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Research Article

Bipolar Membran Elektrodiyaliziyle Simüle Atıksu Çözeltisinden KOH ve HCl Üretimini Etkileyen Parametrelerin Belirlenmesi İçin Kesirli Faktöriyel Tasarım Uygulaması

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Öz

Bu çalışmanın amacı, kesirli faktöriyel tasarımını kullanarak bipolar membran elektrodiyaliz ile bir simüle atık çözelti olarak hazırlanan potasyum klorür çözeltisinden potasyum hidroksit ve hidroklorik asit üretimini etkileyen önemli faktörleri belirlemektir. Deneylerde kullanılan membran hücresi asit, tuz ve baz bölmelerinden oluşmaktadır. Asit ve baz üretimini etkileyen parametreleri değerlendirmek için kesirli faktöriyel 2^{4-1} tasarımı kullanılmıştır. Proses dört ana faktörün fonksiyonu olarak incelenmiştir. Bu faktörler, başlangıç asit ve baz konsantrasyonları, başlangıç tuz konsantrasyonu, akım yoğunluğu ve elektrolit konsantrasyonudur. Normal olasılık grafiği ve Pareto diyagramı, başlangıç tuz konsantrasyonunun bipolar membran elektrodiyaliz sistemini etkileyen en önemli parametre olduğunu ortaya koydu. Sonuçlar ayrıca ana etki grafikleri ve ANOVA yöntemi kullanılarak istatistiksel olarak analiz edildi. Başlangıç tuz konsantrasyonunun en etkin parametre olduğu her iki istatiksel bulguyla da doğrulandı.

Anahtar Kelimeler: Bipolar membran, Elektrodiyaliz, Kesirli faktöriyel tasarım.

Fractional Factorial Design Application for the Determination of Parameters Affecting KOH and HCl Generation From Simulated Wastewater Solution By Bipolar Membrane Electrodialysis

Abstract

The aim of the study is to determine the significant factors influencing the generation of potassium hydroxide and hydrochloric acid from simulated potassium chloride solution by bipolar membrane electrodialysis using fractional factorial design. The membrane stack with acid, dilute (salt), and base compartments was used in the experiments. Fractional factorial design 2^{4-1} was employed to evaluate the parameters affecting the production of base and acid. The process has been investigated as a function of four main factors namely, initial concentrations of acid and base, initial salt concentration, current density, and electrolyte concentration. Normal probability plot and Pareto charts revealed that the initial salt concentration is the most significant parameter affecting the bipolar membrane electrodialysis system performance. The results were also statistically analyzed by using the main effects plots and the ANOVA method. The significance of initial salt concentration was confirmed by both statistical findings.

Keywords: Bipolar membrane, Electrodialysis, Fractional factorial design.

1. Introduction

Sodium chloride (NaCl), potassium chloride (KCl), and bromide salts are extractable constituents from seawater. Seawater is accepted as a universal potassium source due to its ~ 390 mg K^+/L content (Ghara et al., 2014; Hussein, Zohdy, & Abdelkreem, 2017). There are several methods studied to recover KCl from seawater. Precipitation of KCl from naturally occurring brines and seawater is one of the most common methods (da Silva, Seckler, Rocha, Saturnino, & de Oliveira, 2017; Ghara et al., 2014; Hussein et al., 2017; Pujiastuti, Sumada, Ngatilah, & Hadi, 2016). In the Dead Sea, brine is evaporated by solar evaporation and it is extracted by the process of thermal dissolution and crystallization. KCl is generated from the Dead Sea in Israel, Jordan and Great Salt Lake in the USA (Epstein, Altaras, Feist, & Rosenzweig, 1975). In many countries, salt (NaCl) is produced from seawater and the waste brines containing KCl return to the sea. The Çamaltı is the largest sea-salt plant in Turkey and huge amounts of waste brines including approximately 30,000 tons of potash with 22.268 tons of KCl is discharged back into the sea after the removal of NaCl (Mordoğan, Ertem, Erbil, & Yamık). KCl is widely used as a raw material for the production of potassium hydroxide (KOH) (O'Brien, Bommaraju, & Hine, 2007). Since KOH is utilized for the manufacture of soap, biodiesel, batteries, fuel cells, and fertilizers, its extraction from seawater waste brines can make an important contribution to the economy of the country. At that point, KOH is mainly produced by the electrolysis of KCl solutions. However, electrolysis is a gas generated process. High operating cost, electrode requirement of each cell, and undesirable products formation are the main drawbacks of the electrolysis process (Tongwen, 2002).

Electrodialysis which is one type of electrically driven membrane process has been widely employed due to its high efficiency for the production of acid and base from the salts. Furthermore, in order to avoid the waste disposal problem, electrodialysis with a bipolar membrane (BMED) has been applied successfully for the recycling salt brines (Y. Yang, X. Gao, A. Fan, L. Fu, & C. J. J. o. m. s. Gao, 2014; Ye et al., 2015). BMED is regarded as one of the most promising technology and the use of BMED for the production of acid and base can allow efficient, waste free, and environmentally friendly valuable raw materials. A bipolar membrane (BM) with a layer ion-exchange structure is composed of a cation selective membrane and an anion selective membrane (Xu, 2001). BMED was first studied for the water splitting by Frilette in 1956 (Frilette, 1956). BMED was reported as an alternative technology in many industries like the recovery of residues and the production of certain chemicals (Badruzzaman, Oppenheimer, Adham, & Kumar, 2009; Fidaleo, Moresi, & research, 2006; Y. Yang, X. Gao, A. Fan, L. Fu, & C. Gao, 2014). Up to now, BMED has been applied to many areas, such as chemical and food processes, biochemical industries and environmental protection. Researchers reported that BMED has an economical potential for recovering organic acids and inorganic acids and basesfor example boric acid and sodium hydroxide (Jülide Erkmen & Yapici, 2016), hydrofluoric acid and sodium hydroxide (J Erkmen et al., 2016), acetic acid and sodium hydroxide (Trivedi et al., 1997), phosphoric acid and sodium hydroxide (Trivedi, Shah, Adhikary, Rangarajan, & Polymers, 1999) citric acid and sodium hydroxide (Tongwen, Weihua, & Intensification, 2002). As a result, BMED is an effective alkali production technique without the generation of oxygen and hydrogen as by products (Jülide Erkmen & Yapici, 2016; J Erkmen et al., 2016; Tongwen, 2002; Tongwen et al., 2002).

In the light of the given literature, the production of KOH and HCl from the simulated KCl solutions by BMED process was investigated in this study. The design of experiments is used to identify the significant and insignificant factors which affect the performance of the BMED process. A fractional factorial design was used to determine the impact of factors with a small number of experiments. Eight experiments were proposed by using 2^{4-1} fractional factorial design to determine the significant factors influencing the acid and base production performance of BMED. The factors are defined as the initial concentration of acid and base, initial salt concentration, current density, and electrolyte concentration. The effectiveness of these factors was evaluated by using different techniques, such as Normal probability plot of effects, Pareto chart of effects, Main effects of plot, and Analysis of variance (ANOVA).

2. Material and Method

2.1. Materials

Chemicals;

HCl (Hydrochloric acid 37%), KCl (Potassium chloride 99%), KOH (Potassium hydroxide 85%), NaOH (Sodium hydroxide 99%), Na_2SO_4 (Sodium sulfate 99%), phenolphthalein indicator, and methyl orange indicator are the chemicals used in the experiments. All chemicals were obtained from Merck Company.

Membranes;

Membranes and spacers used BMED were produced by PCCell in Germany. The electrodialysis stack with the bipolar membrane is composed of two electrodes made of titanium coated with mixed metal oxide (MMO). Anion exchange membrane, cation exchange membrane, bipolar membrane, and electrodialysis spacer are installed according to the order of bipolar membrane (BM)-cation exchange membrane (CEM)-anion exchange membrane (AEM)-bipolar membrane (BM). The spacer thickness between two membranes is 0.5 mm and the membrane size is 11 cm ×11 cm. The active surface area of each membrane is equal to 64 cm^2. The main characteristics of ion exchange membranes are shown in Table 1.

Table 1. The main characteristics of ion exchange membranes

Membrane	Thickness (µm)	Water content (%)	Area resistance (Ωcm2)	Transport number (%)	Water splitting voltage %
BM (PC BP)	200-350			>0.95	0.8-1
CEM (PC SK-ED)	160-200	9	2,5	>0.95	
AEM (PC Acid 60)	160-200	7	2	>0.95	

2.2. Method

The BMED system configuration consists of the repeated BM-CEM-AEM-BM units. As seen in Figure 1, an electrolyte dilute solution (MX) is introduced into the feed compartment limited by the CEM and the AEM. The acid compartment is located between BM and AEM, while the base compartment is between BM and CEM. Water splitting is carried out inside a bipolar membrane (BM) by using the DC power supply. Protons (H^+) and hydroxyl ions (OH^-) formed during the process move towards the cathode and anode, respectively. Similar to H^+ and OH^- transfer, the applied voltage also initiates the transition of both cations (M^+) crossing to CEM and anions (X^-) crossing to AEM to the related electrodes. During the ion transfer, MOH formation in the base compartment and HX formation in the acid compartment take place. Na_2SO_4 is used electrode rinsing solution.

The conversion from the dissolved ions to acid and base was shown in the following reactions:

$$H_20 \rightarrow H^+ + OH^- \quad \text{(Interphase of bipolar membrane)}$$

$$H^+ + Cl^- \rightarrow HCl \quad \text{(Acid compartment)}$$

$$OH^- + K^+ \rightarrow KOH \quad \text{(Base compartment)}$$

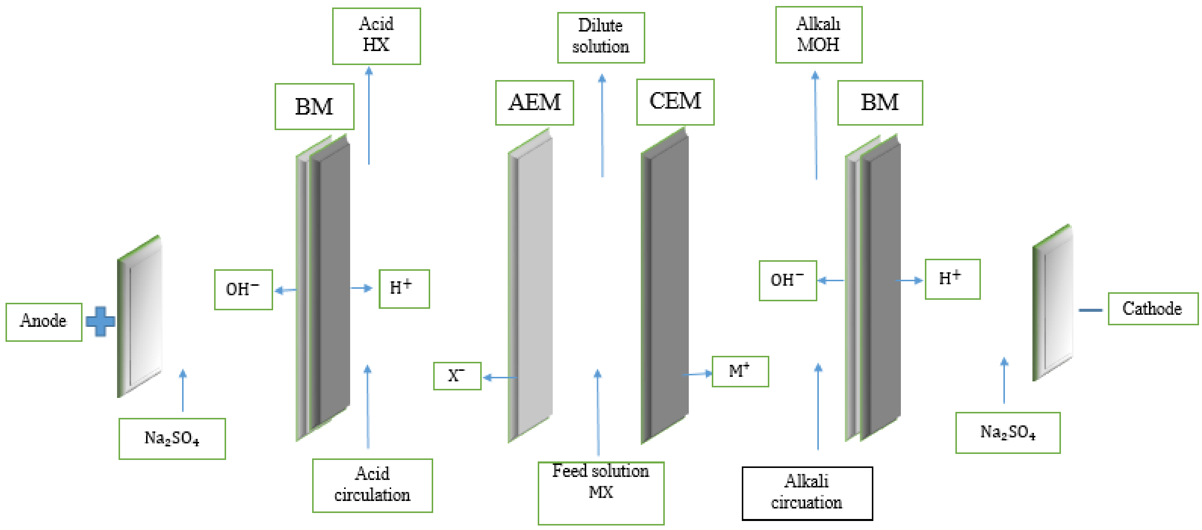

Figure 1. Configuration of BMED stack. BPM: Bipolar membrane, AEM: Anion exchange membrane, CEM: Cation exchange membrane, X^-: Cl^- ion; M^+: K^+ ion

2.3. Laboratory scale experiments

In this study, the electrodialysis system used in the lab–scale is PCCell ED 64-004 stack with three compartment units. There are five cell triplets in the stack and each cell contains a dilute, an acid, a base compartments, and Na_2SO_4 solution as electrode rising. Since every cell trio needs the voltage drop of 1.5V and 6V for the water splitting in BM membranes, the maximum voltage was estimated as 16V by taking into considerations of possible losses (Ghyselbrecht et al., 2014). The process was carried out at 25°C and solutions were circulated at flow rate of 15 L/h. During the BMED process, the pH value and temperatures of dilute and base solutions were measured, regularly. The concentrations of KOH and HCl produced by BMED were determined by titration with standardized of NaOH and HCl solutions in the presence of methyl orange and phenolphthalein as indicators, respectively.

The performance criteria is the molar amount of acid and base produced for the BMED process and it is calculated by using the following equation:

$$C = M.V \tag{1}$$

M: Molarity of acid and base (*mol/L*) V_t: Volume of acid or base (*L*)

2.4. Fractional factorial design of experiments

In order to obtain the significant factors affecting acid and base generation by BMED, the fractional factorial design was carried out. The factorial design applied by Fisher (1935) for the first time was employed to estimate both the main effects and interaction between the factors. It is widely used in engineering and industrial applications to study the relationship between two or more variables. The factorial design consists of full factorial and fractional factorial. The fractional factorial is partial number of a full factorial design. When the number of factors is too high, the fractional factorial design is preferred. The fractional factorial design allows to define the significant factors by a minimum number of experiments. In addition to economical, it can test the difference between various levels of each factor and the interactions between the factors (Chang, Teng, & Ismail, 2011; Gunst & Mason, 2009; Montgomery, 2017).

A fractional factorial design is used to decrease the number of experiments. In this work, initial concentration of acid and base, initial concentration of salt, current density and electrolyte concentration were employed as factors for a fractional factorial design. A minitab[18] software program was used to arrange the experimental design and fractional factorial design in n^{k-q} consisting of number of levels (n), number of factors (k), and generators (q). The total number of experiments needed for the investigation is 2^{4-1} for four factors. In Table 2, the factors of fractional factorial design, their codes, and their high and low levels are defined.

Table 2. Experimental factors and levels

Factors	**Coded symbol**	**Level (-1)**	**Level (+1)**
Initial concentration of Acid and Base (mol/L)	A	0.05	0.1
Initial concentration of Salt (g/L)	B	20	90
Current density (A/cm^2)	C	0.031	0.078
Electrolyte concentration (mol/L)	D	0.05	0.1

Table 3 shows the screening approach to find the significant factors affecting the responses. In Table 3, '-1' and '+1' represent two levels of each factor in the matrix, while Y1 and Y2 are the response variables of base concentration and acid concentration, respectively.

The regression equation with four factors and their interactions is defined by Akhnavarovsa and Katarov (Kleijnen, 2015).

$$Y = b_0 + b_1A + b_2B + b_3C + b_4D + b_{12}AB + b_{13}AC + b_{14}AD + b_{23}BC + b_{24}BD + b_{34}CD + b_{45}DE \tag{2}$$

In Equation 2, b_0, b_1, b_2, b_3 and b_4 are the linear coefficients, while b_{12}, b_{13}, b_{14}, b_{23}, b_{24}, b_{34} and b_{45}, are the second order intersection terms. Additionally, A, B, C, and D are the dimensionless coded factors of the parameters studied. The sequence in which these trials are carried out is randomized.

Table 3. Parameters in their reduced and normal forms

Experiment	Blocks	A	B	C	D	(Y_1)	(Y_2)
1	1	-1	-1	-1	-1	0.250	0.253
2	1	1	-1	-1	1	0.268	0.255
3	1	-1	1	-1	1	0.960	1.090
4	1	1	1	-1	-1	1.033	1.107
5	1	-1	-1	1	1	0.296	0.301
6	1	1	-1	1	-1	0.303	0.312
7	1	-1	1	1	-1	1.031	1.084
8	1	1	1	1	1	1.038	1.163

The data presented in Table 3 is employed to prepare the Normal probability plot, Pareto chart, Main effects plot, and ANOVA table. The experiments are analyzed to determine the significant factors.

3. Results and discussion

The aim of the study is to determine the effects of factors on the performance of producing potassium hydroxide (KOH) and hydrochloric acid (HCl) by the BMED system, statistically. In order to define the effects of four factors and their interactions, normal probability plot, Pareto chart, and main effects plot were formed by using fractional factorial design. ANOVA table was also used to verify the findings of fractional factorial design.

3.1 Normal probability plot of effects

The normal probability plot of the effects was prepared by the Minitab[18] program to specify which effects are important. In Figure 2, the effects of factors (A, B, C, and D) and their interactions (AB, AC, and AD) were evaluated together. The effects normally distributed with mean zero and falling to the same line represent the insignificant effects, while the important effects are located far from this line [25]. As seen in Figure 1a and 1b, the most important factor affecting the performance is the salt concentration coded B.

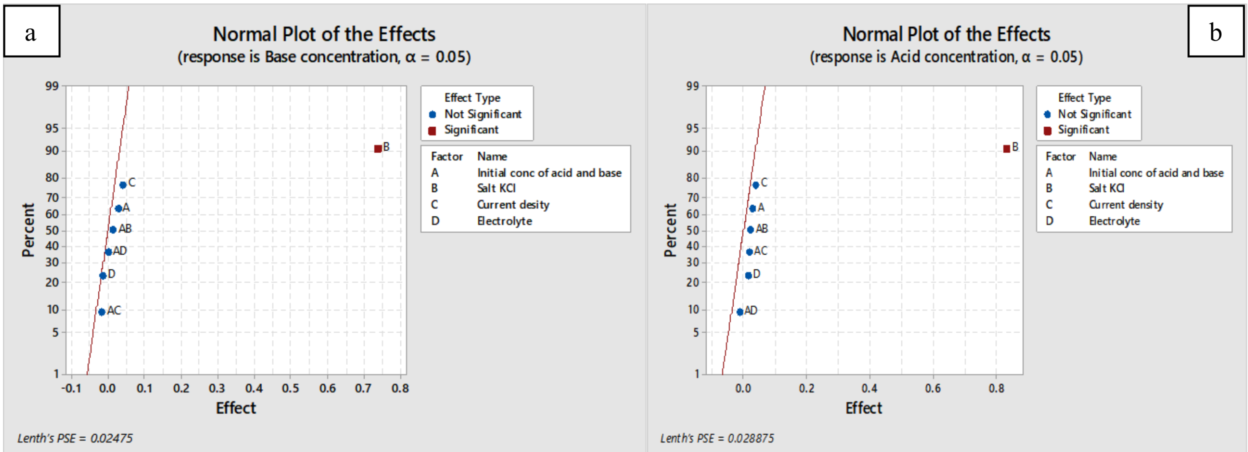

Figure 2. Normal probability plot of the effects for Y_1 (a) and Y_2 (b)

3.2 Pareto chart of the effects

The results obtained from the Normal probability plot of the effects were also confirmed by a Pareto chart as shown in Figure 3 (a and b). The vertical line in the Pareto chart is the reference line showing statistically the minimum degree of significance for α=0.05, while the horizontal column size proportional to the degree of significance for each effect. Any effects or interactions exceeding the vertical line are considered as significant (Antony, 2014). The Pareto chart of the effects also exhibits that factor B has the highest significance.

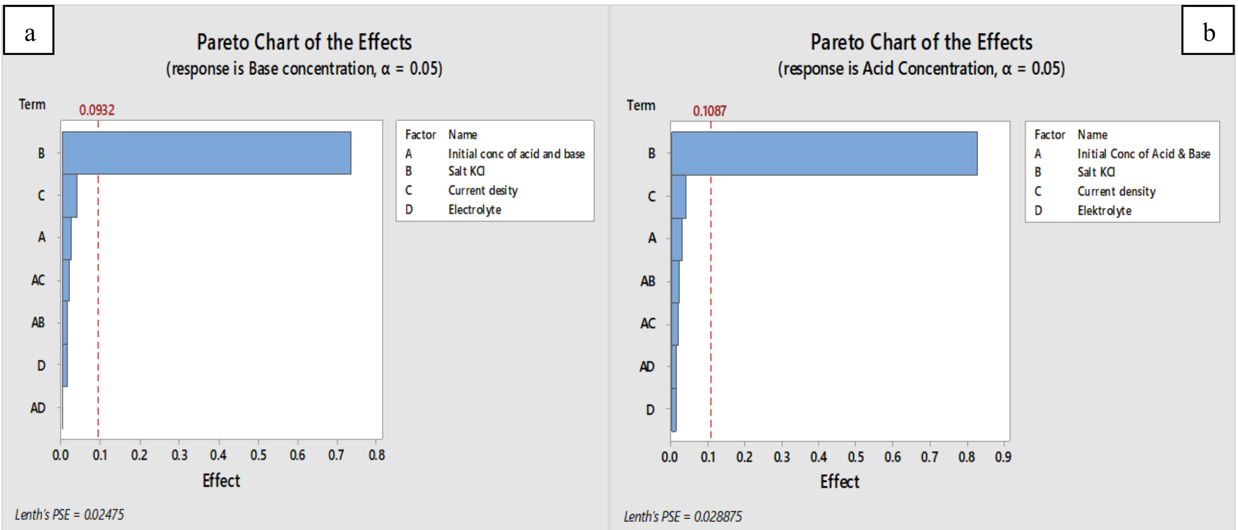

Figure 3. Pareto chart of the effects for Y_1 (a) and Y_2 (b)

3.3 Main effects Plot

The main effects plots indicate all effects behavior in Figure 4 (a and b). Main effect plot uses to determine the significant and insignificant factors. According to the main effect plot, the factor is considered as significant when the difference between the response values at the low level and the high level of a factor is high (El-Taweel & Haridy, 2014). In Figure 4, base and acid concentrations are evaluated with respect to four factors. When the effects of factors are compared, the most distinctive behavior is observed for the factor of initial salt concentration. The similar response of the initial salt concentration factor for both base and acid concentrations reveals that initial salt concentration is the most important factor affecting the performance of the BMED system. This result also confirms the findings obtained from Normal probability plot of effects and Pareto chart of the effects. The straight lines obtained for the other main effects in Figure 4 show no effect of factors on the performance of the BMED system.

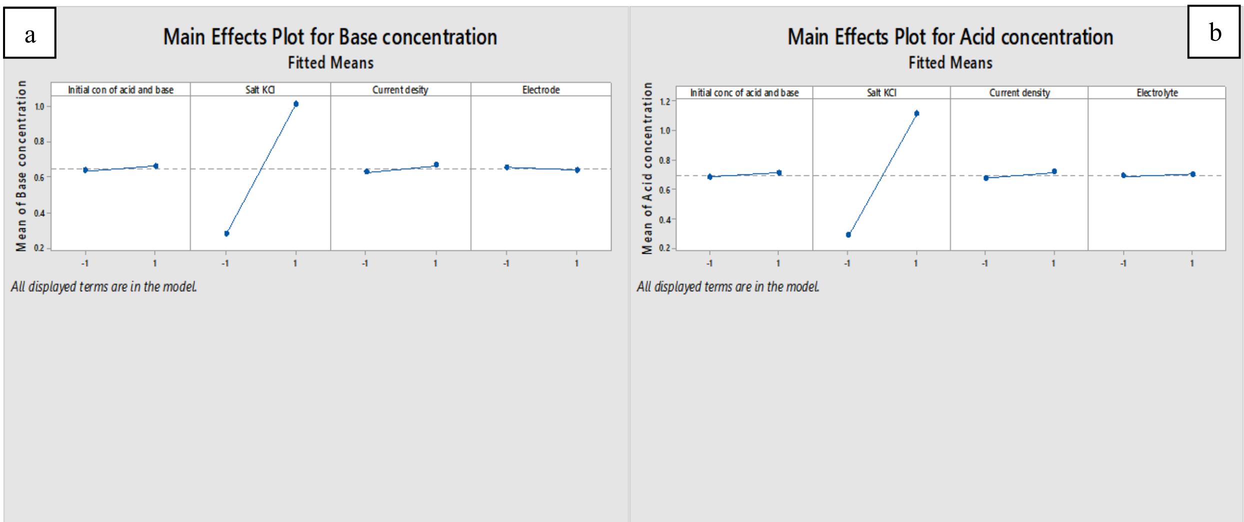

Figure 4. Main effects plots for Y_1 (a) and Y_2 (b)

3.4 Regression model analysis

Minitab[18] software program was used to examine the significance of each individual regression coefficient. According to the findings obtained from fractional factorial design, a reduced regression model was produced. Regression equations of Y_1 (base concentration) and Y_2 (acid concentration) can be written as follows;

Regression Equation for Y_1

$$Y_1 = 0.6474 + 0.01313A + 0.3681B + 0.01963C - 0.006875D + 0.006875AB - 0.009625AC - 0.000625AD \quad (3)$$

(R^2=100%)

Regression Equation for Y_2

$$Y_2 = 0.6956 + 0.01362A + 0.4154B + 0.01938C + 0.006625D + 0.01038AB + 0.008875AC - 0.006875AD \quad (4)$$

(R^2=100%)

As shown in Equation (3) and (4), the estimated effects and regression coefficients of Normal probability plot and Pareto chart can be obtained. Factors with positive signs in equations are proportional to the measured responses. Therefore, initial salt concentration coded B having the biggest coefficient with a positive sign indicates its strongest effect on Y_1 and Y_2.

3.5 Analysis of Variance

The analysis of variance (ANOVA) was employed to determine the significant factors affecting the performance characteristics. F values are used to check the statistical significance of the regression equation, while the significance of each coefficient is examined by the p-values (Hamzaoui, Jamoussi, & M'nif, 2008). Table 4 indicates the analysis of variance findings. In the table, the first three columns show the degrees of freedom (DF), sum of squares (SS), and mean squares (MS), respectively. F-value and p-value are located in the last two columns in Table 4. Mean squares are the sum of squares divided by degrees of freedom. F value is the ratio of mean square error (MS) to the residual error (Ata, Kanca, Demir, & Yigit, 2017). F value for 95% of confidence level, 1 of DF and 8 of factorial tests (F 0.05, 1, 7) is equal to 5.59 (Sharp, 2012). When the model is source, the F-values are 1091.45 and 1234.47 for Y_1 and

Y_2, respectively, while the p-values are 0.00 for both. The smaller p-values show the more significance of the corresponding variables. Furthermore, P values close to zero imply the effects with high significance (Chérif et al., 2016). Since all effects with both F values higher than 5.59 and P values close to zero are significant, the initial concentration of acid and base (A), current density (C), and electrolyte concentration (D) are not significant factors in the performance of BMED system. As a result, F-values and p-values verify that initial salt concentration is the most statistically significant factor for the BMED system.

Table 4. Analysis of variance (ANOVA) at 95% confidence level for Y_1 and Y_2 obtained by fractional factorial regression

Response Y_1: Base Concentration

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	1	108.413	108.413	1091.45	0.000
Linear	1	108.413	108.413	1091.45	0.000
B	1	108.413	108.413	1091.45	0.000
Error	6	0.00596	0.00099		
Total	7	109.009			

Response Y_2: Base Concentration

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	1	138.029	138.029	1234.47	0.000
Linear	1	138.029	138.029	1234.47	0.000
B	1	138.029	138.029	1234.47	0.000
Error	6	0.00671	0.00112		
Total	7	1.387			

3.6 Effect of initial salt concentration on KOH and HCl production

The results of the normal probability plot, Pareto chart, and the main effects plot indicate that initial salt concentration has the highest effect on the performance of the BMED system. Since the higher KCl concentration can decrease the electrical resistance in the salt compartment, processing time and voltage drop can increase with increasing initial KCl concentration (Wei et al., 2012; Ye et al., 2015).

The results in Table 3 show that the higher initial concentration of KCl is a favor for the production of acid and base with higher concentrations by BMED. Moreover, acid and base concentrations produced at the beginning of the experiment is higher than at the end of the experiment. The decrease in concentration gradient can be considered as the main reason for the decrease in acid and base yields. Additionally, water electricity penetration in the KCl compartment can be responsible for the time dependent decrease in acid and base production. Migration of water ions (H^+ and OH^-) from feed tank under electrical field leads to an increase in volume or decrease in concentrations of acid and base tanks (Li et al., 2016).

4. Conclusion

Bipolar membrane electrodialysis experiments were performed to produce KOH and HCl from simulated KCl by the BMED system. Initial acid and base concentrations, initial salt concentration, current density, and electrolyte concentration were defined as the factors affecting the acid and base production yield. In order to define the effects of four factors and their interactions, normal probability plot, Pareto chart, and main effects plot were formed by using fractional factorial design. The Normal probability plot and Pareto chart reveal that the most significant factor is the initial salt concentration. Addition to the main effects plot, F-values and p-values obtained from ANOVA verify the accuracy of Normal probability plot and Pareto chart for the BMED system. Therefore, the fractional factorial design can be applied for the statistical analysis of BMED systems.

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