



Research Paper

Effect of Operational Parameters on Recovery of Lithium from Brine with Bipolar Membrane Electrodialysis

Tuğçe Zeynep Kaya ¹, Ezgi Çermikli ^{1,3}, Yakubu Abdullahi Jarma ¹, Esra Altıok ¹, Deniz İpeççi ¹, Müşerref Arda ², Nalan Kabay ^{1,*}

¹ Ege University, Faculty of Engineering, Chemical Engineering Department, 35100 Izmir, Turkey

² Ege University, Faculty of Science, Chemistry Department, 35100 Izmir, Turkey

³ Ege University, Graduate School of Science, Division of Environmental Sciences, Izmir, Turkey

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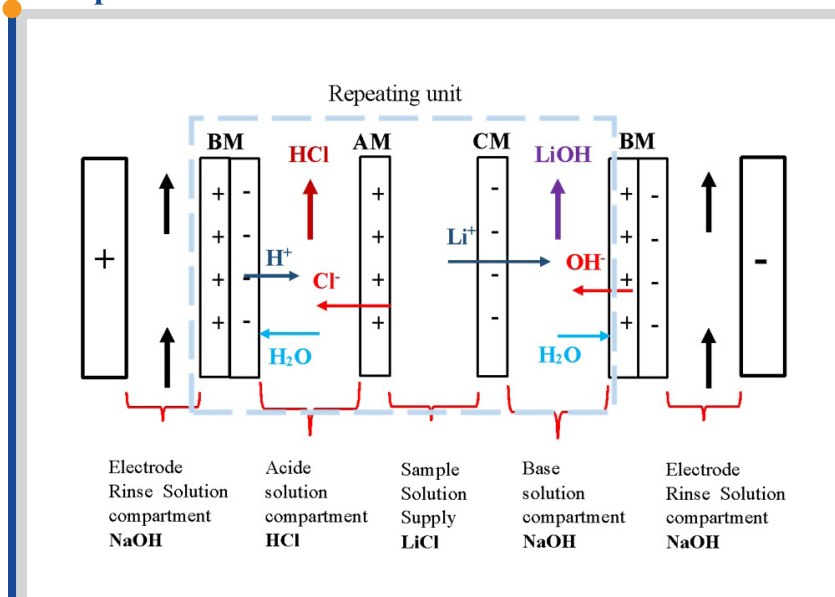
Keywords

Bipolar membrane
Electrodialysis
Ion exchange membrane
Lithium recovery
Lithium separation

Highlights

- Simultaneous removal and recovery of lithium from brine by ED using bipolar ion-exchange membranes were achieved.
- Maximum removal of lithium was above 99% while the maximum recovery was 75.5%.
- The mass transfer coefficient of lithium increased at high electrical potential but it decreased with increasing lithium concentration.

Graphical abstract



Abstract

In this research, the effect of operational parameters on removal and recovery of lithium simultaneously from brine by electrodialysis (ED) method with bipolar ion-exchange membranes (BM) having 10 membrane triplets of cation exchange membranes (CEMs), anion exchange membranes (AEMs) and bipolar membranes (BMs) was investigated. The Mega EDR-Z-Full-V4 model BMED system was employed to produce lithium hydroxide from brine containing lithium ions. Four different concentrations of LiCl solutions were used in the sample compartments 34, 68, 170, and 340 mg Li⁺/L. Also, the effects of concentrations of acid (HCl) and base (NaOH) solutions (0.003 M and 0.05 M) in the acid and base compartments in addition to the electrical potentials (20 and 25 V) were investigated. A NaOH solution with 0.1 M concentration was used as the electrode solution for all tests run. As a result of the study operated with 0.05 M HCl and 0.05 M NaOH solutions at 20 V, the lithium removal percentages were obtained as 98.6, 99.2, 99.7, and 99.6% while the lithium recoveries were 75.5, 54.5, 55.4, 51.2% at four different concentrations of LiCl as 34, 68, 170, 340 mg Li⁺/L, respectively. When the lithium concentration of the sample solution increased, the lithium removal remained constant. But the lithium recovery decreased and the lithium concentration in the base recovery compartment increased. The mass transfer coefficient of lithium was high when the electrical potential applied is high but it decreased with an increase in lithium concentration.

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1. Introduction

Lithium has many applications in various sectors including lithium-ion batteries, polymer production, ceramics and glass, the nuclear sector as well as steel and aluminum production [1]. The increased demand for lithium in many sectors has increased in recent years, therefore, it is of

paramount importance to recover or extract lithium from the available sources. Several lithium resources include terrestrial brine, which is the main source of lithium in nature at around 59%, hard rock (such as petalite, spodumene, and eucriptite) containing approximately 25%, hectorite (7%), underground brine

* Corresponding author: nalan.kabay@ege.edu.tr (N. Kabay)

(3%) and lithium-ion battery recycling [2-4]. According to Shahmansouri et al. [5], industrial lithium extraction from aqueous sources has lower costs because about 85% of the lithium available in the aqueous phase can be recovered. Geothermal waters contain a significant concentration of lithium and they also contain less coexisting ion concentrations compared to seawater, hence, it is much easier to recover lithium from geothermal water than from seawater [5].

Because of its broad range of uses in nuclear fusion, chemical, and metallurgical sectors, and notably in rechargeable lithium-ion batteries, lithium is one of the most significant commodities [6]. The battery industry is in high demand for lithium due to the exponential growth of the electrical car and energy storage businesses. Sales of electrical vehicles and lithium demand are expected to double due to the growing importance of renewables. Lithium is a significant component of the new group of minerals known as "battery minerals" in this scenario [7]. It has been stated that the expected rise in EV sales is 56 million by 2040 [6]. Therefore, a significant increase in lithium demand has been observed in recent years. The global use of lithium compounds is increasing at a rate of 6% per year and its forecast consumption is 95,000 tons by 2025 [6,7].

There are several techniques such as solvent extraction [8], electro dialysis (ED) [9], precipitation [10], adsorption [11], and ion exchange [12] for lithium removal and recovery from brines and geothermal water. Membrane-based technologies such as nanofiltration (NF) electro dialysis (ED) and capacitive membrane deionization (CDI) are also being used for lithium recovery [13].

Hoshino [14, 15] investigated lithium recovery from seawater having Na^+ , Mg^{2+} , Ca^{2+} and K^+ ions by using ED having an ionic liquid membrane and dialysis method on a laboratory scale. When this technique was employed for lithium recovery, the dialysis process required about 30 days of operation for lithium recovery of 49.4%.

Recently, the bipolar membrane electro dialysis (BMED) method has drawn a lot of attention with its broad array of applications, including the separation of organic acids in enzymatic processes, acid and base productions from various available salts [16, 17], fruit juice pH adjustment [18, 19], cleaning of organic and inorganic substances as well as ultrapure deionized water production [20]. Wei et al. [21] investigated the regeneration of sodium hydroxide from the caustic via BMED. Jiang et al. [22] worked with BMs combined with an ED system for the production of acid and base from saline water which was obtained with the processing of wastewater resulting in the cold-rolling method. For this purpose, different systems were integrated as ED, reverse osmosis (RO), and BMED. In the BMED operation, three membrane modules having different membrane types (FKB/BP-1E/FAB, CMX/BP-1E/AMX, and CMB/BP-1E/AHA) were used. The most suitable membrane module that resulted in a high efficiency was proposed as CMX/BP-1E/AMX because of their low area resistances and high capability of water splitting. Yao et al. [23] worked on a continuous process of BMED for the generation of choline hydroxide using choline chloride.

The BMED method is useful for both the concurrent removal and recovery of ions and it combines the ED process with bipolar membranes (BMs) [24]. It sequentially contains the cation exchange membrane (CEM), BM, and anion exchange membrane (AEM) as a repeating unit of the so-called cell [25]. If a certain electrical potential is applied, the water-splitting occurs in the boundary layer of the BM where H^+ and OH^- ions are generated for both acid and base productions. In the meantime, the cations pass through to the CEMs whereas the anions transfer through to the AEMs to combine with the respective H^+ and OH^- ions obtained from water splitting in BM. The corresponding acid and base productions from a salt solution are therefore carried out in discrete units [26, 27]. BMED is an economical method employed in resource recovery and therefore it can be used for lithium recovery from lithium salts as well [28].

There are several usage areas of BMs for the production of lithium from different compositions of brines. For instance, by a combination of BMs and conventional ED methods, Jiang et al. [29] studied the production of LiOH from synthetic lithium brine solutions prepared from the model solutions containing LiCl, MgCl_2 , and CaCl_2 , LiNO_3 , LiOH, Na_2SO_4 , and HCl. The effect of the feed solution concentration and the current density on the operating cost of LiOH production was investigated in their study. According to the results they obtained, the minimum cost of LiOH production was estimated as 2.59 \$/kg of LiOH produced when the current density was 30 mA/cm² and the lithium concentration of feed solution was 0.18 M.

Simultaneous removal and recovery of lithium and boron were investigated in several studies by using different BMED systems. Bunani et al. [30, 31] performed such studies with two different ED systems with BMs. They investigated the effect of the operational parameters such as electrical

potential applied, the volume, and the initial pH of sample solution on the BMED system performance [30]. Efficiencies of lithium and boron separations and recoveries were improved by the increase in electrical potential applied and sample pH. When the electrical potential applied to the system was increased, the current efficiency decreased but the specific power consumption increased [31].

In this study, recovery of lithium in the form of LiOH from model LiCl solution was investigated by BMED method using heterogeneous ion exchange membranes and BMs.

2. Experimental

A lab-scale ED system consisting of BMs (Mega EDR-Z-Full-V4 model) was employed in this study. The ED system consists of 11 CEMs, 10 AEMs, and 10 BMs. Cell dimensions in the BMED module are 56 × 206 mm while the effective area of each membrane is 64 cm² [25].

The BMED stack is composed of anode and cathode made with Ti/Pt and 10 triple units including Ralex model CEMs (CMH-PES), AEMs (AMH-PES), and BMs. The configuration of the membranes in the module was in the series of a CEM, an AEM, and a BM (CMH-AMH-BM). There is a polyethylene spacer with a thickness of 0.8 mm between the membranes. All the membranes used in this study are heterogeneous in nature and the other properties of the ion exchange membranes are given in Table 1.

The flow diagram of the used ED system and experimental setup for recovery of LiOH in this study are depicted in Figs. 3 and 4, respectively.

For BMED tests, 2 L of LiCl solution prepared at various lithium concentrations (34, 68, 170, and 340 mg Li⁺/L) was used as the feed solution. Two different concentrations of HCl and NaOH solutions (500 mL of each) (0.003 M and 0.05 M) were used in both acid and base compartments, respectively. A 250 mL of 0.1 M NaOH solution was employed in the electrode compartment.

Additionally, two experiments were performed at 20 V for lithium recovery in the presence of Na^+ ions. In these experiments, the mixtures including 0.01 M Li⁺ with 0.01 M Na⁺ and 0.01 M Li⁺ with 0.02 M Na⁺ in the sample compartment were employed. The acid and base compartments solutions were 0.05 M HCl and 0.05 M NaOH (500 mL of each), respectively while 0.1 M NaOH solution (250 mL) was used as the electrode solution.

The duration of each test lasted for 2 h. Samples were taken from acid, base, and sample compartments for analysis of lithium concentration every 20 min of the study. The concentration of lithium was determined using the Shimadzu AA-7000 model of Atomic Absorption Spectrophotometer.

Table 1
The membrane characteristics in ED system [26]

Type	CMH-PES	AMH-PES	BM
Application	ED EDI	ED EDI	
Ion exchange group	R-SO ₃ ⁻	R-(CH ₃) ₃ N ⁺	
Ionic form (counter ion)	Na ⁺	Cl ⁻	
Bond	Polyethylene	Polyethylene	
Reinforcement fabrics	PES-PP	PES-PP	
Thickness of membrane (Dry) (mm)	< 0.45	< 0.45	
Electrical Resistance			
Counter-ion transport number (0.5/0.1 M KCl)	< 0.95	< 0.95	NS*
Permselectivity (%) (0.5/0.1 M KCl)	> 90	> 90	
After swelling (%)			
Thickness	< 65	< 60	
Length	< 3	< 3	
Width	< 3	< 4	
Weight	< 65	< 60	
IEC			
(meq/g)	2.2	1.8	

* Not specified

EDI: Electrodeionization

IEC: Ion exchange capacity

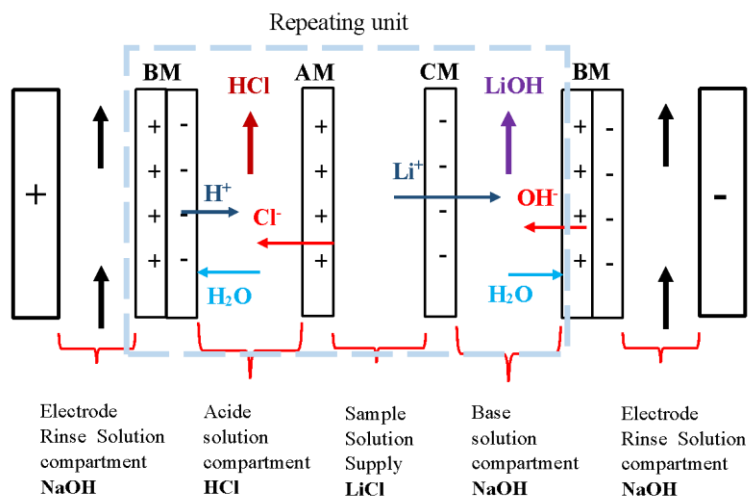


Fig. 1. The flowsheet of the ED system for simultaneous separation and recovery of lithium. (AM: Anion Exchange membrane; BM: Bipolar membrane; CM: Cation Exchange membrane)

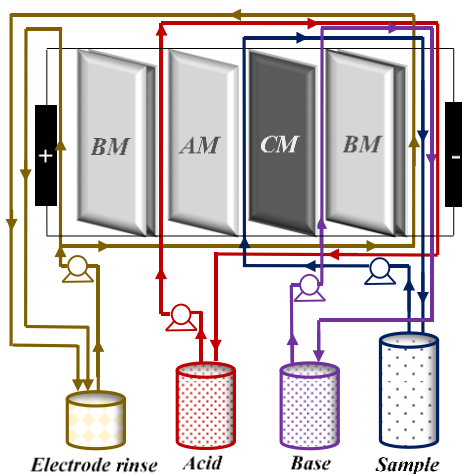


Fig. 2. Schematic presentation of the experimental setup

Equations 1 and 2 were used for assessing the performance of the ED system during this study. Lithium removal efficiency (S , %) from the sample compartment and the percent recovery of lithium (β , %) in the base compartment were calculated using Equations 1 and 2, respectively.

$$S(\%) = \frac{100 * (C_{Li,o} - C_{Li})}{C_{Li,o}} \quad (1)$$

$$\beta = \frac{\left(\frac{C_n}{n}\right)}{C_i} * 100 \quad (2)$$

where, $C_{Li,o}$ is the lithium concentration at the beginning of the experiment (mg Li^+/L), C_{Li} is the lithium concentration at the end of the experimental period (mg Li^+/L), and C_n is the lithium concentration in acid and base compartments at the end of the experiment (mg Li^+/L).

3. Results and discussion

3.1 Effect of lithium concentration

In this study, influence of lithium concentration in the sample compartment on lithium removal and recovery was investigated by means of ED having BMs. In the sample compartment, model solutions of LiCl having four different lithium concentrations (34, 68, 170, and 340 mg/L) were used. In acid and base compartments, 0.05 M HCl and 0.05 M NaOH solutions

were employed as initial acid and base solutions, respectively. Each test was carried out under a constant applied electrical potential (20 V).

In Fig. 3(a), lithium removal versus time plot was illustrated. According to the test results obtained in this study, it was clearly seen that irrespective of the initial lithium concentration in the feed compartment, there were not any considerable changes in terms of lithium removal from the sample compartment at the end of our experimental time (2 h) as depicted in Fig. 3(a). The percent removals obtained for the sample solutions having initial lithium concentrations of 34, 68, 170, and 340 mg Li^+/L were found as 98.6, 99.2, 99.7, and 99.6%, respectively. On the other hand, the kinetics of lithium removal was faster for the sample solution with lower lithium concentration than that with high lithium concentration (Fig. 3(a)). The study performed with the sample solution having 34 mg Li^+/L reached a plateau earlier compared to other sample solutions (68, 170, and 340 mg Li^+/L). When the concentration of lithium in the sample solution increased, the lithium removal rate decreased until a plateau was attained.

Fig. 3(b) depicts the relationship between $\ln(C_{Li}/C_{Li,o})$ and experimental time according to change in lithium concentration in the sample compartment. The active membrane area was 0.064 m^2 for 10 triple ion exchange membranes (CM-AM-BM) and the volume of the sample chamber was 0.002 m^3 (2 L). The change in the linearized lithium concentration of the sample solution was plotted against time as shown in Fig. 3(b). It can be clearly seen that a good linear relation between $\ln(C_{Li}/C_{Li,o})$ and t was attained. Mass transfer coefficients (k_{Li}) were found as 4.06×10^{-5} , 3.44×10^{-5} , 2.50×10^{-5} , and 2.19×10^{-5} m/s for the sample solutions of 34, 68, 170 and 340 mg Li^+/L , respectively. The highest mass transfer coefficients were obtained as 4.06×10^{-5} m/s with 34 mg Li^+/L of LiCl solution.

The lithium mass transfer coefficients were calculated with the help of Fick's first diffusion law. Mass flux equations given in Equations 3 and 4 were used to obtain Equation 5 which was eventually used for the calculation of mass transfer coefficients (k , m/s) [27].

$$J = k * C \tag{3}$$

$$J = \left(\frac{V}{A}\right) \frac{dC}{dt} \tag{4}$$

$$\ln\left(\frac{C}{C_0}\right) = -k\left(\frac{A}{V}\right)t \tag{5}$$

Where C is the concentration (mol/m^3); J is the mass flux ($\text{mol}/(\text{m}^2\text{s})$); V is the volume of the sample chamber (m^3); A is the active membrane area (m^2); k is the mass transfer coefficient (m/s) and t is the experimental time (min).

As indicated in Fig. 4(a), maximum lithium recoveries were obtained as 75.5%, 54.5%, 55.4%, and 51.2% for the sample solutions having the initial lithium concentrations of 34, 68, 170, and 340 mg/L, respectively. So, the highest lithium recovery was 75.5% by using the sample solution having the lowest lithium concentration of 34 mg/L.

Fig. 4(b) shows the value of lithium concentrations in the base compartment at different lithium concentrations of the sample solution. The highest lithium concentration in the base compartment was 706.3 mg Li^+/L when a solution of 340 mg Li^+/L was used in the sample compartment. The lithium concentrations in the base compartment at the end of 2 h of operation were found as 109.7, 143.1, 349.8, and 706.3 mg Li^+/L for the sample solutions having a lithium concentration of 34, 68, 170, and 340 mg Li^+/L , respectively. The higher amounts of acid and base productions were achieved by the increase in the lithium concentration of the sample solution [33]. The lithium concentration in the base compartment has increased with increasing lithium concentration in the sample solution since there is high ionic mobility with a high concentration of sample solution. As the concentration of lithium

in the sample solution increased, the lithium ion mobility also increased. The membrane resistance decreased with the sample solution having high ionic mobility and this helped to facilitate the transfer of lithium ions through the membranes to the base compartment. Consequently, the resistance of the stack decreased with the increasing concentration of sample solution [34]. Similarly, Pan et al. [35] investigated the relation between overall stack resistance and solution resistance resulting from the feed solution concentration. They obtained a graph of resistance versus time. For the first stages of their experiment, the stack resistance has sharply declined, since the BMs released a great number of protons and hydroxide ions by means of water-splitting at the beginning of the experiment. Also, when the concentration of the feed solution increased, the energy consumption, electrical conductivity of the sample solution, and membrane conductivity increased [36].

In all tests performed in this study, lithium recovery values were lower than their corresponding lithium removals due to possible reasons explained below:

- Leaking of lithium ions across membranes to the electrode and acid compartments.
- Lithium-ion retention on the surface of CEMs.
- Lithium ions migration from the sample compartment to the electrode and acid compartments.

It was considered that some of the lithium ions in the sample compartment were possibly retained on the surface of the CEMs. Therefore, some amounts of the lithium ions removed from the sample compartment cannot be transferred into the base compartment. Bunani et al. [31] reported that the configuration of the ED system consisting of two ends CEMs might likely result in the migration of some lithium ions to the electrode compartment. For that reason, it is very hard to have equal lithium removal and recovery values when the ED systems with such configurations are employed. Thus, the lithium removals acquired were higher than the lithium recoveries. For solving this problem, different IEMs having lower membrane resistance or thickness can be used or the experimental period can be extended to ensure maximization of the ion transfer [37].

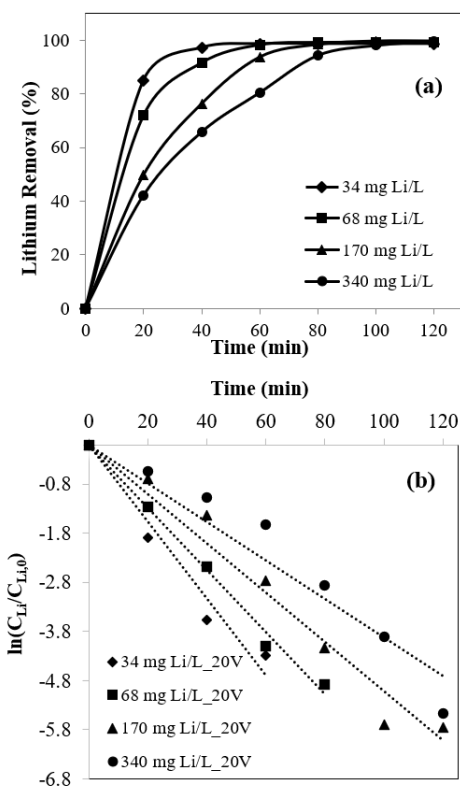


Fig. 3. The influence of lithium concentration of sample solution on a) percent removal of lithium b) linearized data of lithium separation

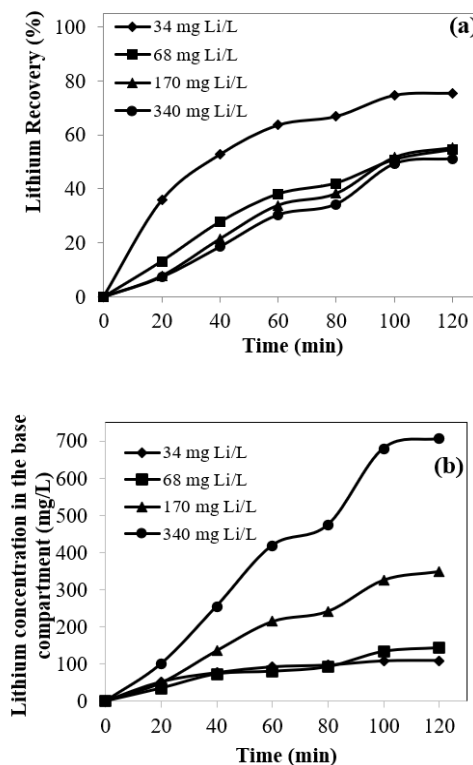


Fig. 4. The influence of lithium concentration of sample solution on a) percent recovery of lithium and b) lithium concentration in the base compartment.

Equation 6 was utilized to obtain Equation 7, which is helpful for the calculation of specific power consumption (E_{SPC} , kWh/m³) in ED operation [26, 27]. The mass transfer coefficients of lithium and E_{SPC} values were calculated from Equations 5-7 and given in Table 2.

$$Q = \int_0^t Idt \tag{6}$$

$$E_{SPC} = \frac{EQ}{V} \tag{7}$$

Where Q is the total electric charge used for the separation process during the experimental time (A.h); I is the current value measured at that time (A) and E is the applied potential (V).

Specific power consumption was calculated in all studies performed by using different concentrations of sample solutions. As shown in Fig. 5, the highest and the lowest E_{SPC} values were obtained as 3.80 kWh/m³ and 1.75 kWh/m³ in the studies performed with 340 mg Li⁺/L and 34 mg Li⁺/L solutions, respectively. As expected, the E_{SPC} values consumed for ionic transport through membranes increased with a high lithium concentration in the feed solution.

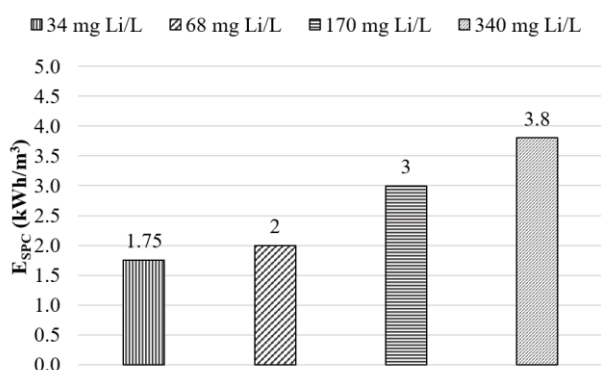


Fig. 5. The influence of lithium concentration of sample solution on the specific power consumption.

Table 2
Mass transfer coefficients of lithium calculated for different sample concentrations

Sample Solution	Acid (HCl) and base (NaOH) solutions	Electrical potential (V)	Mass transfer coefficient of lithium $k_{Li} \cdot 10^5$ (m/s)	E_{SPC} (kWh/m ³)
34 mg Li ⁺ /L	0.05 M – 0.05 M	20	4.06	1.75
68 mg Li ⁺ /L			3.44	2.00
170 mg Li ⁺ /L			2.50	3.00
340 mg Li ⁺ /L			2.19	3.80

3.2 Effect of applied electrical potential on BMED system

For understanding the impact of applied electrical potential on lithium removal and recovery, the ED system was operated at two different electrical voltages (20 and 25 V). In this study, a model solution having lithium with 68 mg Li⁺/L of concentration was used. The solutions of 0.003 M HCl and 0.003 M NaOH were employed in acid and base compartments, respectively.

As depicted in Fig. 6(a), lithium removals were 99.3% and 99.2% at 25 and 20 V, respectively. The results obtained in this study are consistent with the findings by Bunani et al. [26]. They showed that the increase in electrical potential up to the optimum value resulted in an increment in the removal performance of lithium. In the case of recovery performance, it was remarked that if the electrical potential is higher than the optimum value, the system performance did not dramatically increase [26]. Figs. 6(b) and 6(c) show the lithium recovery values and the lithium concentrations recovered in the base compartment, respectively. As can be seen in Fig. 6(b), maximum lithium recovery was obtained when the applied electrical potential was 20 V. Lithium recovery values were 56.0 and 48.7% at 20 and 25 V, respectively.

Lithium concentrations at the end of the study (2 h) were 138.5 and 131.9 mg/L at 20 and 25 V of applied electrical potentials, respectively.

Fig. 6(d) shows the specific power consumption values calculated using the data obtained at two different electrical potentials. E_{SPC} values at the end of 2 h were 0.80 kWh/m³ and 1.25 kWh/m³ at 20 V and 25 V, respectively. As expected, specific power consumption increased with an increase in the electrical potential applied, as expected.

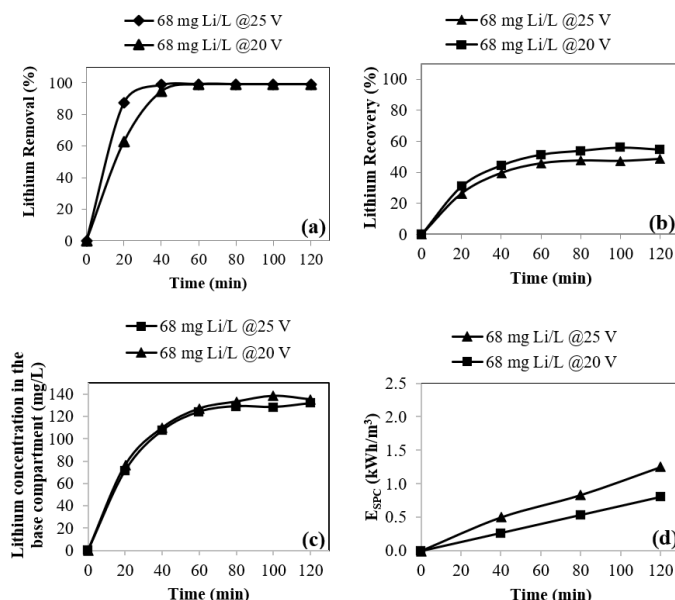


Fig. 6. The effect of the electrical potential applied on a) lithium removal b) lithium recovery c) recovered lithium concentration in the base compartment d) specific power consumption values.

3.3 Effects of acid and base concentrations in respective acid and base compartments

The influence of the initial concentrations of acid and base solutions on lithium recovery by ED having BMs was also investigated. For this, HCl and NaOH solutions with 0.05 M and 0.003 M concentrations were employed in the respective acid and base compartments. The solution used in this study contained 68 mg/L of lithium concentration. The tests were conducted at a constant electrical potential of 20 V. The experimental time was maintained constant as 2 h.

The results of the study were depicted in Fig. 7. The parameter of initial acid and base concentrations at the respective acid and base compartments did not make a big difference in terms of lithium removal at the end of 2 h. Lithium removal value was 99.2% for both experiments run with acid and base compartments solutions of 0.003 M HCl-0.003 M NaOH and 0.05 M HCl-0.05 M NaOH solutions (Fig. 7(a)). However, the lithium recovery of the experiment conducted with 0.003 M HCl-0.003 M NaOH solutions was faster than those with 0.05 M HCl-0.05 M NaOH solutions initially. Nevertheless, after 100 min of the study, lithium recovery values of both conditions were similar (Fig. 7(b)). The maximum lithium recovery value was around 55-56%.

When 0.05 M HCl and 0.05 M NaOH solutions were employed in acid and base compartments, respectively, lithium concentration recovered in the base compartment after 120 min was 143 mg Li⁺/L (Fig. 7(c)). The respective lithium concentration was 139 mg Li⁺/L in the base compartment for the study with 0.003 M HCl and 0.003 NaOH solutions. It was considered that increasing acid and base concentrations from 0.003 M to 0.05 M caused an increase in the osmotic pressure in the both acid and base compartments. This may cause a fall in the supply of water into the BMs and restricts the water dissociation and lead to an increase in the required time for the process [33]. Indeed, the recovery rate of lithium declined especially in the initial 80-100 min when the concentrations of acid and base solutions were higher.

In Fig. 7(d), specific power consumption (E_{SPC}) was calculated for different concentrations of acid and base solutions employed in the acid and base compartments. It was observed that the E_{SPC} was influenced by the concentration of acid and base solutions as reported by Ipekçi et al. [24]

In the work conducted by Ipekçi et al. [24], removals of lithium and boron increased by increasing the initial acid and base concentrations in acid and base compartments. As the initial concentration of acid and base

increases, a higher conductive medium is created. However, in their study, lithium and boron recovery values were high whenever acid and base solutions were employed at lower concentrations. They explained that when HCl and NaOH were used in acid and base compartments, respectively, the increase in their concentrations resulted in lower recovery performance due to back diffusion [25]. The consequences obtained in this study agreed well with the finding by Ipekci et al. [24].

Table 3 depicts the lithium mass transfer coefficients calculated for the experiments performed at different initial acid and base concentrations (0.003 M and 0.05 M) in acid and base compartments, respectively, and at different applied electrical potentials (20 and 25 V) by comparing with the data given in the literature. Our studies were carried out using a LiCl solution having 68 mg Li⁷/L. As seen in Table 3, the mass transfer coefficient of lithium ion increased when the electrical potential applied was higher. The mass transfer rate of lithium is expected to increase because of the rise in the mobility of lithium ions through the ion exchange membranes at a higher electrical potential. When the initial concentrations of acid and base solutions were increased from 0.003 M to 0.05 M in the respective acid and base compartments, the mass transfer coefficient of lithium declined. When the obtained results were compared with the literature, it was seen that the average mass transfer coefficient reported by Ipekci et al. [27] using 812 ± 56.15 mg B/L and 256 ± 33.11 mg Li/L as the feed solution along with 0.003 M H₃BO₃ and LiOH in acid and base compartments, respectively was lower (3.13x10⁻⁵ m/s) than that found in this study.

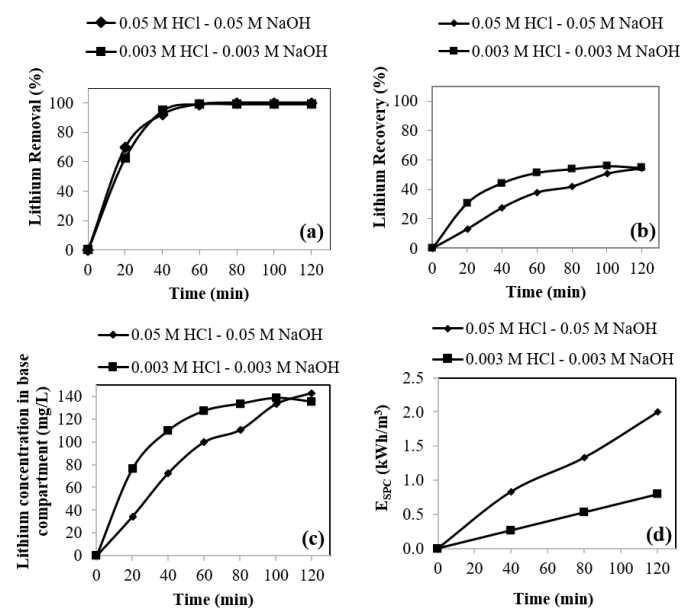


Fig. 7. The studies were performed using different acid and base concentrations in acid and base compartments a) the percent removal of lithium b) the percent recovery of lithium c) lithium concentration in the base compartment d) Specific power consumption values for different concentrations of acid and base solutions.

Table 3
Mass transfer coefficients of lithium obtained by BMED

Salt solution	Solution concentrations of acid and base	Electrical potential (V)	Mass transfer coefficient- $k_{Li} \cdot 10^5$ (m/s)	Ref.
LiCl (68 mg Li/L)	0.003 M HCl 0.003 M NaOH	25	4.69	Our study
	0.003 M HCl 0.003 M NaOH	20	4.06	
	0.05 M HCl 0.05 M NaOH	20	3.44	
	0.05 M HCl 0.05 M NaOH	25	3.13	
Li ₂ B ₄ O ₇ ·5H ₂ O (812±56.15 mg B/L 256±33.11 mg Li/L)	0.003 M HCl 0.003 M NaOH	25	3.13	[27]

3.4 Effect of Sodium-Ion on Lithium Recovery

The effect of sodium ions existing in the feed solution together with lithium ions on lithium recovery was investigated by adjusting the molar ratios of lithium and sodium ions to 1:1 (M Li⁺: M Na⁺) and 1:2 (M Li⁺: M Na⁺). According to Fig. 8, lithium ions removal was faster by using LiCl solution only. On the other hand, the existence of sodium ions in the feed solution reduced the removal rate of lithium ions. But maximum removals of both lithium and sodium ions were almost the same (99%) in each study.

Fig. 9(a) shows the lithium recovery in the absence and presence of sodium ions. The lithium recovery was obtained as 54.5% in the experiment performed using only 0.01 M LiCl solution. On the other hand, when 0.01 M Na⁺ and 0.02 M Na⁺ were added to the sample solution, the percent lithium recoveries were 66.8% and 69.3%, respectively. As can be seen in Fig. 9(b), the presence of sodium ions in the sample solution caused an increase in the specific power consumption.

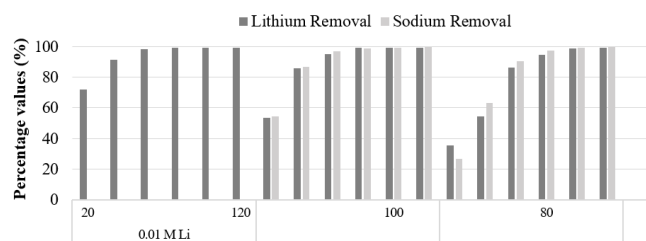


Fig. 8. Removal of lithium and sodium by BMED

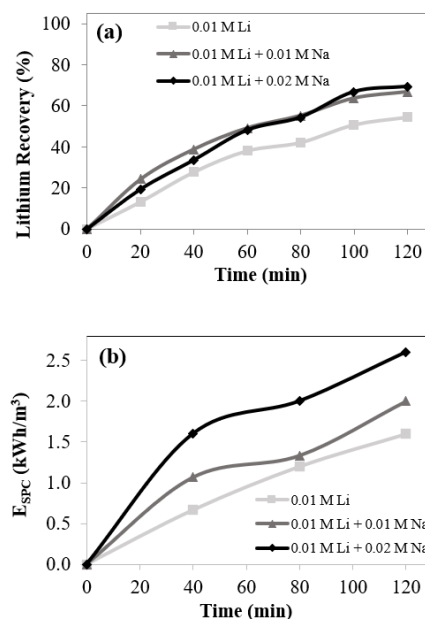


Fig. 9. a) Lithium recovery by BMED b) specific power consumption values in the presence and absence of sodium ion

For the calculation of mass transfer coefficients of lithium and sodium ions, the linearized data of lithium and sodium separations were used (Fig. 10). In Table 4, the mass transfer coefficients calculated for lithium and sodium ions were given. It was obtained that there was some decrease in the mass transfer coefficient of lithium in the co-existence of sodium ions in the solution. This result agreed well with the literature [38].

Table 5 summarized all results obtained in this study. When the sample solution containing both sodium and lithium ions was used, the performance of lithium removal was almost similar. On the other hand, lithium recovery slightly increased by the addition of sodium ions to the sample solution. The effect of sodium ions on lithium separation was observed in mass transfer coefficients. The mass transfer coefficient of lithium was 3.44x10⁻⁵ in the absence of sodium ions. However, this value decreased to 2.81x10⁻⁵ with the addition of sodium ions (0.1 M) to the sample solution. Also, when the concentration of sodium ions was increased from 0.01 M to 0.02 M, the mass transfer coefficients of lithium decreased from 2.81x10⁻⁵ to 1.88x10⁻⁵.

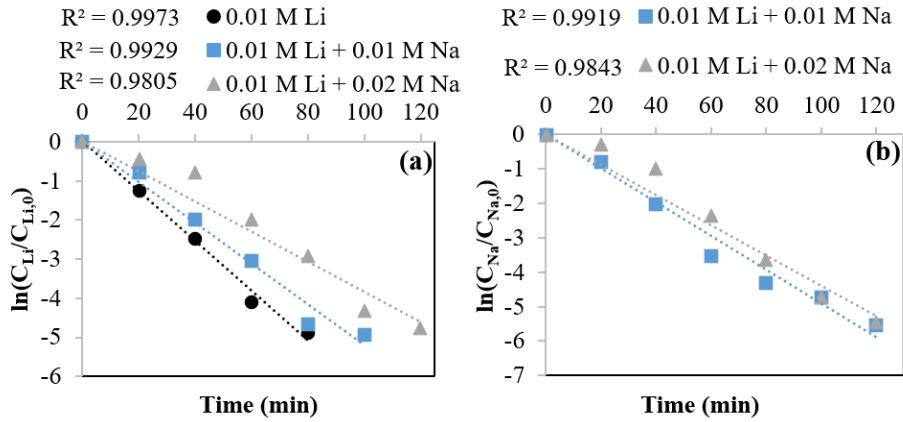


Fig. 10. Linearization of a) Lithium and b) Sodium data in BMED MEGA system

Table 4
Mass transfer coefficients of lithium and sodium for different sample solutions

Sample Solution	Mass transfer coefficients of Lithium ($k_{Li} \cdot 10^5$)	Mass transfer coefficients of Sodium ($k_{Na} \cdot 10^5$)
0.01 M Li	3.44	-
0.01 M Li + 0.01 M Na	2.81	2.50
0.01 M Li + 0.02 M Na	1.88	2.19

Table 5
Summary of the data obtained in comparison with literature

Ref.	Sample solution	Acid and base solutions	Electrical potential (V)	Recovery of lithium (%)	Removal of lithium (%)	Mass transfer coefficient of Lithium $k_{Li} \cdot 10^5$ (m/s)	Mass transfer coefficient of Sodium $k_{Na} \cdot 10^5$ (m/s)		
Our study	LiCl	0.05 M HCl 0.05 M NaOH	20	75.5	98.6	4.06	-		
				54.5	99.2	3.44			
				55.4	99.7	2.50			
				51.2	99.6	2.19			
				56.0	99.2	4.06			
	68 mg Li/L	0.003 M HCl 0.003 M NaOH	25	48.7	99.3	4.69			
[25]	Mixture of LiCl and NaCl	0.05 M HCl 0.05 M NaOH	20	66.8	99.3	2.81	2.50		
				69.3	99.2	1.88	2.19		
	924 mg B/L and 313 mg Li/L			0.003 M HCl 0.003 M NaOH	25	63.9	99.8	-	-
	812 ± 56.15 mg B/L and 256 ± 33.11 mg Li/L			0.003 M HCl 0.003 M NaOH	25	73.0	99.0	3.13	-
[27]	Li ₂ B ₄ O ₇ ·5H ₂ O	0.003 M HCl 0.003 M NaOH	25	66.0	99.0	-	-		
[24]	1000 mg B/L and 340 mg Li/L	0.05 M HCl 0.05 M NaOH	20	30.8	57.0	-	-		

According to results obtained by Jarma et al. [25] using the same ED system, maximum lithium recovery and removal were 63.9 and 99.0%, respectively at 20 V, when acid and base solutions were 0.003 M of HCl and 0.003 M of NaOH, respectively. The lithium recovery results obtained in our study are lower than their results. The difference in removal and recovery

values of lithium is related to the difference in type and concentration of the sample solution. In the study performed by Jarma et al. [25], the sample solution was prepared from Li₂B₄O₇·5H₂O and it contains 924 mg B/L and 313 mg Li/L while the sample solution used in this study contains only 68 mg Li/L. In the experiment performed by the Astom Acilyzer EX3B model

ED system, Ipekçi et al. [24] found that the maximum removal and recovery of lithium were 57.0% and 30.8%, respectively at 20 V using a mixture of 1000 mg B/L and 340 mg Li⁺/L along with 0.05 M HCl-0.05 M NaOH as acid and base compartments solutions, respectively. In our study, the maximum removal and recovery values of lithium were obtained as 99.6% and 51.2% using similar process conditions. The major reason for the differences in both results is the presence of boron in the sample solution and the pH of the feed solution. In another study performed by Ipekçi et al. [27] at 20 and 25 V, the sample solution having 812 ± 56.15 mg B/L and 256 ± 33.11 mg Li⁺/L together with 0.003 M of acid and base solutions were used. Respective lithium recovery and removal were 66.0% and 99.0% at 20 V, while specific power consumption was 3.21 kWh/m³. When the electrical potential applied was increased to 25 V, the lithium recovery and the specific power consumption calculated increased to 73.0% and 4.11 kWh/m³, respectively while the lithium removal value remained constant. In our study performed with the sample solution containing only 68 mg Li⁺/L, the respective lithium recovery values were 56.0% (at 20 V) and 48.7% (at 25 V). Ipekçi et al. [39] stated that by the increase in the amount of lithium ion transferred, the specific power consumption increased also. However, specific power consumption values obtained were 1.25 kWh/m³ and 0.80 kWh/m³ at 25 V and 20 V, respectively in this study. As indicated by Jarma et al. [25], when the electrical potential is high, back diffusion occurs due to the increase in concentration polarization, so much more electrical potential is required for ion transfer through IEMs.

4. Conclusions

In this study, BMED was considered to be an effective method for simultaneous lithium removal and recovery from brine. Generally, the separation efficiency was higher than lithium recovery because of the configuration of the membrane stack in the ED system. Due to the existence of CEMs at both ends of the ED stack, it was considered that some amounts of lithium ions were transferred to the electrode compartment. Indeed, the presence of lithium ions was detected in the electrode compartment. For increasing lithium recovery, the ED system configuration should be redesigned perhaps. Although the presence of a coexisting Na⁺ ion in the sample solution did not affect lithium removal, lithium recovery in the base compartment increased.

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