The adsorption cycle time is determined to be about 20 h and overall lithium recovery approaches 72%.

It was reported that mixed lithium chloride/sodium chloride stream could be separated by elution (regeneration) using aqueous hydrochloric acid and molar selectivity of Li^+ vs. Na^+ up to 2,300 times could be achieved [13]. Purification of Li salt carrying stream is a subject for current investigations. Lithium chloride salt could be finally produced adopting well known concentration methods such as crystallization [43].

3.4. Process sensitivity and Limitations

The estimated amounts of produced salts may be increased by more than 50% due to:

- Enhanced solar pond operation time which may increase lithium concentration in the final effluent.
- Basis for calculations was 20,000 m^3/d of fresh water but the proposed system is promising for higher capacities.
- Possible variations of the different types of RO membrane process design and process conditions (recovery, rejection, feed temperature, number of stages… etc), the estimated salt production may vary significantly due to uncertainties which govern such types of integrated desalination and salt recovery schemes.
- We built our system on the most reliable lithium selective adsorbent, while adsorbents under investigation (such as lithium iron phosphate [47]) could be investigated for more efficient lithium recovery. This will increase the process efficiency, selectivity and estimated produced salts and decrease the adsorbent amount required.
- Increasing trends to use NF for pretreatment before RO may further increase process reliability [48] and eliminate chemical precipitation and lead to system compactness and process efficiency.
- Also, conservative measure for loading efficiency has been adopted due to uncertainties pertinent to scaling up calculations. Work is still ongoing to improve adsorbent loading.

4. Conclusions

An innovative 20,000 m^3/d integrated approach for salt recovery from seawater was proposed for the selective recovery of lithium from desalination brine as an end product. The proposed scheme incorporated chemical treatment, membrane separation, thermal separation process and ion exchange. Reported data on equilibrium and kinetics of lithium adsorption using inorganic adsorbents have been collected, screened, analyzed and compared in terms of their performance. The features of reliability, environmental and process flexibility of the developed recovery scheme are obvious. The developed seawater desalination/salt recovery scheme enabled overall water recovery of about 30% and also the recovery of raw calcium carbonate, magnesium hydroxide and sodium chloride salts of 113, 186 and 1,670 ton/d, respectively. About 575 ton/d of mixed potassium salts were separated, while 29.4 kg/d lithium chloride was produced from brine with overall lithium recovery 72%. In view of the reported lithium adsorption equilibrium data, the required amount of a selective manganese oxide adsorbent for lithium was estimated to be 500 kg/column bed.

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