

MATHEMATICAL MODELING OF DESALINATION BY ELECTRODIALYSIS

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ABSTRACT

In this study, desalination of brackish water by electro dialysis (ED) was modeled based on separation experimental data of sodium ions. At steady-state operation of ED, the outlet concentration of dilute stream was measured at different voltages, flow rates and feed concentrations. The model started from a differential equation of steady state mass balance. Neglecting resistances of ion exchange membranes compared with resistances of bulk solutions in dilute and concentrate compartments and substituting a relation for solution resistance as a function of concentration, the final one-parameter model was obtained. Concentration gradient was also assumed to be constant along the membrane surface due to the very short residence time in dilute compartment and constancy of current density. The model parameter was determined by the experimental data. The approached model gives concentration of dilute compartment or separation percent for various voltages, flow rates and feed concentrations. In order to assess the reliability of the model, the predicted data were compared with measured experimental. It was found that the model could be used to well predict the process.

Keywords: Desalination, Sodium Ions, Electrodialysis, Mathematical Modeling

INTRODUCTION

Water is of great importance in any industrial, domestic and agricultural consumption so that its shortage is one of the most important limitations of life, agriculture and industries. Most of the earth surface is covered by water, which is in the form of the oceans, the seas and the ices in the poles. However, only one percent of these waters which are in the form of surface or underground water is used by human being and that is because the water of the oceans and the seas has very high salt content and it is not directly utilizable and therefore it needs some special processes to be desalinated [1].

Suitable desalinating methods for water treatment of seawater can be effective to overcome the water shortage. ED is one of these methods which has been used for many years. ED is an electrochemical process for the separation of ions across charged membranes from one solution to another under the influence of an electrical potential difference used as a driving force. This process has been widely used for production of drinking and process water from brackish and seawater, treatment of industrial effluents, recovery of useful materials from effluents and salt production. The basic principles of ED have been reviewed in the literature [2].

In a typical ED cell, a series of anion and cation exchange membranes are arranged in an alternating pattern between an anode and a cathode to form individual cells. When a DC potential is applied between two electrodes, positively charged cations move toward the cathode, pass through the negatively charged cation exchange membrane and retained by the positively charged anion exchange membrane. On the other hand, negatively charged anions move toward the anode, pass through the positively charged anion exchange membrane and retained by the negatively charged cation exchange membrane. At the end, ion concentration increases in alternate compartments with a simultaneous decrease of ion concentration in other compartments. A schematic view of an ED cell is presented in Figure 1.

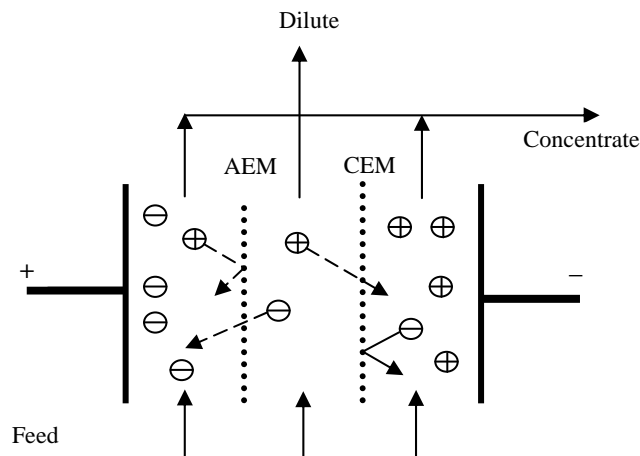


Figure 1- A schematic view of an ED cell

In this research, effect of different operating conditions in water treatment of seawater by an experimental ED cell was studied and a mathematical model was derived to predict the cell behavior.

Experimental Unit

The ED unit consisted of a feed tank where seawater was stored, a pump (MOTOJEN, P = 0.37 kW) and a self designed electrodesalination cell (Figure 2). The cell was packed

with a pair of ion exchange membranes (cation and anion) and a pair of platinum electrodes (anode and cathode) [3-5].

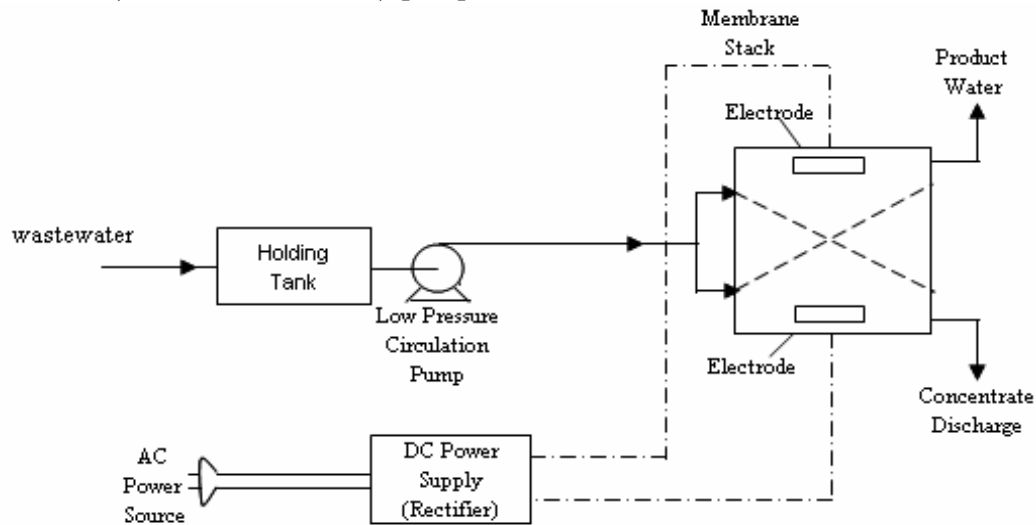


Figure 2- A simplified diagram of an ED unit

The cation exchange membrane (CR67MK111) which was a flexible cation permeable sheet of cloth-rein forced resin cation exchange membrane was amber in color. The anion exchange membrane (AR204SXR412) which was a flexible anion permeable sheet of cloth-rein forced resin anion exchange membrane was pale yellow. Effective area of each membrane was $60 \times 65 \text{ mm}^2$ while thickness of dilution cell (center) was 4 mm and thickness of each concentrate cell (left and right) was 3 mm.

An electric potential was applied to the electrodes. A rectifier (RST SPASTELL TRFO) supplied required DC power at different voltages. Both electrodes were made of pure platinum. Area of each electrode was $4.2 \times 4.2 \text{ mm}^2$ [3-5].

An analytical grade salt (sodium chloride, Merck) was used in all experiments to produce solutions with seawater qualities. The purpose of these experiments was to study the effect of voltage, flow rate and concentration on ED cell performance [3].

Mathematical Modeling

A differential element of the dilute compartment is illustrated in Figure 3.

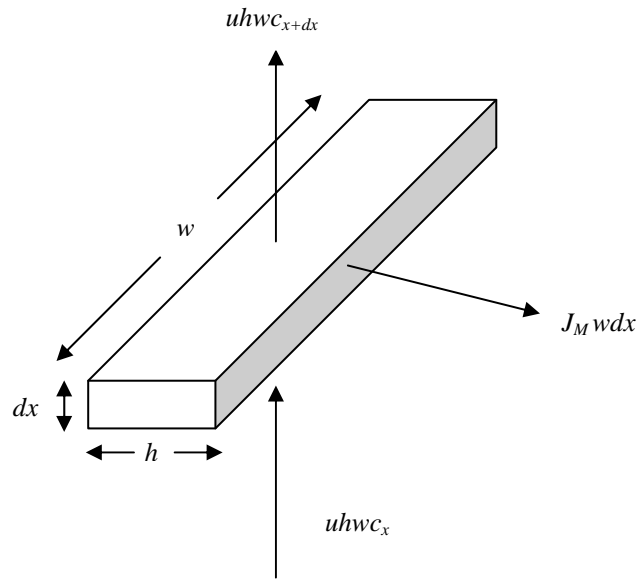


Figure 3- Differential element of the dilute compartment

The mass balance of sodium ions in the compartment is as follows:

$$(uC_x - uC_{x+dx})h = J_M dx \tag{1}$$

Or:

$$uhdC = -J_M dx \tag{2}$$

Where, J_M is the molar flux through the dilute compartment, u is the flow velocity, h is the thickness of dilute compartment and C is the ion concentration. Also, the molar flux through the dilute compartment in term of current density is as follows:

$$J_M = \frac{\eta}{F} \frac{dI}{dA_M} \tag{3}$$

Where, η is the current efficiency, F is the Faraday constant, I is the current intensity and A_m is the effective area of each ion exchange membrane. The assumption of constant η and J_M in the dilute compartment gives [6]:

$$\frac{dI}{dA_M} = \frac{I}{A_M} \tag{4}$$

Hence, Equation 2 can be written as follows:

$$uhdC = \frac{\eta}{F} \frac{I}{A_M} dx \tag{5}$$

To use integrate form of this equation with operational variables, η needs to be stated as a function of velocity. At any point, molar flux can be written as follows:

$$J_M = k(C_{bulk} - C_i) = k\Delta C \quad (6)$$

Where, C_{bulk} and C_i are concentrations at the bulk of dilute stream and at the membrane surface, respectively. Due to very short residence time in dilute compartment and constancy of current density (dI/dA_m), ΔC can be assumed to be constant along the membrane surface [6]. Using Equations 3, 4 and 6, η can be written as follows:

$$\eta = \frac{\Delta C F A_M}{I} k = \delta k \quad (7)$$

The relationship between k and u can be derived using the following correlation [7].

$$Sh = 3.30 \left(\frac{y}{l} Re Sc \right)^{1/3} \quad Re < 1000 \quad (8)$$

Where l is the channel length, Sh is Sherwood number, defined by kh/D_{AB} , Re is Reynolds number, defined by $Re = \rho u h / \mu$ and Sc is Schmidt number, defined by $Sc = \mu / \rho D_{AB}$. All experiments were carried out at different flow rates but at the same chemical and operational conditions and using the same geometrical system. Thus, only u varies and as a result k can be represented as follows:

$$k = \alpha u^{1/3} \quad (9)$$

In ED, the basic relation between current (I), effective electrical motive force (E) and system resistance (R) can be described by Ohm's law:

$$I = \frac{E}{NR} \quad (10)$$

Now, mass transfer resistances in the cell should be considered. Four resistances can be taken into account in a single cell: R_{cm} , the resistance of cation exchange membrane, R_{am} , the resistance of anion exchange membrane, R_d , the resistance of dilute solution and R_c , the resistance of concentrate solution [8].

$$R = R_{cm} + R_{am} + R_d + R_c \quad (11)$$

Since solutions are relatively dilute, $R_{cm}, R_{am} \ll R_d, R_c$, Therefore,

$$R = R_d + R_c \quad (12)$$

Neglecting membranes resistances, as discussed above, solution resistance can be expressed as a function of concentration. Resistance of a material increases with its length and decreases with its cross-sectional area [9,10]:

$$R = \frac{h}{\kappa A_m} \quad (13)$$

Where, κ is conductivity of the material and is proportional to its concentration.

$$\kappa = \Lambda_M C \quad (14)$$

Where, Λ_M is the molar conductivity of the material. At low concentrations, the molar conductivity of strong electrolytes is calculated using the following equation [11]:

$$\Lambda_M = \Lambda_M^0 - AC^{0.5} + BC \quad (15)$$

Where, A and B are constants (89.21 and 82.07 for NaCl solution, respectively) and Λ_M^0 is the limiting molar conductivity, i.e. the molar conductivity in the limit of zero concentration (when the ions do not interact with each other). Kohlrausch indicated that Λ_M^0 can be expressed as the sum of contributions of individual ions. If the limiting molar conductivity of cations is denoted λ_+ and that of anions is denoted λ_- , his law of the independent migration of ions is [9]:

$$\Lambda_M^0 = \nu_+ \lambda_+ + \nu_- \lambda_- \quad (16)$$

Where ν_+ and ν_- are the numbers of cations and anions per an electrolyte molecule (e.g. $\nu_+ = \nu_- = 1$ for NaCl, ZnSO₄, PbSO₄, CuSO₄ etc.). λ_+ and λ_- are molar conductivity of each ion (5.01 and 7.63 m²Smol⁻¹ for Na⁺ and Cl⁻, respectively).

Hence, by substitution of Equations 7, 9, 10 and 13 into Equation 5 and after rearrangement, the following equation can be derived:

$$\frac{uh^2 FN}{\delta\alpha^{1/3} EC(12.64 - 8.92C^{0.5} + 8.21C)} dC = dx \quad (17)$$

By substitution of $1/\delta\alpha = \beta$, $u = Q/A_m$ and $N = 1$ and using the boundary condition, at $x=0 \rightarrow C=C_0$, the integral is ready to be calculated numerically or analytically:

$$\frac{\beta Q^{2/3} h^2 F}{EA_m^{2/3}} f(C_0, C) = \int_0^l dx \quad (18)$$

Where,

$$f(C_0, C) = \int_{C_0}^C \frac{1}{C(12.64 - 8.92C^{0.5} + 8.21C)} dC \quad (19)$$

Final solution for the model parameter (β) is as follows:

$$\beta = \frac{EA_m^{2/3} l}{Q^{2/3} h^2 F} f(C_0, C) \quad (20)$$

Using experimental data, the following equation was fitted for β as a function of flow rate, voltage and feed concentration:

$$\beta = \frac{[a + b \ln Q + c(\ln Q)^2 + d(\ln Q)^3 + eE]}{(1 + f \ln Q + gE + hE^2)} \quad (21)$$

Where, a, b, c, d, e, f, g and h are third degree polynomial functions of feed concentration:

$$a, b, c, d, e, f, g, h = pC_0^3 + qC_0^2 + rC_0 + s \quad (22)$$

The values of p, q, r and s are listed in Table 1.

Table 1- The values of p, q, r and s in the 3rd degree polynomial functions of feed concentration

Coeff. Cons.	p	q	r	s
a	1.8712	-1.4305	0.2721	-0.0142
b	0.4207	-0.3228	0.0623	-0.0035
c	0.0315	-0.0243	0.0048	-0.0003
d	0.0008	-0.0006	0.0001	-8×10^{-6}
e	-0.0001	0.0001	-3×10^{-5}	3×10^{-6}
f	1.3871	-0.7093	0.0658	-0.0068
g	-6.6452	9.9892	-3.6798	-0.0267
h	1.4544	-1.7639	0.5964	-0.0221

Taking a look to the experimental data, β is assumed to be zero at the conditions presented in Table 2.

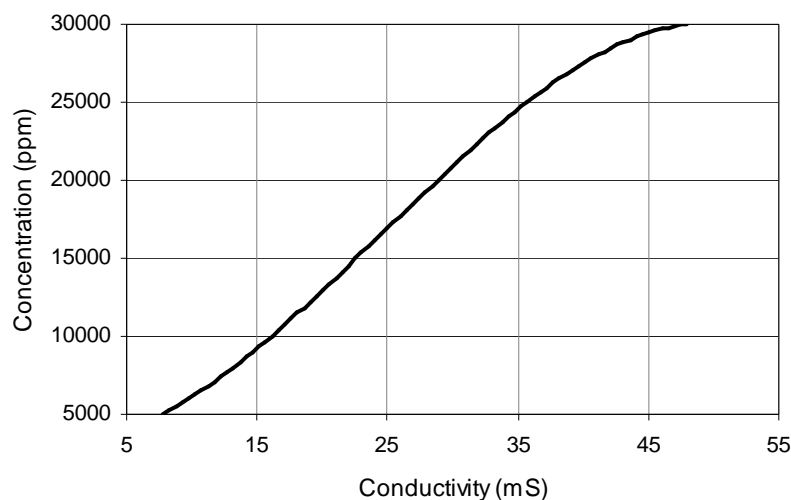
Table 2- Conditions at which the value of β is zero

Flow rate (cc/s)	Concentration (ppm)		
	E=6 V	E=4 V	E=2 V
$2500 < C_0 < 7500$	$Q > 1.5$	$Q > 0.75$	$Q > 0.5$
$7500 < C_0 < 15000$	$Q > 1.5$	$Q > 1.0$	$Q > 0.75$
$15000 < C_0 < 25000$	$Q > 2.0$	$Q > 1.5$	$Q > 1.0$
$25000 < C_0 < 35000$	$Q > 4.0$	$Q > 3.0$	$Q > 2.0$

With the aid of Equation 19, 20 and 21 and using MATLAB, the model gives values of concentration in the dilute compartment for various feed concentrations, flow rates and voltages.

RESULTS AND DISCUSSION

Experiments were conducted at different feed concentrations (5000, 10000, 20000 and 30000 ppm), flow rates (0.1, 0.3, 0.5, 0.75, 1, 1.5, 2, 3, 4 and 5 mL/s) and voltages (2, 4 and 6 V). Concentration of cations (Na^+) only in the dilute compartment was measured at various operating conditions. In all experiments, a conductometer (HANNA, model HI 8633, made in Portugal) was used to measure the amount of salt in water. Water conductivity directly depends on its salt content. This dependency (calibration curve of the conductometer) is shown in Figure 3.

**Figure 3- Calibration curve of the conductometre**

Effect of flow rate on the cell performance at different voltages and concentrations was studied. In order to verify whether the developed model represents the actual behavior of the ED system, the model data were then compared with the experimental data. Both calculated as well as experimental results are plotted in Figure 4.

As can be seen, at higher flow rates the amount of separated salt falls and separation performance decreases. Because a greater flow rate means a lower residence time, it means ions that are between the membranes do not have enough time to transfer through the membranes. Obviously, at a constant concentration, the cell performance increases by increasing voltage and as a result the amount of salt in the product water decreases.

As seen in Figure 4, there is a good agreement between the experimental and calculated results. Maximum error observed between the model and experimental values was about 1.22 %.

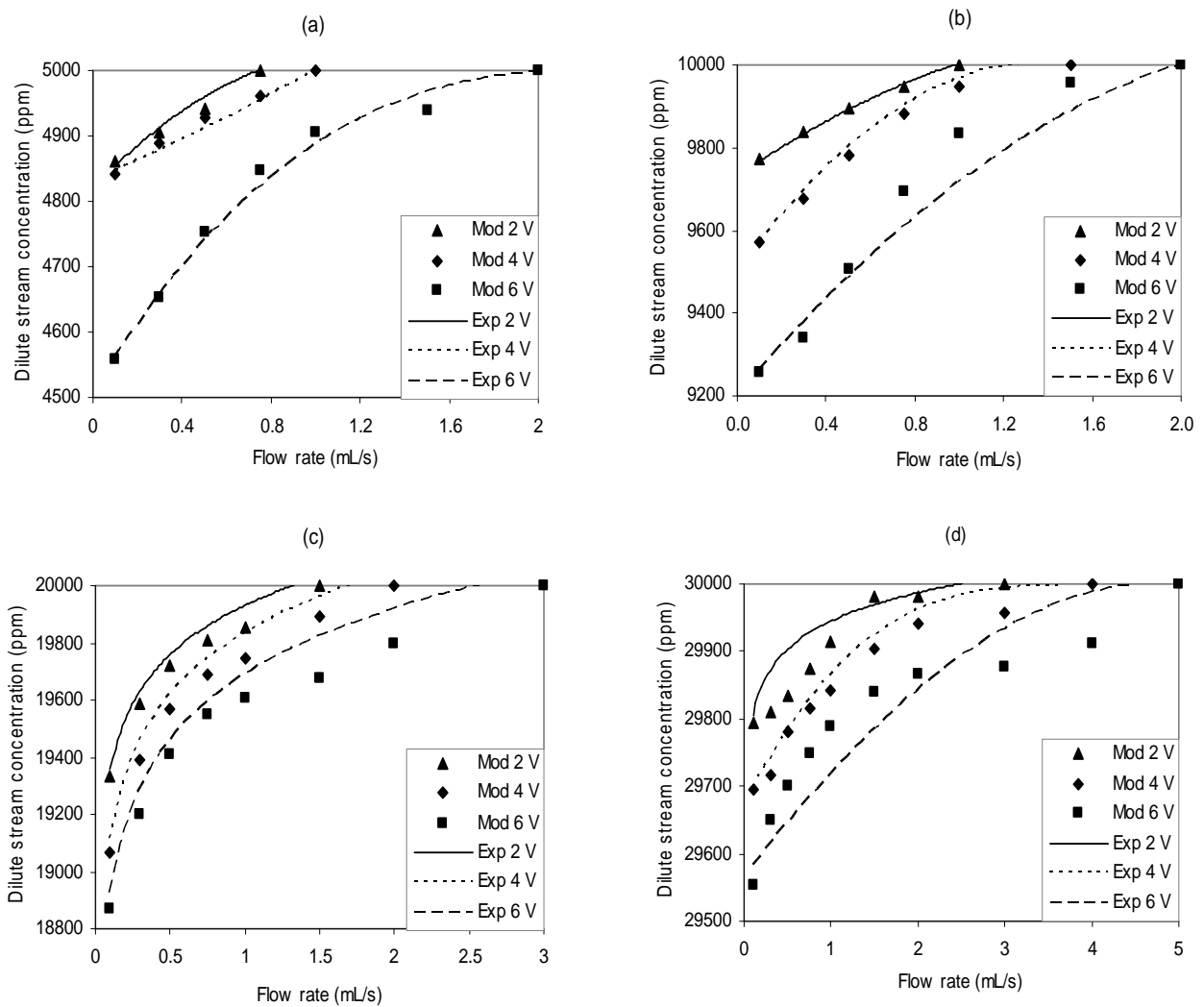


Figure 4- Concentration in dilute compartment at different flow rates, voltages and feed concentrations of (a) 5000, (b)10000, (c) 20000 and (d) 30000 ppm

In order to investigate the effect of feed concentration on ED cell performance, separation percent ($S\% = (C_0 - C)/C_0 \times 100$) is plotted as a function of feed concentration for both model and experimental results as shown in Figure 5. According to this figure, increasing concentration decreases ED cell performance due to the fact that concentration polarization phenomenon is more important at high concentrations. The result confirms that ED process is more useful for low feed concentrations, i.e. it is applicable as a post treatment process after reverse osmosis for concentrations of even lower than 1000 ppm.

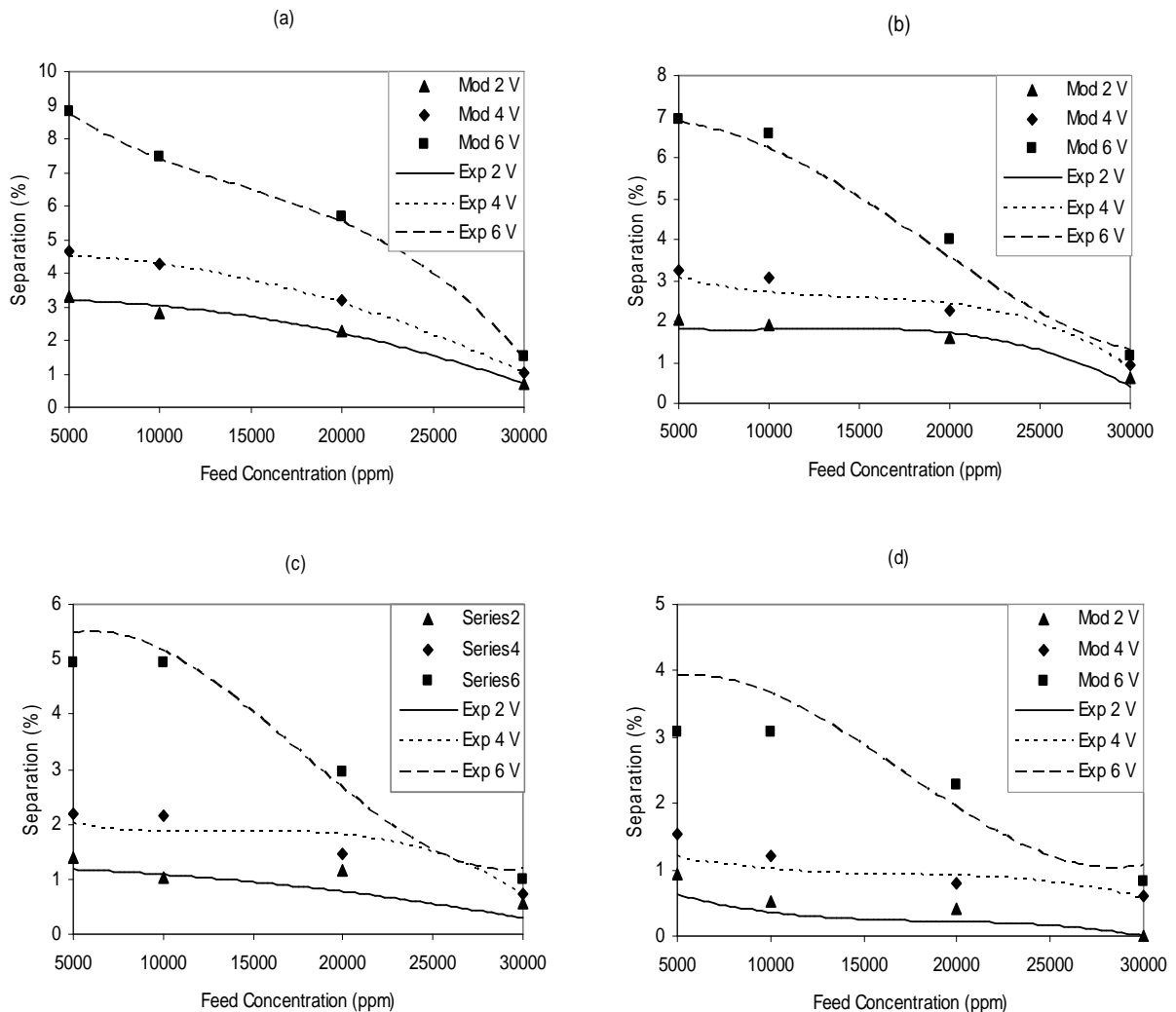


Figure 5- Separation percent at different feed concentration, voltages and flow rates of (a) 0.1, (b) 0.3, (c) 0.5 and (d) 0.75 mL/s

Figure 5 compares separation percent values of the experimental and calculated data at different flow rates. The result shows that there is a good consistency between the experimental and predicted results. This confirms that the developed model is reliable and expresses the actual behavior of the ED system.

CONCLUSIONS

In the present work, a mathematical model was developed using an ED channel mass balance and the fundamental electrochemical equations. Experiments were conducted to investigate the effect of voltages, flow rates and feed concentrations on ED cell performance and the model parameter was calculated using the outlet concentration in the dilute compartment. The developed model makes it possible to predict concentration of dilute stream or separation percent of an ED cell at different operating conditions. Experimental data were finally compared with the values predicted by the model. It was found that there is a good consistency between the model predictions and the experimental data. It means that this model can be used for prediction of ED desalination process.

Notations

u	Flow velocity (m s^{-1})
h	Thickness of dilute compartment (m)
C	Concentration (kmol m^{-3})
J	Molar flux ($\text{kmol m}^{-2} \text{s}^{-1}$)
x	coordinate (m)
i	Current density (A m^{-2})
F	Faraday constant (C kmol^{-1})
A_m	Effective area of ion exchange membrane (m^2)
I	Current intensity (A)
l	Flow length in channel (m)
Sh	Sherwood number
Re	Reynolds number
Sc	Schmidt number
D	Diffusivity ($\text{m}^2 \text{s}^{-1}$)
k	Mass transfer constant (m s^{-1})
E	Electrical potential (V)
N	Number of cell pairs
\mathcal{R}	Universal gas constant ($\text{J kmol}^{-1} \text{K}^{-1}$)
Q	Flow rate ($\text{m}^3 \text{s}^{-1}$)
λ	Molar conductivity of ions ($\text{S m}^2 \text{kmol}^{-1}$)
R	Resistance (Ω)
a, b, c, d, e, f, g, h	Constant
p, q, r, s	Constant
S	Separation percent (%)

Greek letters

η	Current efficiency
κ	Conductivity (S m^{-1})
Λ_M	Molar conductivity ($\text{S m}^2 \text{kmol}^{-1}$)
Λ_M°	Limiting molar conductivity ($\text{S m}^2 \text{kmol}^{-1}$)
ν	Stoichiometric constant

δ	Constant ($\text{m}^{1/3} \text{s}^{2/3} \text{A C}^{-1} \text{kmol}^{-1}$)
α	Constant ($\text{m}^{2/3} \text{s}^{-2/3}$)
β	Constant ($\text{kmol C m}^{-1} \text{A}^{-1}$)

Subscript

<i>M</i>	Molar
<i>m</i>	Membrane
<i>cm</i>	Cation exchange membrane
<i>am</i>	Anion exchange membrane
<i>c</i>	Concentrate compartment
<i>d</i>	Dilute compartment
+	Cation
-	Anion
0	Initial condition

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