

**EGE UNIVERSITY GRADUATE SCHOOL OF
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(MASTER OF SCIENCE THESIS)**

**SEPARATION OF BORON AND LITHIUM FROM
AQUEOUS SOLUTIONS BY BIPOLAR MEMBRANE
ELECTRODIALYSIS (BMED)**

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Deniz İpekçi tarafından yüksek lisans tezi olarak sunulan "Separation of Boron and Lithium From Aqueous Solutions By Bipolar Membrane Electrodialysis (BMED)" başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 11.01.2019 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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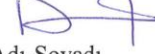
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İmzası



Adı-Soyadı

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ÖZET

Bipolar Membran Elektrodializ (BMED) Yöntemi ile Sulu Çözeltilerden Bor ve Lityum'un Ayrılması

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Bu çalışmada bipolar membran elektrodializ (BMED) metoduyla sulu çözeltilerden bor ve lityum giderimi ve geri kazanımı incelenmiştir. Bu amaçla, deneyler bor ve lityum içeren model çözeltiler kullanılarak yapılmıştır.

Farklı iyon değiştirici membranlar içeren üç farklı BMED sistemi kullanılmış ve prosesi etkileyebileceği düşünülen bazı parametreler incelenmiştir. Çalışmalarda ASTOM ACILYZER model BMED sistemi, MEGA model BMED sistemi ve PC-Cell model BMED sistemleri kullanılmıştır. ED sisteminde bulunan asit ve baz bölmelerinde kullanılan asit ve baz çözeltilerinin türü ve derişimleri ile elektriksel potansiyelin etkisi ASTOM ACILYZER ve MEGA model BMED sistemleri kullanılarak incelenmiştir. Ek olarak, örnek çözeltinin akış hızının ve pH değerinin sisteme olan etkisi MEGA model BMED sistemi kullanılarak incelenmiştir. Proses parametreleri optimize edildikten sonra, MEGA model ve ASTOM ACILYZER model BMED sistemleri için optimum çalışma koşulları belirlenmiştir. Optimum koşullar bu iki BMED sistemi için de farklılık göstermiştir. Bu sonuç optimum çalışma koşullarının kullanılan BMED sistemine göre değişebileceğini göstermiştir. MEGA BMED sistemi ve ASTOM ACILYZER BMED sistemi için belirlenen optimum koşullar, PC-Cell BMED sistemine de uygulanarak elde edilen sonuçlar karşılaştırılmıştır.

BMED deneylerinin sonucunda maksimum lityum ve bor geri kazanımları MEGA model BMED sistemi ile 25 V'luk elektriksel potansiyel altında, asit-baz bölmelerinde kullanılan asit baz derişimleri 0.003 M HCl-0.003 M NaOH, akış hızı 50 L/h ve örnek çözelti pH değeri 10 iken sırasıyla %71 ve %66 olarak elde edilmiştir. ASTOM ACILYZER model BMED sistemi ile elde edilen maksimum

lityum ve bor geri kazanımları ise, 30 V elektriksel potansiyel altında, asit-baz bölmelerinde kullanılan asit baz derişimleri 0.05 M HCl-0.05 M NaOH iken, % 62 ve %50 olarak elde edilmiştir. Asit baz bölmelerinde kullanılan asit ve baz derişimleri 0.05 M HCl-0.05 M NaOH iken 20 V elektriksel potansiyel altında çözelti pH'ı 9.11 olduğunda maksimum lityum ve bor geri kazanımları PC-Cell BMED sistemiyle sırasıyla %76 ve %49 olarak elde edilmiştir.

Anahtar kelimeler: Bor, lityum elektrodializ, bipolar membran elektrodializ, geri kazanım.



ABSTRACT

Separation of Boron and Lithium from Aqueous Solutions by Bipolar Membrane Electrodialysis

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In this study, the feasibility of bipolar membrane electrodialysis (BMED) method for recovery of boron and lithium from aqueous solutions has been investigated. For this purpose, experiments were carried out with model solutions containing boron and lithium.

Three different BMED systems containing different ion exchange membranes were used and some parameters affecting the process performance were investigated. ASTOM ACILYZER BMED system, MEGA BMED system and PC-Cell BMED system were used in studies. The influences of type and of acid base solutions in acid base chambers and the electrical potential applied were investigated using ASTOM ACILYZER and MEGA BMED systems. In addition, the influence of the feed flow rate and the pH of the feed solution on process were investigated using the MEGA BMED system. Once the process parameters have been optimized, the optimum conditions for the MEGA BMED system and the ASTOM ACILYZER BMED system have been determined. Optimal conditions were different for these two BMED systems. This result showed that the optimum conditions could change according to the BMED system used. Optimum conditions for MEGA BMED system and ASTOM ACILYZER BMED system were applied to PC-Cell BMED system.

As a result of BMED experiments, the highest recoveries of lithium and boron were obtained as 71% and 66% respectively under 25 V of electrical potential with MEGA BMED system while initial concentrations of acid and base were 0.003 M HCl-0.003 M NaOH, feed flow rate was 50 L/h and pH value of the sample solution was 10. The highest recoveries of lithium and boron were obtained as 62% and 50%, respectively under electrical potential of 30 V of with ASTOM ACILYZER model BMED system while initial acid base concentrations

were 0.05 M HCl-0.05 M NaOH. However, when three different BMED systems were compared and the experimental conditions were kept constant (0.05 M HCl-0.05 M NaOH), the highest recoveries of lithium and boron were achieved by PC-Cell BMED system as 76% and 49% under 20 V electrical potential.

Keywords: Boron, lithium, electro dialysis (ED), bipolar membrane, recovery.



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CONTENT

	<u>Page</u>
ÖZET	vii
ABSTRACT	ix
TEŞEKKÜR	xi
ACKNOWLEDGEMENT	xii
NOMENCLATURE	xix
1 INTRODUCTION.....	1
1.1 Separation Methods for Boron and Lithium from Water	1
1.1.1 Separation Methods for Boron.....	1
1.1.2 Separation Methods for Lithium.....	7
1.2 Electrodialysis (ED).....	9
1.2.1 Ion Exchange Membranes	9
1.2.2 Theory and Applications of ED method.....	11
1.2.3 Cost of Electrodialysis (ED).....	13
1.3 Bipolar Membrane Electrodialysis (BMED).....	14
1.4 Separation of Boron and Lithium by BMED.....	15
1.5 Aim of this study	16
2.0 EXPERIMENTAL.....	17
2.1 Experiments with ASTOM ACILYZER model BMED System.....	17
2.1.1 Influence of Acid and Base Concentrations in Acid and Base Chambers....	18

CONTENT (Continued)

	<u>Page</u>
2.1.2 Influence of Acid and Base Types in Acid and Base Chambers	19
2.1.3 Influence of Electrical Potential Applied.....	19
2.2 Experiments with MEGA model BMED System	19
2.2.1 Influence of Concentrations of Acid and Base Solutions Used in Acid and Base Chambers	21
2.2.2 Influence of Applied Electrical Potential.....	22
2.2.3 Influence of Acid and Base Types Used in Acid and Base Chambers	22
2.2.4 Influence of pH of the sample solution.....	22
2.2.5 Influence of Feed Flow Rate.....	22
2.3 Comparative Tests with ASTOM ACILYZER, MEGA and PC-Cell model BMED Systems.....	23
2.3.1 Experiments with PC-Cell and MEGA Model BMED Systems (Test I).....	23
2.3.2 Experiments with PC-Cell and MEGA Model BMED Systems (Test II)	24
2.4 Equipments.....	24
2.4.1 pH-meter	24
2.4.2 ICP-AES.....	24
2.4.3 Atomic Absorption Spectrometer (AAS).....	25
2.4.4 Uv/vis Spectrophotometer.....	25
2.5 Calculations.....	26
3.0 RESULTS AND DISCUSSION	28

CONTENT (Continued)

	<u>Page</u>
3.1 Lithium and Boron Separations and Recoveries from Aqueous Solutions by ASTOM ACILYZER Model BMED System.....	28
3.1.1 Influence of Concentrations of Acid and Base Solutions in Acid and Base Chambers	28
3.1.2 Influence of Applied Electrical Potential	32
3.1.3 Influence of Acid and Base Types Used in Acid and Base Chambers	36
3.2 Lithium and Boron Separations and Recoveries from Aqueous Solutions by MEGA Model BMED System.....	44
3.2.1 Influence of Concentrations of Acid and Base Solutions in Acid-Base Chambers	44
3.2.2 Influence of Applied Electrical Potential	48
3.2.3 Influence of Acid and Base Types in Acid and Base Chambers	54
3.2.4 Influence of sample solution pH.....	58
3.2.5 Influence of Feed Flow rate	63
3.3 Comparison of test results obtained by three different BMED systems.....	67
3.4 Comparison of Results obtained with PC-Cell and MEGA model BMED System Results.....	69
3.4.1 Comparison at 20 V	69
3.4.2 Comparison at 15 V	72
3.5 Cost Analysis	74
3.5.1 Cost Analysis for ASTOM ACILYZER Model BMED System.....	74
3.5.2 Cost Analysis for Mega Model BMED System	77

CONTENT (Continued)

	<u>Page</u>
4.0 CONCLUSIONS.....	82
REFERENCES.....	87
CV	94
APPENDIX (Raw data)	1



LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
Figure 1.1. Illustrations of the (a) fixed bed system and (b) the integrated system (Koltuniewicz et al., 2004)	4
Figure 1.3. Bipolar Membrane (Bunani et al., 2017).....	11
Figure 1.4 Conventional Electrodialysis (Strathmann, 2010).....	12
Figure 1.5. Bipolar membrane electrodialysis process (Bunani et al., 2017)	14
Figure 1.6. Illustration for removal and recovery of boron and lithium (Bunani et al., 2017).....	16
Figure 3.1. Removal of boron with different acid and base concentrations by ASTOM ACILYZER model BMED system	28
Figure 3.2. Removal of lithium with different acid and base concentrations by ASTOM ACILYZER model BMED system	29
Figure 3.3. Recovery of boron with different and base concentrations by ASTOM ACILYZER model BMED system	30
Figure 3.4. Recovery of lithium with different acid and base concentrations by ASTOM ACILYZER model BMED system	30
Figure 3.5. Linearization of boron separation data for ASTOM ACILYZER model BMED system.....	31
Figure 3.6. Linearization of lithium separation data for ASTOM ACILYZER model BMED system.....	31
Figure 3.7. Mass transfer coefficients of boron and lithium with different acid base concentrations by ASTOM ACILYZER model BMED system.....	32
Figure 3.16. Removal of lithium using different acid and base solutions in acid-base chambers by ASTOM ACILYZER model BMED system.....	38

LIST OF TABLES

<u>Table</u>	<u>Pages</u>
2.1 Characteristics of membranes in Astom Acilyzer model BMED system.....	18
2.2 Characteristics of membranes in MEGA model BMED system.....	20
2.3. The characteristics of membranes in PC-Cell BMED system	23
3.1. Mass transfer coefficients with different acid and base type by ASTOM ACILYZER model BMED system.....	40
3.2. Mass transfer coefficients with different acid and base types used in acid and base chambers.....	44
3.3. Mass transfer coefficients with different acid-base concentrations by MEGA model BMED system.....	48
3.4. Mass transfer coefficients calculated at different flow rates by MEGA model BMED system.....	65
4.1. Boron and lithium recoveries and SPC values obtained with ASTOM ACILYZER model BMED system	85
4.2. Boron and lithium recoveries and SPC obtained with MEGA model BMED system.....	85
4.3. A comparison for boron and lithium recoveries and SPC by different BMED systems.....	86

NOMENCLATURE

ED	Electrodialysis
BMED	Bipolar Membran Electrodialysis
SPC (kwh/m ³)	Specific Power Consumption
C _i (mol/l)	Initial concentration of the species
C _f (mol/l)	Final Concentration of the species
k (m/s)	Mass Transfer Coefficient
R (%)	Separation Efficiency
B (%)	Recovery of boron/lithium in acid and base chambers, respectively
n	The proportion of sample solution volume at the beginning to acid /base solutions volume at the beginning in acid and base chambers
V (L)	Volume of the sample chamber
A (m ²)	Effective Membrane Area



1 INTRODUCTION

1.1 Separation Methods for Boron and Lithium from Water

1.1.1 Separation Methods for Boron

1.1.1.1 Ion Exchange

Ion exchange is a mass transfer process for ionic species from liquid solution to solid ion exchange resins. Ion exchange is based on three factors:

- Ions can be removed by replacing another ionic species that has same charge sign. The critical point is that ions can be displaced in equivalent amounts.
- When solution is directly contacted with ion exchange resin, the solute transfers to the ion exchange resin. After transferring of ions to the ion exchange resin, ions eluted in regeneration step. Hence, solution with much higher concentration of ions is obtained.
- Ion exchange resins have different affinity for different species. That means “selectivity” and selectivity is a crucial parameter for the separation (Rodrigues, 1983).

Ion exchange method is utilized to remove of boron from aqueous solutions especially at low salt concentrations. Effective boron separation can be achieved via boron-specific ion exchange resins (Güler et al., 2015). Kabay et al. (2007) utilized commercial ion exchange resins (Diaion CRB and Dowex XUS) for separation of boron from seawater. While the authors studied with these resins, it was observed that decreasing particle size of resin resulted with the increase in boron removal. Li et al. (2011) worked with N-methyl-D-glucamine functionalized silica–polyallylamine composites for separation of boric acids because of the fact that molecules with vicina diols are enable to form tetraborate complexes even if it is in aqueous solutions. Additionally, amine functional group is needed for chelating of boric acid. Removal of boric acid was achieved as effectively by this chelating ion exchange resin with or without foreign ions in aqueous solutions. Santander (2013) et al. synthesized a new type of ion exchange resin (poly(N-(4-vinylbenzyl)-N-methyl-D-glucamine) for boron separation and

this resin was compared to commercial boron selective resin. According to their results, the authors did not observe high separation difference for boron separation when these resins compared in terms of boron separation. Boron separation was achieved around 80% with both resins.

In the literature, it has been also reported that boron separation was achieved by polystyrene-based resin grafted with glycidol and equilibrium was occurred end of the 24 h (Kluczka et al., 2015).

According to Wolska and Bryjak, (2013), commercially available boron selective ion exchange resins are enable to remove 93-98% of boron from solutions.

1.1.1.2 Membrane Processes

Membranes are semi-permeable barriers and these barriers enable to divide the feed stream as concentrate and permeate streams. Hyperfiltration that is also known as reverse osmosis (RO) is one type of membrane process enable to remove very small particles having 10^{-3} - 10^{-4} μm diameters (Alonso et al., 2018). However, effective separation of boron by conventional RO could not be possible because removal of boron highly depends on operating conditions and pH of the feed stream (Güler et al., 2011). Boron separation by RO could be provided by increasing pH and applied pressure (Chiang et al., 2013). Therefore, ion exchange following conventional RO systems is a favorable process for removal of boron. In the literature, it was reported that boron was removed from seawater by using different SWRO membranes. The influences of applied pressure, temperature and pH were investigated by using two different types of RO membranes in that study. A highest of 89% boron separation was obtained at natural pH values of seawater (Güler et al., 2011). Öner et al. (2011) tested four different types of RO membranes in order to compare boron separation performances of membranes. These membranes were AD-SWRO (GE Osmonics), AG-BWRO (GE Osmonics), BW-30-BWRO (FILMTEC) and AK-BWRO (GE Osmonics). When the authors compared performance of these membranes in terms of salt rejection and permeate flux, they found that BWRO membranes gave better result than others. Öztürk et al. (2008) used RO method for separation of boron. They obtained a 69% of boron removal from aqueous solution including 5 mg B/L at adjusted pH 9 by RO. In the literature, Cengeloglu et al. (2008) also studied on boron separation from water by RO. Three types of RO membranes (SWHR, BW-30 (FILMTEC) and AG (GE

Osmonics)) were tested at different operational conditions (pH of the sample, boron concentration in feed and operating pressure). The best rejection efficiency was obtained by seawater RO and least by AG. These studies demonstrated that boron removal from water by RO highly depends on membrane properties. Recently, RO membranes designed specifically for boron removal were developed. Wang et al. (2018) developed polyamide RO membranes enable to remove large amount of boron. Interfacial polymerization (IP) with *m*-phenylenediamine (MPD) and 1,3,5-benzenetricarbonyltrichloride (TMC) were used to produce boron selective membrane. Polyisobutylene (PIB) was also added to the organic phase prior to IP. Boron removal tests were conducted after the characterization of membrane and good separation performance was obtained by using these RO membranes at low PIB concentrations (0.30%, m/v). Vincenzo et al. (2017) studied on thin-film composite membranes (TFC) functionalized by polyol to improve transport properties of membranes and to separate boron. Sequential IP method is used to create functional polyamide layer on polysulfone support. Sample solution including 5 mg/L boric acid was used to test of separation performance of boron. Bilayer membranes demonstrated a 90% boron removal at pH 5.2, when boron was mostly been as neutral boric acid.

1.1.1.3 Sorption-Membrane Filtration Hybrid Process

Hybrid process includes combinations of sorption system and membrane filtration. The illustrations of the hybrid process are shown in Figure 1.1. This system enables to obtain high efficiency of separation (Koltuniewicz et al., 2004). Polymer enhanced ultrafiltration (PEUF) and adsorption membrane filtration (AMF) are typical hybrid methods. Dilek et al. (2002) used continuous PEUF for separation of boron from aqueous solutions. The selective boron separation can be provided by producing target-specific polymers. Smith et al. (1999) produced boron selective polymers (poly(amidoamine) and poly(ethyleneimine) instead of PVA), however they observed one third of polymers loss after the four cycles of separation-regeneration experiment. Main disadvantages of this process are membrane fouling, cost of ultrafiltration and cost of preparation of water soluble polymers (Wolska and Bryjak, 2013). Kabay et al. (2013) utilized hybrid method that includes commercial ion exchange resin and ultrafiltration membranes for boron separation from geothermal water. Authors have determined that boron removal could be enhanced while using high amount of resin.

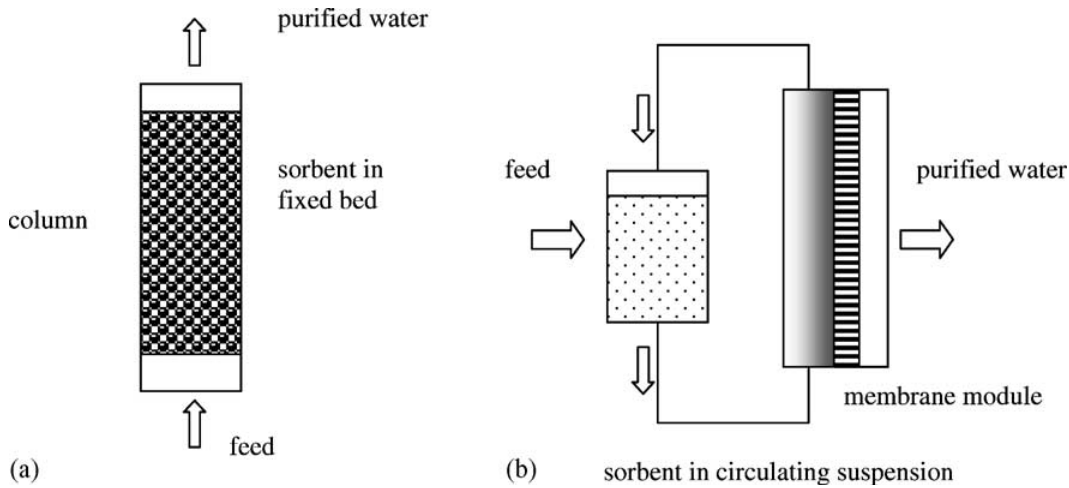


Figure 1.1. Illustrations of the (a) fixed bed system and (b) the integrated system (Koltuniewicz et al., 2004)

The main advantages of this process are that high pressures are not needed and membranes can operate below critical flux conditions (Wang et al., 2014). Wolska and Bryjak (2011) studied on boron separation by sorption membrane filtration. The authors prepared three polymeric microspheres types including different amount of vinylbenzyl chloride, styrene and divinylbenzene. They used N-methyl-D glucamine for modification of synthesized particles. Samatya et al. (2015) utilized sorption-nanofiltration hybrid method to produce irrigation water from geothermal water. Since boron concentration in irrigation water is crucial for plants, they measured boron concentration in water after this process and they found that boron concentration decreased from 11 mg/L to less than 1 mg/L.

1.1.1.4 Electrocoagulation (EC)

This method comprises a cell containing a metal EC, a metal anode cell (aluminum or iron) and direct current is used in it. The ability to achieve separation via simple equipment is the factor that makes this process more favorable. Electrode selection is very crucial for this process (Sayiner et al., 2008). In the literature, iron and aluminum electrodes or zinc electrodes were used for removal of boron in EC process (Vasudevan et al., 2013 and Sayiner et al., 2008). Sayiner et al. (2008) obtained a 70% boron removal by the aluminum electrode after 50 min in case that initial concentration of boron is 100 mg/L and current density was 30 mAcm^{-2} . They found that when boron concentration was high in the feed solution, boron removal was higher. The authors obtained a 95% of boron removal both for iron and aluminum electrodes when initial feed boron

concentration of solution was 1000 mg/L. Dolati et al. (2017) also used EC method to separate boron from aqueous solutions. They obtained a 70% of boron removal at a concentration of 100 mg/L at pH 8 after 60 min reaction time. The authors indicated that when water contains more than 50 mg/L of boron, EC process can be applied for boron removal.

1.1.1.5 Solvent Extraction

Solvent extraction has been used for separation of boron. In the literature, there are many different extractants for separation of boron. Certain alcohols, such as monohydric alcohol, dibasic alcohols and mixed alcohols were used as extractants in solvent extraction processes (Zhang et al. 2016). It was reported that 2-ethylhexanol as an extractant was used for separation of boron from brine. According to the results of that study, when 2-ethylhexanol was used as an extractant for boron separation, a 99.5% boron was extracted with a 99.5% of purity (Zhang et al. 2016).

Ionic liquids which are known as green solvents are also used for boron extraction. It was shown that these solvents can be used for boron extraction even in chloride medium and 60% of boron could be extracted from solution that includes 0.5 M boron by this method under the optimum conditions (Fortuny et al., 2012).

1.1.1.6 Capacitive Deionization (CDI)

Sample solution is fed along electrodes in this method while highly reversible electrostatic ionic adsorption occurs after applying a potential difference between electrodes. Ions are attracted to oppositely charged electrodes. After the adsorption of ions on electrodes, deionized sample solution is obtained (Xu et al., 2008 and Avraham et al., 2011). Avraham et al. (2011) studied on boron removal from water by CDI and they found that boron can be removed by CDI method while it present in boric acid form in water solution. Their preliminary experimental results demonstrated that a 30% of boron from the sample solution was removed. This process was shown in Figure 2.

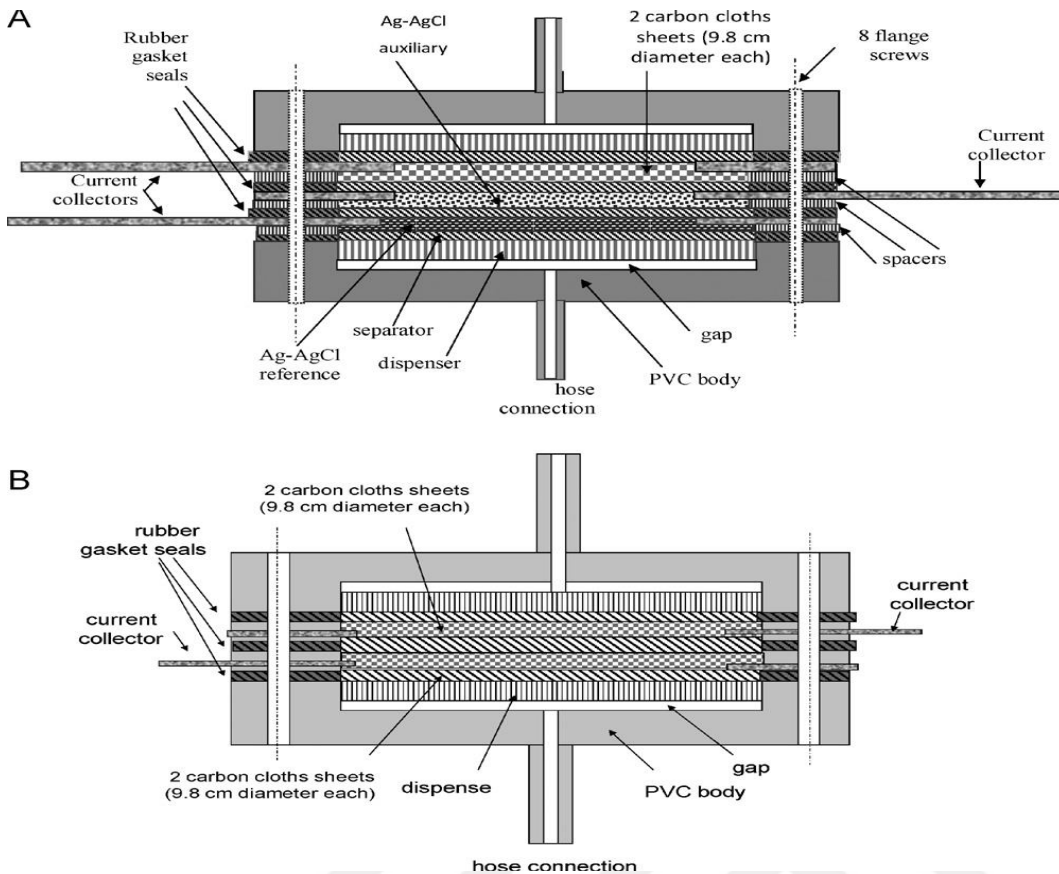


Figure 1.2. Illustrations of two types of cells. (a) CDI cell with three electrodes (b) CDI cell with two electrodes (Avraham et al., 2011)

1.1.1.7 Adsorption

Adsorption is a type of effective method for removal of boron at very low concentrations. There are many adsorbents used for removal of boron. Some of these adsorbents are activated carbon, biological materials, clays, fly ash, layered double hydroxides, mesoporous silica, natural minerals, nanoparticles, oxides (Guan et al., 2016). Karahan et al. (2006) researched on separation of boron and by adsorption with using clays and modified clays. They used bentonite, sepiolite and illite clay samples and the used these clay samples were modified with nonylammonium chloride to increase the adsorption capacity. Kluczka et al. (2007) studied on removal of boron by activated carbon and its impregnated states with zirconium dioxide, silica aerosol and activated alumina. The boron adsorption ability increased with impregnation of activated carbon. Activated carbon with mannitol gave best result for adsorption of boron in that study. Adsorptive capacity of 2.0 mg/g boron was obtained with activated carbon impregnated with mannitol. Köse et al. (2011) studied on separation of boron by using activated carbon. The maximum boron capacity was obtained as 3.5 mg/g at

initial pH of 5.5. Polowczyk et al. (2013) utilized fly ash for adsorption of boron. They obtained a 90% boron separation and the adsorption capacity was found as 6.9 mg/g. Zohdi et al. (2014) utilized carbon nanotube functionalized with tartaric acid as an adsorbent for separation of boron. They found that maximum of 1.97 g/mg adsorption capacity was at pH 6.0. Demey et al. (2014) studied on boron separation from seawater with using chitosan/Fe(OH)₃-based sorbent. It was found that this sorbent is stable for continuous column study.

1.1.2 Separation Methods for Lithium

1.1.2.1 Ion exchange and Adsorption

Lithium can be separated by ion exchange material which was prepared specifically for separation of lithium. Nishihama et al. (2011) studied on lithium recovery from seawater by using integrated ion exchange method. Granulated λ -MnO₂ adsorbent was utilized to concentrate lithium from seawater in first step. After the first step, solution was contacted with cation exchange resin and solvent impregnated resin. In that study, strongly acidic cation exchange resin provides separation of divalent ions while β -diketone/TOPO impregnated resin provides removal of Na⁺ and K⁺. Lastly, (NH₄)₂CO₃ saturated solution was used to obtain recovery of lithium as Li₂CO₃ precipitation. According to the results, a 56% of lithium was recovered as Li₂CO₃ with more than 99.9% of purity. Lemaire et al. (2014) utilized four types of sorbents and the maximum lithium separation was obtained as 20-25 mg Li/g with Amberlite IR 120 resin and molecular sieve 13X. In the literature, it has been also reported that manganese oxide ion sieve (MnO₂·0.5H₂O) can be utilized for separation of lithium. While manganese oxide was used as adsorbent, Li_{1.6} Mn_{1.6} O₄ was used as precursor. The authors found that adsorption capacity of this adsorbent was 10.5 mg/g from seawater (Liu et al., 2015). Park et al. (2015) researched on separation of lithium from seawater. They used manganese oxide and lithium hydroxide to synthesize lithium manganese oxide. After synthesizing lithium manganese oxide, 0.5 M HCl and synthesized lithium manganese oxide were mixed in order to replace lithium manganese oxide with manganese oxide. The results demonstrated that Langmuir isotherm is fitted with experimental data and 11.9 mg/g sorption capacity was obtained in seawater. Recepoğlu (2017) et al. used λ -type manganese dioxides (λ -MnO₂) for lithium separation from geothermal water and authors determined that λ -type manganese dioxides (λ -MnO₂) adsorbent gave good results in terms of lithium separation from geothermal water.

1.1.2.2 Solvent Extraction

The solvent extraction method is often used for separation of lithium. Shi et al. (2016) researched on separation of lithium from brine by solvent extraction using tri n- butyl phosphate as an extractant. The authors investigated influence of several parameters such as acidity of the brineratios of phases. The single extraction of lithium efficiency was obtained as 92.37% at optimum conditions. Zhou et al. (2011) studied on feasibility of lithium extraction from brine. The authors selected coextracting agents (FeCl_3 , ZnCl_2 and CrCl_3 solutions) and they used tributyl phosphate (TBP) in kerosene, in methyl isobutyl ketone (MIBK), and in 2-octanol as extractants. FeCl_3 as a co-extractant gave better results than others. MIBK in TBP yielded highest extraction capacity while TBP/2-octanol gave the lowest.

1.1.2.3 Membrane Processes

Separation of lithium by membrane process is a one of the popular subject in recent years. Park et al. (2016) studied on flow-through membrane adsorber and produced polysulphone (PSF) based mixed matrix nanofiber (MMN) dispersed with lithium ion sieves (LIS) as a lithium adsorber. MNNs were not lead to any problem for membranes because of the fact that their water permeability high even under small trans-membrane pressure values. Their results showed that MNN membrane absorber for continuous Li separation from seawater can be evaluated as an alternative method. Chung et al. (2008) researched on inorganic adsorbent ($\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$) containing polymeric membrane reservoir for recovery of lithium from seawater. Seawater which contains lithium was exposed with membrane reservoir and after that, this membrane reservoir put in the 0.5 M HCl solution. The main advantage of this process, including the use of membranes, was that lithium can be used directly to separate from seawater. Umeno et al. (2002) used spinel type manganese oxide which is a membrane type adsorbent for lithium recovery from seawater. It was found that the adsorption rate was highly influenced by preparation conditions. Maximum lithium adsorption in seawater was obtained as following conditions; initial PVC concentration 8% and 20% PVC additive content.

RO and nanofiltration (NF) processes have been used for separation of lithium from aqueous solutions (Swain, 2017). Sun et al. (2015) studied on removal of magnesium and lithium from brine using NF membrane because of the fact that salt lake brines having high relative concentrations of magnesium to

Lithium in China. The results of this study demonstrated that separation of lithium and magnesium by NF process were highly influenced by pH, Mg^{2+}/Li^+ proportion and operating pressure. The authors found that while lithium penetrating into the membrane and it was concentrated, while magnesium was mostly rejected. Therefore, magnesium/lithium separation was provided by this way. In the literature, NF and low pressure RO membranes (LP-RO) were utilized for separation of lithium from brine (Somrani et al., (2013)). The authors compared NF90 membrane with XLE which is a LP-RO membrane for separation of lithium. It was found that XLE did not gave good results for lithium extraction from diluted brine while comparing NF90 because of its lower permeability to pure water. The results of NF90 membrane demonstrated that a total separation of magnesium and only 15% lithium separation were obtained. Totally a 85% separation of magnesium-lithium was provided at low pressures (<15 bars).

1.2 Electrodialysis (ED)

Electrodialysis (ED) is a method that has been used for over 50 years to produce drinkable water from brine. Several modified ED process have been formulated such as electrodeionization, capacitive deionization, bipolar membrane electrodialysis (BMED) through years. Despite the fact that NF is more widely used today for desalination of salt water, ED and modified ED processes are also used to produce high quality industrial process water (Strathmann, 2010).

1.2.1 Ion Exchange Membranes

Several ion exchange membranes have been developed from laboratory scale to industrial scale in last 50 years because of the fact that it has high potential for commercial impact. These membranes are especially used to concentrate or separate foods and pharmaceutical products (Xu, 2005).

Ion exchange membranes are important components of separation mechanism for electro-membrane process (Vogel and Haack, 2014). Ion exchange membranes are categorized as cation or anion exchange membranes according to type of their ionic groups (Ran et al., 2017). The cation exchange membranes are consisted of negatively charged fixed groups like PO_3^{2-} , SO_3^- , COO^- . Cations in the feed solution pass through the cation exchange membranes by the interaction between anionic groups on the membrane surface and the cations in feed the solution. Most common preparation method of cation exchange membranes is the

attachment of sulfonic acid groups onto the chain polymer backbone by either copolymerization via polycondensation or post-sulfonation. In order to improve cation conductivity, which is the main problem occurring in this method, cation exchange membranes can be synthesized based on block copolymers and by creating cation-conductive channels in membrane structure. Anion exchange membranes contain positively charged groups like NH_3^+ , NR_3^+ , NRH_2^+ and anions in feed solution move through the anion exchange membranes depending on interaction between the cationic groups on the membrane surface and anions in the feed solution (Xu, 2005). Anion exchange membranes are most commonly synthesized by reaction of a polymer including trimethylamine (TMA) and benzyl halide groups due to the simplicity of the method. Moreover, some other tertiary amines are reported to increase the physical durability and stability of membrane. However, improvement of anionic conductivity and tolerance to alkalinity could not be reached effectively until today for anionic exchange membranes (Ran et al., 2017).

Additionally, anion and cation exchange membranes are categorized as strong acid-base or weak acid-base. The categorization of ion exchange membranes as weak acid/strong acid or weak base/strong base depends on the degree of dissociation of the charged groups (Strathmann, 2010). Ion exchange membranes are also classified as homogenous and heterogeneous membrane which depends on connection type of their charged groups to matrix or chemical structure where in homogenous membranes, charged groups are chemically bonded to matrix while in heterogeneous ones; they are physical mixed with it. However, most of the preferred ion exchange membranes for use in the studies are homogeneous and generally contain the fluoro carbon or hydrocarbon polymer film ion groups (Xu, 2005).

Bipolar membranes are special types of ion exchange membranes that include a cation and an anion exchange membranes and a hydrophilic layer between anion and cation exchange membranes. Bipolar membranes give H^+ and OH^- ions by the dissociation of water during the process. Under the electrical potential water dissociation is occurred in the transition region (Huang and Xu 2006). A representation of bipolar membrane was illustrated in Figure 1.3 (Bunani et al., 2017).

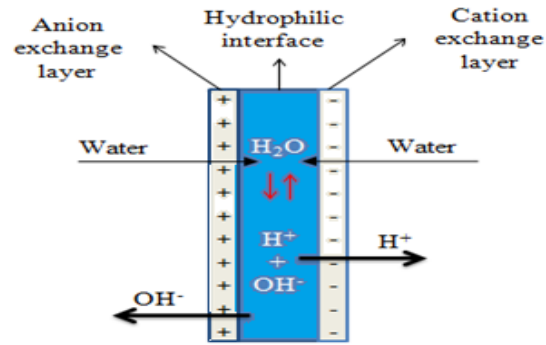


Figure 1.3. Bipolar Membrane (Bunani et al., 2017)

A favorable ion exchange membrane should be chemically stable and have a high perm-selectivity, good mechanical strength, low electrical resistance (Vogel and Haack, 2014).

1.2.2 Theory and Applications of ED method

Electrodialysis (ED) is an electro-membrane process that provides transferring of ions from one solution to another solution under the applied electrical potential. Main driving force is electrical potential difference between cathode and anodes. By this way, two main streams as concentrate and permeate are obtained. Concentrate part includes high amount of ions, while dilute part contains less amounts of ions. Therefore, electrical conductivity of concentrate part is higher than dilute part. The principal of conventional ED system was given as Figure 1.4 (Strathmann, 2010).

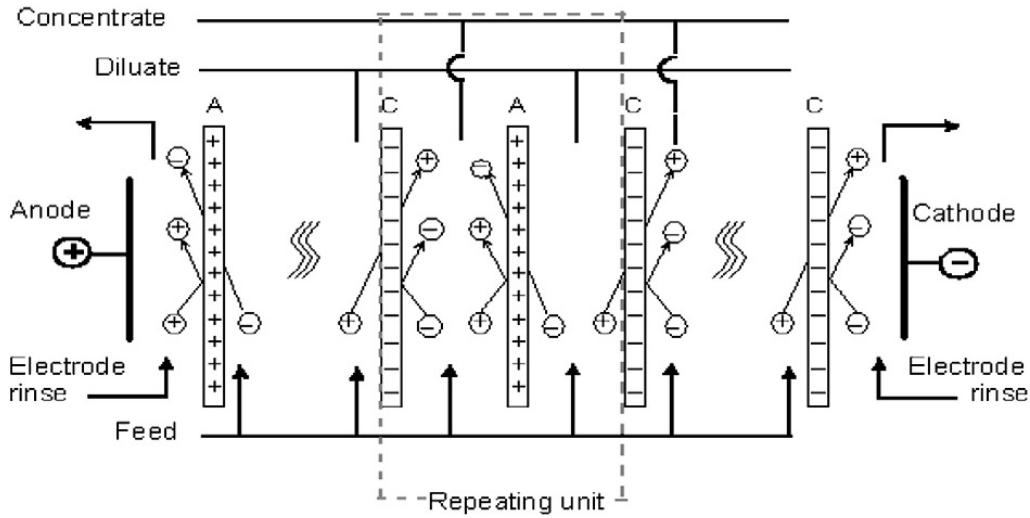


Figure 1.4 Conventional Electrodialysis (Strathmann, 2010)

Conventional ED process contains two membrane types, a cation exchanger membrane and an anion exchanger membrane, and spacers between membranes. Here, the spacers are not used only to isolate membranes; they are also used to mix the solution properly in the cell (Strathmann, 2010). In ideal situation, anions move through the anion exchange membranes while cations are moving through the cation exchange membranes (Kwak et al., 2013).

In the literature, Nernst-Planck equation generally was used to explain transport of ions through membranes. This equation includes migration and diffusion terms (Sistat and Pourcelly, 1999, Mier et al., 2008, Tado et al., 2016).

$$J_i = -D_i \frac{dc_i}{dy} - D_i \frac{z_i F C_i}{RT} \frac{dV}{dy} + C_i v \quad (1)$$

where; C_i is the concentration of species (mol/m^3), y is the coordinate (m), D_i is the diffusivity of the species (m^2/s), z_i charge number of the ion i , R gas constant (J/mol K), T is the temperature (K), V is the electrical potential, F is the Faraday constant (A s eq^{-1}), v is the species velocity (m/s) and J_i is the molar flux of species or ions ($\text{mol/m}^2\text{s}$).

ED is generally used to produce process and drinking water from brackish water, minimize industrial effluents, to produce salt and recover valuable materials. Factors that may affect the process are membrane properties, electrical potential, feed flow rate, pH of the feed solution and current density (Xu et al., 2018).

Zhang et al. (2011) researched about wastewater reclamation from RO concentrates by using ED method. They carried out experiments with pilot ED system for evaluation of RO concentrate in order to increase water recovery. Decarbonation process was applied in order to prevent scaling. After this decarbonation, ED process was utilized and 95% water recovery from RO concentrate acquired from integrated RO-ED system. They proposed that ED could be utilized for evaluation of RO concentrates.

1.2.3 Cost of Electrodialysis (ED)

Cost of ED includes the system capital expenditure and operating fee. Capital expenditure for ED processes contains cost of ED units, pipelines, valves, electrical equipment, pumps, tanks and process control devices (Melnikov et al., 2016). Operating costs highly depend on electrical consumption of ED processes. Specific power consumption (SPC) is an important parameter in the operating fee. This value calculated by multiplication of electrical potential by integrated current divided to volume of feed solution. It includes only electrical consumption; it does not include pumping cost. Therefore, pumping cost should be calculated separately (Demircioğlu et al., 2001). As it has seen economical perspective, the overall cost of ED process highly depends on country, volume and composition of the feed solution, properties of membranes used for ED (Melnikov et al., 2016). Moreover, there are some studies about optimizing cost of ED system in the literature (McGovern et al., 2014, Shah et al., 2018, McGovern et al., 2014). McGovern et al. (2013) conducted a cost analysis on desalination of feed solutions with high salinity by ED method and the authors found that optimization of electrical potential can reduce the cost of ED between 60% and 30%. Shah et al. (2018) studied the optimization of the cost of ED in the domestic desalination of brackish water by ED. The authors established that pumping cost was 46% of the total capital cost in their study. McGovern et al. (2014) researched on cost analysis of ED process for feed solutions having different salinity. It has been determined that partial desalination by ED method is the most effective method to optimize cost while working with brackish water. Especially, if produced water is not needed to have high purity, ED processes could be economical way.

1.3 Bipolar Membrane Electrodialysis (BMED)

Bipolar membrane electro dialysis process (BMED) is a combination of conventional ED and bipolar membranes. When electrical potential is applied, dissociation of the water molecules in the interphase of the bipolar membranes takes place. After that, H^+ ions that come from the bipolar membrane combines with the anions which pass across the anion exchange membranes while OH^- ions that comes from the bipolar membrane combines with the cations which pass across the cation exchange membranes. Acid production occurs as a result of the combination of H^+ ions with anions that is in the feed solution, base production also occurs as a result of combination of OH^- ions with cations that is in the feed solution in the similar way (Badruzzaman et al., 2009). The flow scheme of BMED processes was shown in Figure 1.5.

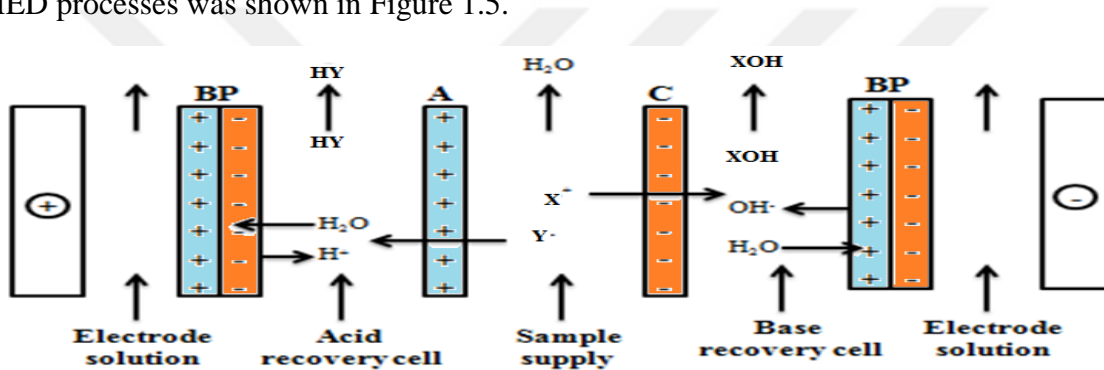


Figure 1.5. Bipolar membrane electro dialysis process (Bunani et al., 2017)

In the literature, BMED processes was defined as attractive method due to its ability to provide acid and base production from the salt solution without adding extra chemical reagents (Li et al. 2016). BMED processes has been utilized for producing organic acid (i.e salicylic acid, lactic acid, ascorbic acid,) in the food industry, producing acid and base from RO concentrate, alkalization and acidification in chemical industries (Badruzzaman et al., 2009).

There are many studies using BMED method in the literature. BMED method is generally used for acid and base production from RO concentrate, production of organic acids, desalination of brackish water and producing acid and base from brackish water. Ibanez et al. (2013) selected BMED method for evaluation of RO concentrate as acid (HCl) and base products (NaOH). The authors reported that BMED can be considered for evaluation of RO concentrate. Results demonstrated that production of 0.1 M or higher concentrated acid and base with current

efficiencies between 60% and 90% was possible by using BMED method. Badruzzaman et al. (2009) also utilized BMED method for reuse of (RO) concentrate. As a result of these studies, it was reported that RO concentrate should be softened as a pretreatment step for BMED processes. BMED method was also used to obtain NH_3 and HCl from synthetic ammonium chloride solution. It was reported that when concentration of ammonium chloride solution was above 8000 mg/L, BMED method for producing NH_3 and hydrochloric acid is an economically feasible (Li et al., 2016). There are also some studies about integration of other membrane methods such as NF or microfiltration (MF) as a pretreatment step with BMED. It was reported that NF 270 membrane was used for removal of Ca^{2+} and Mg^{2+} ions and after nanofiltration, precipitation with Na_2CO_3 and NaOH was used before the BMED processes. After the pretreatment processes, seawater desalination brine was fed through the BMED process, and thus HCl and NaOH were produced (Reig et al., 2016). Since BMED process is an environmentally-friendly method, production of acid and base without using harmful chemicals by BMED is an also intensive research subject. BMED method is used for production of salicylic acid in order to avoid using sulphuric acid. Because, salicylic acid is generally produced by using sodium salicylate by adding sulphuric acid that is a harmful chemical. The authors investigated that possible stack configuration and co-solvent to obtain a soluble sodium salicylate solution. The results show that the use of 1-propanol as a co-solvent and the use of a bipolar membrane with two cation exchange membranes as a stack configuration of BMED are the best options for its production (Rottiers et al., 2017). It has been suggested in the literature that citric acid fermented liquid can be recovered by BMED method. The highest recovery percentage as 97.1% of acid recovery was achieved in that study. The results also demonstrated that increasing of current density lead to increase in recovery rate (Sun et al., 2017).

1.4 Separation of Boron and Lithium by BMED

In the literature, Bunani et al. (2017) studied on removal and recovery of lithium and boron from aqueous solutions by BMED method as in this study. The authors found that some parameters as sample solution volume, pH of the sample solution and electrical potential affect recovery of lithium and boron from aqueous solutions in BMED process.

Sample solution containing boron and lithium is fed between anion and cation exchange membranes in BMED processes. While Li^+ ions are moving across the cation exchange membrane, anions B(OH)_4^- ions move across the anion exchange membrane. B(OH)_4^- ions that pass through the anion exchange membranes combines with the H^+ ions that comes from bipolar membrane. Li^+ ions that move across the cation exchange membrane combine with the OH^- ions that come from bipolar membrane by the similar way. As a result, H_3BO_3 and LiOH are produced by this way (Figure 1.6).

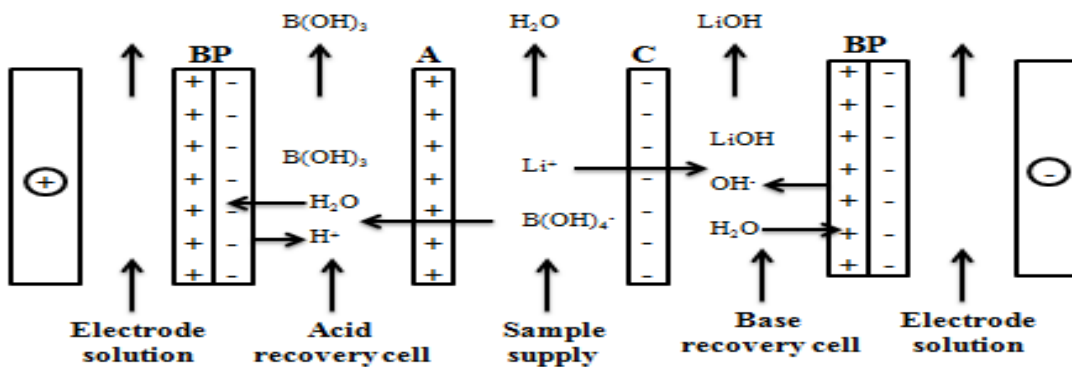


Figure 1.6. Illustration for removal and recovery of boron and lithium (Bunani et al., 2017)

1.5 Aim of this study

Scope of this study is to investigate impacts of some process parameters on removal and recovery of lithium and boron from aqueous solutions by BMED method. Following parameters were investigated using ASTOM ACILYZER and MEGA Model BMED systems:

- Acid and base types and acid and base concentrations of solutions in acid/base chambers,
- Electrical potential,
- pH of the sample solutions
- Types of BMED systems (using Mega, PC-Cell and Astom Acilyzer Model BMED systems)

2.0 EXPERIMENTAL

2.1 Experiments with ASTOM ACILYZER model BMED System

ASTOM ACILYZER EX3B model lab-scale BMED system was used for experiments in first step (Figure 2.1). Model solutions that used for BMED experiments were prepared by using $\text{Li}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$. Lithium and boron concentrations in the feed solution were kept constant as 340 mg/L and 1000 mg/L, respectively. The characteristics of membranes employed in ASTOM ACILYZER BMED system are given in Table 2.1.



Figure 2.1. Astom Acilyzer EX3B model BMED system

Table 2.1 Characteristics of membranes in Astom Acilyzer model BMED system

MEMBRANE	CMB	AHA
Type	Strong acid	Strong base
Characteristics	Alkali resistance High mechanical strength	Alkali resistance High mechanical strength
Thickness (mm)	0.21	0.22
Electrical Resistance (ohm-cm ² , 25 °C)	4.5	4.1
Mullen Burst Strength (MPa)	≥0.40	≥0.90
Temperature Stability (°C, maximum)	≤60	≤60
NEOSEPTA BP-1E		
Water splitting voltage (V) ^a	1.2 ^b	
Water splitting efficiency (%) ^a	≥98	
Burst strength (MPa)	≥0.40	
Thickness(mm) ^a	0.22	

^a 1N NaOH and 1N HCl 10A/dm² 30°C

^b Measured between Ag-AgCl electrodes

Experimental parameters and experimental conditions were summarized below.

2.1.1 Influence of Acid and Base Concentrations in Acid and Base Chambers

Influence of concentrations of acid and base solutions used in acid and base chambers on removal and recovery of lithium were investigated. Sample solution containing 340 mg Li/L and 1000 mg B/L was used. HCl and NaOH solutions were used in acid and base chambers respectively to determine optimum initial acid-base concentrations. For this purpose, 0.1 M HCl-0.1 M NaOH, 0.05 M HCl-0.05 M NaOH and 0.005 M HCl-0.005 M NaOH acid-base pairs were used. These concentrations were tested under 30 V of electrical potential.

2.1.2 Influence of Acid and Base Types in Acid and Base Chambers

Sample solution containing 340 mg Li/L and 1000 mg B/L was used. Acid and base types in acid and base chambers were changed after optimum initial acid-base concentrations were determined. For this HCl, NaOH, H₃BO₃ and LiOH solutions were used in acid and base chambers. 0.1 M HCl-0.1 M NaOH, 0.1 M H₃BO₃-0.1 M LiOH acid base pairs and 0.05 M HCl-0.05 M NaOH and 0.05 M H₃BO₃-0.05 M LiOH acid-base pairs were used. These solutions were tested under 30 V of electrical potential.

2.1.3 Influence of Electrical Potential Applied

Sample solution containing 340 mg Li/L and 1000 mg B/L was used. 0.05 M HCl-0.05 M NaOH solutions were used in acid and base chambers for these tests. Experiments were carried out by using three different electrical potentials (15, 20, 30 V)

2.2 Experiments with MEGA model BMED System

In this step, MEGA EDR_Z-FULL V4 model lab-scale BMED system was used for experiments. Model solutions that used for BMED experiments were prepared by using Li₂B₄O₇·5H₂O. Lithium and Boron concentrations in the solution were kept constant as 340 mg/L and 1000 mg/L, respectively. The characteristics of MEGA BMED system membranes were given in Table 2. MEGA BMED system was shown in Figure 2.2.

Table 2.2. Characteristics of membranes in MEGA model BMED system

Ion Exchange Membrane	Cation exchange	Anion exchange
Ion Exchange Group	$R-SO_3^-$	$R-(CH_3)_3N^+$
Matrix	Polyethylene	Polyethylene
Ion Exchange Capacity (meq/g)	2.2	1.8
Thickness (mm)		
Dry	<0.45	<0.45
Swelled	<0.70	<0.75
Electrical Resistance (ohm-cm ²)	<8	<7.5
Changes During Swelling (%)		
Thickness	<3	<3
Length	<4	<4
Width	<65	<65
Weight	<60	<65

**Figure 2.2.** MEGA model BMED system

The membrane modules of MEGA model BMED system and flow scheme of this system are given in Figures 2.3 and 2.4.

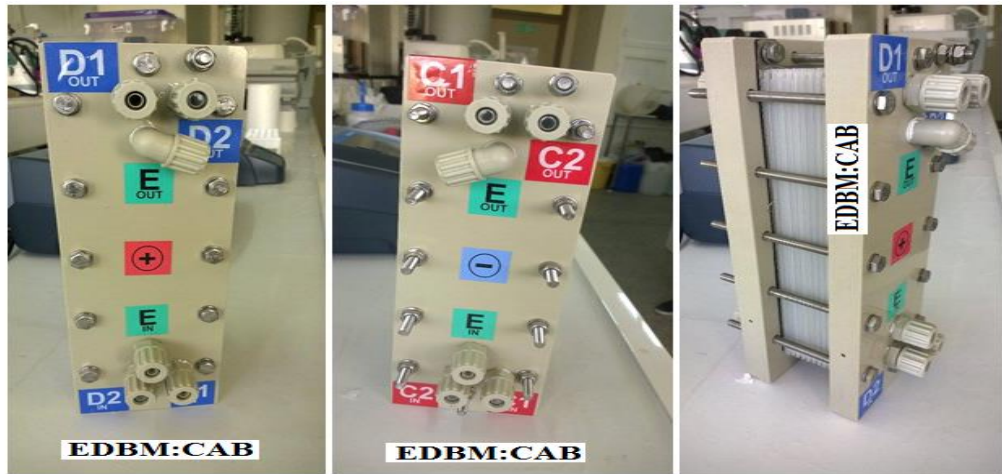


Figure 2.3. Membrane module of MEGA model BMED system

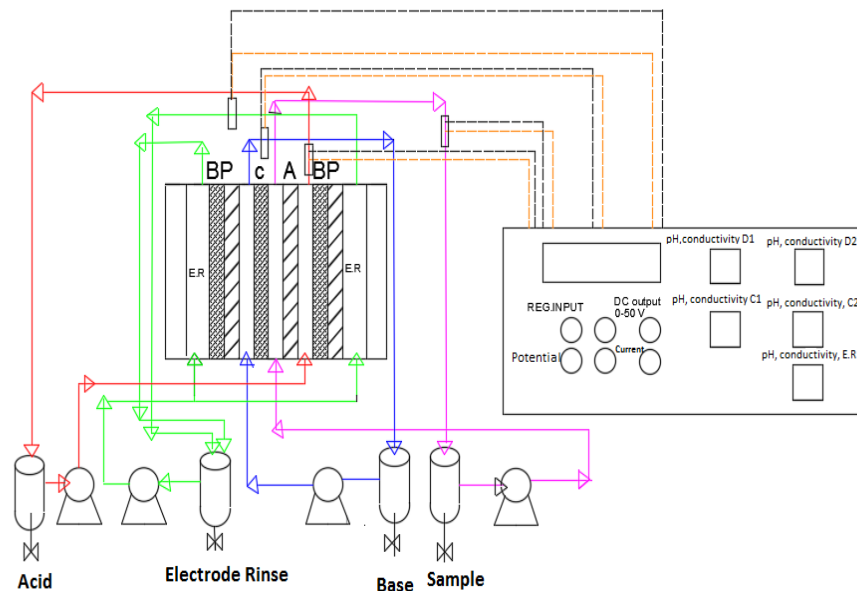


Figure 2.4. A flow sheet of MEGA model BMED system

2.2.1 Influence of Concentrations of Acid and Base Solutions Used in Acid and Base Chambers

Influence of acid and base solutions that used in acid and base chambers on separation and recovery of lithium and boron were examined by using MEGA model BMED system. HCl and NaOH solutions were used in acid and base chambers respectively. Sample solution containing 340 mg Li /L and 1000 mg B/L was used and 20 V electrical potential was applied. 0.05 M HCl-0.05 M

NaOH, 0.005 M HCl-0.005 M NaOH and 0.003 M HCl-0.003 M NaOH acid-base pairs were used.

2.2.2 Influence of Applied Electrical Potential

Sample solution containing 340 mg Li/L and 1000 mg B/L was used. Optimum concentrations of acid and base solutions (0.003 M HCl-0.003 M NaOH) were used in acid and base chambers for these tests. Experiments were carried out by using four different electrical potentials (15, 20, 25, 30 V) in order to determine optimum electrical potential.

2.2.3 Influence of Acid and Base Types Used in Acid and Base Chambers

Sample solution containing 340 mg Li/L and 1000 mg B/L was used. Types of acid and base solutions in acid and base chambers were changed. HCl, NaOH, H_3BO_3 and LiOH were used in acid and base chambers, respectively. In this step, 25 V of electrical potential was applied and flow rate of feed solution was adjusted as 50 L/h. 0.003 M HCl-0.003 M NaOH, 0.05 M H_3BO_3 -0.003 M LiOH, 0.003 M H_3BO_3 -0.003 M LiOH and 0.05 M H_3BO_3 -0.05 M LiOH solutions were used in acid and base chamber for these tests.

2.2.4 Influence of pH of the sample solution

After determining optimum initial acid and base concentrations (0.003 M HCl-0.003M NaOH) and optimum applied electrical potential (25 V), tests were carried out by adjusting pH of the sample solution. LiOH.H₂O was used in order to adjust pH of the sample solution. The pH of the sample solutions that used in this step are 9.11, 10.00, and 11.00. Flowrate of the feed was adjusted as 50 L/h.

2.2.5 Influence of Feed Flow Rate

Sample solution containing 340 mg Li/L and 1000 mg B/L was used. pH of the sample solution was 9.11. Two different feed flow rates were tested in the MEGA model BMED system. Flow rates applied were 30 L/h and 50 L/h. In this step, 0.003 M HCl-0.003 M NaOH solutions were used in acid and base chambers. A 15 V of electrical potential was applied.

2.3 Comparative Tests with ASTOM ACILYZER, MEGA and PC-Cell model BMED Systems

In these tests, some of the studies made with MEGA and ASTOM ACILYZER model BMED systems were also made with PC-Cell model BMED system and the results obtained with these three systems were compared. Because different ion-exchange membranes exist in these three systems, this study also allowed us to obtain the influence of the membrane type. The characteristics of the membranes in the PC-Cell model BMED system were given in Table 3.

Table 2-3. The characteristics of membranes in PC-Cell BMED system

Membrane	CMK	AMK
Ionic form as shipped	Sodium	Chloride
Type	Strongly acidic sulfonic acid	Strongly alkaline ammonium
Thickness (μm)	160-200	180-220
Resistance ($\text{ohm}\cdot\text{cm}^2$)	~2.5	~1.8
Burst Strength (kgcm^{-2})	4-5	4-5
Maximum Operating Temperature ($^{\circ}\text{C}$, maximum)	50	60
Water content (wt %)	~9	~14
Reinforcement	Polyester	Polyester

When compared the results obtained with these three systems, the experimental conditions and all initial parameters were kept constant. The sample was a solution of lithium concentration of 340 mg/L and boron concentration of 1000 mg/L. The acid and base solutions of 0.05 M HCl and 0.05 M NaOH were used in acid-base chambers. The experiments were carried out at 20 V of electrical potential. pH of the sample solution was 9.11.

2.3.1 Experiments with PC-Cell and MEGA Model BMED Systems (Test I)

Experiments were carried out by using MEGA model BMED system and PC-Cell model BMED system. Sample solution having boron of 1000 mg/L and lithium of 340 mg/L. 0.003 M HCl and 0.003 M NaOH in acid and base chambers

were used. Experiments were carried out under the 20 V applied electrical potential.

2.3.2 Experiments with PC-Cell and MEGA Model BMED Systems (Test II)

Second comparison study was carried out by using PC-Cell and Mega model BMED systems using the following experimental conditions. Sample solution containing 340 mg Li/L and 1000 mg B/L was used. 0.003 M HCl and 0.003 M NaOH solutions were used in acid and base chambers and 15 V of electrical potential was applied. Flowrate of the feed was adjusted as 50 L/h

2.4 Equipments

2.4.1 pH-meter

pH values of the sample solution were measured by digital pH meters (Hach Lange HQ40d multi meter and WTW pH 3110). The photos of devices were shown in Figure 2.5.



Figure 2.5. WTW pH 3110 pH-meter and Hach Lange HQ40d pH-meter

2.4.2 ICP-AES

Boron and lithium were analyzed by the help of ICP-AES (Shimadzu ICPE-9000 Model with auto sampler ASC-6100) in Japan for the experiments run with ASTOM ACILYZER model BMED system. ICP-AES device was shown in Figure 2.6.



Figure 2.6. ICP-AES (Shimadzu ICPE-9000 Model with auto sampler ASC-6100)

2.4.3 Atomic Absorption Spectrometer (AAS)

Lithium was analyzed by Shimadzu AA7000 model AAS in Turkey for the experiments carried out with MEGA model BMED system and PC-Cell BMED system. This device was shown in Figure 2.7.



Figure 2.7. Atomic Absorption Spectrometer (Shimadzu AA7000 model AAS)

2.4.4 Uv/vis Spectrophotometer

Boron was analyzed by Azomethine-H method by Jasco V-530 model UV/Vis spectrophotometer in our laboratory for the experiments carried out with

MEGA model BMED system and PC-Cell model BMED system. This device was shown in Figure 2.8.



Figure 2.8. UV/vis spectrophotometer (Jasco V-530 model)

2.5 Calculations

Performance parameters of BMED such as removal efficiency (R , %), percentage recoveries of lithium and boron in acid and base chambers (β , %) and specific power consumption (SPC, kWh/m³) were calculated by equations given below (Bunani et al., 2017).

$$R(\%) = \frac{100 * (C_i - C_f)}{C_i} \quad (2)$$

$$\beta = \frac{C_{rt}}{C_i} * 100 \quad (3)$$

$$SPC = \frac{E * \int_0^t I dt}{V} \quad (4)$$

where

C_i is concentration of species at beginning of the process in sample chamber (lithium and boron) (mg/L)

C_f is concentration of species in sample chamber at the end of 2 h of experimental time (mg/L)

C_{rt} is the concentration of species in acid and base chambers after 2 h of experimental time (mg/L)

n is the proportion of sample solution volume at the beginning to acid /base solutions volume at the beginning in acid and base chambers

E is the electrical potential (V)

I is the electrical current (A)

V is the volume of the sample solution (m^3)

The kinetic study related to the experiments was carried out by Fick's first law of diffusion (Bunani et al., 2017):

$$J = kC \quad (5)$$

$$J = (V/A) * dC/dt \quad (6)$$

$$\ln(C/C_0) = -k (A/V)t \quad (7)$$

where;

J : Mass flux ($mol/(m^2s)$)

C_0 : Concentration of boron or lithium at beginning of the process (mg/L)

C : Concentration of boron or lithium at the end of 2 h of experimental time (mg/L)

V : Volume of sample chamber (m^3)

A : Effective membrane area (m^2)

k : Mass transfer coefficient of boron or lithium (m/s)

3.0 RESULTS AND DISCUSSION

3.1 Lithium and Boron Separations and Recoveries from Aqueous Solutions by ASTOM ACILYZER Model BMED System

3.1.1 Influence of Concentrations of Acid and Base Solutions in Acid and Base Chambers

Acid and base concentrations in acid and base chambers are two important parameters for separation and recovery of boron and lithium by BMED process. Three different acid and base concentrations were used under 30 V electrical potential. When relatively high initial acid-base concentrations were used in acid and base chambers, boron and lithium removals from sample chamber were fast. In all experiments, boron removal was over 70% and lithium removal was over 80%. According to results obtained, it was understood that lithium removal in all tested initial acid and base concentrations was easier than boron removal (Figures 3.1 and 3.2).

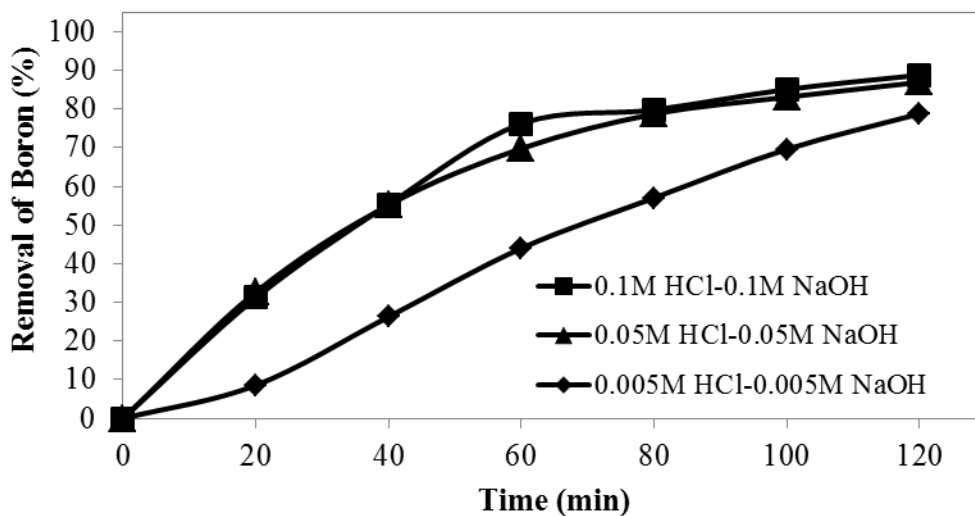


Figure 3.1. Removal of boron with different acid and base concentrations by ASTOM ACILYZER model BMED system

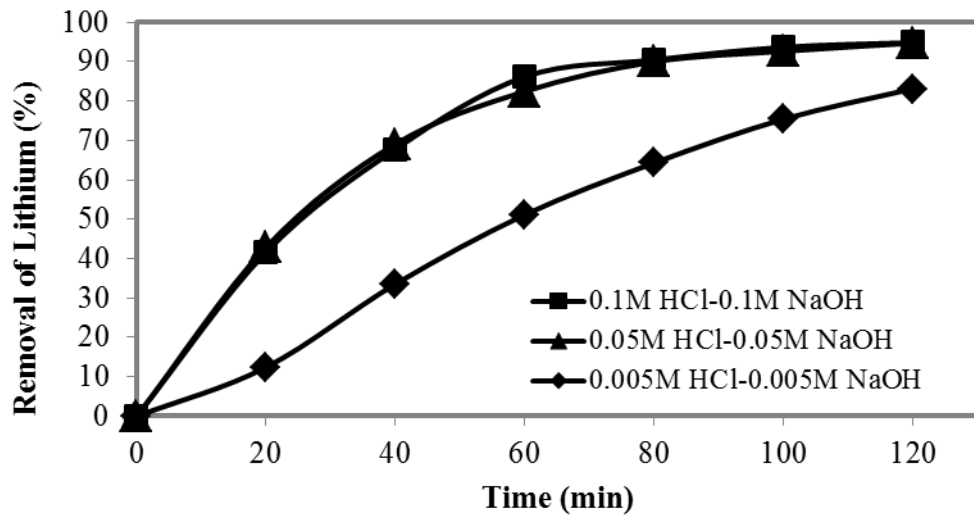


Figure 3.2. Removal of lithium with different acid and base concentrations by ASTOM ACILYZER model BMED system

As it can be seen from Figures 3.3 and 3.4, using of low concentrations of initial acid-base solutions in acid and base chambers resulted in decreasing of boron and lithium recoveries as well as boron and lithium removals from sample chamber. This situation originates from that using low initial acid-base concentrations in acid and base chambers lead to increasing resistance of solutions in these chambers. As a result of this, removals and recoveries of boron and lithium were lower for low acid-base concentrations in acid-base chambers. Using high initial acid-base concentrations lead to increase in removal rates of lithium and boron, however, recoveries of boron and lithium were much lower in base and acid chambers, respectively at this condition. This problem was solved by using moderately high initial acid-base concentrations in acid and base chambers. According to the obtained results, optimum initial acid-base concentrations were determined as 0.05 M HCl and 0.05 M NaOH in acid and base chambers. In this case, 50% of boron and 62% of lithium recovery were obtained in acid and base chambers, respectively.

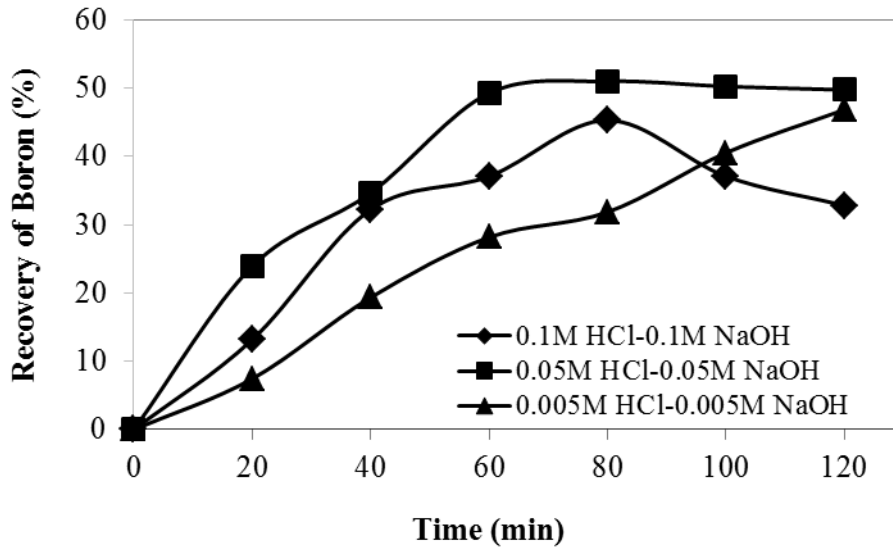


Figure 3.3. Recovery of boron with different acid and base concentrations by ASTOM ACILYZER model BMED system

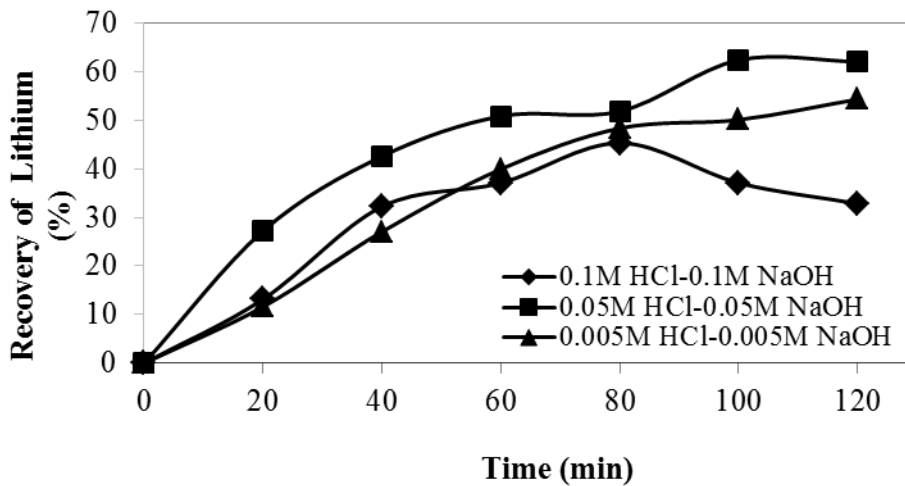


Figure 3.4. Recovery of lithium with different acid and base concentrations by ASTOM ACILYZER model BMED system

Figure 3.5 shows the relationship between $\ln(C_B/C_{B0})$ vs time. As it can be understood from Figure 3.5, there is a good linear relationship between $\ln(C_B/C_{B0})$ and time. Also, there is good linear relationship between $\ln(C_{Li}/C_{Li0})$ (Figure 3.6).

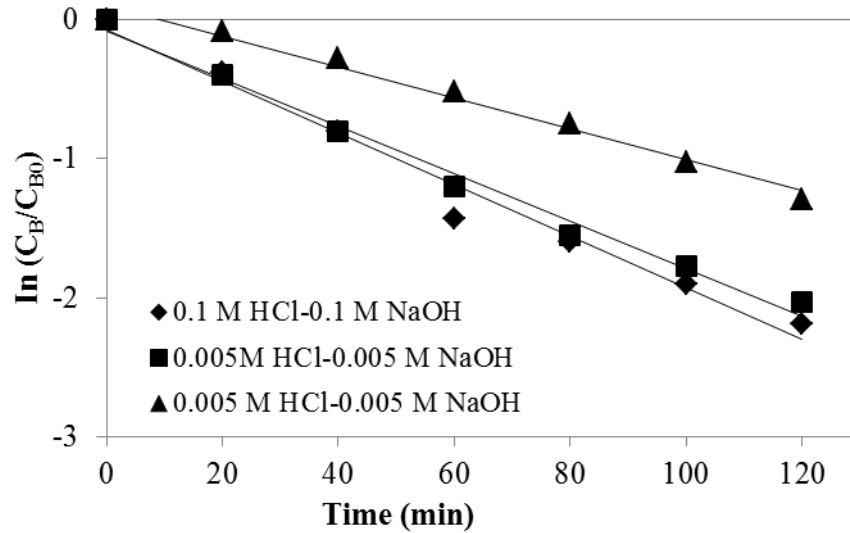


Figure 3.5. Linearization of boron separation data for ASTOM ACILYZER model BMED system

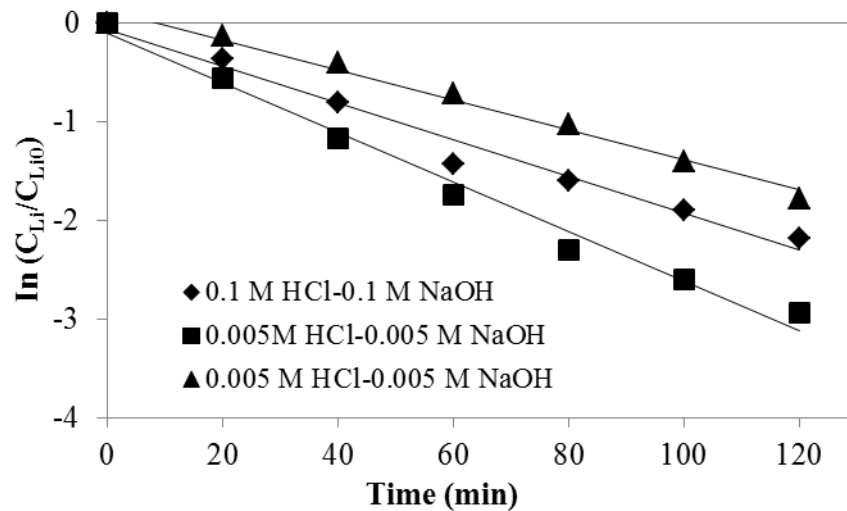


Figure 3.6. Linearization of lithium separation data for ASTOM ACILYZER model BMED system

In case of the use of high initial acid-base concentrations in acid and base chambers, mass transfer coefficients of boron and lithium were higher. The use of high initial acid-base concentrations in acid and base chambers accelerates removals of boron and lithium from sample chamber, therefore mass transfer coefficients would be high. However, recovery of boron and lithium ions in acid and base chambers decreased by the increase in acid-base concentrations (Figure 3.7).

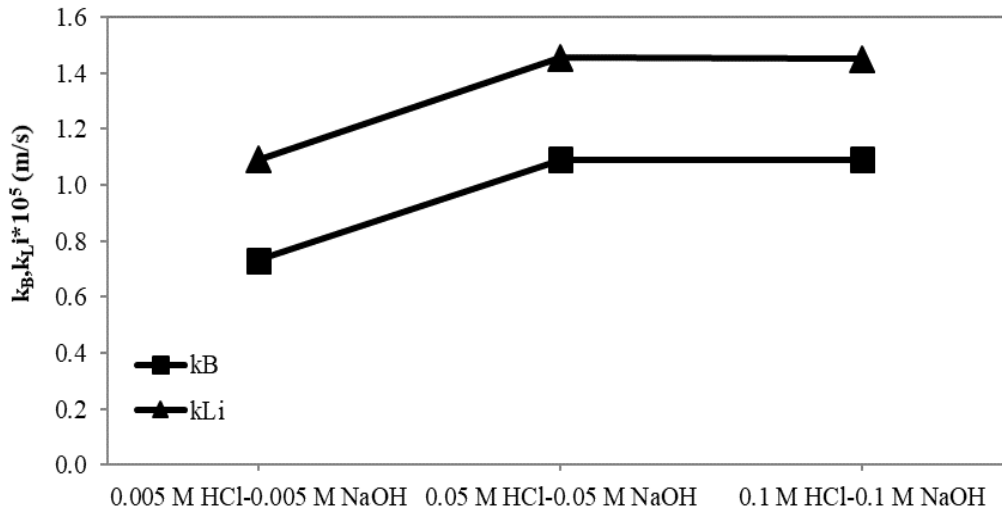


Figure 3.7. Mass transfer coefficients of boron and lithium with different acid base concentrations by ASTOM ACILYZER model BMED system

3.1.2 Influence of Applied Electrical Potential

In this part, 0.05 M HCl and 0.05 M NaOH solutions were used in acid and base chambers. Experiments were carried out at three different electrical potentials (15, 20 and 30 V) to investigate the influence of electrical potential on separation and recovery of boron and lithium by BMED.

As it can be seen in Figures 3.8 and 3.9 clearly, when electrical potential applied was increased, boron and lithium removals increased remarkably. This result is not unexpected, since BMED processes is an electrical driven process. The highest removal of boron and lithium obtained at 30 V were 87% and 95%, respectively. As it was expected, ions that are in the sample solution were transferred from the sample solution to acid and base chambers during the experiment and removals of ions from sample solution decreased after a while because of decreasing of ions in the sample chamber.

According to the obtained results, it can be said that transferred amounts of boron and lithium ions from sample chamber increased with increasing applied electrical potential. As a result of this, the amount of boron and lithium in acid and base chambers increased (Figures 3.10, 3.11). Since electrical potential is the driving force for electro-membrane process, that is an expected result as it was mentioned in literature (Bunani et al., 2017, Demircioğlu et al., 2001).

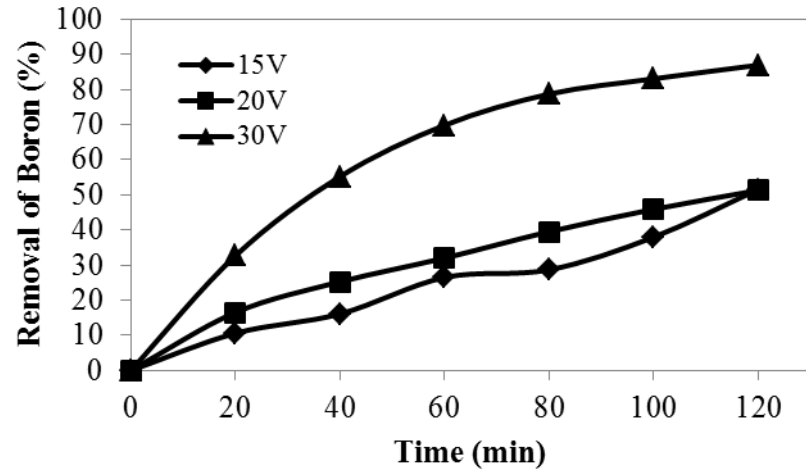


Figure 3.8. Removal of boron at different applied electrical potentials by ASTOM ACILYZER model BMED system

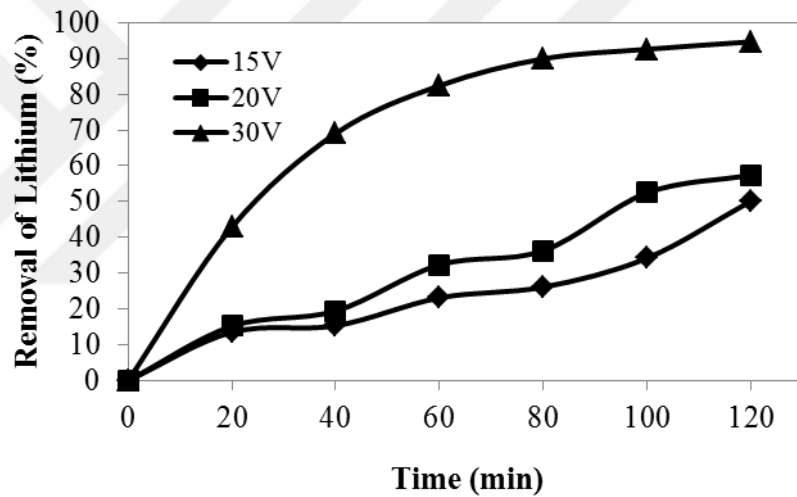


Figure 3.9. Removal of lithium at different applied electrical potentials by ASTOM ACILYZER model BMED system

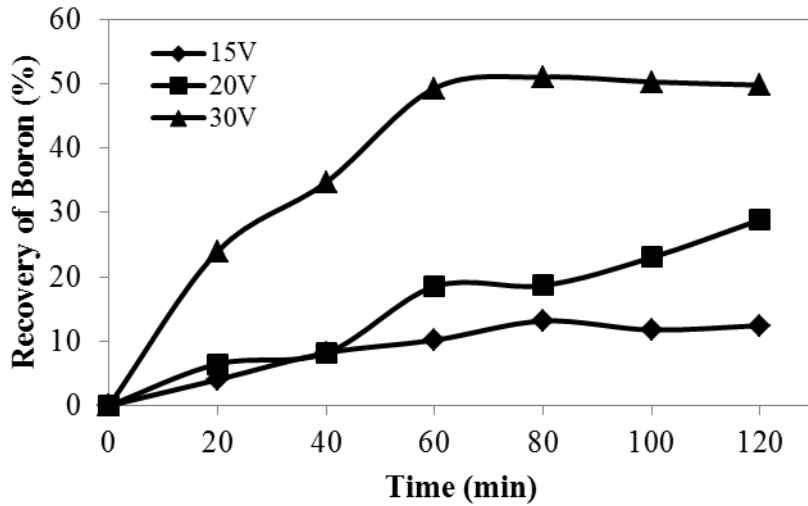


Figure 3.10. Recovery of boron at different applied electrical potentials by ASTOM ACILYZER model BMED system

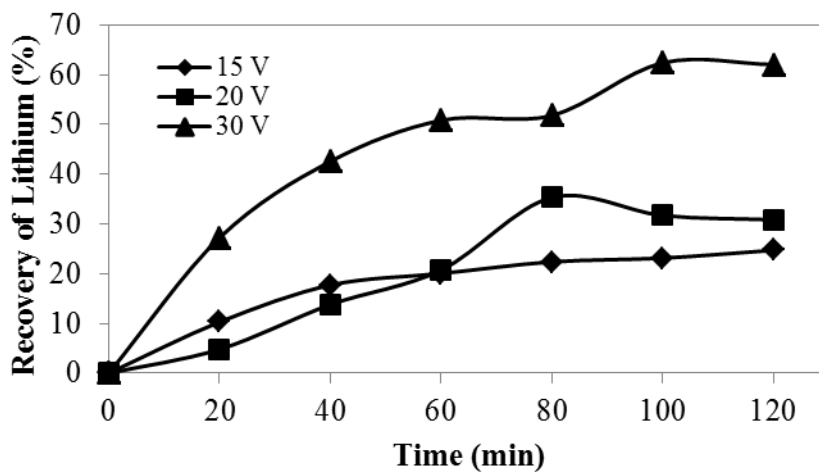


Figure 3.11. Recovery of lithium at different applied electrical potentials by ASTOM ACILYZER model BMED system

In (C_B/C_{B0}) and $\ln(C_{Li}/C_{Li0})$ vs time graphs were illustrated Figures 3.12 and 3.13. It was observed that there is a good linear relationship between the ratio of initial concentrations to final concentrations and time.

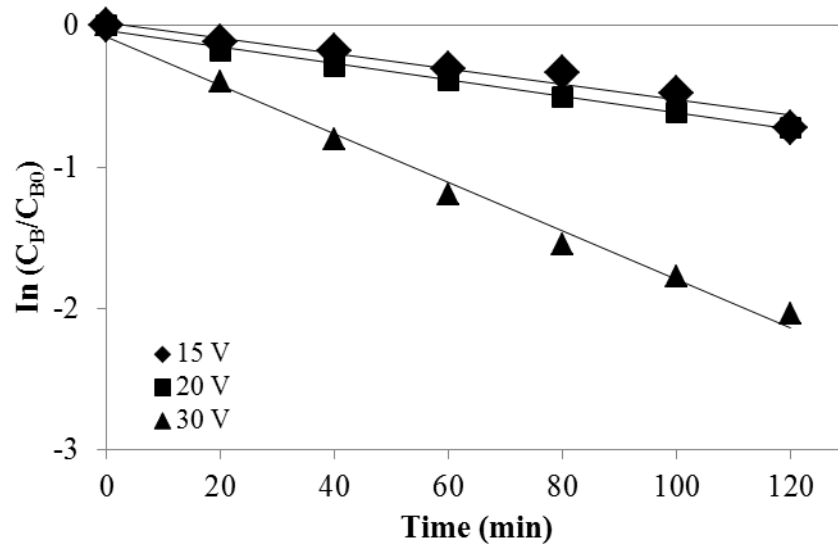


Figure 3.12. Linearization of boron concentration ratios at different applied electrical potentials

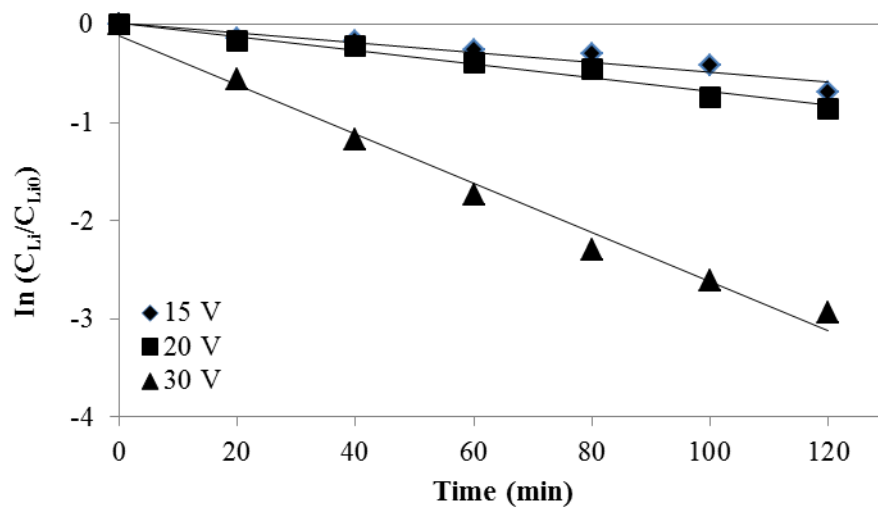


Figure 3.13. Linearization of lithium concentration ratios at different applied electrical potentials

Mass transfer coefficients with respect to electrical potentials were shown in Figure 3.14. Mass transfer coefficients of boron and lithium were increased with increased applied electrical potential. Since electrical potential is a driving force for electro-membrane processes, boron and lithium mass transfer coefficients increased with increasing applied electrical potential as expected. In the literature, Bunani et al. (2017) observed the same phenomenon while they were using ASTOM ACILYZER BMED system.

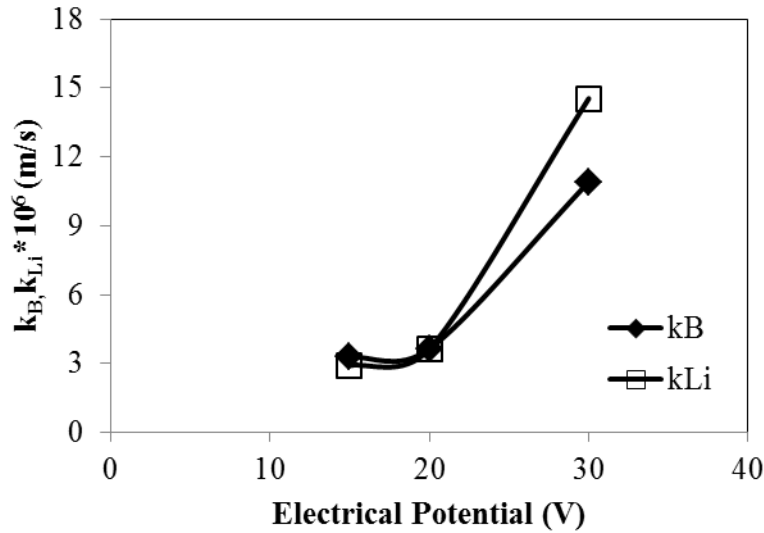


Figure 3.14. Mass transfer coefficients at different applied electrical potentials by ASTOM ACILYZER BMED system

3.1.3 Influence of Acid and Base Types Used in Acid and Base Chambers

Influence of acid and base solutions on removal and recovery of boron and lithium was investigated by using H_3BO_3 and $LiOH$ instead of HCl and $NaOH$ solutions employed in acid and base chambers. Main purpose of these studies was recovery of boron as boric acid and recovery of lithium as lithium hydroxide. When H_3BO_3 and $LiOH$ were used in acid and base chambers, there will be no need for extra separation process to obtain H_3BO_3 and $LiOH$ with high purity by BMED process. In this step, tests were carried out by using H_3BO_3 - $LiOH$ as acid and base solutions at 30 V.

3.1.3.1 0.05 M H_3BO_3 -0.05 M $LiOH$ as Acid-Base Pair

The test was carried out using H_3BO_3 and $LiOH$ solutions as an initial acid-base pair in acid and base chambers instead of HCl and $NaOH$ solutions. While removals and recovery values of lithium and boron were calculated, initial lithium and boron amounts in acid and base chambers were analyzed and subtracted from lithium and boron concentrations measured in acid and base chambers at the end of experiment to see the difference.

When 0.05 M H_3BO_3 and 0.05 M LiOH solutions were used, maximum removals of boron and lithium were similar with the results obtained with 0.05 M HCl-0.05 M NaOH solutions. The highest removals of boron and lithium from sample solutions were 86.9% and 94.7%, respectively, with 0.05 M HCl-0.05 M NaOH pair (Figures 3.15 and 3.16). Boron recoveries were obtained as 50.1% (0.05 M HCl-0.05 M NaOH) and %21.1 (0.05 M H_3BO_3 -0.05 M LiOH). Boron recoveries decreased with using 0.05 M H_3BO_3 -0.05 M LiOH solution. Lithium recoveries were obtained as 62.0 % (0.05 M HCl-0.05 M NaOH) and %49.0 (0.05 M H_3BO_3 -0.05 M LiOH). Using of H_3BO_3 solution in acid chamber led to generate low conductive medium for transferring of H_3BO_3 ions from sample chamber to acid chamber. It was considered that concentrations of acid-base pair should be increased when H_3BO_3 -LiOH acid-base pair was used to increase recovery of boron and lithium.

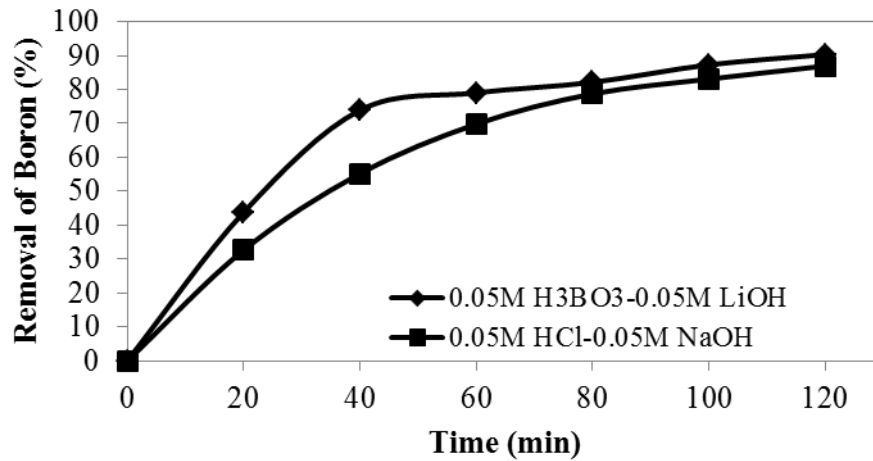


Figure 3.15. Removal of boron using different acid and base solutions in acid-base chambers by ASTOM ACILYZER model BMED system

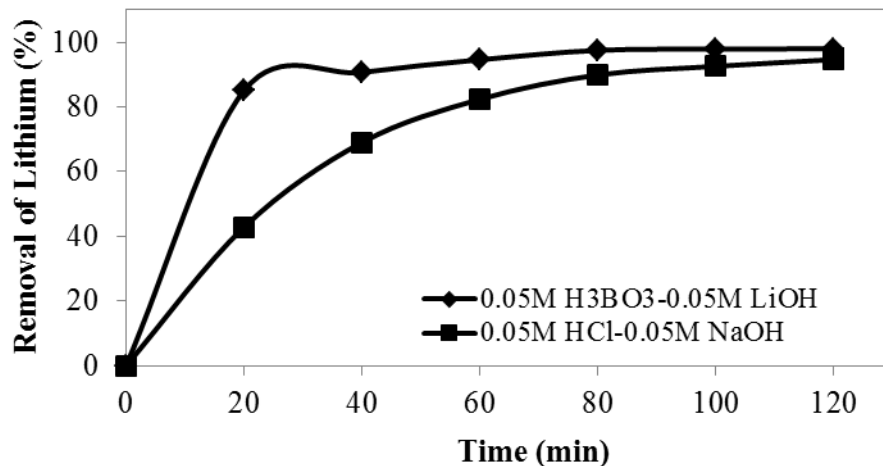


Figure 3.16. Removal of lithium using different acid and base solutions in acid-base chambers by ASTOM ACILYZER model BMED system

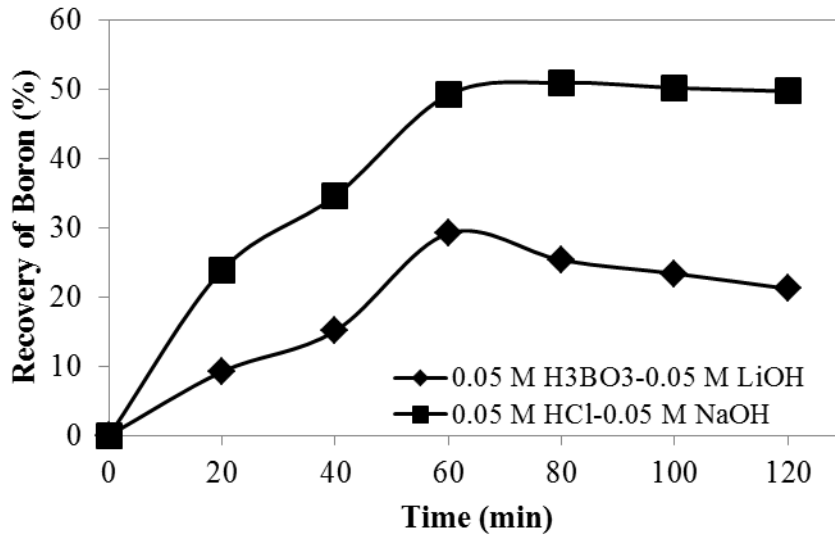


Figure 3.17. Recovery of boron using different acid and base solutions in acid-base chambers by ASTOM ACILYZER model BMED system

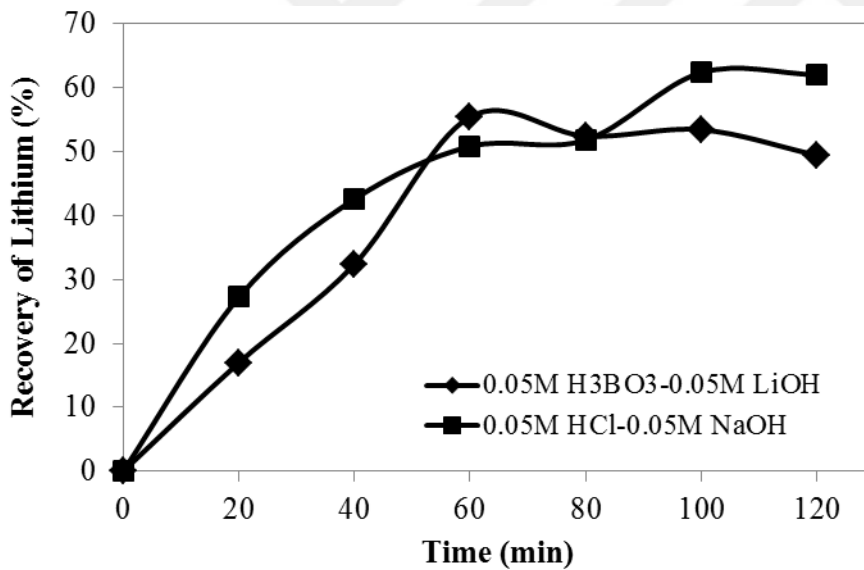


Figure 3.18. Recovery of lithium using different acid and base solutions in acid-base chambers by ASTOM ACILYZER model BMED system

In (C_B/C_{B0}) and $\ln(C_{Li}/C_{Li0})$ vs time graphs were illustrated Figures 3.19 and 3.20. As it can be seen from Figures 3.19 and 3.20, there is a good linear relationship between $\ln(C_B/C_{B0})$ and $\ln(C_{Li}/C_{Li0})$ versus time. The differences between points in linearization graphs for lithium at these two conditions stem

from that differences in separations of lithium with using 0.05 M H_3BO_3 and 0.05 M LiOH instead of 0.05 M HCl and 0.05 M LiOH.

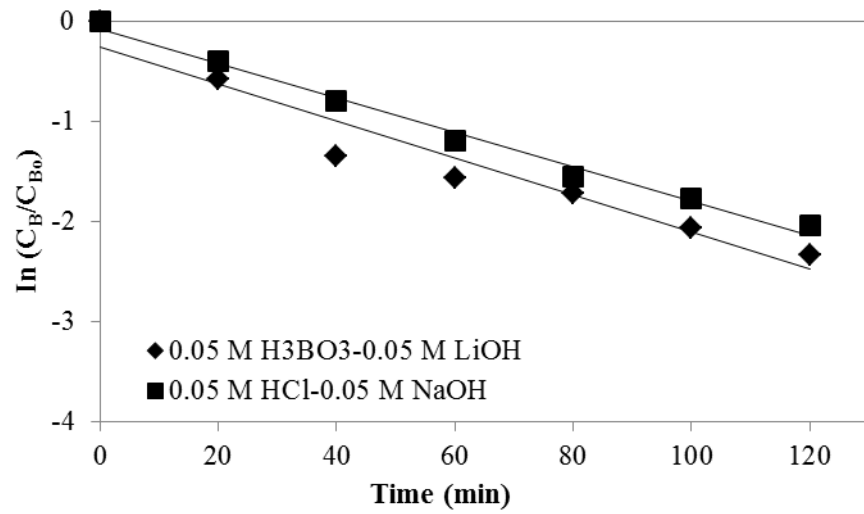


Figure 3.19. Linearization of boron separation data with different acid and base solutions

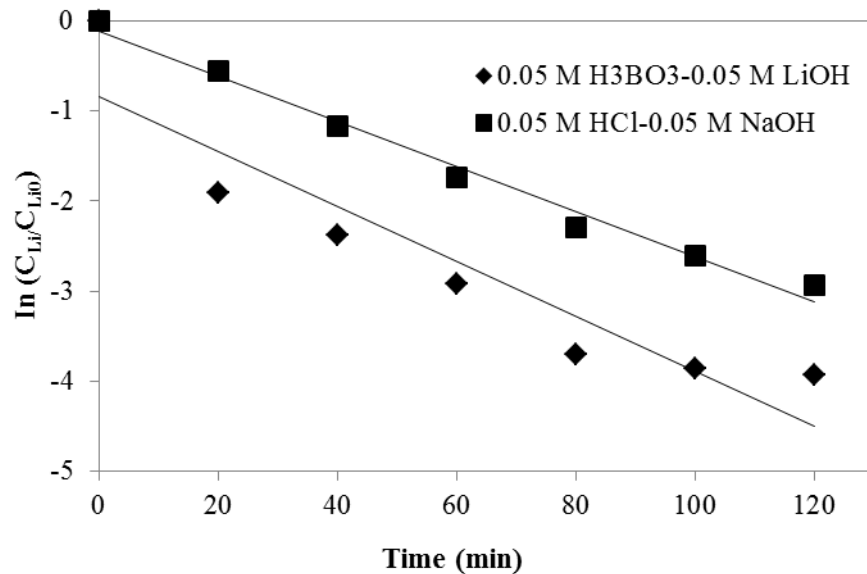


Figure 3.20. Linearization of lithium separation data with different acid and base solutions

When 0.05 M HCl-0.05 M NaOH acid-base pair was replaced with 0.05 M H_3BO_3 -0.05 M LiOH acid-base pair, mass transfer coefficients of lithium were different. Separation rates of lithium were higher when 0.05 M HCl-0.05 M NaOH in acid and base chamber were replaced with 0.05 M H_3BO_3 -0.05 M LiOH. Therefore, when 0.05 M H_3BO_3 -0.05 M LiOH solutions were used in acid and base chamber, mass transfer coefficient of lithium ions was found as higher.

However, mass transfer coefficients of boron was found as nearly same for both situation because, removal rates of boron did not change significantly with changing of acid-base pair (Table 3.1).

Table 3.1. Mass transfer coefficients with different acid and base type by ASTOM ACILYZER model BMED system

	0.05 M H ₃ BO ₃ -0.05 M LiOH	0.05 M HCl-0.05 M NaOH
$k_B \cdot 10^6$ (m/s)	10.91	10.91
$k_{Li} \cdot 10^6$ (m/s)	18.18	14.55

3.1.3.2 0.1 M H₃BO₃-0.1 M LiOH Acid-Base Pair

Separation of boron and lithium was carried out at 30 V of applied electrical potential using H₃BO₃ solution (0.1 M) instead of HCl solution in the acid chamber and LiOH solution (0.1 M) in the base chamber instead of NaOH solution. The highest removals of boron and lithium from feed were 87.0% and 93.3%, respectively (Figures 3.21 and 3.22). The highest boron and lithium recoveries were 62.0% and 56.0%, respectively (Figures 3.23, 3.24).

When used acid-base pair (0.1 M HCl-0.1 M NaOH) was replaced with 0.1 M H₃BO₃-0.1 M LiOH in acid-base chambers, it was observed that there were no significant differences between boron and lithium removals. However, the recovered amount of boron and lithium were different when 0.1 M H₃BO₃-0.1 M LiOH pair was used. The recoveries were better than the recoveries obtained with 0.1 M HCl-0.1 M NaOH acid-base pair. When H₃BO₃ and LiOH are used, it was considered that there was not back diffusion from acid and base chambers to the sample chamber (Figures 3.21-3.24).

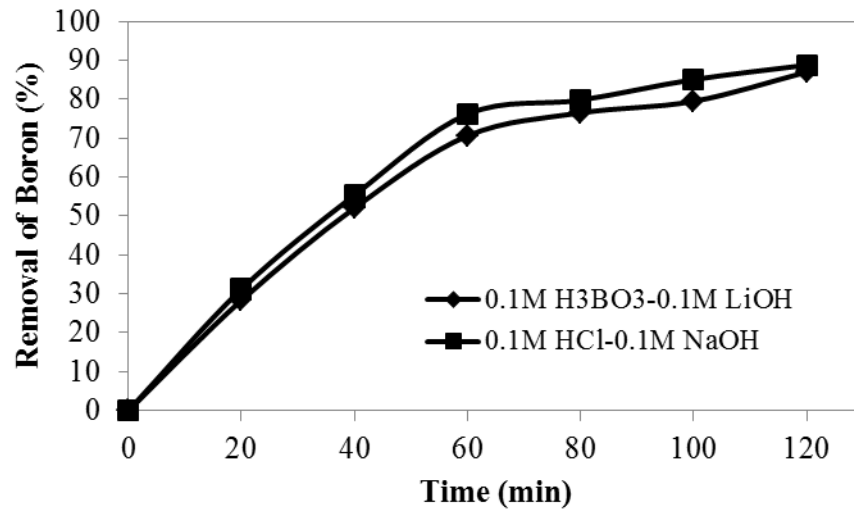


Figure 3.21. Removal of boron with different acid and base solutions by ASTOM ACILYZER model BMED system

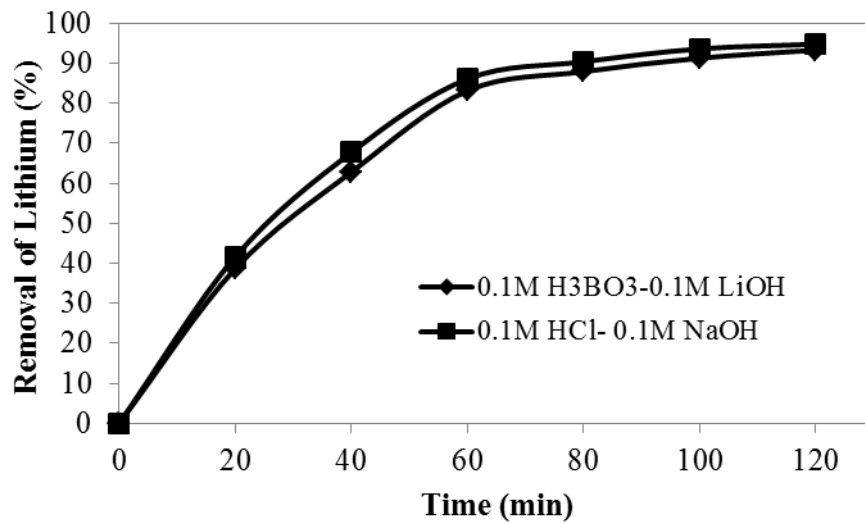


Figure 3.22. Removal of lithium with different acid and base solutions by ASTOM ACILYZER model BMED system

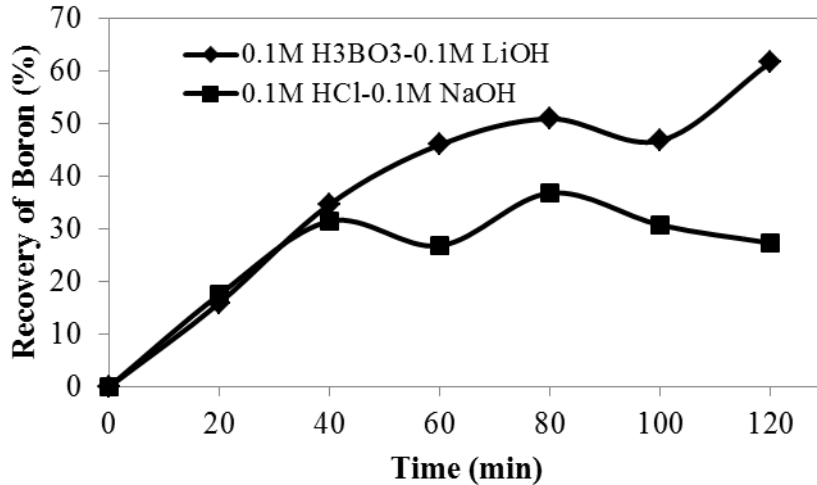


Figure 3.23. Recovery of boron using different acid and base solutions by ASTOM ACILYZER model BMED system

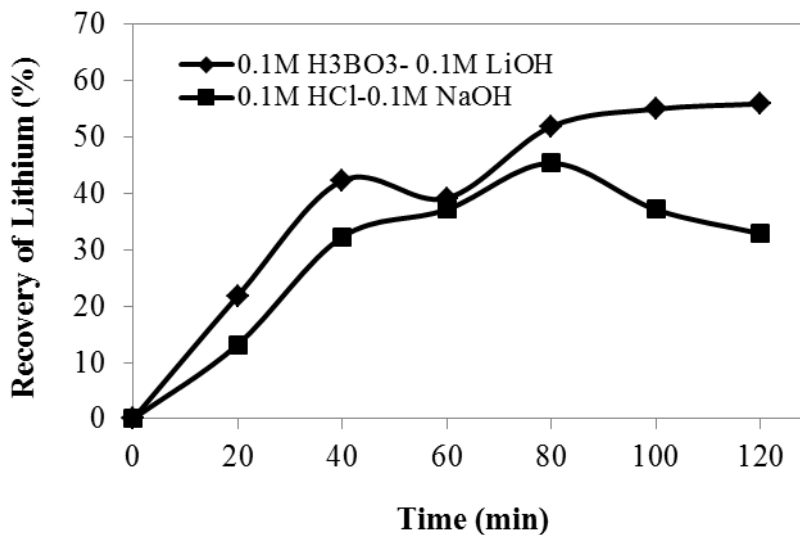


Figure 3.24. Recovery of lithium with different acid and base solutions by ASTOM ACILYZER model BMED system

In (C_B/C_{B_0}) and $\ln(C_{Li}/C_{Li_0})$ vs time graphs were illustrated Figures 3.25 and 3.26. As it can be seen from Figures 3.25 and 3.26, there is a good linear relationship between $\ln(C_B/C_{B_0})$ and $\ln(C_{Li}/C_{Li_0})$ and time. According to the experimental results, separations of boron and lithium from sample chamber did not change significantly when 0.1 M H₃BO₃-0.1 M LiOH solutions were used instead of 0.1 M HCl-0.1 M NaOH solutions. The differences between points in linearization graphs for boron and lithium at these two conditions stem from that small differences in separations of boron and lithium. Therefore, slopes of linearizations of boron and lithium separations graphs were found as almost same.

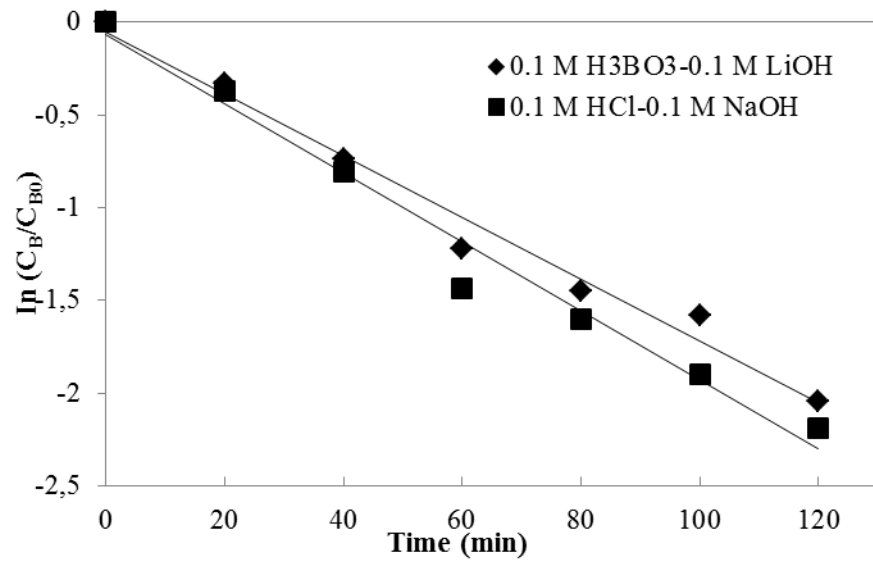


Figure 3.25. Linearization of boron separation data for different acid and base solutions by ASTOM ACILYZER model BMED system

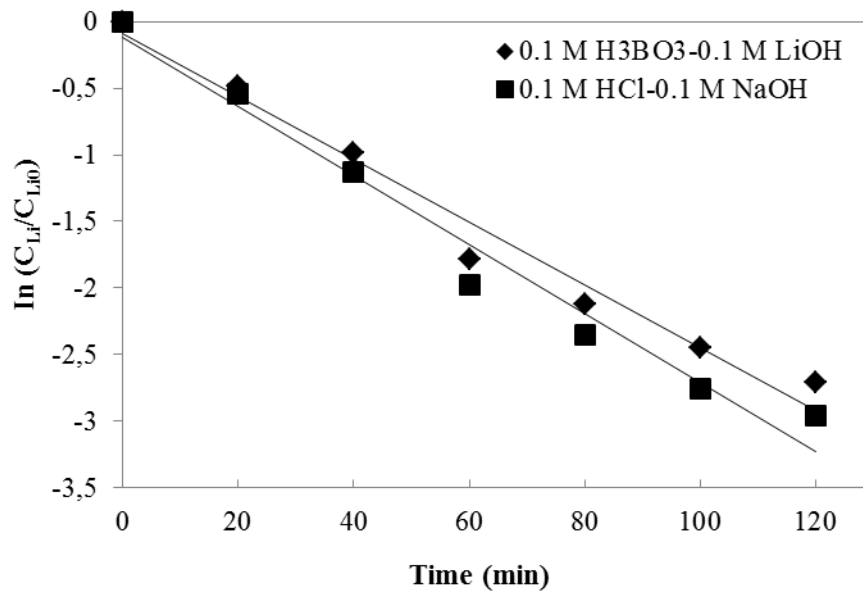


Figure 3.26. Linearization of lithium separation data for different acid and base solutions by ASTOM ACILYZER model BMED system

When used 0.1 M HCl-0.1 M NaOH acid-base pair was replaced with 0.1 M H₃BO₃-0.1 M LiOH, mass transfer coefficients of boron and lithium were not found remarkably different since removal rates of lithium and boron from sample

chamber did not change significantly with changing acid-base pair at these initial concentrations (Table 3.2).

Table 3.2. Mass transfer coefficients with different acid and base types used in acid and base chambers

	0.1 M H ₃ BO ₃ -0.1 M LiOH	0.1 M HCl-0.1 M NaOH
$k_B \cdot 10^6$ (m/s)	10.91	10.91
$k_{Li} \cdot 10^6$ (m/s)	14.55	14.55

3.2 Lithium and Boron Separations and Recoveries from Aqueous Solutions by MEGA Model BMED System

3.2.1 Influence of Concentrations of Acid and Base Solutions in Acid-Base Chambers

For these tests, 0.05 M HCl-0.05 M NaOH, 0.005 M HCl-0.005M NaOH and 0.003 M HCl-0.003 M NaOH acid base pairs were used. Maximum lithium removal from the sample solution was found to be over 99% in all tested acid and base concentrations. Lithium removal was faster when 0.05 M HCl - 0.05 M NaOH solutions were used in acid-base chambers. When the solutions with high acid-base concentration were used in acid and base chambers, these solutions have a high electrical conductivity and a good conductive field for ion transfer. However, the lithium recovery was 37% with 0.05 M HCl-0.05 M NaOH solutions in acid-base chambers. This is probably due to the back diffusion of lithium at high concentrations. The highest lithium recovery was achieved when 0.003 M HCl-0.003 M NaOH solutions were employed in acid and base chambers. In this case, the maximum lithium recovery in the base chamber was found to be 66% (Figures 3.27 and 3.29).

Maximum removal of boron was over 70% at all tested conditions. It was observed that there was not any important difference between boron removals at the end of two hours experiment. However, boron was removed rapidly when 0.05 M HCl-0.05 M NaOH solutions were used in acid-base chambers. Again, when high acid-base concentrations were used, these solutions create good conductive area for transfer of ions. Maximum boron recovery was obtained as 55% with 0.003 M HCl-0.003 M NaOH solutions in acid and base chambers. Boron recoveries were obtained as 41% (0.005 M HCl-0.005 M NaOH) and 36% (0.05 M HCl-0.05 M NaOH). When high initial acid-base concentrations were used, recovery of boron would be low as seen in case of lithium recovery.

This situation is probably due to the back diffusion because of the rapid ion transfer (Figures 3.28 and 3.30).

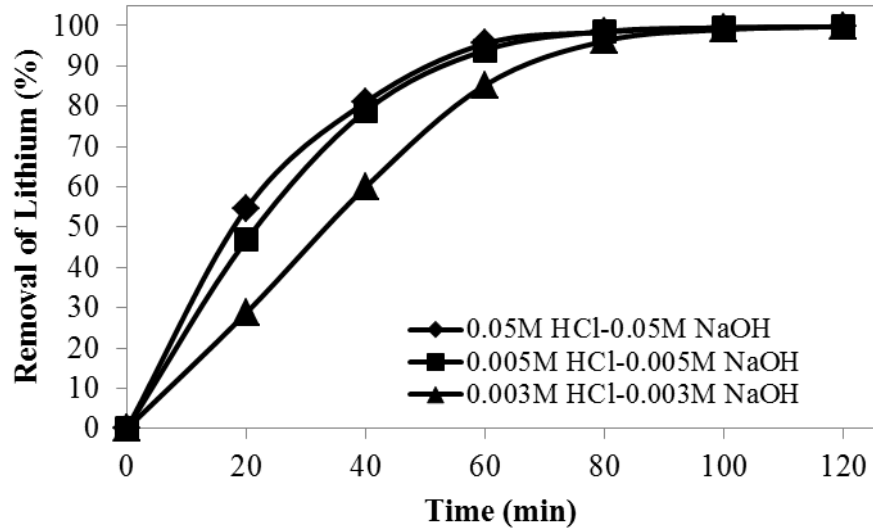


Figure 3.27. Removal of lithium with different acid and base concentrations used in acid-base chambers by MEGA model BMED system

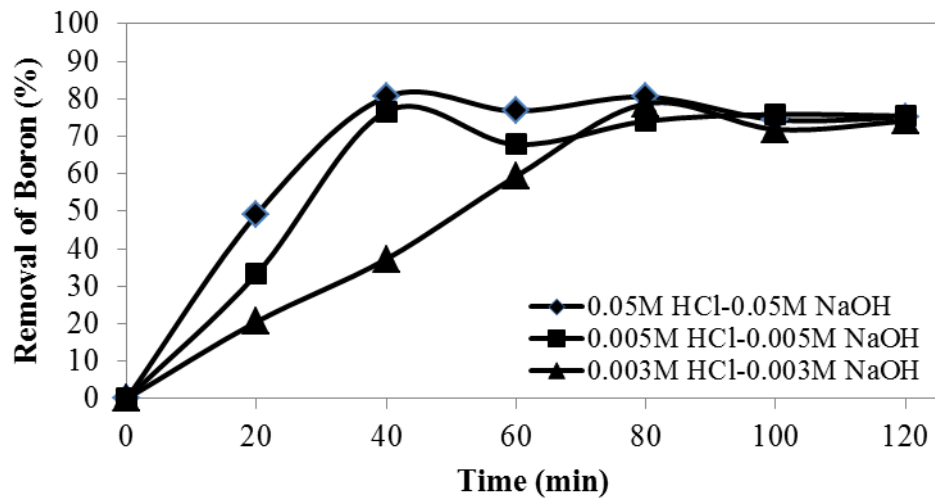


Figure 3.28. Removal of boron with different acid and base concentrations used in acid base chambers by MEGA model BMED system

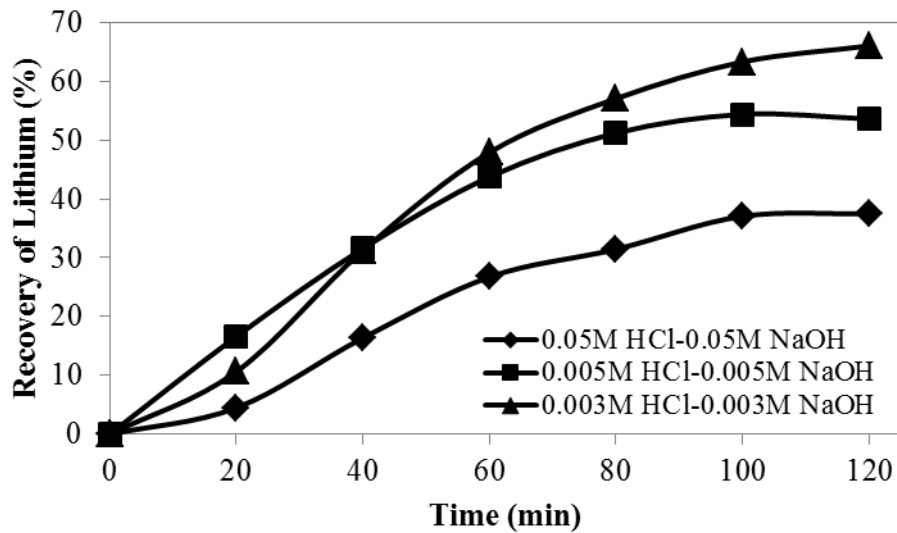


Figure 3.29. Recovery of lithium with different acid and base concentrations used in acid-base chambers by MEGA model BMED system

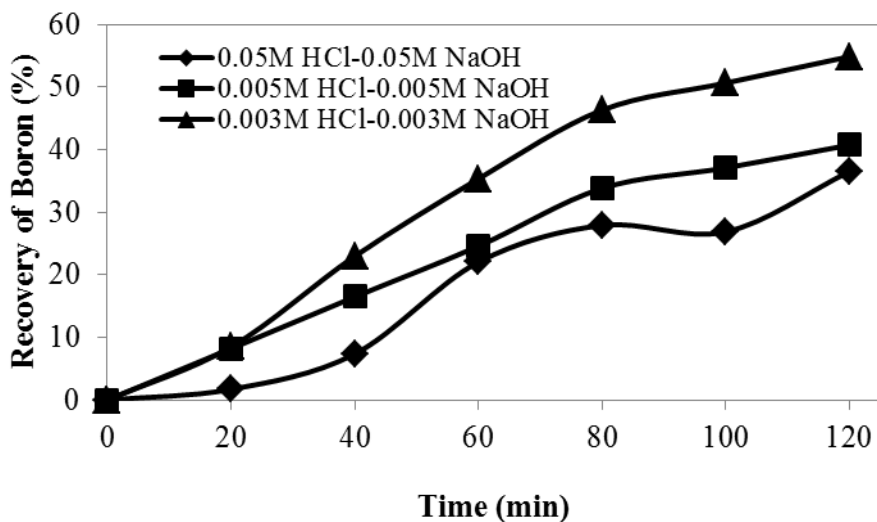


Figure 3.30. Recovery of boron with different acid and base concentrations by MEGA model BMED system

Linearization of experimental data for boron and lithium were shown in Figures 3.31 and 3.32. There is a very good linear relationship between $\ln(C_B/C_{B0})$ and time while using MEGA BMED system at optimum acid base concentration (0.003 M HCl-0.003 M NaOH) in acid and base chambers. However, in contrast to ASTOM ACILYZER BMED system, there is not a good relationship between $\ln(C_B/C_{B0})$ and time while using MEGA BMED system at other acid base concentrations (0.05 M HCl-0.05 M NaOH and 0.005 M HCl-0.005 M NaOH). This difference between ASTOM ACILYZER BMED system

and MEGA BMED system could be stem from that they have different membranes in terms of thickness, electrical resistance and effective surface area. Because, ion transport mechanism depends on membrane characteristics. Especially, membrane thickness is a key factor for the linearization graphs. Because, linear relationship between final concentrations to initial concentration at any time depends on that concentration profiles do not change with membrane thickness. If the membranes are thick, high molecular weight ions such as $B(OH)_4^-$ may not pass through the membranes and partial adsorption on the surface of the membrane and back diffusion from the membrane surface may be seen. Concentration profile would be as a function of time and membrane thickness in this situation. However, the effect of membrane thickness for thick membrane does not observed significantly after sufficient conductive medium create for transferring of ions. Because, ions will be transferred easily without depending on membrane thickness almost. The differences between points in linearization graphs for boron and lithium at these three conditions stem from that differences in separation of boron and lithium at these three conditions.

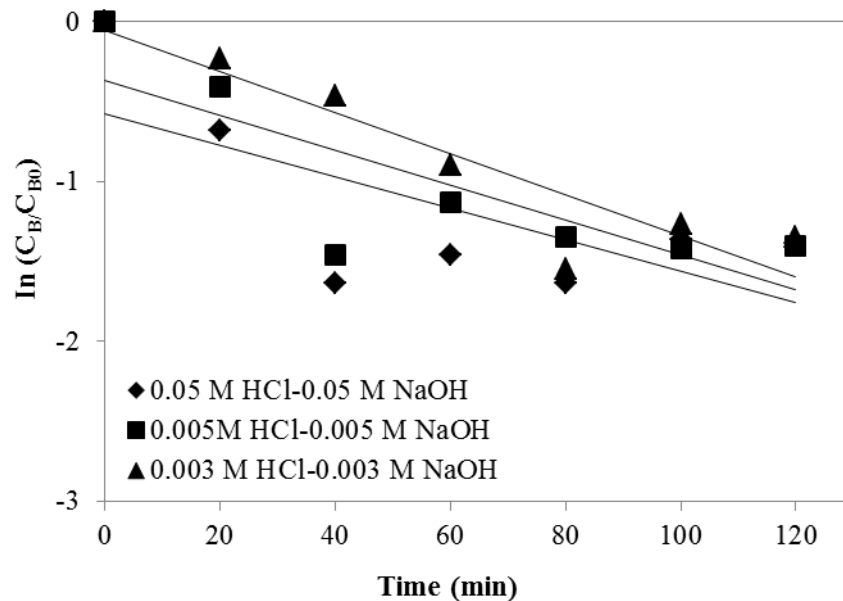


Figure 3.31. Linearization of boron separation data by MEGA model BMED system

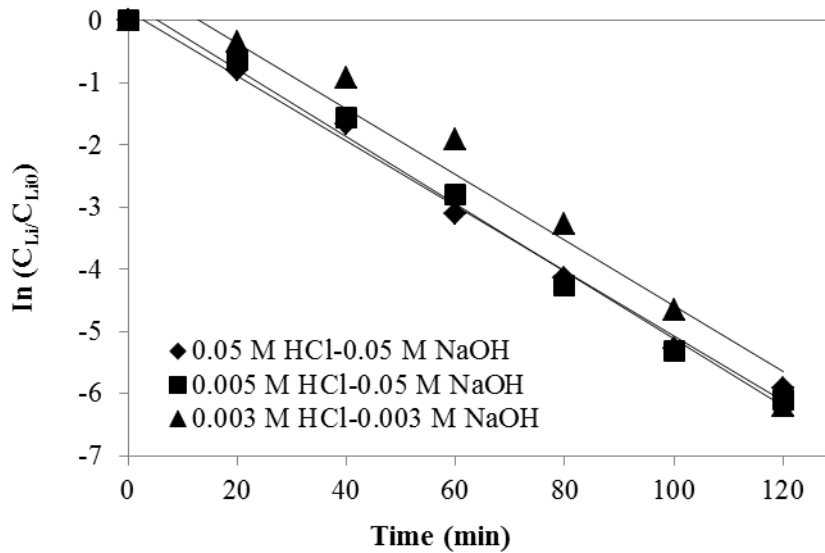


Figure 3.32. Linearization of lithium separation data by MEGA model BMED system

Mass transfer coefficients of boron and lithium were found by using different initial acid-base concentrations were used in acid and base chambers. When acid-base pairs having different concentrations were used, there were no significant differences for mass transfer coefficients of boron and lithium. However, mass transfer coefficient of lithium was found as higher than mass transfer coefficient of boron as it was an expected. Since molecular weight of the borat ions higher than molecular weight of lithium ions, transferring of borat ions were more slowly than lithium ions. The difference between mass transfer coefficients of boron and lithium was stem from this situation (Table 3.3).

Table 3.3 Mass transfer coefficients with different acid-base concentrations by MEGA model BMED system

	0.05 M HCl-0.05 M NaOH	0.005 M HCl-0.005 M NaOH	0.003 M HCl-0.003 M NaOH
$k_B \cdot 10^5$ (m/s)	0.625	0.625	0.625
$k_{Li} \cdot 10^5$ (m/s)	2.81	2.81	2.81

3.2.2 Influence of Applied Electrical Potential

For these tests, **0.003 M HCl-0.003 M NaOH** acid-base pair in acid-base chambers was used. The studies were performed using four different electrical potentials (15, 20, 25 and 30 V).

As it can be seen from Figures 3.33 and 3.34, removal rates of boron and lithium from sample solution increased when applied electrical potential was high. Increasing removal rate of lithium and boron with increased applied electrical potential is an expected outcome because of the fact that electrical potential is a main driving force for electro-membrane process.

When 20, 25 and 30 V of electrical potentials were applied, maximum removal of lithium was over 99%. Lithium removal from sample solution was obtained as 93% when 15 V of electrical potential was applied. According to this result, it was seen that there is no significant influence of electrical potential above 20 V. However, removal rate was highest with 30 V of electrical potential.

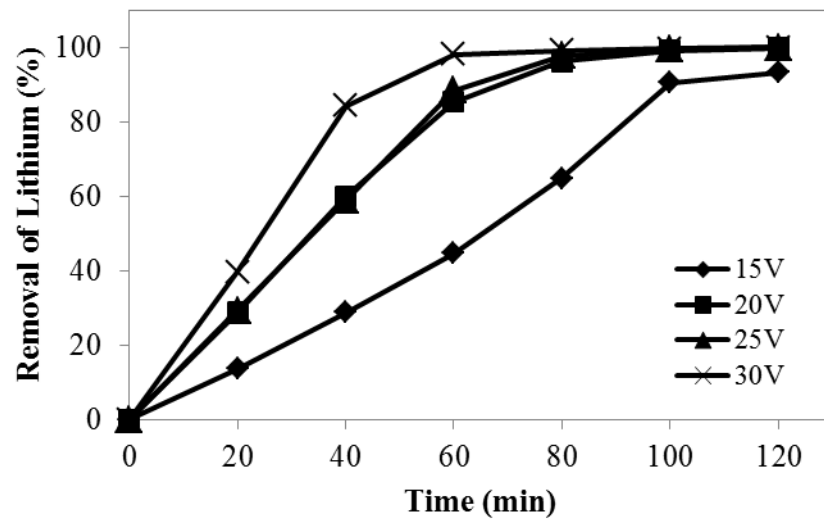


Figure 3.33. Removal of lithium at different electrical potentials by MEGA model BMED system

When boron removal was examined at different electrical potentials, it was seen that the maximum removal of boron was 69% or more at all electrical potentials. Similarly, as electrical potential increased, removal rate was faster. When 25 V and 30 V of electrical potentials were applied, boron removal was 74% at both electrical potentials at the end of the two-hour test.

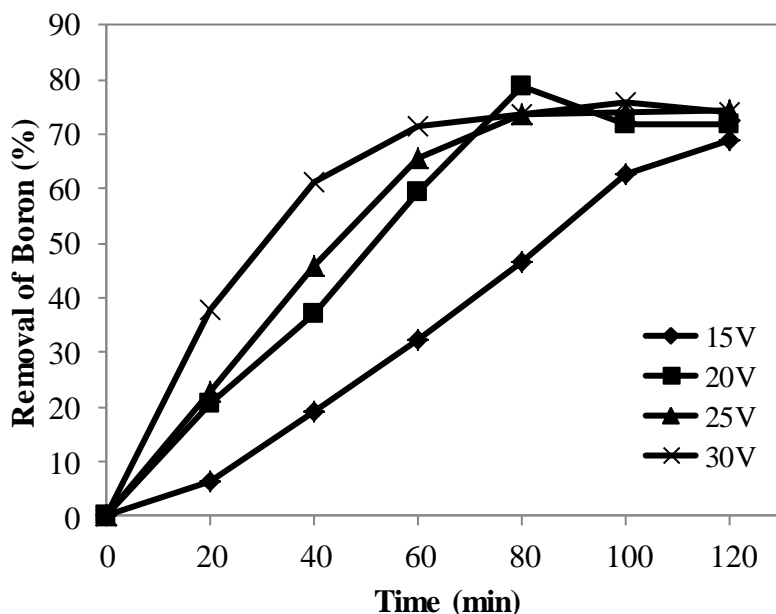


Figure 3.34. Removal of boron at different electrical potentials by MEGA model BMED system

When recoveries of lithium were investigated at different electrical potentials, recovery of lithium was more rapid with increasing electrical potential. This result was possibly due to the electrical potential as a driving force for electro-membrane processes. When 15, 20, 25 and 30 V of electrical potentials were applied, recoveries of lithium were 57%, 66 %, 73% and 74%, respectively. Lithium recovery increased with increasing electrical potential (Figure 3.35). Parsa et al. (2015) observed this phenomenon while they were working on recovery of lithium from lithium bromide solution that contains sodium by ED method. The authors applied 3 V, 5 V and 7 V of electrical potential to sample solution and 1.5%, 4.5 % and 14% of lithium recoveries were obtained, respectively. However, when 30 V electrical potential was applied, recovery of lithium increased for a while and it stayed as constant.

It was seen that influence of pH is another factor for recovery of boron. When 30 V electrical potential was applied, the removal took place rapidly and pH value of the sample solution showed a faster decline than at other three electrical potentials. For this reason, borate ions in the sample chamber are transformed into boric acid in molecular form. Since boric acid is not charged, it cannot be transferred to the acid chamber (Figures 3.36 and 3.37).

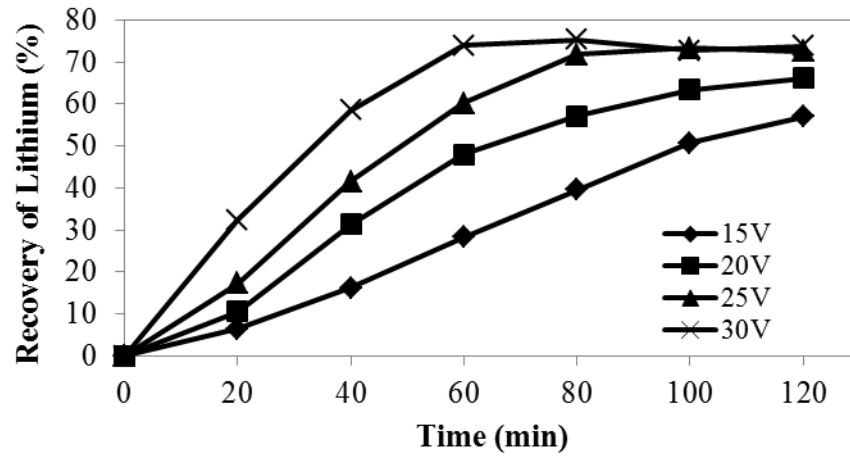


Figure 3.35. Recovery of lithium at different electrical potentials by MEGA model BMED system

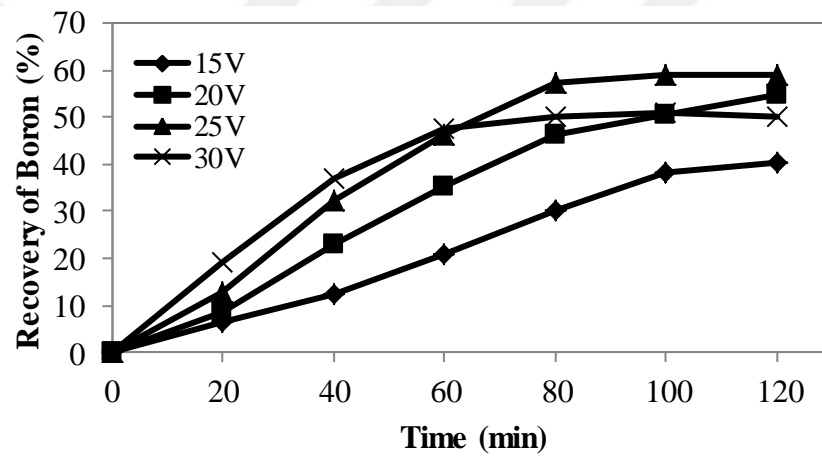


Figure 3.36. Recovery of boron at different electrical potentials by MEGA model BMED system

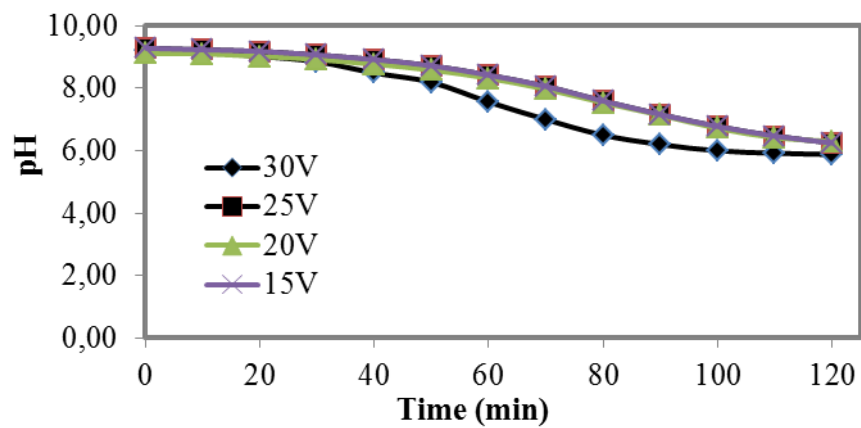


Figure 3.37. pH of the sample solution during experiments by MEGA model BMED system at various electrical potentials

According to the obtained results, maximum boron recovery obtained was 59% at 25 V. Maximum lithium recovery was obtained as 75% at 30 V of electrical potential. However, lithium recovery was 74% at 25 V of electrical potential. Since there is no significant difference between 25 and 30 V for recovery of lithium and maximum boron recovery was obtained under the 25 V of electrical potential, optimum electrical potential was determined as 25 V.

$\ln(C_{Li}/C_{Li0})$ and $\ln(C_B/C_{B0})$ vs time graphs as a function of applied electrical potential were given in Figures 3.38 and 3.39. There is relatively good linearship between $\ln(C_{Li}/C_{Li0})$ and $\ln(C_B/C_{B0})$ with time.

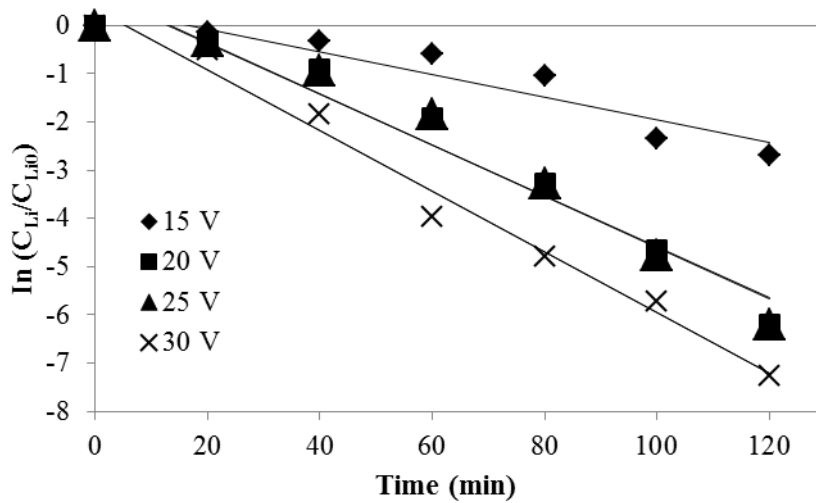


Figure 3.38. Linearization of lithium separation data as a function of electrical potential for MEGA model BMED system

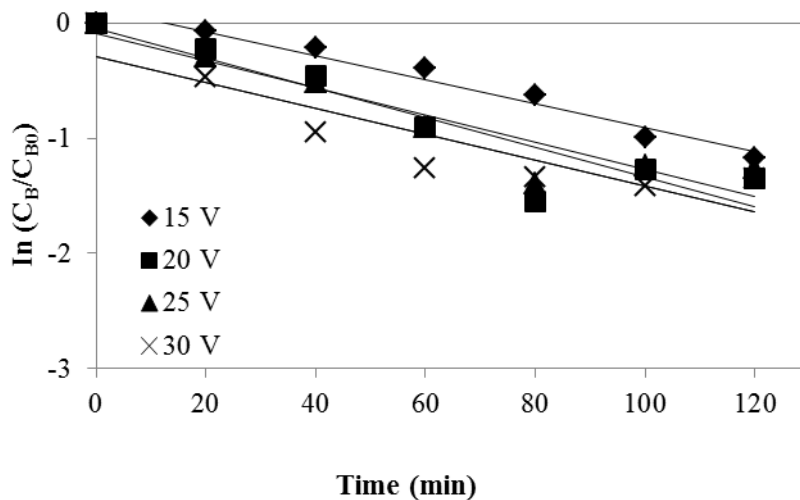


Figure 3.39. Linearization of boron separation data as a function of electrical potential for MEGA model BMED system

Mass transfer coefficients of lithium and boron at different electrical potentials were given in Figure 3.40. There is a great difference between mass transfer coefficients of boron and lithium. This situation was stem from that there is a great difference between molecular weight of lithium and molecular weight of borat ions. Since molecular weight of $B(OH)_4^-$ ions is much higher than molecular weight of Li^+ ions, mass transfer coefficient of boron was found as lower than lithium at all tested conditions.

Mass transfer coefficints of boron and lithium is related with removal of boron and lithium from sample compartment to ion exchange membrane surface. Mass transfer coefficients lithium at 30 V applied electrical potential were found as higher. Increasing mass transfer coefficient of lithium with increasing applied electrical potential was an expected result because of that electrical potential is main driving force for electro-membrane processes. However, boron mass transfer coefficients were found as almost same. Because, boron separation was constant after a while even if electrical potential was increased. Maximum boron separation from sample compartment was found as approximately 73% at all tested conditions. It was considered that the pH of the sample solution had a much more strong effect upon the removal of boron at this situation (Figure 3.40).

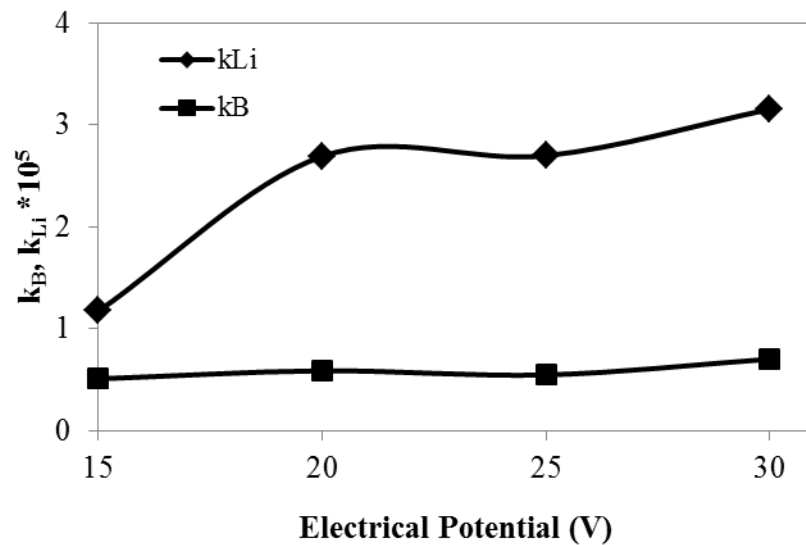


Figure 3.40. Mass transfer coefficients of boron and lithium at different electrical potential by MEGA model BMED system

3.2.3 Influence of Acid and Base Types in Acid and Base Chambers

Impact of acid and base types in acid and base chambers was investigated while HCl and NaOH solutions changed with H_3BO_3 and LiOH solutions in acid and base chambers. Main goal of this experiment is recovery of boron as a boric acid and recovery of lithium as lithium hydroxide. Tests were performed with H_3BO_3 -LiOH solutions with different acid and base concentrations under 25 V of electrical potential. For acid and base chambers, 0.05 M H_3BO_3 - 0.003 M LiOH; 0.003 M H_3BO_3 -0.003 M LiOH and 0.05 M H_3BO_3 -0.05 M LiOH acid-base pairs initially were used.

Influence of acid and base types on removal of boron and lithium from sample solution was investigated. Maximum lithium removal was determined as above 99 % at all tested conditions at the end of 2 h. Maximum removal of boron was above 75% at the same conditions. As it can be understand from Figures 3.41 and 3.42, changing acid and base types does not create a serious influence on removal of boron and lithium from sample solutions. Lithium recovery was slightly slower when H_3BO_3 -LiOH was used as the acid-base pair in acid and base chambers. However, there was no critical difference between the lithium recovery values at the end of the two-hour test period. Maximum lithium recoveries were obtained as 73% (0.003 M HCl-0.003 M NaOH), 67% (0.05 M H_3BO_3 -0.003 M LiOH), 72% (0.003 M H_3BO_3 -0.003 M LiOH), and 71% (0.05 M H_3BO_3 -0.05 M LiOH) respectively (Figure 3.43). Maximum boron recoveries were obtained as 59%, 50%, 51% and 57%, respectively at the respective experimental conditions (Figure 3.44).

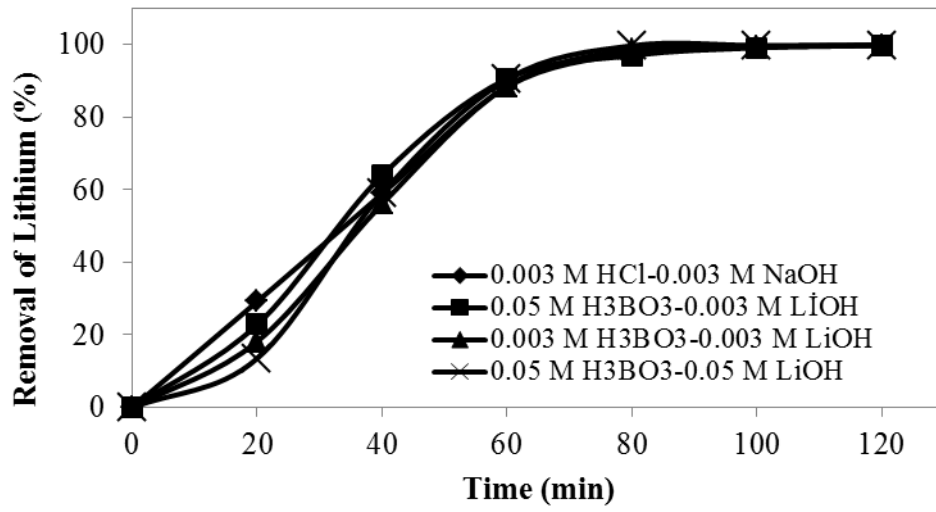


Figure 3.41. Removal of lithium with different acid and base solutions by MEGA model BMED system

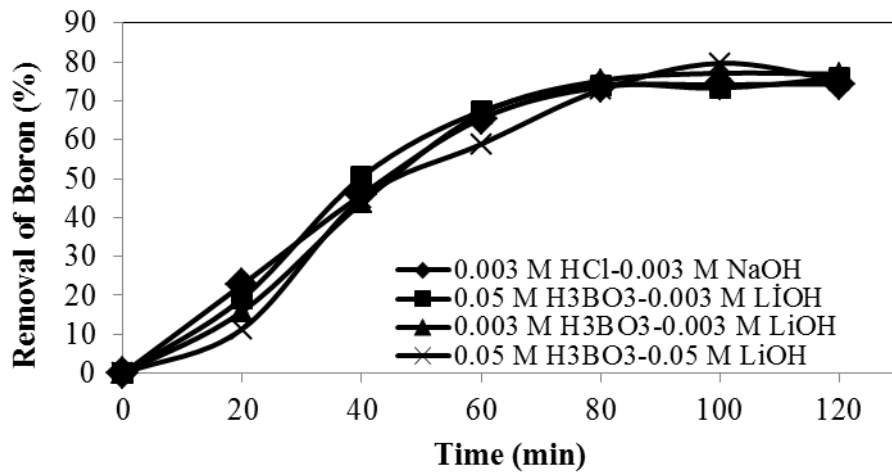


Figure 3.42. Removal of boron with different acid and base solutions by MEGA model BMED system

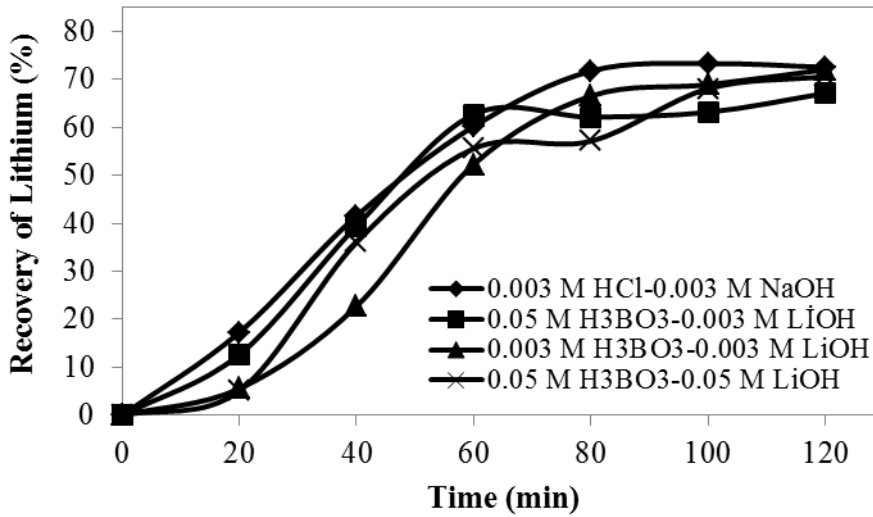


Figure 3.43. Recovery of lithium with different acid and base solutions for MEGA model BMED system

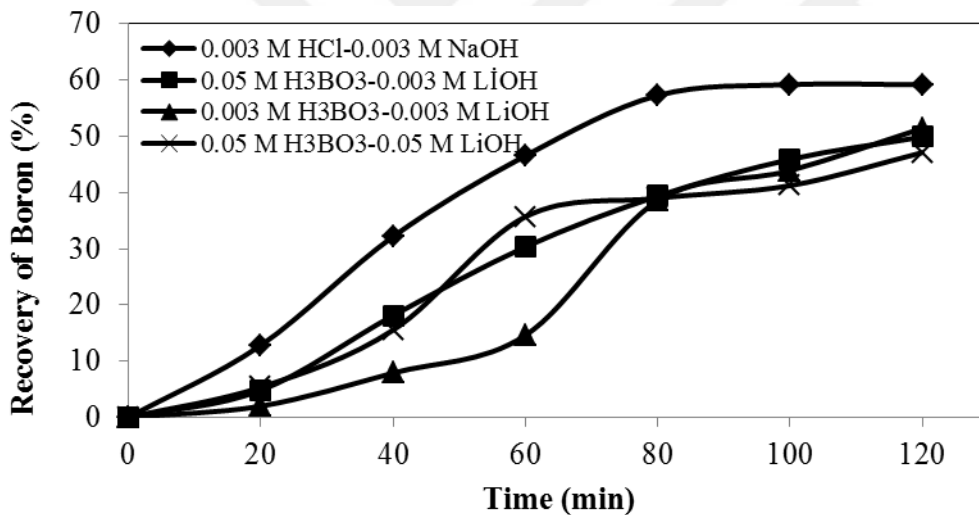


Figure 3.44. Recovery of boron with different acid and base solutions for MEGA model BMED system

Linearizations of boron and lithium separation data by using different initial acid and base concentrations in acid-base chambers are shown in Figures 3.45 and 3.46. The small differences between points in linearization graphs for boron and lithium at these three conditions stem from that small differences in separation of boron and lithium at these four conditions.

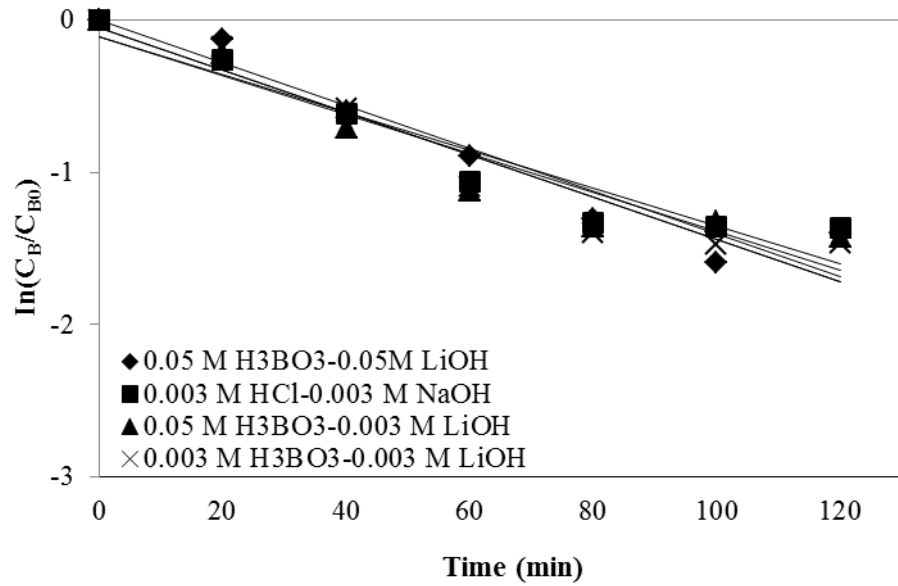


Figure 3.45. Linearization of boron separation for different acid and base types in acid and base chambers for MEGA model BMED system

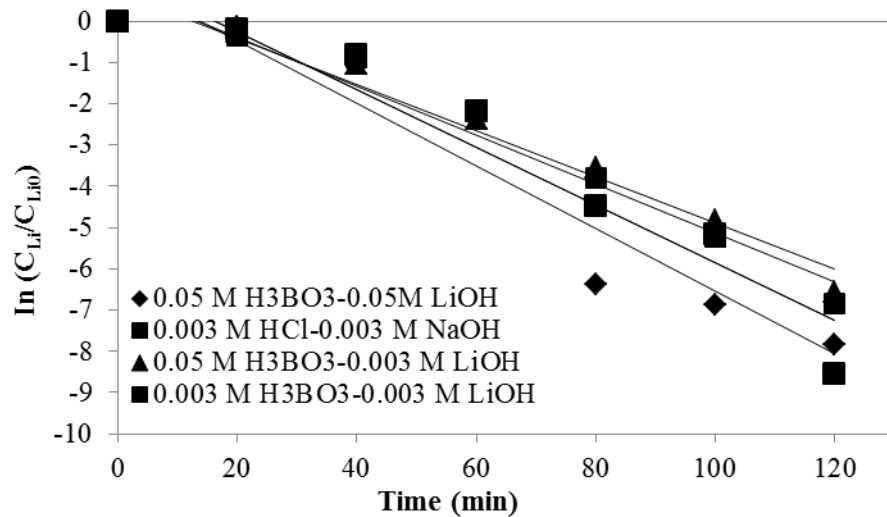


Figure 3.46. Linearization of lithium separation data for different acid and base types for MEGA model BMED system

Mass transfer coefficients of lithium and boron at different acid base type in acid and base chambers were given in Figure 3.47. Mass transfer coefficients of boron and lithium did not change significantly since removals of boron and lithium did not change when acid base concentrations in acid-base chambers changed. Mass transfer coefficients of boron were found as lower than mass transfer coefficient of lithium. This situation stem from that molecular weight of borate ions have higher than lithium ions. Therefore, lithium mass transfer coefficients were found as higher at all tested conditions.

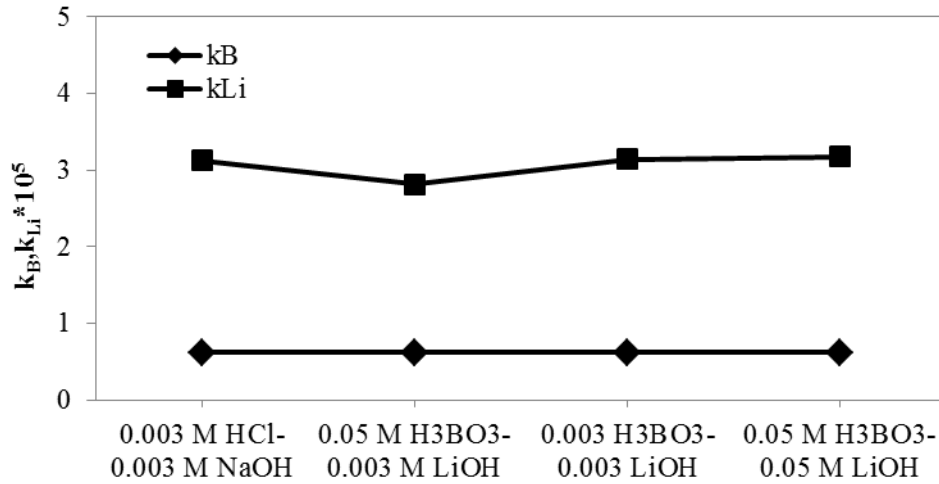


Figure 3.47. Mass transfer coefficients at different acid and base type by MEGA model BMED system

3.2.4 Influence of sample solution pH

Tests were conducted using 0.003 M HCl-0.003 M NaOH solutions in acid-base chambers under 25 V of applied electrical potential in this step. Sample solution was prepared using $\text{Li}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ with boron concentration of 1000 mg/L and lithium concentrations of 340 mg/L. pH of the this solution was 9.19 ± 0.07 . In order to change pH value of the solution, $\text{LiOH} \cdot \text{H}_2\text{O}$ was added to the solution as needed, and solutions having pH values of 10 and 11 were obtained. The solutions with pH values 10 and 11 had lithium concentrations of 363.23 mg/L and 483.59 mg/L, respectively.

When pH of the sample solution was increased, there was no significant decrease in removal of lithium at the end of 2h of experimental period but removal rate of lithium decreased (Figure 3.48). The removal of boron increased with increasing pH (Figure 3.49). In terms of lithium recovery, the maximum lithium recovery was 64% when the pH value was 11 and it was reduced by about 7%. Because, LiOH was used to adjust pH of the sample solution. Increased Li ion concentration in the sample compartment led to limiting of recovery of lithium ions. Therefore, recovery of lithium decreased when pH of the sample solution was adjusted as 11. The removal of boron increased with increasing pH of feed. When pH of feed was adjusted as 10 and 11, maximum removals of boron from sample chamber were obtained as 94% (pH 10) and 98% (pH 11). The recovery of boron increased when the pH value of sample solution was 10 but when pH value of sample solution was 11, recovery of boron decreased. It was considered that

this situation could be stem from competition between OH^- ions and $\text{B}(\text{OH})_4^-$. Anion exchange membranes that were in MEGA BMED system showed a higher selectivity to OH^- ions than $\text{B}(\text{OH})_4^-$ ions. The highest boron and lithium recoveries were obtained as 66.14% and 71.40% when pH value of feed was 10 (Figures 3.50 and 3.51).

According to the results, it was understood that pH of the sample solution seriously affects removal and recovery of boron. In the literature, Banasiak et al. (2009) studied on separation of fluoride, boron and nitrate in the existence of organic matter by ED method. The authors observed same phenomenon and noted that more boron could be recovered with increasing pH of feed.

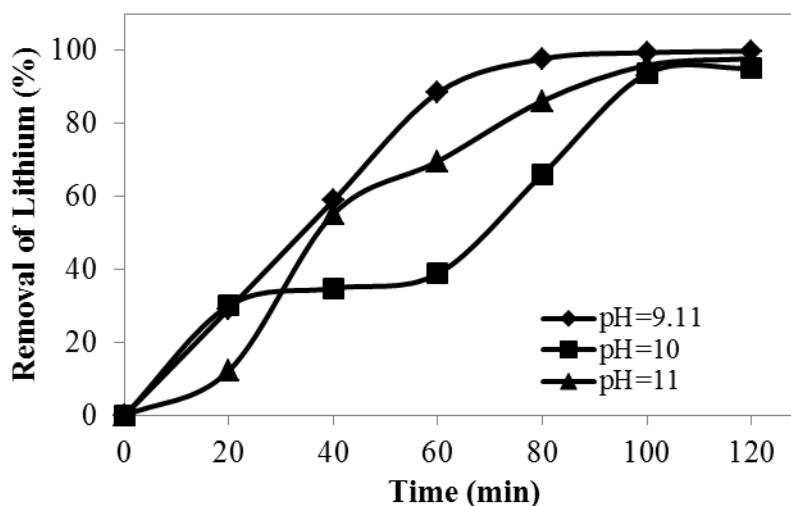


Figure 3.48. Removal of lithium at different pH by MEGA model BMED system

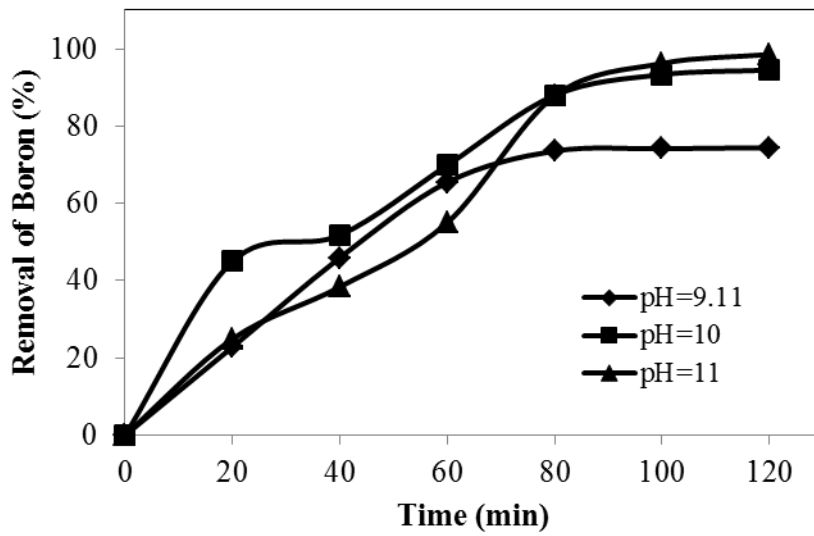


Figure 3.49. Removal of boron at different pH by MEGA model BMED system

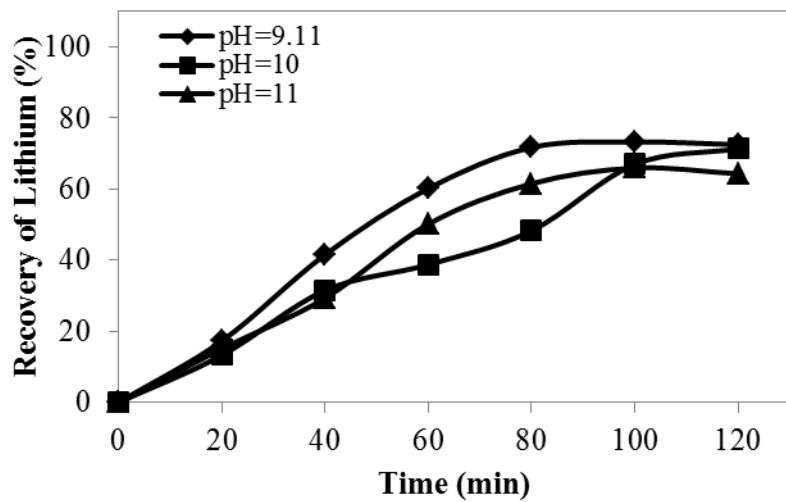


Figure 3.50. Recovery of lithium at different pH by MEGA model BMED system

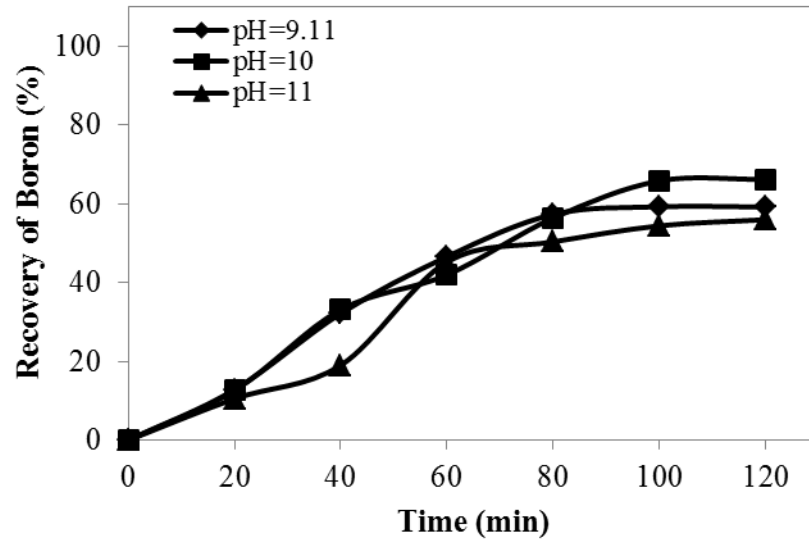


Figure 3.51. Recovery of boron at different pH by MEGA model BMED system

Linearization of experimental data for boron and lithium separations at different pH and mass transfer coefficients were given below as Figures 3.52-3.53.

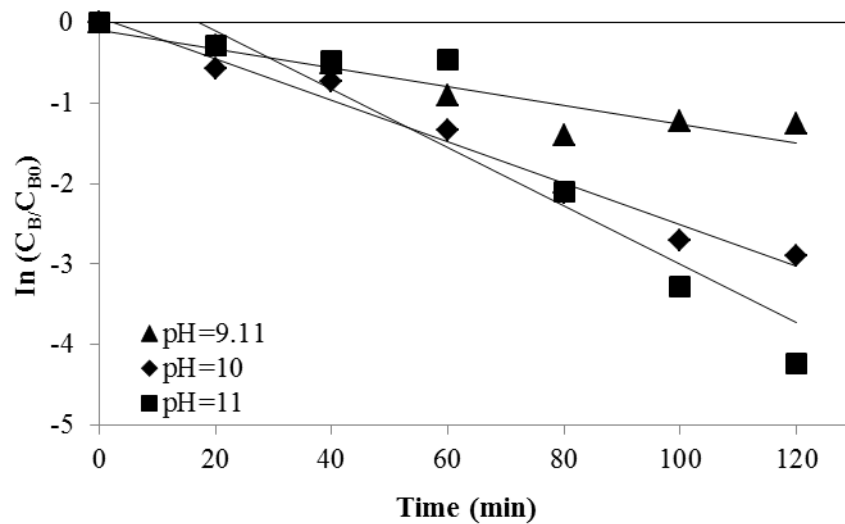


Figure 3.52. Linearization of separation data for boron at different pH for MEGA model BMED system

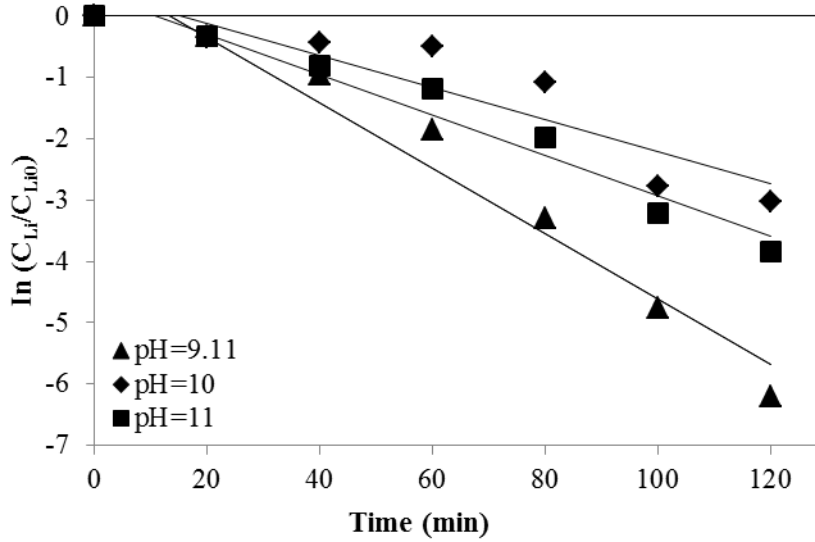


Figure 3.53. Linearization of separation data for lithium at different pH by MEGA model BMED system

Mass transfer coefficients at different pH of feed were given in Figure 3.57. Mass transfer coefficient of lithium decreased with increasing pH of feed. Because, LiOH solution was used to arrange pH of the sample solution. The transfer of lithium ions from sample chamber was slower with increasing pH because the amount of lithium ion to be transferred from the feed solution increased but the test period and electrical potential was kept constant. As a result of that, when sample solution pH was adjusted as 10 and 11, mass transfer coefficient of lithium ions were found as lower than mass transfer coefficient of lithium ions at natural pH of model solution. Since removal of boron increased with increasing pH of feed, mass transfer coefficient of boron increased with increasing pH of feed (Figure 3.54).

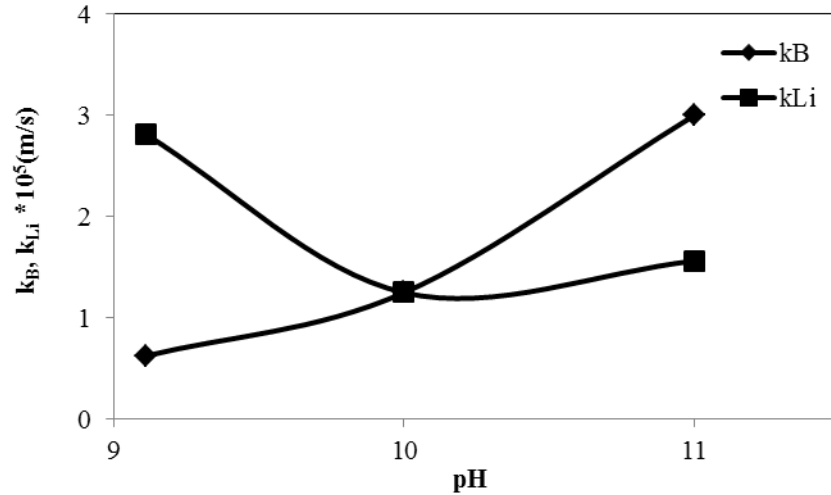
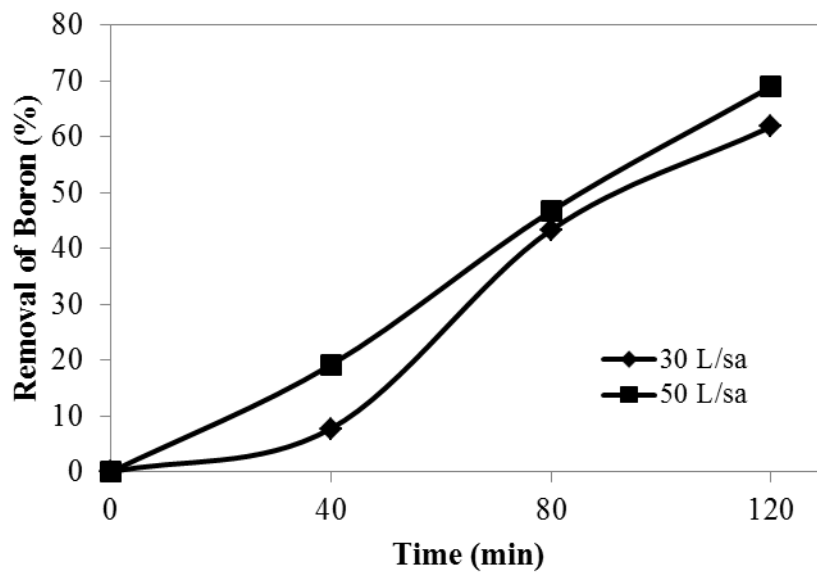
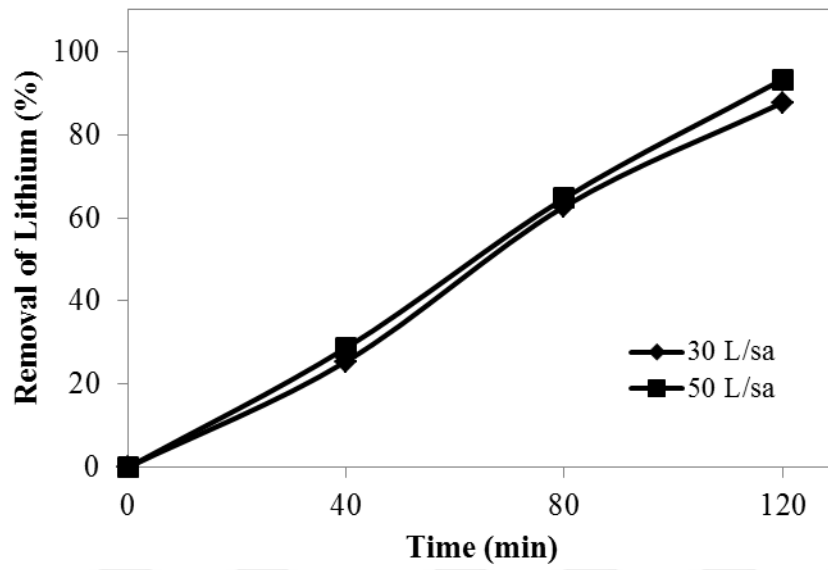


Figure 3.54. Mass transfer coefficients at different pH by MEGA model BMED system

3.2.5 Influence of Feed Flow rate

In order to determine the influence of flow rate on removal and recovery of boron and lithium from water by BMED, experiments were carried out with flowrates of 30 L/h and 50 L/h. Experiments were conducted with MEGA model BMED system using 0.003 M HCl-0.003 M NaOH solutions in acid and base chambers using 15 V of electrical potential. Lithium and boron concentrations were kept constant as 340 mg/L and 1000 mg/L in feed solution for each flow rates. Lithium and boron removals and recoveries were low while feed flow rate of sample solution was 30 L/h. Decreasing flow rate of feed lead to increase sample solution contact time with membranes and this situation probably lead to partial adsorption of ions on the membrane surface. According to the results obtained at a flow rate of 30 L/h, the experiment time increased at low flow rates. Optimum flow rate of the feed solution was determined as 50 L/h and removal of lithium and boron were 93.3% and 69.0%, respectively at this flow rate (Figures 3.55 and 3.56). Recoveries of boron and lithium were found as 40.5% and 57.0% at this condition (Figures 3.57 and 3.58). Since optimum flow rate of sample solution was determined as 50 L/h, all tests after this step were conducted at 50 L/h of flow rate.

Figure 3.55. Removal of lithium at different flow rates by MEGA model BMED system**Figure 3.56.** Removal of boron at different flow rates by MEGA model BMED system

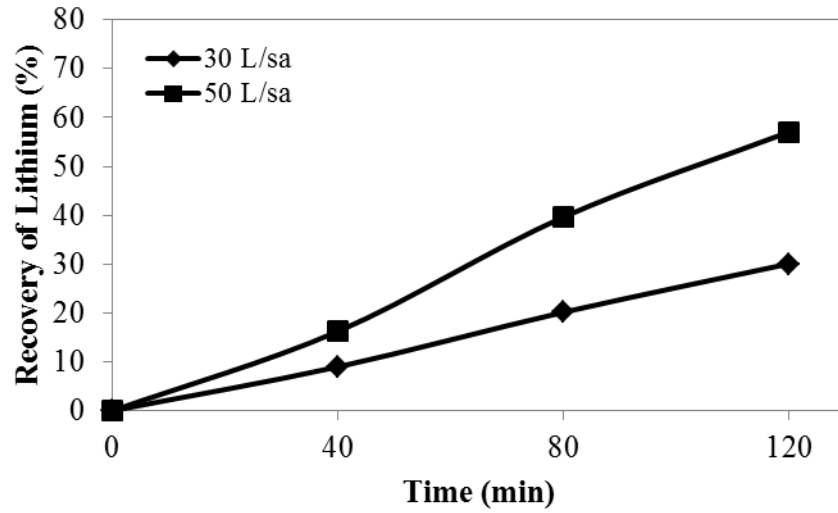


Figure 3.57. Recovery of lithium at different flow rates by MEGA model BMED system

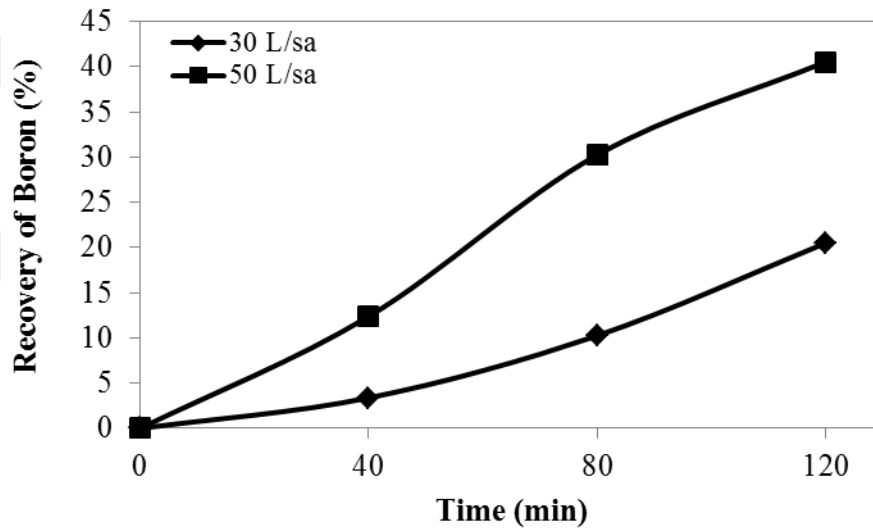


Figure 3.58. Recovery of boron at different flow rates for MEGA BMED system

Linearizations of concentration changes (C/C_0) of boron and lithium versus time plots in sample chamber were given in Figures 3.59 and 3.60. Mass transfer coefficients for boron and lithium calculated at different flow rates by MEGA model BMED system were given in Table 3.4.

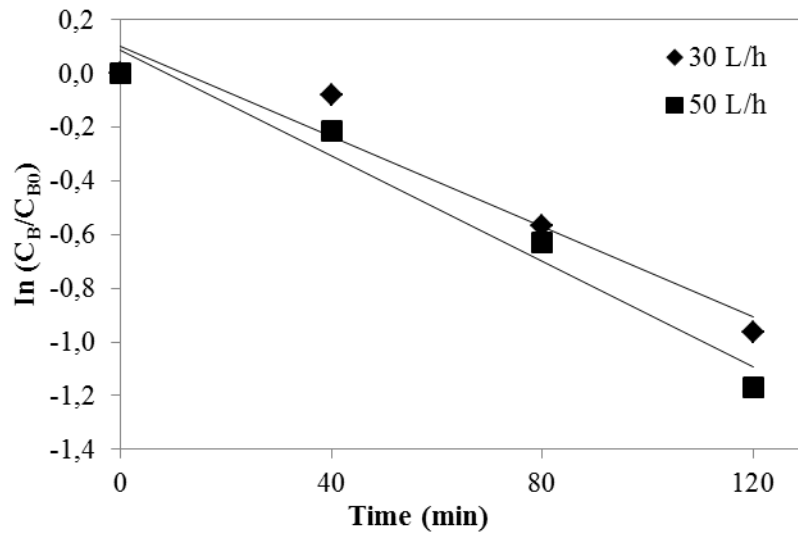


Figure 3.59. Linearization of boron concentrations ratio vs time plots obtained at different flow rates by MEGA model BMED system

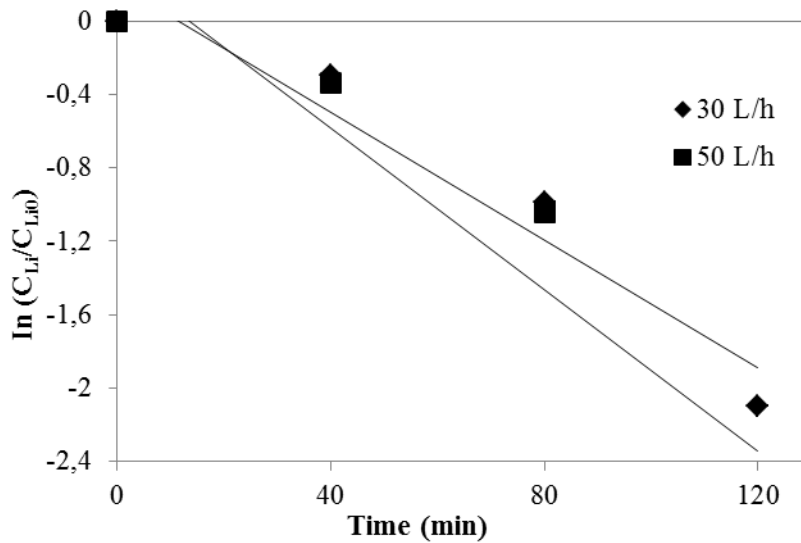


Figure 3.60. Linearization of lithium concentrations ratio vs time plots obtained at different flow rates by MEGA model BMED system

Mass transfer coefficients calculated at different flow rate of feed were given in Table 3.4. Mass transfer coefficients of lithium and boron increased when flow rate of feed was increased. Since removal of boron and lithium were increased when flow rate of the sample solution was increased, mass transfer coefficient of boron and lithium increased accordingly.

Table 3.4. Mass transfer coefficients calculated at different flow rates by MEGA model BMED system

	30 L/h	50 L/h
$k_B \cdot 10^6$ (m/s)	4.18	5.07
$k_{Li} \cdot 10^6$ (m/s)	9.10	11.72

3.3 Comparison of test results obtained by three different BMED systems

In this step, some tests which were carried out with MEGA and ASTOM ACILYZER BMED systems are conducted with PC-Cell BMED system and the results obtained by these three different BMED systems were compared. This study was useful to see the influence of membranes in different BMED systems since three BMED systems have different ion exchange membranes.

When three BMED systems were compared, all experimental conditions and initial parameters were kept constant. Lithium and boron concentrations in sample solutions were set as 340 mg/L and 1000 mg/L, respectively. A solution of 0.05 M HCl and 0.05 M NaOH solutions were employed in acid and base chambers and experiments were conducted at 20 V.

From the boron and lithium removal point of view, the best results were obtained with MEGA model BMED system. A 75.1% boron and 99.7% lithium from sample solution were removed with using this system (Figures 3.61 and 3.62). However, when the amount of boron in the acid chamber was calculated as boron recovery (%), the situation was completely different. Maximum lithium and boron recoveries were obtained with PC-Cell BMED system. Maximum boron and lithium recoveries obtained with PC-Cell BMED system were 48.9% and 76.3%, respectively (Figures 3.63 and 3.64).

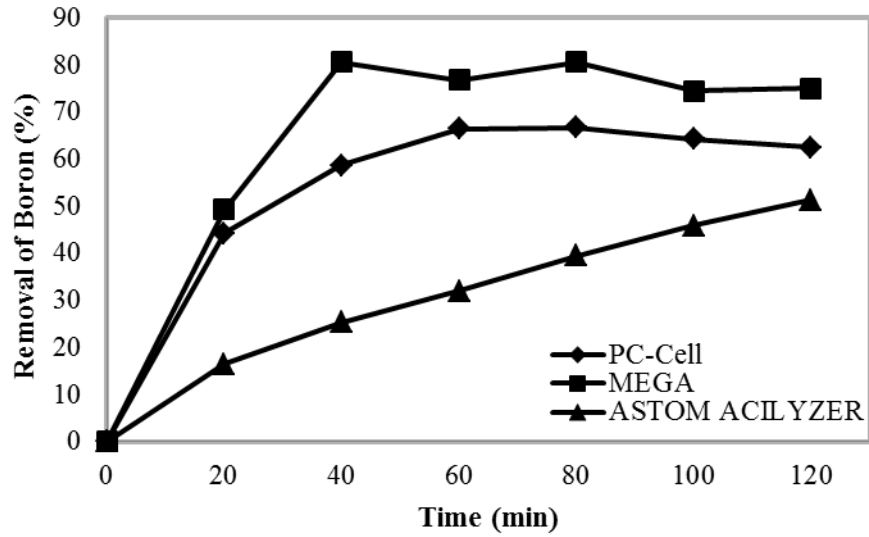


Figure 3.61. Removal of boron vs time by different BMED systems

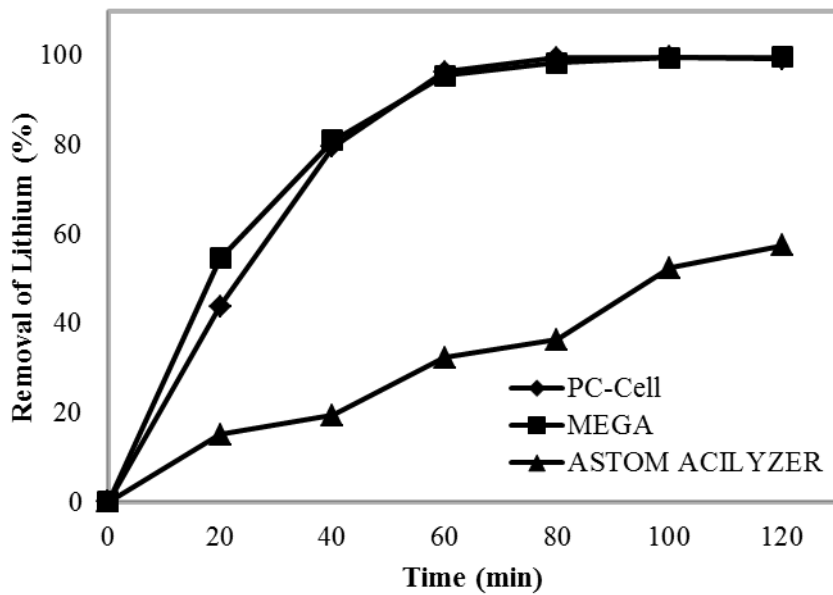


Figure 3.62. Removal of lithium vs time by different BMED systems

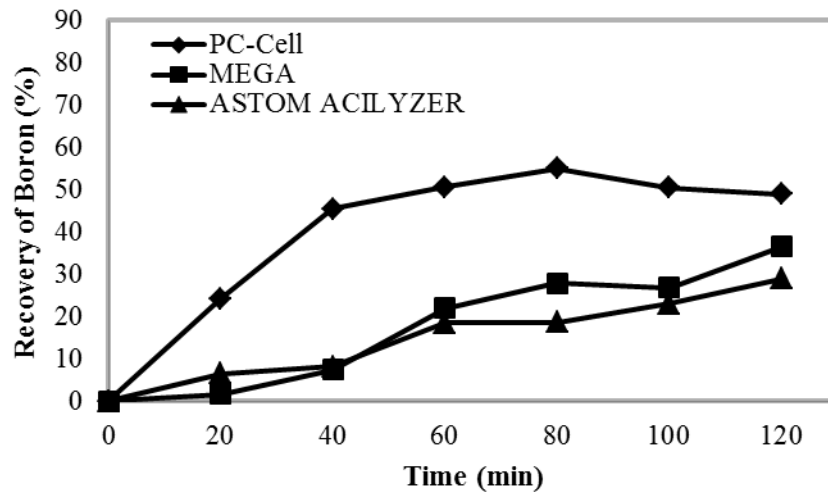


Figure 3.63. Recovery of boron vs time by different BMED systems

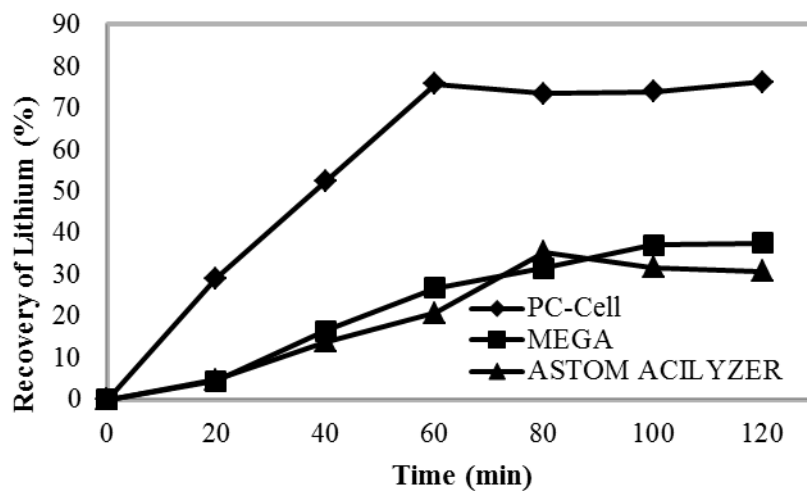


Figure 3.64. Recovery of lithium vs time by different BMED systems

3.4 Comparison of Results obtained with PC-Cell and MEGA model BMED System Results

3.4.1 Comparison at 20 V

Experiments were conducted at constant experimental conditions with MEGA and PC-Cell BMED systems. Results of these experiments obtained by two systems were compared. While these two different systems were compared, all experimental conditions and initial parameters kept constant. The sample solution had a boron concentration of 1000 mg/L and a lithium concentration of

340 mg/L. In acid base chambers, 0.003M HCl and 0.003 M NaOH solutions were used and experiments were conducted at 20 V of electrical potential.

When MEGA and PC-CELL BMED systems were compared, removals of lithium and boron from feed were faster when PC-CELL model BMED system was used. However, boron and lithium removals with two different BMED systems obtained at the end of 2 h were close to each other. Maximum removals of lithium and boron obtained with MEGA BMED system were 99.8% and 71.6%, respectively at the end of 2 h. Maximum removals of boron and lithium with PC-Cell BMED system were 99.7% and 71.6%, respectively at the end of 2 h. (Figures 3.65 and 3.66).

Maximum lithium recovery obtained with PC-Cell BMED system was 68.3% while maximum lithium recovery obtained with MEGA BMED system was 63.9%. According to the result, it can be said that PC-Cell BMED system membranes performed better for lithium recovery (Figure 3.67). However, the situation was different when boron recovery was examined. Although, removal and recovery of boron obtained with PC-Cell BMED system were better during initial an hour, it was observed that removal and recovery of boron decreased to some extent with PC-Cell BMED system. The reason for this situation was considered to be possibly back diffusion of boron after 1 h. The same situation was not observed while MEGA BMED system was used and recovery of boron was increased constantly, after a while this increment was constant as expected. The highest boron recovery obtained with MEGA BMED system was 53.4% while maximum boron recovery obtained with PC-Cell BMED system was 47.6% (Figure 3.68).

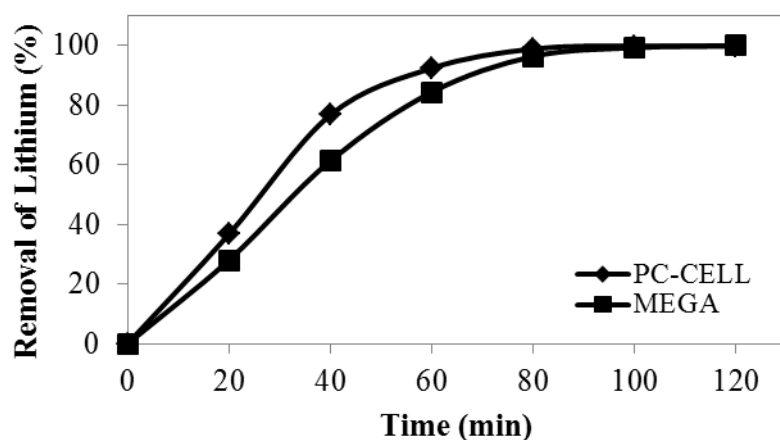


Figure 3.65. Removal of lithium by two different BMED systems

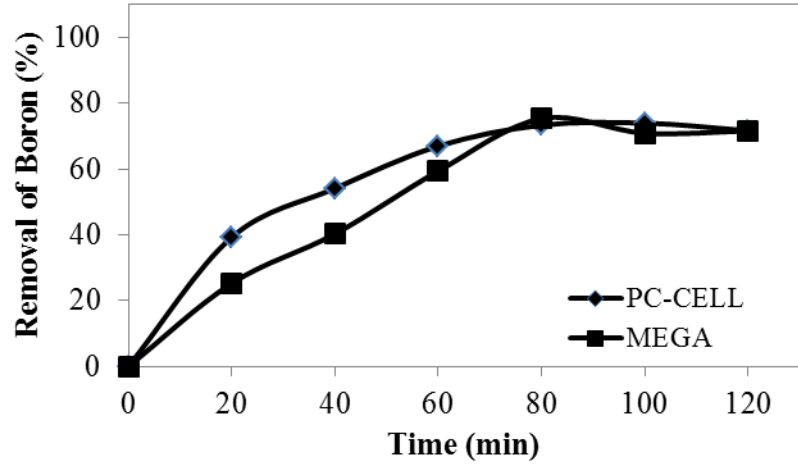


Figure 3.66. Removal of boron by two different BMED systems

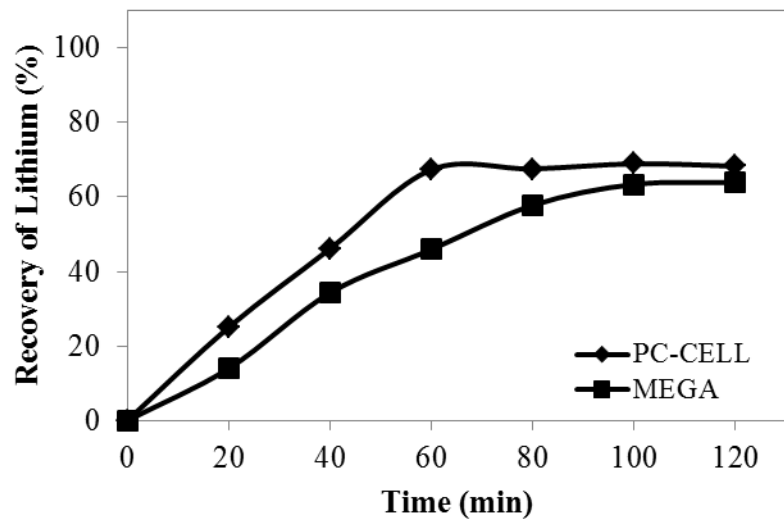


Figure 3.67. Recovery of lithium by two different BMED systems

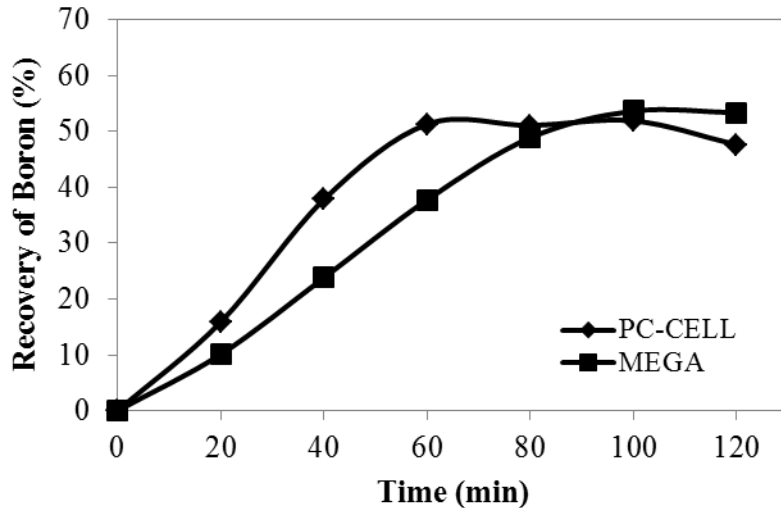


Figure 3.68. Recovery of boron by two different BMED systems

3.4.2 Comparison at 15 V

A second comparative study with PC-CELL and Mega model BMED systems was conducted with constant experimental conditions and the obtained results were compared. The sample solution had a boron concentration of 1000 mg/L and a lithium concentration of 340 mg/L. In acid-base chambers, 0.003 M HCl and 0.003 M NaOH solutions were used. The electrical potential applied was 15 V. When maximum removals of boron and lithium were compared for these BMED systems, there were almost no significant differences. Removal of lithium from sample solutions by PC-Cell and MEGA model BMED systems were obtained as 93.3% and 93.2%, respectively. Removal of boron from sample solution by PC Cell and MEGA BMED systems were obtained as 61.9% and 68.9%, respectively (Figures 3.69 and 3.70).

When these two systems were compared in terms of boron and lithium recovery, it was observed that PC-CELL BMED system results were better than MEGA BMED system results. Lithium recoveries obtained with PC-Cell and MEGA BMED systems were 78.0% and 57.0%, respectively. Recoveries of boron by PC Cell and MEGA BMED systems were 48.9% and 40.5%, respectively (Figures 3.71 and 3.72). This situation showed once more that PC-Cell BMED system membranes performed better than MEGA model BMED system for lithium and boron recoveries. Back diffusion of boron occurred in previous experiment conducted with PC-Cell BMED systems at 20 V of electrical potential. However, when electrical potential decreased to 15 V, back diffusion of boron was not occurred at PC-Cell model BMED system. Based on this result,

when working with the PC-CELL BMED system, it is possible to study at lower electrical potentials than with MEGA BMED system to achieve better lithium and boron recoveries. The reason for the need to work at higher electrical potentials when working with the MEGA BMED system is the electrical resistance of membranes during ion transfer because the membranes in the stack of the MEGA BMED system are thicker than the membranes of the PC-Cell BMED system membrane module. For this reason, when working with MEGA BMED system, higher electrical potentials are needed.

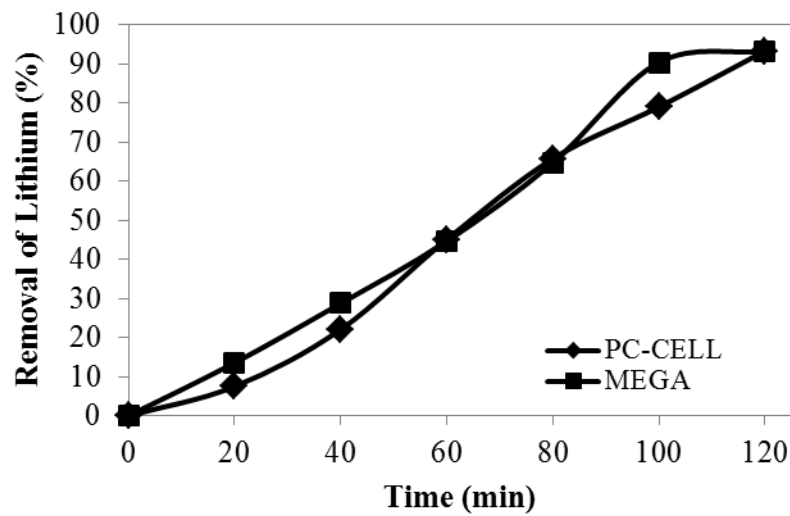


Figure 3.69. Removal of lithium by two different BMED systems

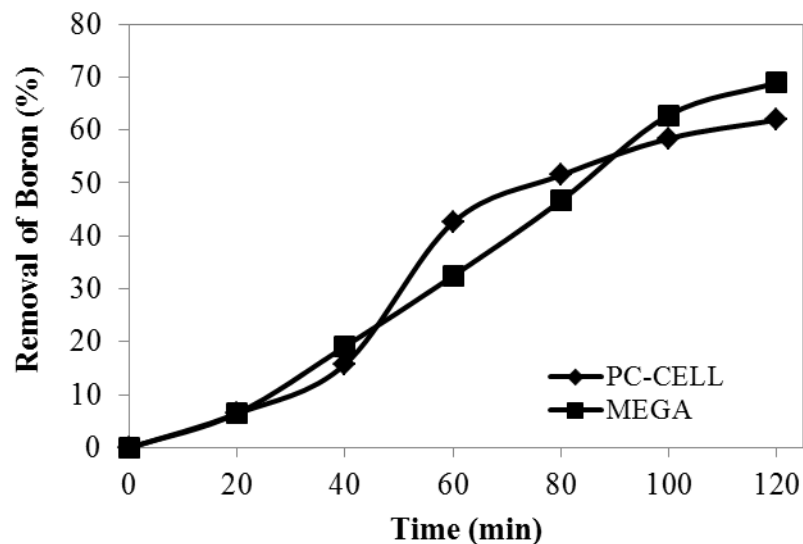


Figure 3.70. Removal of boron by two different BMED systems

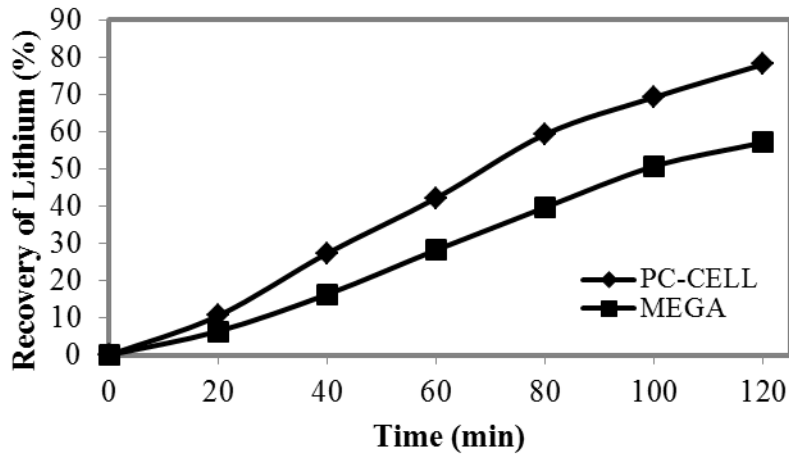


Figure 3.71. Recovery of lithium by two different BMED systems

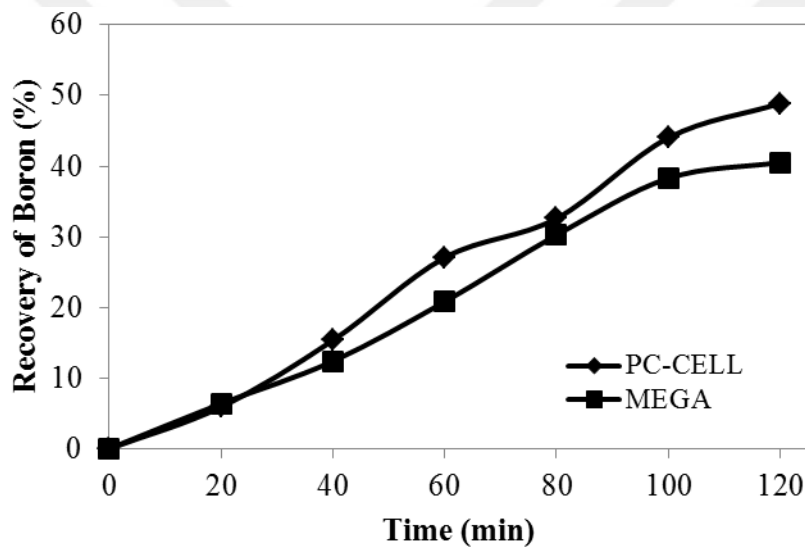


Figure 3.72. Recovery of boron for by two different BMED systems

3.5 Cost Analysis

3.5.1 Cost Analysis for ASTOM ACILYZER Model BMED System

The specific power consumptions calculated for three different acid-base solutions with different concentrations used in acid and base chamber were 8.9 kWh/m^3 (0.1 M HCl-0.1 M NaOH), 7.9 kWh / m^3 (0.05 M HCl-0.05 M NaOH), and 5.3 kWh/m^3 (0.005 M HCl-0.005 M NaOH). As the acid and base concentrations were increased, electrical current passed through the sample solution increased and this situation lead to increase in specific power consumption (SPC). But the fact that the SPC is high does not mean that the recovery is also high. When the percentage recoveries of boron and lithium in acid

and base chambers are taken into account, it is possible to say that HCl and NaOH solutions with a concentration of 0.05 M are the most suitable solutions for the study. The SPC using 0.05 M HCl and 0.05 M NaOH solutions in acid and base chamber is 7.9 kWh / m³ (Figure 3.73).

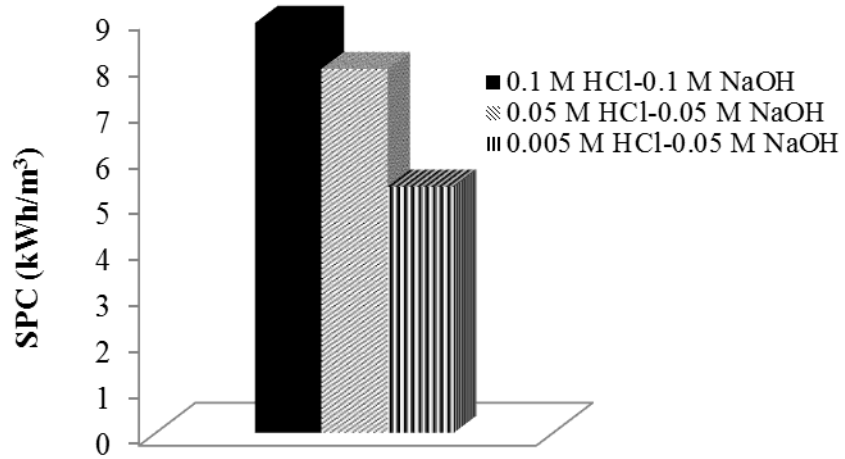


Figure 3.73. Influence of acid and base solutions on SPC calculated for ASTOM ACILYZER model BMED system

When the SPC values obtained at several electrical potentials (15, 20 and 30 V) was considered, SPC increased with an increase in electrical potential as expected. When 0.05 M HCl-0.05 M NaOH was used as the acid and base solutions in the acid and base chambers, SPC for 15, 20 and 30 V electrical potentials were respectively 1.6, 3.3 and 7.9 kWh / m³ (Figure 3.74).

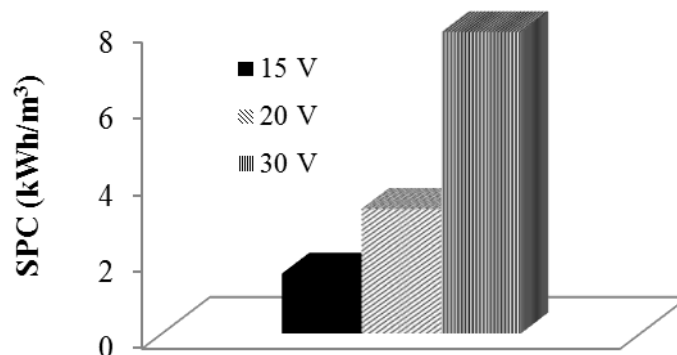


Figure 3.74. Influence of electrical potential applied on SPC calculated for ASTOM ACILYZER model BMED system

When 0.05 M HCl-0.05 M NaOH solutions were changed with 0.05 M H_3BO_3 -0.05 M LiOH in acid and base chambers under 30 V of electrical potential, SPC also increased. In this case, SPC increased from 7.9 kWh/m³ to 9.4 kWh/m³ (Figure 3.75).

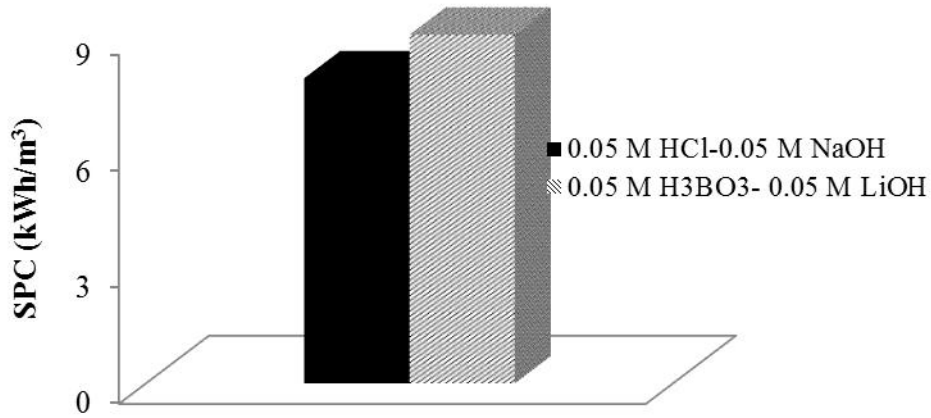


Figure 3.75. SPC obtained with different acid and base types for ASTOM ACILYZER model BMED system

When the HCl-NaOH acid-base pair was changed with H_3BO_3 -LiOH in acid and base chambers and initial concentrations of the solutions were increased, 0.1 M H_3BO_3 - 0.1 M LiOH solutions under the 30 V of electrical potential gave higher SPC as well. When 0.1 M H_3BO_3 and 0.1 M LiOH acid-base pairs were used under the 30 V electrical potential, the SPC was calculated as 8.9 kWh/ m³ (Figure 3.76).

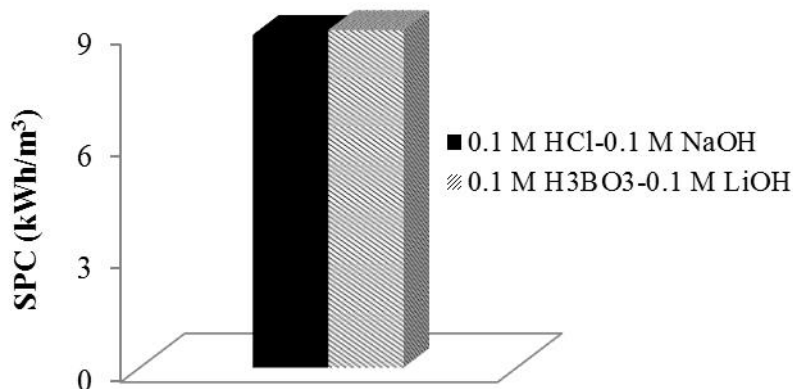


Figure 3.76. SPC obtained using different acid and base solutions for ASTOM ACILYZER BMED system

3.5.2 Cost Analysis for Mega Model BMED System

When we look at the SPC at different acid-base concentrations, the MEGA model BMED system gave similar results with the ASTOM ACILYZER model BMED system. As the concentrations of acid-base solutions in acid and base chambers were increased, SPC also increased. The optimum acid-base concentrations for the MEGA model BMED system were found as 0.003 M HCl-0.003 M NaOH. The specific power consumption for optimum conditions at 20 V electrical potential was found as 3.2 kWh/m³ (Figure 3.77).

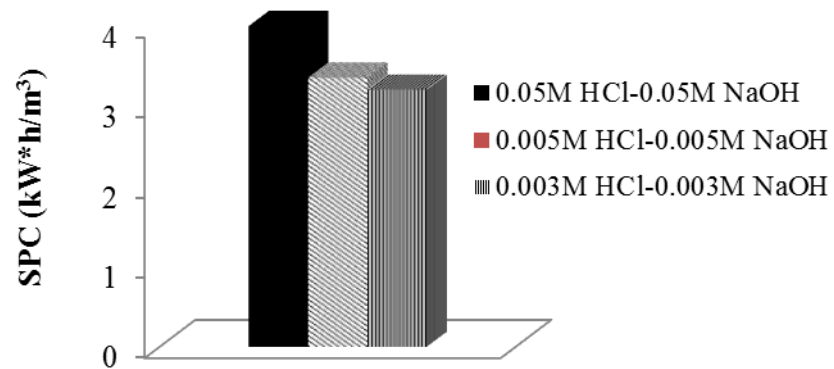


Figure 3.77. SPC obtained at different acid and base concentrations for MEGA model BMED system

As the electrical potential increased the specific power consumption also increased. When 0.003 M HCl-0.003 M NaOH was used in acid and base chambers, the SPC at 25 V with using which is the optimum electrical potential, was calculated as 4.1 kWh/m³ (Figure 3.78).

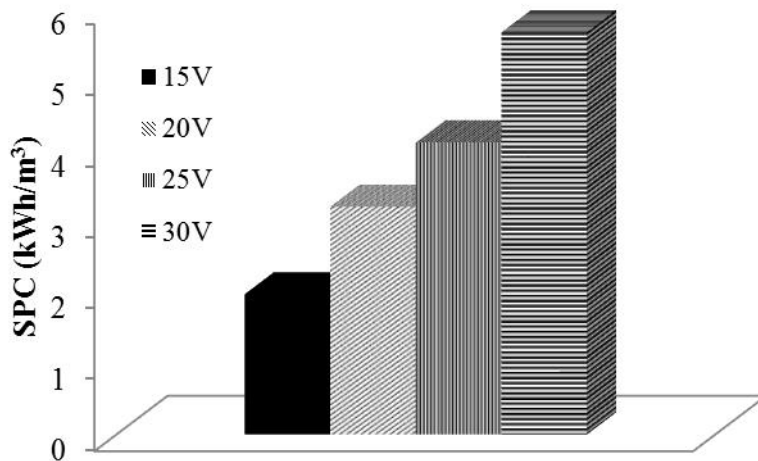


Figure 3.78. SPC obtained at different applied electrical potentials for MEGA BMED system

As in the ASTOM ACILYZER model BMED system, using of H_3BO_3 -LiOH instead of HCl-NaOH under the constant electrical potential (25 V) were resulted in slight increase in SPC for MEGA model BMED system (Figure 3.79).

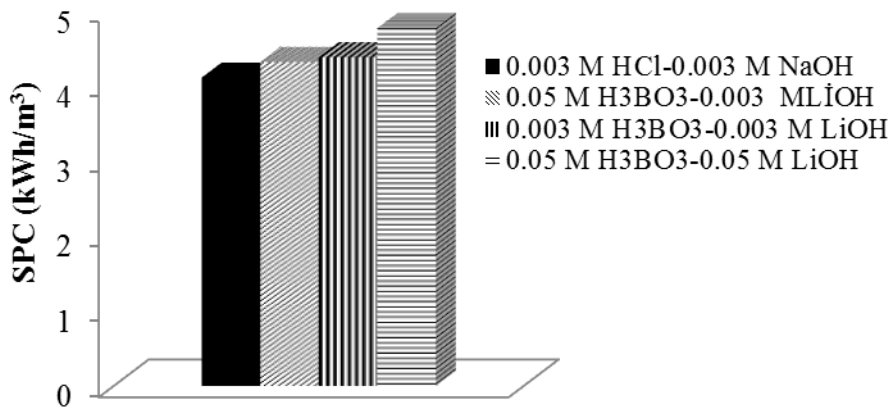


Figure 3.79. SPC obtained with different initial acid and base solutions for MEGA model BMED system

As it can be seen in Figure 3.80, the SPC increased with pH increase in sample solution. SPC was calculated as 3.2 kWh/m^3 , 7.2 kWh/m^3 and 8.5 kWh/m^3 for pH 9.11, pH 10.00 and pH 11.00, respectively under 25 V electrical potential when used 0.003 M HCl-0.003 M NaOH in acid and base chambers (Figure 3.80).

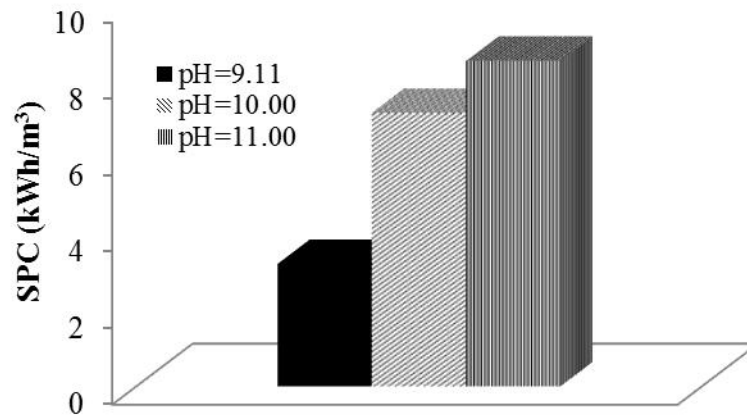


Figure 3.80. SPC at different pH of the sample solution for MEGA model BMED system

As shown in Figure 3.81, SPC decreased with increasing feed flow rate. However, in this case, it would not be right to do a cost analysis based solely on SPC due to electrical current by ion transport. Because increasing flow rate of the solution lead to increase electrical power for pumping cost also. However, SPC does not include pumping cost.

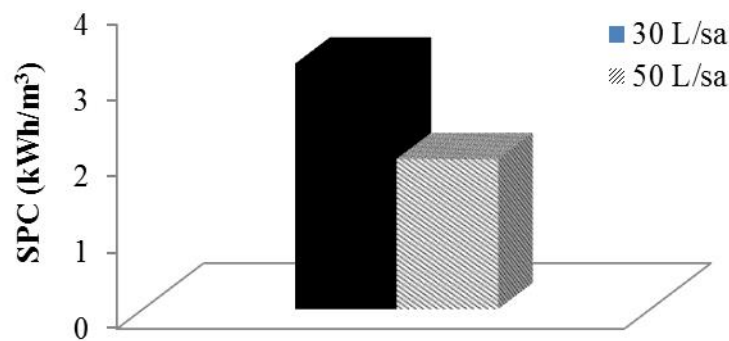


Figure 3.81. SPC at two different flow rates for MEGA model BMED system

In experiments with BMED systems containing three different BMED stacks, SPC were calculated and compared. For these tests, sample solution containing 340 mg Li/L and 1000 mg B/L was prepared. 0.05 M HCl-0.05 M NaOH was used in acid and base chambers and 20 V of electrical potential was applied. The SPC calculation was based on electrical energy required to transfer boron and lithium to acid and base chambers from 1 m³ of sample solution. The SPC values were calculated for ASTOM ACILYZER, MEGA and PC-Cell

BMED systems were 3.25 kWh/m^3 , 4.00 kWh/m^3 and 4.31 kWh/m^3 respectively (Figure 3.82).

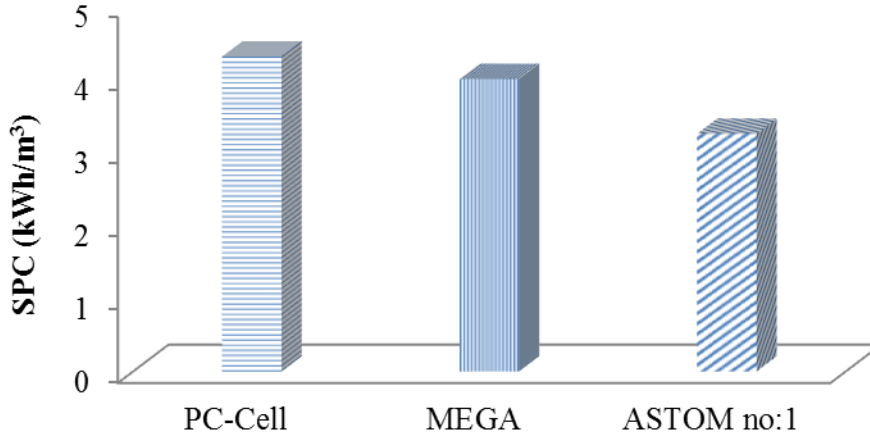


Figure 3.82. SPC values calculated for three different BMED systems

When comparing MEGA and PC-Cell BMED systems for SPC, the SPC value of the PC-CELL BMED system was slightly higher than the SPC of the MEGA BMED system. For these tests, sample solution containing 340 mg Li/L and 1000 mg B/L was prepared. 0.003 M HCl and 0.003 M NaOH solutions were used in acid and base chambers and 20 V of electrical potential was applied. PC-Cell and MEGA BMED systems have SPC of 3.46 kWh/m^3 and 3.21 kWh/m^3 , respectively under this condition (Figure 3.83).

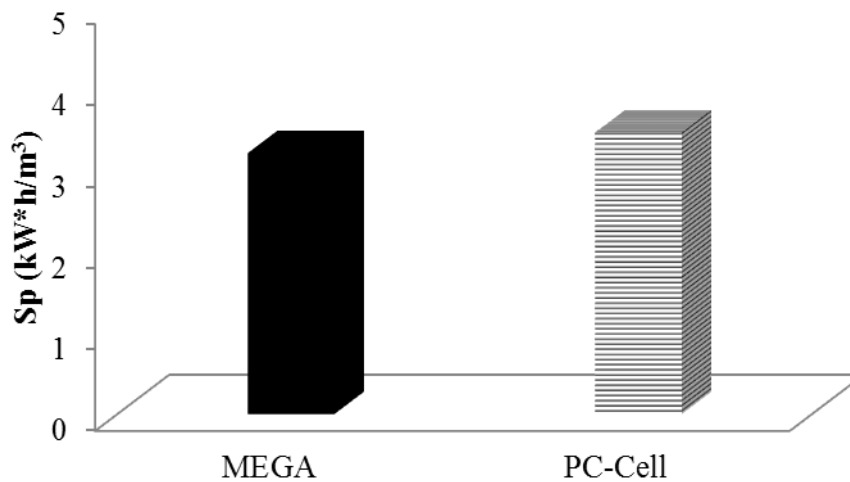


Figure 3.83. SPC values for two different BMED system

Compared to MEGA and PC-CELL BMED systems for SPC, the PC-CELL BMED system was found to have higher SPC in the first experimental conditions as well as in the second experimental conditions. For these tests, sample solution containing 340 mg Li/L and 1000 mg B/L was prepared. 0.003 M HCl-0.003 M NaOH was used in acid and base chambers and 15 V of electrical potential was applied. The SPC obtained with the MEGA BMED system and the PC-CELL BMED systems were 1.98 kWh/m³ and 2.89 kWh/m³, respectively (Figure 3.84).

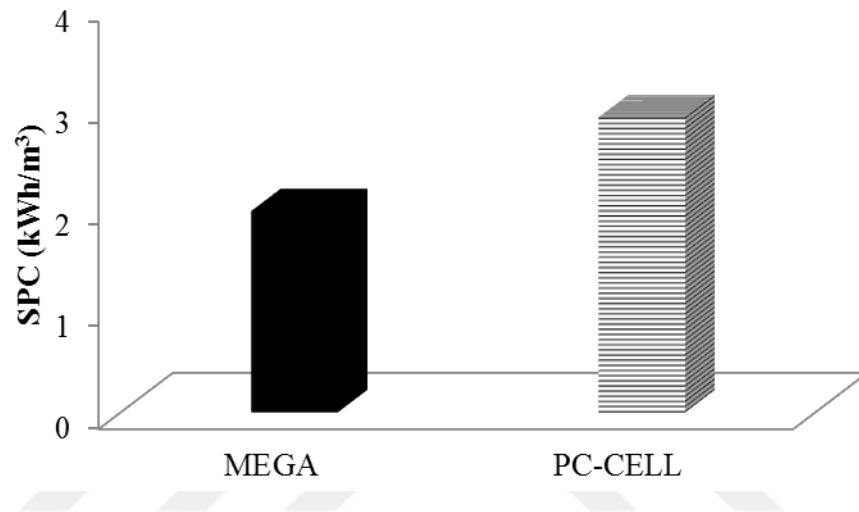


Figure 3.84. SPC values for two different BMED systems

4.0 CONCLUSIONS

In this research, removals and recoveries of lithium and boron from aqueous solutions by BMED method was investigated. Three different BMED systems were used in experiments. Influences of acid and base types and acid and base concentrations employed in acid and base chambers, and applied electrical potential on removal and recovery of boron and lithium from aqueous solution were investigated by using ASTOM ACILYZER BMED system. Influences of feed flow rate and pH of the sample solution on removals and recoveries of lithium and boron were also investigated in addition to the above parameters with MEGA BMED system used as second BMED system. The third BMED system was PC-Cell BMED system. Some of experiments that were carried out by other BMED systems were also done by using PC-Cell BMED system and these three different BMED systems were compared. The results obtained were listed below:

1) The initial concentrations of acid-base solutions in acid and base chambers have a significant influence on removals and recoveries of lithium and boron from aqueous solutions as a result of experiments with ASTOM ACILYZER and MEGA BMED systems. It was determined that the high initial acid-base solutions concentrations in acid and base chambers may cause back diffusion in boron and lithium recovery, while low acid and base concentrations were not able to form a good conductive area for ion transfer.

2) When applied electrical potential was increased, separations and recoveries of lithium and boron from sample solutions increased unless a significant pH drop occurs in the sample solution. Additionally, the using of H_3BO_3 and LiOH instead of HCl and NaOH did not cause to any leakage problem. However, when H_3BO_3 and LiOH solutions in acid-base chambers was used instead of HCl –NaOH solutions, initial acid and base concentrations should be increased to create a good conductive area.

3) It was found that optimum process conditions were different for ASTOM ACILYZER model BMED system and MEGA model BMED system. The reason for this is that the membranes in the membrane stacks of both systems have different characteristics. Optimum process conditions were determined as 30 V of electrical potential, 0.05 M HCl-0.05 M NaOH solutions in acid and base chambers for ASTOM ACILYZER BMED system. When MEGA BMED system was used, optimum process conditions were 25 V of electrical potential and 0.003 M HCl-0.003 M NaOH solutions in acid-base chambers.

4) Influences of feed flow rate and pH of the sample solution were investigated by using MEGA BMED system. Two different flow rates were tested (30 L/h and 50 L/h) and it was seen that recoveries of boron and lithium decreased with decreasing flow rate. This situation is caused by the increased partial adsorption of lithium and boron on the membrane surface because of the increasing contact time between solution and membranes at low feed flow rate. However, this might be prevented by increasing experiment duration or increasing feed flow rate.

Influences of sample solution pH were investigated by using MEGA model BMED system. Two different pH values were tested in addition to pH of sample solution itself. More boron can be recovered by increasing pH of the sample solution. When pH of the sample solution was not adjusted, borate ions in the sample solution are converted into boric acid with decreasing sample solution pH. Since boric acid is neutral, boron transfer to acid chamber from sample solution does not take place. According to the obtained results, the highest boron and lithium recoveries were obtained when pH of the sample solution was arranged to 10.

5) According to the all experimental results carried out by using MEGA model BMED system, optimum process conditions were determined as 50 L/h of feed flow rate, 25 V of electrical potential, 0.003 M HCl-0.003 M NaOH solutions in acid and base chambers and pH 10.

6) After optimization of ASTOM ACILYZER BMED system and MEGA BMED system, some experiments were also carried out by PC-Cell BMED system using the optimal conditions of other two BMED systems. These BMED systems that have different membranes were compared. As result of these comparisons studies, highest lithium and boron recoveries were obtained by using PC-Cell BMED system. In order to compare three BMED systems, sample solution containing 340 mg/Li/L and 1000 mg B/L and 0.05 M HCl-0.05 M NaOH solutions in acid and base chambers were used and 20 V of electrical potential was applied. As a result of comparison studies, it was possible to say that PC-Cell BMED system membranes have better performance for boron and lithium than other two systems.

7) From the standpoint of SPC, the SPC changes according to applied electrical potential. The SPC also increased when high concentrations of acid-base solutions were used. This is caused by concentration polarization that occurs

when acid-base solutions with high initial concentrations were used. This prevents the ion transfers to the acid and base chambers. When the flow rate of the feed solution is increased, the SPC required for ion transfer from the membranes decreased. Flow rate increase resulted with the partial adsorption reduction of ions on the membrane, thus transfer of ions was carried out easily. The increasing of the flow rate of the feed decreased the SPC but it caused increase in the electrical power consumed by pumps. When the pH of the solution was increased by using LiOH to increase boron recovery, the SPC increased again. This is due to the increase in the amount of lithium ion transferred, due to the increase in lithium ions in the solution. The increase in the amount of lithium ion transferred resulted in an increased integrated current, which in turn increased the SPC.

8) SPC values were different when different BMED systems were used at constant experimental conditions. The reason of this result is that these three BMED systems include different membranes. Thickness of the membranes increases the ion transfer resistance and membrane electrical resistance, thus for decreasing electrical current. Since there is direct proportion between SPC and integrated electrical current, increasing of electrical current that passing through membranes lead to increase in SPC. As membranes in the PC-Cell BMED device are thinner than the membranes in the ASTOM ACILYZER BMED system and MEGA BMED system, electrical current passing through membranes are higher than other two systems. As a result of this, the SPC obtained with PC-Cell BMED device is more than that of the ASTOM ACILYZER BMED and MEGA BMED system.

All experimental conditions and results were summarized by Tables 4.1-4.3

Table 4-1. Boron and lithium recoveries and SPC values obtained with ASTOM ACILYZER model BMED system

Acid and Base Solutions in Acid-Base Chambers	Electrical Potential (V)	Recovery (%)		SPC (kWh/m ³)
		Boron	Lithium	
0.1 M HCl-0.1 M NaOH	30	27	33	8.9
0.05 M HCl-0.05 M NaOH	30	50	62	7.9
0.005 M HCl-0.005 M NaOH	30	47	54	5.3
0.05 M HCl-0.05 M NaOH	15	12	25	1.6
0.05 M HCl-0.05 M NaOH	20	29	31	3.3
0.05 M H ₃ BO ₃ -0.05 M LiOH	30	21	49	9.4
0.1 M H ₃ BO ₃ -0.1 M LiOH	30	62	56	9.4

Table 4-2. Boron and lithium recoveries and SPC obtained with MEGA model BMED system

Acid-Base Solutions in Acid-Base Chambers	Electrical Potential (V)	Flow rate (L/h)	pH	Recovery (%)		SPC (kWh/m ³)
				Boron	Lithium	
0.003 M HCl-0.003 M NaOH	15	30	9.19±0.07	21	30	3.23
0.003 M HCl-0.003 M NaOH	15	50	9.19±0.07	41	57	1.98
0.05 M HCl-0.05 M NaOH	20	50	9.19±0.07	37	38	4.0
0.005M HCl-0.005 M NaOH	20	50	9.19±0.07	41	54	3.4
0.003M HCl-0.003 M NaOH	20	50	9.19±0.07	55	66	3.21
0.003 M HCl-0.003 M NaOH	25	50	9.19±0.07	59	73	4.11
0.003M HCl-0.003 M NaOH	30	50	9.19±0.07	50	74	5.66
0.05M H ₃ BO ₃ -0.003 M LiOH	25	50	9.19±0.07	50	67	4.3
0.003 M H ₃ BO ₃ -0.003 M LiOH	25	50	9.19±0.07	51	72	4.4
0.05 M H ₃ BO ₃ -0.05 M LiOH	25	50	9.19±0.07	47	71	4.8
0.003 M HCl- 0.003 M NaOH	25	50	10.00	66	71	7.2
0.003 M HCl-0.003 M NaOH	25	50	11.00	56	64	8.5

Table 4-3. A comparison for boron and lithium recoveries and SPC by different BMED systems

Acid-Base Solutions in Acid-Base Chambers	Electrical Potential (V)	Flow rate (L/h)	pH	Recovery (%)		SPC (kWh/m ³)
				Boron	Lithium	
0.003 M HCl-0.003 M NaOH	15	30	9.19±0.07	21	30	3.23
0.003 M HCl-0.003 M NaOH	15	50	9.19±0.07	41	57	1.98
0.05 M HCl-0.05 M NaOH	20	50	9.19±0.07	37	38	4.0
0.005M HCl-0.005 M NaOH	20	50	9.19±0.07	41	54	3.4
0.003M HCl-0.003 M NaOH	20	50	9.19±0.07	55	66	3.21
0.003 M HCl-0.003 M NaOH	25	50	9.19±0.07	59	73	4.11
0.003M HCl-0.003 M NaOH	30	50	9.19±0.07	50	74	5.66
0.05M H ₃ BO ₃ -0.003 M LiOH	25	50	9.19±0.07	50	67	4.3
0.003 M H ₃ BO ₃ -0.003 M LiOH	25	50	9.19±0.07	51	72	4.4
0.05 M H ₃ BO ₃ -0.05 M LiOH	25	50	9.19±0.07	47	71	4.8
0.003 M HCl- 0.003 M NaOH	25	50	10.00	66	71	7.2
0.003 M HCl-0.003 M NaOH	25	50	11.00	56	64	8.5

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Oral Presentations

- İpekçi, D., Bunani, S., Kabay, N., Arda, M., Yuksel, M., (2017), Separation of Boron and Lithium From Aqueous Solutions Via Bipolar Membrane Electrodialysis (BMED)-Influence of Initial Acid and Base Concentrations”, 2nd IWA Regional Symposium on Water, ORAL PRESENTATION, ABSTRACT
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Posters

- Altıok, E., Bunani, S., İpekçi, D., Kabay, N., Arda, M., Yuksel, M., (2016), Concentrate Management of Groundwater Reverse Osmosis Brine by a Hybrid Process Based on Electrodialysis (ED) and Electrodeionization (EDI) “, Recycle& Reuse, İstanbul.-POSTER, ABSTRACT
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APPENDIX (Raw data)

Table A1. Astom Acilyzer Experimental Results with 0.1 M HCl-0.1M NaOH in acid and base chambers at 30 V (Figures 3.1, 3.2, 3.3, 3.4, 3.5, 3.6 , 3.7 3.22, 3.23, 3.24, 3.25, 3.26, 3.27,3.28)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	1025	329	0	0
20	705	192	1797	433
40	457	106	3225	1060
60	244	45,6	2750	1220
80	207	31,4	3775	1490
100	153	20,9	3150	1220
120	115	17	2800	1080

Table A2. Astom Acilyzer Experimental Results with 0.05 M HCl-0.05 M NaOH in acid and base chambers at 30 V (Figures 3.1, 3.2, 3.3 , 3.4, 3.5, 3.6, 3.7, 3.15, 3.16, 3.17,3.18, 3.19, 3.20 and 3.21)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	1010	303	0	0
20	680	173	2415	825
40	452	93	3500	1290
60	305	53	4975	1540
80	215	31	5150	1570
100	171	23	5075	1890
120	132	16	5025	1880

Table A3. Astom Acilyzer Experimental Results with 0.005 M HCl-0.005 M NaOH in acid and base chambers at 30 V (Figures 3.1, 3.2, 3.3 , 3.4, 3.5,3.6 ,3.7)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	950	285	0	0
20	875	250	705	331
40	720	190	1838	772
60	565	140	2675	1140
80	451	102	3025	1380
100	341	70	3850	1430
120	261	48	4450	1550

Table A4. Astom Acilyzer Experimental Results with 0.05 M HCl-0.05 M NaOH in acid and base concentrations at 15 V (Figures 3.8, 3.9,3.10,3.11,3.12, 3.13, 3.14 and)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	1000	333	0	0
20	990	288	476	343
40	970	282	965	589
60	868	256	1200	667
80	842	246	1550	745
100	732	219	1388	770
120	572	166	1468	823

Table A5. Astom Acilyzer Experimental Results with 0.05 M HCl-0.05 M NaOH in acid and base chambers at 20 V (Figures 3.8, 3.9, 3.10, 3.11, 3.12 and 3.13)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	1000	303	0	0
20	835	257	648	145
40	748	244	818	417
60	680	205	1850	628
80	605	193	1865	1070
100	541	144	2300	960
120	487	129	2885	934

Table A6. Astom Acilyzer Experimental Results with 0.05 M H₃BO₃-0.05 M LiOH in acid and base chambers at 30 V (Figures 3.15, 3.16, 3.17,3.18, 3.19, 3.20 and 3.21)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	1030	299	540	292
20	579	44	1490	800
40	269	28	2097	1260
60	216	16	3550	1950
80	184	7	3150	1860
100	131	6	2950	1890
120	100	6	2725	1770

Table A7. Astom Acilyzer Experimental Results with 0.1 M H₃BO₃-0.1 M LiOH in acid and base chambers at 30 V (Figures 3.22, 3.23, 3.24, 3.25, 3.26, 3.27,3.28)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	970	323	885	527
20	695	198	2430	1230
40	465	120	4250	1890
60	285	54	5350	1790
80	228	39	5825	2200
100	199	28	5425	2300
120	126	22	6875	2330

Table A8. MEGA BMED system Experimental Results with 0.05 M HCl -0.05 M NaOH in acid and base chambers at 20 V (Figures 3.29, 3.30, 3.31, 3.32 , 3.33 and 3.34)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	914	287	0	0
20	464	130	62	51
40	178	54	269	187
60	213	13	805	307
80	178	5	1020	361
100	234	2	982	425
120	228	0,8	1334	431

Table A9. MEGA BMED system Experimental Results with 0.005 M HCl -0.005 M NaOH in acid and base chambers at 20 V (Figures 3.29, 3.30, 3.31, 3.32 , 3.33, 3.34,3.35 and 3.35)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	886	254	0	0
20	591	135	291	169
40	207	54	584	321
60	285	15	871	445
80	230	4	1199	521
100	214	1	1315	553
120	218	0,6	1445	545

Table A10. MEGA BMED system Experimental Results with 0.003 M HCl -0.003 M NaOH in acid and base chambers at 20 V (Figures 3.29, 3.30, 3.31, 3.32 , 3.33, 3.34, 3.35 and 3.43)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	760	260	0	0
20	604	185	258	110
40	477	104	699	324
60	309	38	1074	498
80	162	10	1408	593
100	214	2,5	1540	658
120	197	0,5	1668	687

Table A11. MEGA BMED system Experimental Results with 0.003 M HCl -0.003 M NaOH in acid and base chambers at 15 V electrical potential (Figure 3.36, 3.37, 3.38, 3.39,3.40 ,3.41 and 3.42 and 3.43)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	834	253	0	0
20	780	218	213	64
40	674	180	413	165
60	564	140	694	285
80	445	89	1009	401
100	310	24	1277	513
120	259	17	1352	577

Table A12. MEGA BMED system Experimental Results with 0.003 M HCl -0.003 M NaOH in acid and base chambers at 25 V electrical potential (Figure3.36, 3.37, 3.38, 3.39,3.40, 3.41 and 3.42, 3.43)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	781	216	0	0
20	6023	153	400	149
40	422	88	1005	359
60	270	25	1454	519
80	207	5	1790	618
100	201	1	1850	632
120	200	0,2	1846	626

Table A13. MEGA BMED system Experimental Results with 0.003 M HCl -0.003 M NaOH in acid and base chambers at 30 V electrical potential (Figure 3.36, 3.37, 3.38, 3.39,3.40, 3.41 and 3.42, 3.43)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	838	243	0,0	0,0
20	520	146	641	314
40	325	38	1246	568
60	238	4,6	1590	717
80	221	2,0	1674	731
100	203	0,8	1713	706
120	218	0,2	1687	716

Table A14. MEGA BMED system Experimental Results with 0.05 M H₃BO₃ -0.003 M LiOH in acid and base chambers at 25 V (Figures 3.44, 3.45 ,3.46, 3.47, 3.48, 3.49, 3.50)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	887	235	344	17
20	715	181	515	140
40	439	84	987	400
60	290	22	1420	626
80	229	6,8	1741	621
100	236	1,8	1972	630
120	213	0,3	2114	669

Table A15. MEGA BMED system Experimental Results with 0.003 M H₃BO₃ -0.003 M LiOH at 25 V ((Figures 3.44, 3.45 ,3.46, 3.47, 3.48, 3.49, 3.50))

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	912	323	29	21
20	766	265	101	93
40	512	142	316	315
60	304	36,8	560	698
80	226	3,6	1433	881
100	208	1,8	1629	912
120	211	0,0628	1904	953

Table A16. MEGA BMED system Experimental Results with 0.05 M H₃BO₃ -0.05 M in acid and base chambers at 25 V (Figures 3.44, 3.45 ,3.46, 3.47, 3.48, 3.49, 3.50))

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	893	289	477	226
20	791	250	668	285
40	492	118	1031	644
60	367	27	1752	871
80	243	0,5	1870	889
100	181	0,3	1950	1015
120	220	0,1	2160	1045

Table A17. MEGA BMED system Experimental Results with 0.003 M HCl -0.003 M NaOH in acid and base chambers at 25 V electrical potential pH=10.00 (Figures 3.51, 3.52, 3.53, 3.54, 3.55, 3.56, 3.57)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	863	363	0	0
20	484	253	435	192
40	416	236	1142	457
60	225	221	1446	563
80	104	123	1944	701
100	58	23	2269	973
120	47	17	2282	1037

Table A18. MEGA BMED system Experimental Results with 0.003 M HCl-0.003 M NaOH in acid and base chambers at 25 V electrical potential pH=11.0 (Figures 3.51, 3.52, 3.53, 3.54, 3.55, 3.56, 3.57)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	841	483	0	0
20	631	345	323	225
40	518	216	639	567
60	526	147	1519	970
80	103	67	1691	1190
100	32	19	1828	1276
120	12	10	1881	1244

Table A19. MEGA BMED system Experimental Results with 0.003 M HCl-0.003 M NaOH in acid and base chambers at 15 V electrical potential, flow rate 30 L/h (Figures 3.58, 3.59, 3.60,3.61, 3.62, 3.63 and 3.64)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	748	243	0	0
40	690	181	101	87
80	424	90	307	196
120	286	30	614	292

Table A20. PC-Cell BMED system Experimental Results with 0.003 M HCl-0.003 M NaOH in acid and base chambers at 20 V (Figures 69, 70, 71 and 72).

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	886	266	0	0
20	538	169	563	266
40	406	62	1342	491
60	293	21	1819	717
80	236	3,2	1812	719
100	231	0,7	1840	734
120	251	0,9	1688	727

Table A21. PC-Cell BMED system Experimental Results with 0.05 M HCl-0.05 M NaOH in acid and base chambers at 20 V (Figures 3.65, 3.66 ,3.67 and 3.68)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	853	262	0	0
20	476	148	825	305
40	352	54	1549	550
60	286	10	1724	795
80	284	1,2	1876	771
100	304	0,8	1721	777
120	319	1,8	1668	802

Table A22. PC-Cell BMED system Experimental Results with 0.05 M H₃BO₃-0.05 M LiOH in acid and base chambers at 20 V electrical potential (Figures 3.69, 3.70, 3.71 and 3.72)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	932	269	619	101
20	734	203	855	251
40	470	78	1686	619
60	286	28	2072	754
80	310	3,4	2102	725
100	288	1,4	2132	802
120	299	2,0	2179	829

Table A23. PC-Cell BMED system Experimental Results with 0.05 M HCl-0.05 M NaOH in acid and base chambers at 20 V (Figures 3.74, 3.3.75, 3.76 and 3.77)

Time (min)	Boron Concentration in Sample Solution (mg/L)	Lithium Concentration in Sample Solution (mg/L)	Boron Concentration in Acid Solution (mg/L)	Lithium Concentration in Base Solution (mg/L)
0	845	219	0	0
20	791	203	200	92
40	712	171	518	239
60	486	120	914	369
80	410	75	1102	519
100	352	46	1488	606
120	322	15	1652	683