

Development of a predictive model of the limiting current density of an electro dialysis process using response surface methodology

Mourad Ben Sik Ali ^{*1,2} and Béchir Hamrouni ²

¹ Engineering Preparatory Institute of Nabeul, Merezka University Campus, Merazka, 8000 Nabeul, Republic of Tunisia

² Desalination and Water Treatment Research Unit, Chemistry Department, Faculty of Sciences of Tunis, El Manar II, 2092, Republic of Tunisia

(Received February 29, 2015, Revised January 26, 2016, Accepted January 29, 2016)

Abstract. Electro dialysis (ED) is known to be a useful membrane process for desalination, concentration, separation, and purification in many fields. In this process, it is desirable to work at high current density in order to achieve fast desalination with the lowest possible effective membrane area. In practice, however, operating currents are restricted by the occurrence of concentration polarization phenomena. Many studies showed the occurrence of a limiting current density (LCD). The limiting current density in the electro dialysis process is an important parameter which determines the electrical resistance and the current utilization. Therefore, its reliable determination is required for designing an efficient electro dialysis plant. The purpose of this study is the development of a predictive model of the limiting current density in an electro dialysis process using response surface methodology (RSM). A two-factor central composite design (CCD) of RSM was used to analyze the effect of operation conditions (the initial salt concentration (C) and the linear flow velocity of solution to be treated (u)) on the limiting current density and to establish a regression model. All experiments were carried out on synthetic brackish water solutions using a laboratory scale electro dialysis cell. The limiting current density for each experiment was determined using the Cowan-Brown method. A suitable regression model for predicting LCD within the ranges of variables used was developed based on experimental results. The proposed mathematical quadratic model was simple. Its quality was evaluated by regression analysis and by the Analysis Of Variance, popularly known as the ANOVA.

Keywords: electro dialysis; concentration polarization; limiting current density; response surface methodology; central composite design

1. Introduction

Electro dialysis (ED) and its related technologies are electrochemical membrane separation processes in which ions are transferred through selective ion-exchange membranes from one solution to another using an electric field as the driving force (Ghyselbrecht *et al.* 2013, Ghyselbrecht *et al.* 2014, Moon and Yun 2014, Xu and Huang 2008).

The interest in using of electro dialysis in desalination process and also to remove excess

*Corresponding author, Ph.D., E-mail: mourad.bensikali@gmail.com

inorganic contaminants such as borate, fluoride and heavy metals from water has increased worldwide (Banasiak and Schäfer 2009, Dermentzis 2010). This is principally due to that electro dialysis is a simple process, does not have many of the defects of chemical processes and mainly the development of new membranes and new sources of energy (Ghyselbrecht *et al.* 2014, Moon and Yun 2014, Banasiak and Schäfer 2009).

In electro dialysis it is desirable to work at high current density in order to achieve fast desalination with the lowest possible effective membrane area (Káňavová *et al.* 2014). In practice, however, operating currents are restricted by the occurrence of concentration polarization phenomena (Krol *et al.* 1999, Meng *et al.* 2005, Geraldes and Afonso 2010a). Concentration polarization was studied using a commercial anion and cation exchange membranes. The current voltage curves showed the occurrence of a limiting current density (LCD). The limiting current density in the electro dialysis process is an important parameter which determines the electrical resistance and the current utilization. Usually, LCD depends on membrane and solution properties as well as on the electro dialysis stack construction and various operational parameters such as the flow velocity of the dilute solution (Káňavová *et al.* 2014, Geraldes and Afonso 2010a). Therefore, a reliable determination of LCD is required for designing an efficient electro dialysis plant (Lee *et al.* 2006a).

Although it is not possible to establish an accurate model for the limiting current density, there are still some systematic methodologies for the determination and or the prediction of his value during an electro dialysis processes. Response surface methodology (RSM) is such one. RSM is an effective technique for analyzing the interactions among factors, exploring the relationships between the response and the independent variables, and optimizing the processes or products where multiple variables may influence the outputs (Wang *et al.* 2010, Zazouli *et al.* 2014, Fouladitajar *et al.* 2014, Mourabet *et al.* 2012, 2013).

The main advantage of RSM is the small number of experimental trials needed to evaluate multiple parameters and their interactions (Wang *et al.* 2010, Zazouli *et al.* 2014, Fouladitajar *et al.* 2014, Boubakri *et al.* 2014a, b), and this makes the optimization process more efficient and cost-effective in terms of both manpower and resources.

Therefore, this research employs RSM to study the effects of two main parameters: the initial salt concentration (C) and the linear flow velocity of solution to be treated (u) on the value of the LCD.

Since the central composite design (CCD) is the most commonly used response surface designed experiment, CCD was employed to investigate the mutual effect of the two factors on the performance of membrane process. All experiments were carried out on synthetic brackish water solutions using a laboratory scale electro dialysis cell.

2. Background

2.1 Principle of electro dialysis

Electro dialysis is a separation process that is based on the selective migration of ions in solution through ion exchange membranes under the activation of an electric field (Xu and Huang 2008, Alvarado and Chen 2014, Zerdoumi *et al.* 2014, Doyen *et al.* 2014).

As shown in Fig. 1, an ED system consists of a series of anion (AEM, anion permeable) and cation exchange membranes (CEM, cation permeable) arranged in a parallel and alternate way between two electrodes. Solutions are through membranes and an electrical potential

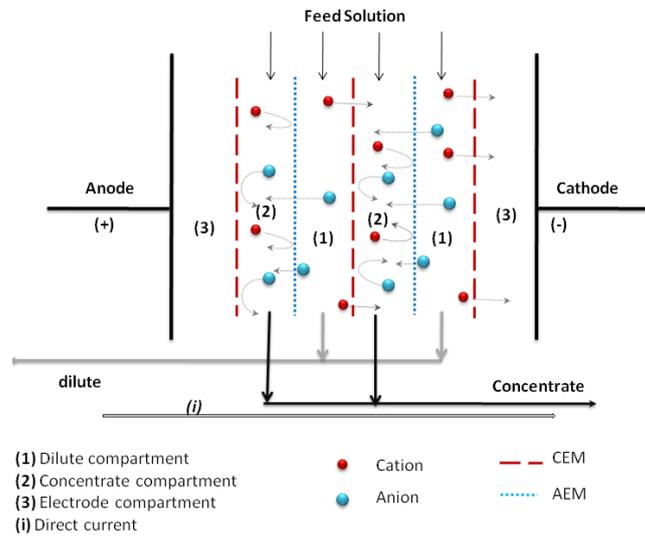


Fig. 1 Principle of electro dialysis

difference is applied between the two electrodes in the process. In response to the presence of the electric field, the ionized dissolved species, such as salts, acids or bases, are transported across the ionic membrane. Cations migrate toward the cathode, whereas anions gravitate to the anode target. However, the interposed CEM blocks the anions and let passing only cations. Whereas AEM blocks the cations and let anions migration. Over time, one of the compartments is stripped of ions (diluted), while the other becomes more ionically populated (concentrated). As consequence, two different compartments are created: concentrating compartment (concentrate) and dilution compartment (dilute).

The electro dialysis is a widely used especially for desalination of brackish water and sodium chloride recovery from sea water (Ghyselbrecht *et al.* 2013, Ben Sik Ali *et al.* 2010, Baker 2004, Noble and Stern 1995, Strathmann 2010).

2.2 Transport limitations and concentration polarization at ion exchange membranes

In electro dialysis, as shown in Fig. 2, concentration polarization can take place at the membrane surface. When current is applied, an electric potential difference is obtained as a response. This is the result of the speed at which the ions are transported within the system. By increasing the potential difference, the current is also amplified as a result of the enhancement of transport velocity of the ions that contact the membrane and then traverse it. However, since the rate of ion transport is much higher within the membrane in contrast to the solution, this increase of the current attains a threshold where the concentration of ions at the membrane/solution interface and precisely at the laminar boundary layer of the membrane surface facing the dilute cell (C_s^d) is degraded to the point that any subsequent increase in the electric field results the dissociation of water. In the other side the transport of charged species is increased at the surface facing the concentrate cell (C_s^c). When the ion concentration at membrane surface will approach the zero, the current density will approach to a maximum value. At this condition the applied current is defined as the limiting current (i_{lim}) and his density is called the limiting current density (LCD) (Lee *et al.* 2006b).

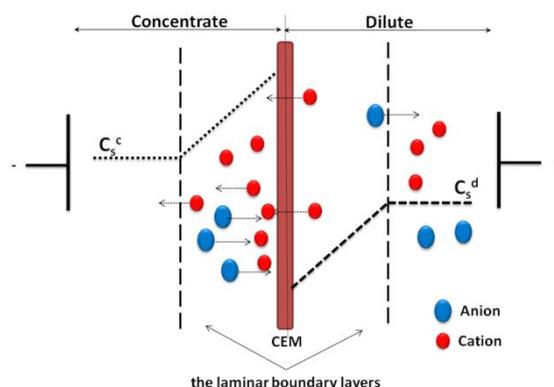


Fig. 2 Schematic diagram of concentration polarization in electro dialysis process

Beyond this point, an increase of cell resistance occurs and the pH of the solution is altered. This is mainly due to the quantity of charged species present at the membrane/solution interface. Effectively, the population of ions in this area is insufficient to carry an appropriate current flow. Hence, the H^+ ions and OH^- products, generated from the dissociation of water, begin to conduct electrical current (Zerdoumi *et al.* 2014, Nikonenko *et al.* 2014). This can cause a decrease in the system efficiency via the requirement for higher energy consumption. Also, the pH changes may lead to the precipitation of insoluble hydroxides on the membrane surface.

The appearance of the concentration polarization phenomenon prevents the treatment of very dilute solutions in ED systems. Hence, it is convenient to operate the system at 80% of i_{lim} in order to harness the full extent of energy via ions transport (Daniels 2014).

To conclude, the limiting current density can be considered as one of the most important parameters in the electro dialysis process. It is, therefore, necessary to determine his value in order to prevent the problems and to operate the electro dialyzer successfully (Káňavová *et al.* 2014, Nikonenko *et al.* 2014, Tanaka 2002).

The magnitude of the concentration polarization is a function of various parameters including the applied current density, the feed flow velocity parallel to the membrane surface, the cell design, and the membrane properties (Lee *et al.* 2006b, Tanaka 2002, Lee *et al.* 2002, Tanaka 2005a, Geraldes and Afonso 2010b, Długołęcki *et al.* 2010). For a designed electro dialysis cell and for a solution treated at the same hydrodynamic condition, the effects of the cell design and membranes characteristics on limiting current density can be considered as constant and can be neglected. In this work, the effect of the two main parameters: the initial salt concentration of the treated solution (C) and his linear flow velocity (u) on the limiting current density value will be studied.

3. Experimental

3.1 Membranes & reagents

PC-SK standard cation exchange membranes and PC-SA standard anion exchange membranes were used for experiments. They are supplied by PCA-Polymerchemie Altmeier GmbH and PCCell GmbH, Heusweiler, Germany. Their corresponding properties are listed in Table 1.

Analytical grade sodium chloride and sodium sulfate salts are used in all experiments.

Table 1 Information on cation (PC-SK) and anion (PC-SA) exchange membranes

Membrane	Thickness (μm)	Ion exchange capacity (meq g^{-1})	Chemical stability (pH)	Permselectivity	Functional groups	Membrane resistance ($\Omega \text{ cm}^2$)
PC-SK	130	~ 1	0-11	> 0.93	$-\text{SO}_3^-$	0.75-3
PC-SA	90-130	~ 1.5	0-9	> 0.96	$-\text{NR}_4^+$	1-1.5

Synthetic brackish water solutions with known amount of compounds were prepared by dissolving sodium chloride in distilled water. Ionic strength was fixed by adjusting the concentration of sodium chloride. Prior to the experiments, pH was adjusted by the addition of 1 M HCl and/or NaOH.

Sodium sulfate salt and distilled water were used to prepare electrode rinse solution.

3.2 Experimental installation

An electrodialysis “PCCell ED 64 002” unit (PCA-Polymerchemie Altmeier GmbH and PCCell GmbH, Heusweiler, Germany), constituted by 2 cell pairs (2 AEM and 3 CEM membranes) stacked between two titan electrodes with a platinum layer, was used to perform the studies. As shown in Fig. 3, plastic separators are placed between the membranes to form the flow paths of the dilute and concentrate streams. These spacers are designed to minimize boundary layer effects and are arranged in the stack so that all the dilute and concentrate streams are manifolded separately. For each membrane, the active surface area is 0.0064 m^2 and the flow channel width between two membranes is 0.5 mm. In the spacer-free stack configuration, the intermembrane distance is maintained uniform.

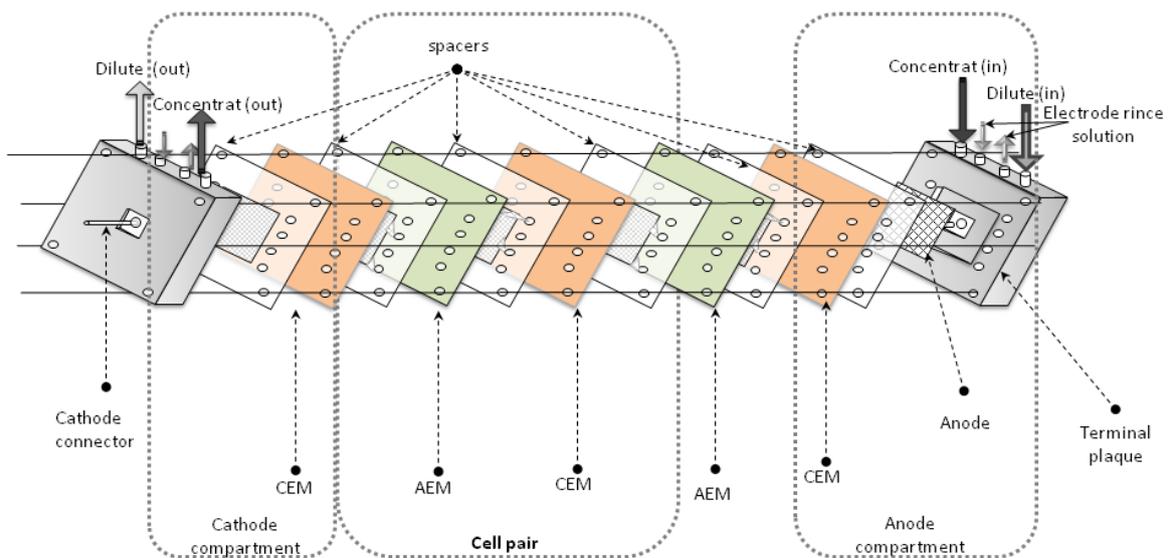


Fig. 3 Schematic of the ED cell used in this study

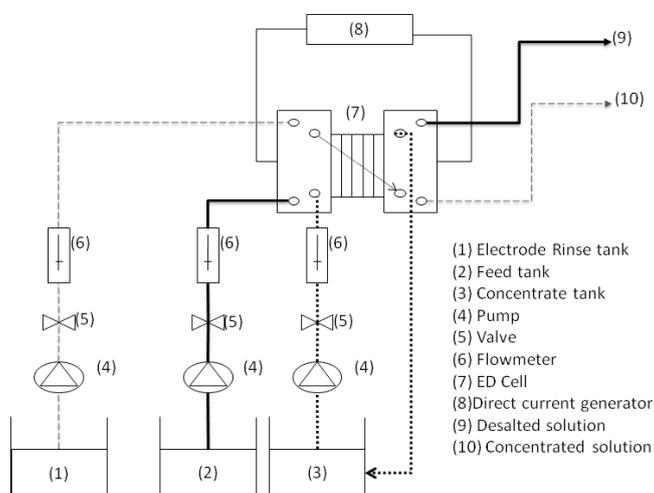


Fig. 4 Schematic of the electro dialysis system used in this study

A power direct current (DC) generator was then connected to ED stack electrodes to assure an applied current between them. The brine, feed and electrodes rinse solutions were circulated in the unit using three centrifugal pumps ($P = 84\text{W}$, total head = 4.2 m) equipped each with a flowmeter and three valves to control their flow rates. Fig. 4 shows a simplified diagram of the electro dialysis setup working in continuous mode.

3.3 Experimental procedure: Determination of the limiting current

In this context, practical and mathematical methods were developed and used to determine or estimate the limiting current density value. As reported in the literature, the limiting current (i_{lim}) and then the limiting current density (LCD) can be determined experimentally by plotting the electrical resistance across the membrane stack ($E \bar{i}^{-1}$) or the pH value in the dilute cell as a function of the reciprocal electric current (i^{-1}). At the inflection point on this graph, the current

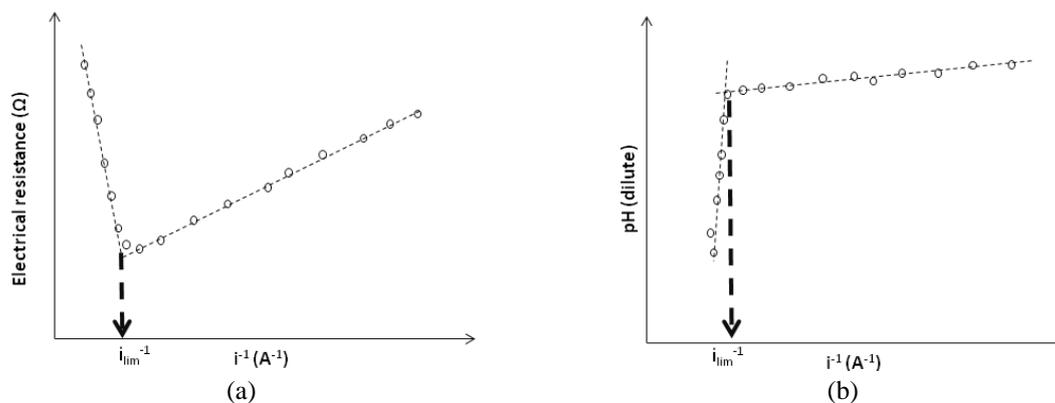


Fig. 5 Experimental determination of i_{lim} by the Cowan–Brown method

intensity divided by the membrane area is considered as the i_{lim} value of the system. This is called a Cowan–Brown plot after its original developers (Baker 2004, Tanaka 2002). Fig. 5 depicts two typical types of curves for the experimental determination of i_{lim} by the Cowan–Brown method.

In order to prevent the generation of chlorine or hypochlorite, which could be hazardous for the electrodes, 0.1 M Na_2SO_4 was used as electrode rinse solution circulating in electrode compartments. Flow rate of electrode rinse solution was fixed to 80 L h^{-1} for all experiments.

During the experiments, the same synthetic brackish water solutions were used as initial concentrate and dilute solutions. Their flow rates (dilute and concentrate) were fixed at the beginning of experiment. Total voltage drop, including voltage drop in the membrane stack as well as on the electrodes, was also fixed at the start of the experiment.

Samples, to be analyzed, were collected at the inlet (before treatment) and outlet (after treatment) of each compartment of electro dialysis cell.

In order to remove any deposits, cleaning solutions of 0.1 M HCl, 0.1 M NaOH and distilled water were circulated through the ED cell for 30 min each at the end of experiment.

Usually, the limiting current depends on membrane and solution properties as well as on the electro dialysis stack construction and various operational parameters (Doyen *et al.* 2014). In this work, the effects of two main parameters on the limiting current density will be studied: the initial salt concentration and the linear flow velocity (u) of the dilute solution.

3.4 Experimental design

As shown in Table 2, a central composite design (CCD) in the form of a 2^2 full factorial design was used to develop the response surface design. Five levels were employed for each factor. According to CCD, a total number of 13 experiments should be performed with 4 orthogonal design points, 4 star points to form a CCD with $\alpha = 1.41421$ and 5 replicate points to estimate the experimental error (Zhang *et al.* 2008).

Based on our preliminary experiment, three key parameters of flow rate in dilute compartment and initial salt concentration with central point values of 0.104 m s^{-1} (15 L h^{-1}), and 0.030 mol L^{-1} were chosen as independent variables, which were converted to dimensionless ones (A, B), with the coded values at five levels: $-\alpha$, -1 , 0 , $+1$ and $+\alpha$.

The experimental plan generated is shown in Table 3. The design involved 13 runs and the response variable measured was the LCD value (A m^{-2}).

The effect of the two independent variables on LCD was modeled using a polynomial response surface. The second-order response function for our experiments was predicted by the following equation (Zhang *et al.* 2008)

$$LCD = \beta_0 + \beta_1 \cdot A + \beta_2 \cdot B + \beta_{12} \cdot A \cdot B + \beta_{11} \cdot A^2 + \beta_{22} \cdot B^2 \quad (1)$$

where LCD is the predicted response, (A) and (B) are the coded values of factors according to

Table 2 Factors and levels investigated for response surface

Factors	Coded levels				
	$-\alpha$	-1	0	$+1$	$+\alpha$
(A) Linear flow velocity (m s^{-1})	0.006	0.035	0.104	0.174	0.202
(B) Initial Salt concentration (mol L^{-1})	0.0017	0.010	0.030	0.050	0.058

Table 3 Design layout and experimental results

Std order	Run order	Blocks	(A) Linear flow velocity	(B) Initial salt concentration	LCD (A m^{-2})	
9	1	1	0	0.104	153.13	
5	2	1	$-\alpha$	0.006	60.30	
13	3	1	0	0.104	153.13	
6	4	1	$+\alpha$	0.202	196.88	
1	5	1	-1	0.035	31.25	
2	6	1	+1	0.174	81.88	
8	7	1	0	0.104	$+\alpha$	342.40
3	8	1	-1	0.035	+1	223.30
12	9	1	0	0.104	0	153.13
4	10	1	+1	0.174	+1	326.20
7	11	1	0	0.104	$-\alpha$	40.00
11	12	1	0	0.104	0	153.13
10	13	1	0	0.104	0	153.13

Table 2, β_0 is a constant, β_1 , β_2 are linear coefficients, β_{12} , are interaction coefficients, and β_{11} , β_{22} are quadratic coefficients.

The statistical software package *STATISTICA* (trial version) was used for the generation of experimental design and regression analysis of the experimental data. Analysis of variance (ANOVA) methodology was used to estimate the statistical parameters.

The response surface and contour plots were generated to understand the interaction of various parameters. The fitting quality of the polynomial model equation was expressed by the coefficient of determination R^2 .

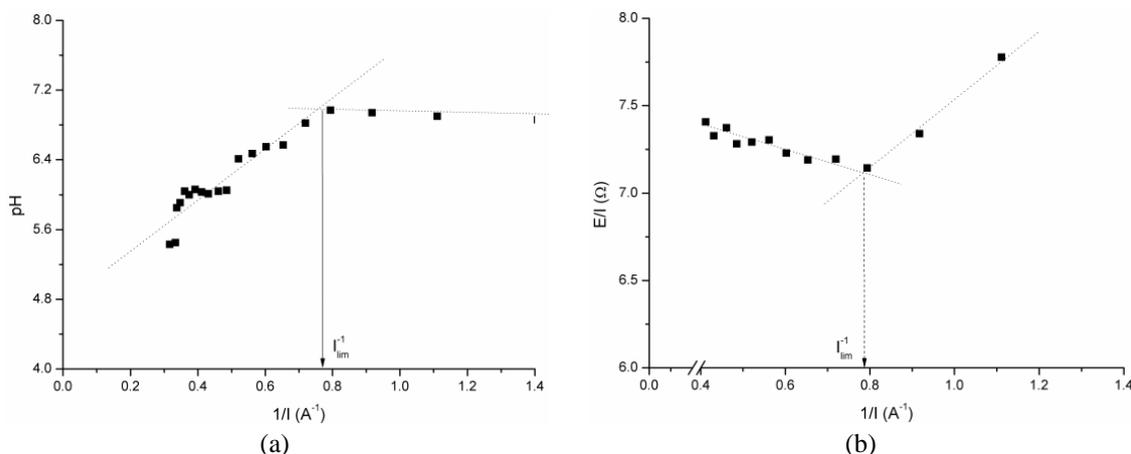


Fig. 6 Variation of the pH of dilute (a) and the cell resistance; (b) versus the reciprocal of the current: The Cowan–Brown method ($C = 0.03 \text{ M}$ and $u = 0.202 \text{ m s}^{-1}$)

4. Results and discussions

4.1 Determination of the limiting current

Figs. 6 show an example of the curves used for the determination of the limiting current from the experimental result by the Cowan-Brown method. These graphs were obtained for 0.03 M NaCl solution treated at 0.202 m s⁻¹ linear feed flow velocity (Run order N^o4).

In the relationship between the dilute pH and the reciprocal current in Fig. 6(a), the limiting current was determined where the slope was changed (Lee *et al.* 2006a, Baker 2004). In addition, the limiting current was determined from the graph showing the cell resistance versus the reciprocal of the current (Fig. 6(b)).

4.2 Application of response surface methodology

4.2.1 Model fitting

The levels of factors (initial feed concentration and the dilute linear velocity) and the effects of their interactions on the value of the limiting current density were determined through the central composite design of RSM. Thirteen experiments were performed at different combinations of the factors (Table 3). Regression analysis and ANOVA were used to fit the model and examine the statistical significance of the model terms. The application of RSM yielded the following regression equation, which was an empirical relationship between the limiting current density value and the test variables in coded units

$$\begin{aligned} LCD (A m^{-2}) = & -22.975 + 810.075 * A + 1346.417 * B \\ & -2241.990 * A^2 + 9401.079 * A * B + 51189.062 * B^2 \end{aligned} \quad (2)$$

Table 4 presents the results of the quadratic response surface model fitting in the form of analysis of variance (ANOVA). The above mathematical quadratic model can sometimes be unsatisfactory to describe the experimental results and then, it is necessary to evaluate the quality of the model fitted using ANOVA and comparing variation sources with Fisher distribution (*F*-test). This allows the identification of the model that best fits the population from which the data were sampled. This statistical test is based on the ratio of two scaled sums of squares reflecting different sources of variability. Therefore, the significance of regressions was evaluated by the ratio between the mean square of regression and the mean square of residuals (difference between

Table 4 Analysis of variance for the limiting current density

Effect	Sum of squares (SS)	Degree of freedom (DF)	Mean square (MS)	<i>F</i> -value	<i>p</i> -value
Intercept	189.421	1	189.421	4.87210	0.063050
A	1594.854	1	1594.854	41.02135	0.000366
A ²	815.829	1	815.829	20.98399	0.002541
B	365.502	1	365.502	9.40111	0.018166
B ²	2916.530	1	2916.530	75.01628	0.000055
A*B	683.038	1	683.038	17.56847	0.004079
Error	272.150	7	38.879		

Table 5 Test of SS whole Model vs. SS Residual

Dependent variable	Multiple R^2	Adjusted R^2	SS Model	DF Model	MS Model	SS Residual	DF Residual	MS Residual	F	p
LCD	0.997	0.996	113231.1	5	22646.22	272.1504	7	38.879	582.485	0.000000

observed and predicted values) (Almeida *et al.* 2011).

Table 5 summarizes the obtained results of test of sum of squares of the whole model versus the sum of squares of residual. The calculated F -value for the regressions was 582.485 for LCD, greater than the minimum tabulated $F_{(5/7)}$ -value of 3.97 required to achieve a 95% confidence level, confirming that all the models are well fitted to the experimental data.

The p -value less than 0.0500 indicates that the model terms are significant, while the value greater than 0.1000 indicates terms that are not significant. The very low p -value obtained in this work fully confirms that the model is significant.

As shown in Table 5, the determination coefficient R^2 of the quadratic regression model was determined to be 0.997. The R^2 value indicates how much of the variability in the data is accounted for by the model. (Gabriel *et al.* 2015)

This implies that 99.70% of the variations for the LCD value are explained by the independent variables and this also means that only about 0.30% of the variations are not explained by the model.

Adjusted R^2 (Adj- R^2) is also a measure of goodness of fit. It modifies the R^2 value by taking into account the number of covariates or predictors in the model. Here, Adj- R^2 value (0.996) was very close to the corresponding R^2 value. This higher R^2 coefficient ensured satisfactory adjustment of the quadratic model to the experimental data.

The checking of model adequacy is also an important part of the data analysis procedure, as it will give poor or misleading results if it is an inadequate fit. The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight

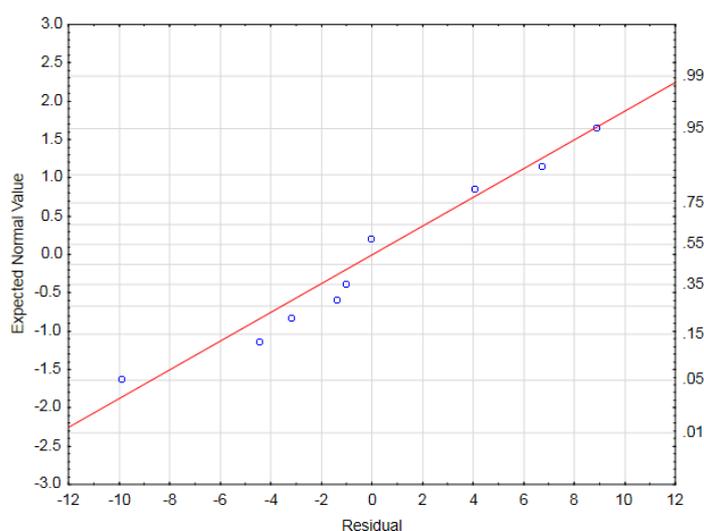


Fig. 7 Expected normal value vs. residual plot

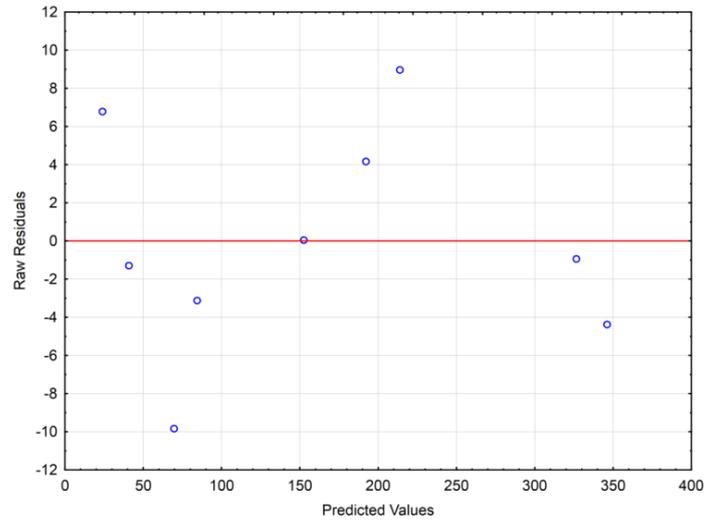


Fig. 8 Raw residues vs. predicted value plot

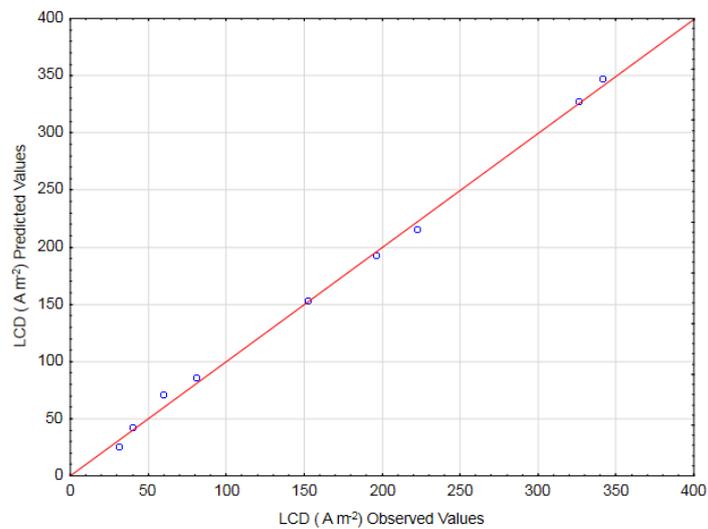


Fig. 9 Predicted vs. Observed plot for LCD value

line. S-shaped curve was not formed according to Fig. 7, indicating that there is no apparent problem with normality and no need for transformation of response.

Furthermore, Fig. 8 shows the raw residues vs. predicted value plot. The residues appear to be randomly distributed around zero deviation, according to the normal distribution expected from the *F*-test, thus discarding the existence of systematic errors (Almeida *et al.* 2011).

The comparison between the predicted values of LCD and the experimental points are presented in Fig. 9. All the points are distributed relatively near to the regression line. The graph confirms that the proposed predicted values are in good agreement with the observed ones (Li *et al.* 2015).

In a literature review, researchers proposed many empirically expressions in which i_{lim} (LCD) is a function of the feed flow velocity in the stack (u) and the concentration of dilute solution (C). For example, Tanaka proposed the following expression

$$i_{lim} = m * C^n \quad (3)$$

With $m = 66.36 + 14.72 * u$ and $n = 0.7404 + 3.585 * 10^{-3} * u$

In his investigation, Tanaka used NaCl solutions and an electro dialysis unit incorporated with an Aciplex A172 anion-exchange membrane (Tanaka 2005b, 2006, Tanaka *et al.* 2012).

Lee and Strathmann (Lee *et al.* 2006a) proposed also an empirically derived expression in which i_{lim} is a function of the feed flow velocity in the stack and the concentration of dilute solution. The correspondent equation, which refers to Lee-Strathmann model, is

$$i_{lim} = a * C * u^b \quad (4)$$

Where the coefficients a and b are constant; a is expressed in $A s^b m^{1-b} keq^{-1}$ and b is dimensionless.

These coefficients (a , b , m and n) are estimated by the measurements of the respective i_{lim} with different flow velocities, a defined dilute concentration and for a specific cell design. Specifically, a and b are estimated from a double logarithmic plot showing i_{lim} divided by the dilute concentration as a function of the linear flow velocity. In another terms, many experiments should be performed to determine their values.

However, in this work the main advantage of the response surface methodologies was exploited. A relatively small number of experimental trials (thirteen) was necessary to find a relationship between the LCD and the two studied parameters. The proposed mathematical model was simple. Its quality was evaluated by regression analysis and ANOVA.

4.2.2 Response surface analysis

Three-dimensional response surface plots were made with the dependent variables LCD related to the two independent variables linear flow velocity (A) and initial salt concentration (B). The

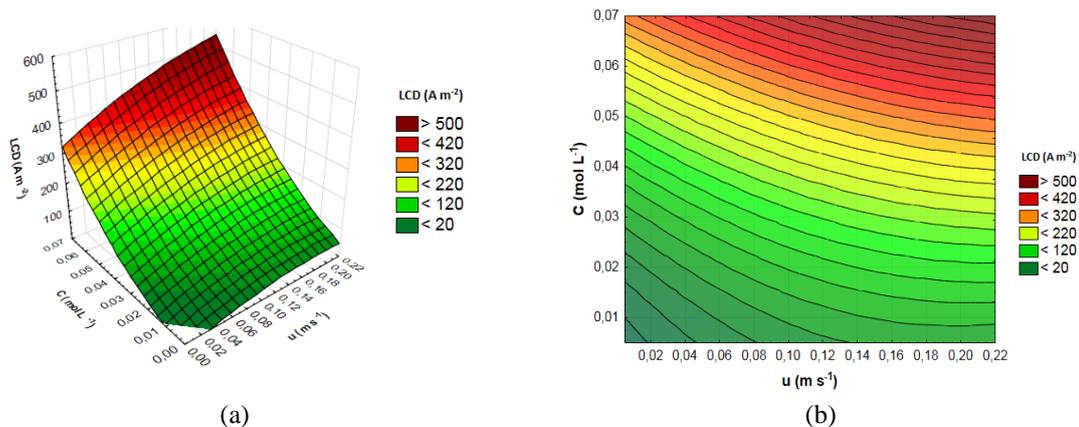


Fig. 10 (a) Response surface; and (b) contours plots for the effect of independent variables (linear flow velocity and Initial salt concentration) on response variables (LCD)

corresponding response surface plot and response contour plot obtained from the RSM equation are presented in Figs. 10(a) and (b).

As seen in Figs. 10, the limiting current density depends closely to both parameters. At fixed initial salt concentration the LCD increases by increasing the linear flow velocity of dilute solution. For solutions with very low initial salt concentration (below 0.01 M) and processed with low linear flow velocity, the LCD is almost equal to zero. This is expected because, for these solutions, the quantity of ionic species is too low that the cell resistance will increase drastically. To avoid this problem an increase of the linear flow velocity is recommended.

On the other hand, for solutions with initial salt concentration in the range of 0.01 to 0.05 M processed at a low flow velocity, the LCD is also low. This can be associated to the remaining time of the solution in each compartment. In fact the ions have more time to be transferred from one compartment to another through the membrane when the velocity or flow rate is lower. As consequence the concentration polarization can be reached with lower applied current.

For higher initial salt concentrations (more than 0.05 M), the LCD value is relatively high. It exceeds 220 A m^{-2} for all flow rates and can reach 500 A m^{-2} . This is due to the fact that the quantities of charged species in the solution are sufficient to assure the transport of current in all compartments and cell resistivity still relatively low. As mentioned before better desalination efficiency will be obtained by increasing the applied current. (Li *et al.* 2015).

5. Conclusions

The purpose of this work was to develop an explicit model to estimate the limiting current density in the electrodialysis of brackish water solutions. CCD was used according to the RSM for this proposal. A relatively small number of experimental trials was necessary to find a relationship between the LCD and the two studied parameters (the linear flow velocity and the initial salt concentration). The proposed mathematical model was simple. Its quality was evaluated by regression analysis and ANOVA.

Three-dimensional response surface plots showed that the limiting current density depends closely to both parameters. At fixed initial salt concentration, LCD increases by increasing the linear flow velocity of dilute solution. For solutions with very low initial salt concentration (below 0.01 M) and processed with low linear flow velocity, the LCD is almost equal to zero. To avoid this problem an increase of the linear flow velocity is recommended. On the other hand, for solutions with initial salt concentration in the range of 0.01 to 0.05 M processed at a low flow velocity, the LCD is also low. As consequence the concentration polarization can be reached with lower applied current.

References

- Almeida, L.C., Garcia-Segura, S., Bocchi, N. and Brillas, E. (2011), "Solar photoelectro-Fenton degradation of paracetamol using a flow plant with a Pt/air-diffusion cell coupled with a compound parabolic collector: Process optimization by response surface methodology", *Appl. Catal., B*, **103**(1-2), 21-30.
- Alvarado, L. and Chen, A. (2014), "Electrodeionization: Principles, strategies and applications", *Electrochim. Acta*, **132**, 583-597.
- Baker, R.W. (2004), *Membrane Technology and Applications*, John Wiley & Sons, Ltd., England, UK.
- Banasiak, L.J. and Schäfer, A.I. (2009), "Removal of boron, fluoride and nitrate by electrodialysis in the

- presence of organic matter”, *J. Membr. Sci.*, **334**(1-2), 101-109.
- Ben Sik Ali, M., Mnif, A., Hamrouni, B. and Dhahbi, M. (2010), “Electrodialytic desalination of brackish water: Effect of process parameters and water characteristics”, *Ionics*, **16**(7), 621-629.
- Boubakri, A., Hafiane, A. and Bouguecha, S.A.T. (2014a), “Application of response surface methodology for modeling and optimization of membrane distillation desalination process”, *J. Ind. Eng. Chem.*, **20**(5), 3163-3169.
- Boubakri, A., Bouchrit, R., Hafiane, A. and Bouguecha, S.A.T. (2014b), “Fluoride removal from aqueous solution by direct contact membrane distillation: theoretical and experimental studies”, *Environ. Sci. Pollut. Res.*, **21**(17), 10493-10501.
- Daniels, J.A. (2014), *Advances in Environmental Research*, (Volume 32), Nova Science Publishers, New York, NY, USA.
- Dermentzis, K. (2010), “Removal of nickel from electroplating rinse waters using electrostatic shielding electro dialysis/electrodeionization”, *J. Hazard. Mater.*, **173**(1-3), 647-652.
- Długolecki, P., Anet, B., Metz, S.J., Nijmeijer, K. and Wessling, M. (2010), “Transport limitations in ion exchange membranes at low salt concentrations”, *J. Membr. Sci.*, **346**(1), 163-171.
- Doyen, A., Roblet, C., L’Archevêque-Gaudet, A. and Bazinet, L. (2014), “Mathematical sigmoid-model approach for the determination of limiting and over-limiting current density values”, *J. Membr. Sci.*, **452**, 453-459.
- Fouladitajar, A., Ashtiani, F.Z., Dabir, B., Rezaei, H. and Valizadeh, B. (2014), “Response surface methodology for the modeling and optimization of oil-in-water emulsion separation using gas sparging assisted microfiltration”, *Environ. Sci. Pollut. Res.*, **22**(3), 2311-2327.
- Gabriel, A.A., Cayabyab, J.E.C., Tan, A.K.L., Corook, M.L.F., Ables, E.J.O. and Tiangson-Bayaga, C.L.P. (2015), “Development and validation of a predictive model for the influences of selected product and process variables on ascorbic acid degradation in simulated fruit juice”, *Food Chem.*, **177**, 295-303.
- Geraldes, V. and Afonso, M.D. (2010a), “Limiting current density in the electro dialysis of multi-ionic solutions”, *J. Membr. Sci.*, **360**(1), 499-508.
- Geraldes, V. and Afonso, M.D. (2010b), “Limiting current density in the electro dialysis of multi-ionic solutions”, *J. Membr. Sci.*, **360**(1-2), 499-508.
- Ghyselbrecht, K., Huygebaert, M., Van der Bruggen, B., Ballet, R., Meesschaert, B. and Pinoy, L. (2013), “Desalination of an industrial saline water with conventional and bipolar membrane electro dialysis”, *Desalination*, **318**, 9-18.
- Ghyselbrecht, K., Silva, A., Van der Bruggen, B., Boussu, K., Meesschaert, B. and Pinoy, L. (2014), “Desalination feasibility study of an industrial NaCl stream by bipolar membrane electro dialysis”, *J. Environ. Manage.*, **140**, 69-75.
- Káňavová, N., Machuča, L. and Tvrzník, D. (2014), “Determination of limiting current density for different electro dialysis modules”, *Chem. Pap.*, **68**(3), 324-329.
- Krol, J.J., Wessling, M. and Strathmann, H. (1999), “Concentration polarization with monopolar ion exchange membranes: current-voltage curves and water dissociation”, *J. Membr. Sci.*, **162**(1-2), 145-154.
- Lee, H.J., Sarfert, F., Strathmann, H. and Moon, S.H. (2002), “Designing of an electro dialysis desalination plant”, *Desalination*, **142**(3), 267-286.
- Lee, H.-J., Strathmann, H. and Moon, S.-H. (2006a), “Determination of the limiting current density in electro dialysis desalination as an empirical function of linear velocity”, *Desalination*, **190**(1-3), 43-50.
- Lee, H.J., Strathmann, H. and Moon, S.H. (2006b), “Determination of the limiting current density in electro dialysis desalination as an empirical function of linear velocity”, *Desalination*, **190**(1-3), 43-50.
- Li, H., Li, Y., Xiang, L., Huang, Q., Qiu, J., Zhang, H., Sivaiah, M.V., Baron, F., Barrault, J., Petit, S. and Valange, S. (2015), “Heterogeneous photo-Fenton decolorization of Orange II over Al-pillared Fe-smectite: Response surface approach, degradation pathway, and toxicity evaluation”, *J. Hazard. Mater.*, **287**, 32-41.
- Meng, H., Deng, D., Chen, S. and Zhang, G. (2005), “A new method to determine the optimal operating current (i_{lim}) in the electro dialysis process”, *Desalination*, **181**(1), 101-108.
- Moon, S.-H. and Yun, S.-H. (2014), “Process integration of electro dialysis for a cleaner environment”, *Curr.*

- Opin. Chem. Eng.*, **4**, 25-31.
- Mourabet, M., El Rhilassi, A., El Boujaady, H., Bennani-Ziatni, M., El Hamri, R. and Taitai, A. (2012), "Removal of fluoride from aqueous solution by adsorption on Apatitic tricalcium phosphate using Box–Behnken design and desirability function", *Appl. Surf. Sci.*, **258**(10), 4402-4410.
- Mourabet, M., El Rhilassi, A., El Boujaady, H., Bennani-Ziatni, M. and Taitai, A. (2013), "Use of response surface methodology for optimization of fluoride adsorption in an aqueous solution by Brushite", *Arab. J. Chem.* DOI: <http://dx.doi.org/10.1016/j.arabjc.2013.12.028> [In Press]
- Nikonenko, V.V., Kovalenko, A.V., Urtenov, M.K., Pismenskaya, N.D., Han, J., Sistas, P. and Pourcelly, G. (2014), "Desalination at overlimiting currents: State-of-the-art and perspectives", *Desalination*, **342**, 85-106.
- Noble, R.D. and Stern, S.A. (1995), "*Membrane Separations Technologies Principles and Applications*", Elsevier Science B.V., Amsterdam, The Netherlands.
- Strathmann, H. (2010), "Electrodialysis, a mature technology with a multitude of new applications", *Desalination*, **264**(3), 268-288.
- Tanaka, Y. (2002), "Current density distribution, limiting current density and saturation current density in an ion-exchange membrane electro dialyzer", *J. Membr. Sci.*, **210**(1), 65-75.
- Tanaka, Y. (2005a), "Limiting current density of an ion-exchange membrane and of an electro dialyzer", *J. Membr. Sci.*, **266**(1-2), 6-17.
- Tanaka, Y. (2005b), "Limiting current density of an ion-exchange membrane and of an electro dialyzer", *J. Membr. Sci.*, **266**(1-2), 6-17.
- Tanaka, Y. (2006), "Irreversible thermodynamics and overall mass transport in ion-exchange membrane electro dialysis", *J. Membr. Sci.*, **281**(1-2), 517-531.
- Tanaka, Y., Uchino, H. and Murakami, M. (2012), "Continuous ion-exchange membrane electro dialysis of mother liquid discharged from a salt-manufacturing plant and transport of Cl⁻ ions and SO₄²⁻ ions", *Membr. Water Treat., Int. J.*, **3**(1), 63-76.
- Wang, Y., Huang, C. and Xu, T. (2010), "Optimization of electro dialysis with bipolar membranes by using response surface methodology", *J. Membr. Sci.*, **362**(1-2), 249-254.
- Xu, T. and Huang, C. (2008), "Electro dialysis-based separation technologies: A critical review", *AIChE J.*, **54**(12), 3147-3159.
- Zazouli, M.A., Dianati Tilaki, R.A. and Safarpour, M. (2014), "Modeling nitrate removal by nano-scaled zero-valent iron using response surface methodology", *Health Scope*, **3**(3), e15728.
- Zerdoumi, R., Oulmi, K. and Benslimane, S. (2014), "Electrochemical characterization of the CMX cation exchange membrane in buffered solutions: Effect on concentration polarization and counterions transport properties", *Desalination*, **340**, 42-48.
- Zhang, X., Lu, W., Yang, P. and Cong, W. (2008), "Application of response surface methodology to optimize the operation process for regeneration of acid and base using bipolar membrane electro dialysis", *J. Appl. Chem. Biotechnol.*, **83**(1), 12-19.