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Experimental Study and Modelling of the Ammonium Sulphate Solution Electrodialysis

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Abstract: An experimental study was carried out on the constant voltage electrodialysis (ED) of ammonium sulphate solution using a laboratory-scale ED stack Eurodia-Tokuyama Model TS 2-5. The evolution of solution concentration has been determined for two feed rates and four voltages at 303 K. A mathematical model was developed to describe this evolution with time. The two empirical constants of the model have been identified by confronting the calculated data with the measured ones. The relative errors of the model with average values of the constants have been estimated. The validated model has been finally used to extrapolate the ED process in order to determine the necessary time for a complete removal of ammonium sulphate, equivalent to a final dilute concentration of 1.5 mol/L.

Keywords: Electrodialysis, Ammonium sulphate, Model validation.

1. Introduction

Electrodialysis (ED) is a unit operation which uses ion exchange membranes to remove electrolytes from solution under the driving force of electrical potential. The principle used in the ED process is the fact that the ion exchange membranes exclude co-ions, and hence only the counter-ions can diffuse through membranes. Thus, cations pass through the cation exchange membrane (CEM) and not through the anion exchange membrane (AEM). Similarly, the anions pass through the AEM and not through the CEM. Thus, if the membranes are arranged in an alternating fashion between the electrodes, this will result in concentrated and diluted compartments being formed between the membranes. In other words, ED is a unit operation which can, starting from a given electrolyte feed stream, produce a concentrated and a diluted product stream. Due to unwanted redox products being generated at the electrodes, it is common practice to use a third process stream, the electrode fluid, to prevent these unwanted products from entering the product streams. For a more elaborate description of the ED process the reader is referred to standard texts [1, 2].

The key parameters that determine the optimum range of ED applicability are: current density, cell voltage, current efficiency, dilute and concentrate solutions. The current density determines the quantity of product transported across the membranes. A higher current reduces the required surface of the ED cells. However, at a high current the cell voltage increases resulting in much higher power consumption. The can also be polarization when the ions are transported faster across the membranes than in the cell solutions to the membrane surface. This results in a very quick cell voltage increase. The *limiting current density* is the maximum allowed to avoid this steep cell voltage increase. Thus, for a given application it is important to first determine this critical parameter. This was done for ammonium sulphate solutions in a previous published paper [3]. Another restriction comes from the conductivity- concentration relation. The minimum dilute concentration is limited by conductivity considerations due to the ohmic resistance of the dilute cells. The conductivity of the ammonium sulphate solutions has been determined and correlated in a previous work [4].The conclusion was that the critical conductivity (0.5 mS/cm) corresponds to a concentration of 0.0003 Eq/L ammonium sulphate , at 308 K. This is equivalent to a concentration factor of 99% when starting with a solution of 0.3 Eq/L. Hence, ED can be applied to recover ammonium sulphate from diluted waste solutions.

This paper is devoted to the kinetic modelling of ammonium sulphate solution ED on the basis of experimental data obtained on a laboratory ED stack operated in batch mode at constant voltage.

2. Experimental

The laboratory–scale ED stack Eurodia-Tokuayama Model TS 2-5 (Fig.1) contained five cell pairs with membrane area of 0.02 m^2 (0.113x0.177 m) with a 0.4 mm intermembrane gap. The membranes used were AMX type anion exchange membranes and CMS type cation exchange membranes (Tokuyama Soda/ Neosepta). The main characteristics of the membranes used are presented in the Table 1. A platinized titanium anode and a 316 stainless steel cathode have been used.

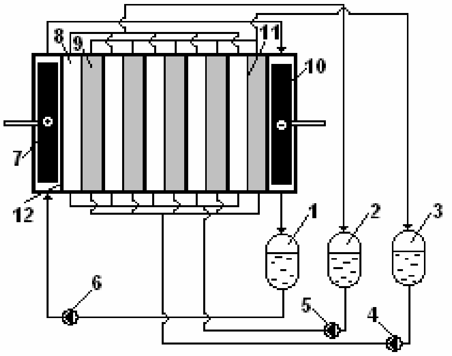

Figure 1.Diagram of the experimental system.
1-electrolyte tank ;2-dilute tank;3- concentrate tank; 4-concentrate pump, 5- dilute pump; 6- electrolyte tank; 7-anode;8-dilute cell; 9- concentrate cell;10- cathode; 11-cation exchange membranes; 12- anion exchange membranes.

The instantaneous concentrations in diluted and concentrated streams have been indirectly determined by measuring the electric conductivity at 303 K with a WTW LF 196 conductivity meter equipped with a TetraCon 96-1.5 conductivity cell with an integrated temperature sensor. The epoxy cell had easy to clean graphite plates with a cell constant of 0.609 cm^{-1}, a response time less than 12 seconds. The cell was calibrated with commonly used standard KCl 0.01 M solution having a conductivity of 1.412 μS/cm at 298 K. This 4 electrode cell reduces the problem of polarization error and fouling of the electrodes. The ammonium sulphate solutions of about 1% w have been prepared analytical grade salt and pre water (0.05 μS/cm).The laboratory unit was equipped with inline instruments for monitoring dilute, concentrate and electrode rinse feed rates and tank temperatures; voltage at the power source , across the stack (including anode and cathode chambers, and across the five cell pairs. Before each experiment the ED unit was thoroughly cleaned to circulate through the unit for five minutes at high flow rates.

Table 1. Characteristics of the membranes used.

Mem-brane	S, %	IEC, Eq/kg	R, Ωcm^2	BS, kg/cm^2	W, g/g dry	δ, mm
AMX	98.0	1.5	3.0	5.0	0.3	0.17
CMS	98.0	2.2	2.0	3.5	0.4	0.15

S- selectivity, IEC- ion exchange capacity, R- electric resistance, BS-burst strength, W- water content, δ-membrane thickness.

3. Results and discussion

The primary experimental results are presented in the Table 2 (total flow rate of 100 L/h, and different constant voltages: 5V; 7.5V; 10V; 12V) , and in the Table 2 (total flow rate of 140 L/h, and the same voltages). They represent the evolution of the dilute stream concentrations. In each run the solution volume (V_D) was 4.56 L, measured with errors from -1.65% to + 1.23%.

Table 2. Experimental results at a total flow rate of 100 L/h , and T= 303 K

Time, (s)	Diluted solution concentration, (mol/m^3)			
	5 V	7.5 V	10 V	12 V
0	91.6061	91.0909	90.7273	89.9015
180	90.1500	88.0200	86.0900	84.3100
360	88.7000	84.9900	81.5700	78.7700
540	87.2500	82.0200	77.1700	73.2900
720	85.8050	79.0950	72.8900	67.8700
900	84.3600	76.2200	68.7400	62.5200
1080	82.9150	73.4000	64.7100	57.2600
1260	81.4750	70.6350	60.8300	52.0850
1440	80.0400	67.9250	57.0800	47.0200
1620	78.6000	65.2700	53.4600	42.0700
1800	77.1700	62.6700	49.9850	37.2650
1980	75.7400	60.1250	46.6500	32.6200

The removal degree of the ammonium sulphate ($X= 1-C/C^0$) after 1980 s (33 minutes) at a total flow rate of 100 L/h increased with the voltage from 17.14% at 5 V to 63.79% at 12 V. At a total flow rate of 140 L/h the removal degree increased from 15% to 66.25% in the same conditions.

Table 3. Experimental results at a total flow rate of 140 L/h, and T= 303 K.

Time (s)	Diluted solution concentration, (mol/m^3)			
	5 V	7.5 V	10 V	12 V
0	90.8788	90.3106	90.2121	88.6591
180	89.5100	87.4200	85.7200	83.1250
360	88.1600	84.5600	81.2600	77.6150
540	86.8250	81.7300	76.8350	72.1300
720	85.5000	78.9300	72.4500	66.6800
900	84.1900	76.1600	68.1050	61.2600
1080	82.9000	73.4250	63.8100	55.8800
1260	81.6200	70.7300	59.5600	50.5500
1440	80.3500	68.0600	55.3750	45.2750
1620	79.1000	65.4400	51.2500	40.0700
1800	77.8700	62.8500	47.1900	34.9400
1980	76.6400	60.3000	43.2150	29.9250

4. Mathematical modelling

A mathematical model , derived on a phenomenological basis, could allow : (I)to predict the behaviour of the system in similar conditions but a larger scale (scale-up) ,(II) to calculate the necessary time for a final desired concentration,(III)to evaluate the necessary of electrical energy for a given application. There are several published attemps to modell the ED operated in a batch recirculation mode [5-11]. The model proposed in this paper is established starting from the molar flux of the ions i (NH_4^+, SO_4^{2-}) from the dilute stream through the membrane. This can be expressed in terms of current density as follows[10,11]:

$$N_i = -\frac{dn_i}{d\tau} = \frac{\eta_c dI}{zFdA_m} \qquad \text{(mol/s)}, \qquad (1)$$

Where: A_m = membrane area (m^2), I= current intensity (A), F=Faraday constant (96500 C/Eq), τ= time (s), n_i = number of moles transferred, η_c = current efficiency .

The assumption of constant flux (N_i) and constant current efficiency in dilute cell gives:

$$\frac{dI}{dA_m} = \frac{I}{A_m} = const. \qquad (2)$$

Concequently, the molar flux at any point of the membrane surface ca be written as follows:

$$N_i = k_L\left(C_i - C_i^s\right) = k_L \Delta C \qquad (3)$$

Where C_i and C_i^s are the concentrations at the bulk and at the membrane surface, respectively.

Due to the very short residence time in the dilute compartment (about one second in our case), and the constancy of the the ratio I/A$_m$, ΔC_i can be assumed to be constant along the membrane surface. Hence, (1) and (3) can be combined to give :

$$\eta_c = \frac{zFA_m}{I} k_L \Delta C = \alpha k_L \qquad (4)$$

where α is a constant. To correlate the mass transfer coefficient k_L the criterial relation (5) , derrived from limiting current measurements [4,5,6], can be used :

$$Sh = 8.093\sqrt{\frac{h}{\Delta l}}\,\mathrm{Re}^{0.13}\,Sc^{1/3} \quad \text{, at} \quad 100 < \mathrm{Re} > 300 \qquad (5)$$

where : h, l = characteristic distances of spacer; Sh, Sc, Re = Sherwood, Schmidt, Reynolds numer respectively.

For a given system, from (4) and (5) results:

$$\eta_c = \beta Q_D^{0.13} \qquad (6)$$

where : β is a constant ,and Q_D is the dilute flow rate.

In the constant voltage operation the current I can be replaced by the Ohm' relation :

$$I = \frac{U}{NR_{cp}} \qquad (7)$$

N= number of cell pairs , R_{cp}= electrical resistance of a cell pair. Neglecting the membranes resistances, the solution resistance can be expressed , at constant temperature, as a function of concentration:

$$R_{cp} = R_{sol} = \frac{1}{\lambda_{sol}} = \frac{p}{c_i} + q \qquad (8)$$

Combining (2), (6), (7), and (8) the differential equation (9) is obtained :

$$\int_0^{\tau} d\tau = \frac{zFV_D}{UQ_D^{0.13}} \int_{C_i}^{C_i^0} \left(\frac{a}{C_i} + b\right) dC_i \qquad (9)$$

where a = p/α , and b= q/α are constants. By integrating (9) with the limit conditions:

at τ =0 , $C_i = C_i^0$

the relation time vs concentration is obtained:

$$\tau = \frac{zFV_D}{UQ_D^{0.13}}\left[a\ln\frac{C_i^0}{C_i} + b\left(C_i^0 - C_i\right)\right] \qquad (10)$$

The constants *a* and *b* from (10) have been identified by confronting the equation with the experimental data. The average values of *a* and *b* , obtained for each experimental kinetic curve at 303 K, are presented in the Table 4.

Table 4. Average values of the constants.

Voltage, (V)	Flow rate, (L/h)	Constants	
		a	b
5	100	1.3691	0.1650
	140	12.4040	0.0626
7.5	100	5.1985	0.0696
	140	3.8253	0.0987
10	100	4.6851	0.0598
	140	1.4613	0.1050
12	100	1.3333	0.0969
	140	0.6300	0.1111

Table 5. Relative errors (ε,%) of the model for Q_D= 140 L/h, and T= 303 K.

Time, (s)	Voltage, V			
	5.0	7.5	10	12
0	0	0	0	0
180	0.069	-0.040	-0.441	-0.107
360	0.014	0.059	-0.300	0.425
540	-0.043	0.224	-0.241	0.062
720	0.083	0.272	-0.234	-0.319
900	0.139	0.257	-0.339	-0.905
1080	0.315	0.043	-1.305	-1.409
1260	0.312	-0.138	-2.235	-1.805
1440	0.318	-0.494	-2.992	-2.122
1620	0.510	-1.206	-4.995	-2.794
1800	0.367	-2.154	-7.048	-3.748
1980	0.682	-2.751	-9.169	-5.997

Table 6.Relative errors(ε, %)of the model for Q_D =140 L/h , and T= 303 K.

Time, (s)	Voltage , V			
	5.0	7.5	10	12
0	0.000	0.000	0.000	0.000
180	-0.087	-0.177	-0.062	0.074
360	0.042	0.144	0.081	-0.073
540	0.033	0.077	0.067	0.403
720	-0.106	-0.164	0.027	0.233
900	-0.097	-0.541	-0.240	-0.348
1080	-0.466	-0.753	-0.285	0.286
1260	-0.493	-1.424	-0.729	0.290
1440	-0.724	-1.835	-0.779	0.362
1620	-0.988	-2.416	-1.409	0.814
1800	-1.137	-3.384	-1.583	1.353
1980	-1.459	-3.957	-1.900	2.056

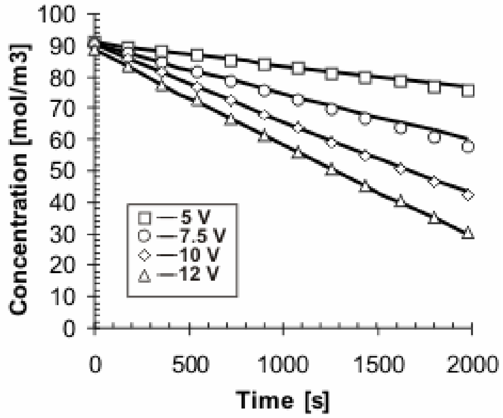

Figure 2. Calculated (lines) versus experimental (symbols) data at Q_D= 100 L/h , and T=303 K.

The concentration corresponding to each experimental point has been recalculated with the model including the constants from the Table 4. A graphical comparison between experimental and comupted concentration is given in Fig. 2 and in Fig.3. The relative errors are summarized in the Table 5 and the Table 6. The adequacy of the model has been testified in this manner.

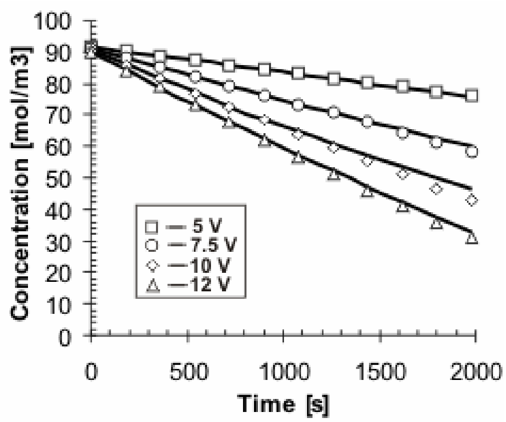

Figure 3. Calculated (lines) versus experimental (symbols) data, at Q_D = 140 L/h , and T= 303 K.

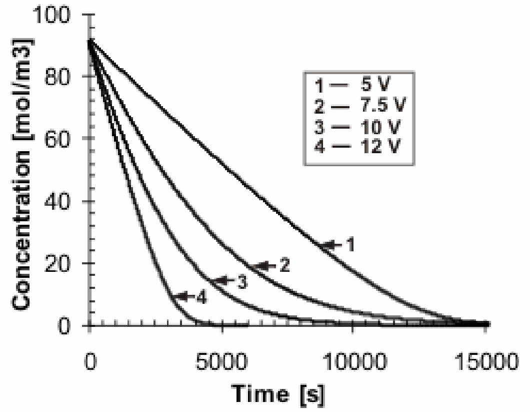

Figure 4. Calculated dilute concentrations at Q_D=100 L/h , and T= 303 K.

Finally, the validated model was used to simulate the electrodialysis exteded to 15 000 seconds (Fig.4) in order to evaluate the necessary time for an almost complete removal of ammonium sulphate from the feed solution. If the residual concentration of the diluted solution is 1.5 mmol/L (removal of over 98%) the necessary time, at a feed rate of 100 L/h, decreases from 3.9 hours at a voltage of 5 V to only 1.1 hours at a voltage of 12 V. A compromise must be adopted because the necessary electrical energy increases with the voltage.

5. Conclusions

- Electrodialysis is a suitable process to recover ammonium sulphate, a valuable fertilizer, from residual diluted solutions.

- The experimental results obtained on a laboratory-scale ED unit at 303 K, operated at constant voltage in a batch recirculation mode, revealed the influence of two important parameters: feed rate (100 L/h, and 140 L/h), and applied voltage (5 V, 7.5 V, 10 V, and 12 V).The results have shown , as expected, that at higher voltages the feed ion concentration was depleted more rapidly thus reducing the duration of the process. The influence of the flow rate is important only at higher voltages (10 V, and 12 V in this system). At higher feed rates the residence time of the solution in the cells becomes too short.

- A mathematical model has been derived and validated with the experimental data. The application of this model allows to predict the system behaviour in various operation conditions and calculate the necessary time for a successful ED of ammonium sulphate solutions, as well as to calculate the necessary electrical energy.

- The model developed in this paper could be applied to commercial ED units (industrial / pilot plants) working in batches with recirculation and controlled potential, which is the usual mode of operation of such equipment when the requirements of treated residual solution are moderated.

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