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SCIENTIFIC PAPER

## STUDY OF THE AMMONIUM SULFATE AQUEOUS SOLUTION ELECTRODIALYSIS

*A mathematical model was derived to describe the concentration evolution with time in a batch – recirculation laboratory – scale electrolysers. The integrated model contains two constants that have been identified by confronting the computed data with the experimental ones. The relative errors of the model including the average values of the identified constants have been estimated. The validated model was finally used to extrapolate the electro dialysis (ED) process in order to determine the necessary time for a complete removal of ammonium sulfate, equivalent to a final dilute content of less than 1.5 mol/m<sup>3</sup> ammonium sulfate.*

*Key words: Electrodialysis, ammonium sulfate, mathematical model, scale-up.*

Electrodialysis (ED) is an electrically driven membrane separation process which is capable of separating, concentrating, and purifying selected ions from aqueous solutions (as well as some organic solvents). The process is based on the property of ion exchange membranes to selectively reject anions or cations. For a more elaborate description of the ED process the reader is referred to standard texts [1,2].

The first use of ED was the desalination of brackish water and seawater. Currently, the desalting plants in about 130 countries worldwide have the capacity to produce over 23 million m<sup>3</sup> of high quality water each day [2]. The second major use of ED was envisaged in Japan where the ED was used to concentrate NaCl from seawater to produce table salt. A third important application of ED was the waste water treatment: the recovery of nickel and copper salts from electroplating rinse waters, removal of nitrate from natural and waste water to produce drinking water, treatment of cooling-tower waste streams.

The use of ED in the food, drug and chemical industry has been studied extensively in recent years [2]. Several applications have great economic significance and are already well established today. The most important by far ones are cheese whey demineralization, and the removal of potassium tartrate from wine. A new important application could be the demineralization of fermentation liquids. Such liquids can contain ammonium sulfate [3]. The paper of Moon et al. [3] suggested us the study of the ED of such diluted solutions in order to recover ammonium sulfate – a valuable fertilizer. Our previous papers were devoted

to the experimental study of the ammonium sulfate solution ED process in order to determine and correlate the limiting current density [4], to measure and correlate the electrical conductivity of the solution [5], and to investigate the influence of the main operating parameters on the separation degree [6].

Despite the important commercial application the mathematical modeling of the ED process is still in infancy. Most published papers on the subject are devoted to the continuous plants used in the sea water desalination. There are also some attempts to model the batch circulating ED plants, but they are devoted to other systems with different mode of operation [7–10].

### EXPERIMENTAL

The objective of the experimental study was to determine the ammonium sulfate concentration in the two main streams (dilute and concentrate) versus the time of electro dialysis in order to evaluate the duration of the process under different values of the parameters: initial solution concentration, temperature, voltage applied to electrodes, solution flow rate, and inter-membranes gap. To this end a laboratory– scale ED unit type TS 2–5 from Eurodia/Tokuyama has been used. The ED stack contained five cell pairs. The membranes used (Table 1) were AMX type anion–exchange membranes and CMS type cation–exchange membranes (from Tokuyama Soda/ Neosepta). Each membrane had a transfer area of 0.02 m<sup>2</sup> (0.113 x 0.177 m). Polypropylene mesh spacers were used for desired inter-membrane and electrode chamber gaps (0.4 mm and 2.0 mm respectively), and to promote turbulence. The two electrodes were made of platinized titanium (anode), and 316 stainless steel (cathode). The instantaneous concentrations of the diluted and concentrated streams were indirectly determined by measuring their electrical conductivity at constant temperature with a WTW LF 196 conductivity meter equipped with a TetraCon 96–1.5 conductivity cell.

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Table 1. The main characteristics of the membranes used

Membrane	Selectivity, %	Ion exchange capacity, Eq/kg	Electric resistance, $\Omega\text{cm}^2$	Burst strength, $\text{kg/cm}^2$	Water content, $\text{kg/kg dry}$	Membrane thickness, 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

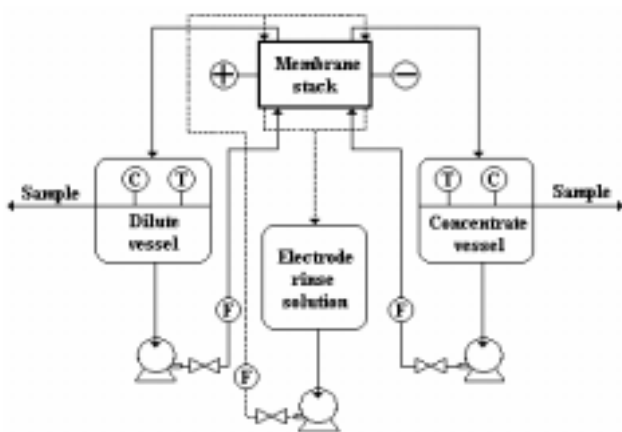


Figure 1. Diagram of the experimental ED system. T, C, and F are temperature, conductivity, and flow rate meters.

The cell was calibrated with the commonly used standard solution of 0.01 M KCl ( $1.412 \mu\text{S/cm}$ , at 298 K).

The ED unit was equipped with in-line instruments for monitoring flow rates (F), temperature (T), conductivity/concentration (C), and voltage (Figure 1). The system was operated in batch recirculation mode at constant voltage. Before each experiment the ED unit was thoroughly cleaned by circulating through the stack standard solution at high flow rate for five minute.

## RESULTS AND DISCUSSION

The experimental results at 303 K are presented in the Table 2 for a total flow rate of  $2.78 \times 10^{-5} \text{ m}^3/\text{s}$ . Similar results have been obtained for a total flow rate of

$3.89 \times 10^{-5} \text{ m}^3/\text{s}$ . The table includes the measured dilute concentrations at four different voltages, and twelve times of electro dialysis, as well as the degree of removal ( $X_D$ ) of ammonium sulfate from the feed stream.

The results from Tables 2 show a strong influence of the potential applied at the electrodes in the constant voltage mode of operation. The salt degree increased from 17.32% at 5V to 63.71% at 12V, after 33 minutes ED time, when the feed rate was  $2.78 \times 10^{-5} \text{ m}^3/\text{s}$ , at 303 K. Similar figures have obtained with a flow rate of  $3.89 \times 10^{-5} \text{ m}^3/\text{s}$ . However, at higher voltage the power consumption became too important and the process inefficient. Therefore, depending on the solution concentration, the maximum voltage per cell must not exceed 0.8 – 1.5 V.

The results have shown a slight influence of the flow rate increasing from  $2.78 \times 10^{-5} \text{ m}^3/\text{s}$  to  $3.89 \times 10^{-5} \text{ m}^3/\text{s}$ . The greatest removal degree after 33 minutes ED time at 12 V was 63.71% working with a flow rate of  $2.78 \times 10^{-5} \text{ m}^3/\text{s}$ , and 66.25% with a flow rate of  $3.89 \times 10^{-5} \text{ m}^3/\text{s}$ .

Future experiments, at lower flow rates, must be done in order to elucidate the complex influence of this parameter.

The third parameter studied was the ED time. This was limited in experiments to 33 minutes. The question is: "What is the necessary time to reach the desired practical removal degree"? Consequently, the second question arose: "What was the maximum degree of removal which can be obtained with given feed solution"? It is known that the minimum conductivity that can be considered in a given application of ED is of 0.5 mS/cm.

Table 2. Experimental results with  $Q_D = 2.78 \times 10^{-5} \text{ m}^3/\text{s}$ ,  $T = 303 \text{ K}$ 

Voltage	5 V		7.5 V		10 V		12 V		
	Time, min.	$C_i, \text{ mol/m}^3$	$X_D, \%$	$C_i, \text{ mol/m}^3$	$X_D, \%$	$C_i, \text{ mol/m}^3$	$X_D, \%$	$C_i, \text{ mol/m}^3$	$X_D, \%$
0		91.61	0.00	91.09	0.00	90.73	0.00	89.90	0.00
3		90.15	1.59	88.02	3.37	86.09	5.11	84.31	6.22
6		88.70	3.18	84.99	6.70	81.57	10.10	78.77	12.38
9		87.25	4.76	82.02	9.89	77.17	14.94	73.29	18.48
12		85.80	6.34	79.09	13.17	72.89	19.66	67.87	24.50
15		84.36	7.91	76.22	16.32	68.74	24.23	62.52	30.46
18		82.91	9.50	73.40	19.42	64.71	28.68	57.26	36.31
21		81.47	11.07	70.63	22.46	60.83	32.95	52.08	42.07
24		80.04	12.63	67.92	25.43	57.08	37.09	47.02	47.70
27		78.60	14.20	65.27	28.34	53.46	41.08	42.07	53.20
30		77.17	15.76	62.67	31.20	49.98	44.91	37.26	58.55
33		75.74	17.32	60.12	34.00	46.65	48.58	32.62	63.71

This value is equivalent to an ammonium sulfate concentration of 1.5 mmol/L at 303 K [6]. In other words, the ammonium sulfate can be extracted by ED until the final dilute solution is depleted to 1.5 mmol/L. Below this concentration the electrical resistance becomes too high, and the process is economically inefficient. The final concentration being fixed, we tried to find the necessary time by mathematical modeling and extrapolation.

A mathematical model was derived, based on the following assumptions: (I) constant mass transfer flux, and constant current efficiency in the cell bulk, (II) a constant ratio  $I/A_m$  along the membranes in each cell due to the very short residence time of the solution in the dilute and concentrate compartments, (III) the electrical resistance of the membranes can be neglected and the cell resistance equals the solution resistance, (IV) the solution resistance is a linear function of concentration. Starting from the mass balance of the ion transfer from the diluted stream, expressed in terms of current density, one obtains:

$$N_i = -dn_i/dt = (\eta/zF) (dI/dA_m), \text{ mol/s} \quad (1)$$

where:  $A_m$  = membrane area ( $m^2$ ),  $I$  = current intensity (A),  $F$  = Faraday constant (96500 C/Eq),  $\tau$  = ED time (s),  $n_i$  = number of moles of ion  $i$  transferred,  $\eta$  = current efficiency.

The assumptions (I) and (II) lead to the constancy of the current density along the membrane area:

$$dI/dA_m = I/A_m \quad (2)$$

As a result, the molar flux at any point of the membrane surface can be written as follows:

$$N_i = k_L (C_i - C_i^s) = k_L \Delta C_i \quad (3)$$

where  $C_i$  and  $C_i^s$  are the molar concentrations at the bulk and at the membrane surface, respectively. Due to the very short residence time of ions in the cell (about one second in our case), and to the constancy of the ratio  $I/A_m$ , the concentration gradient can also be considered as constant along the membrane surface. Hence, from (1) and (3) results:

$$\eta = (z F A_m/I) k_L \Delta C_i = \alpha k_L \quad (4)$$

where  $\alpha$  is a constant for the given system. To correlate the mass transfer coefficient  $k_L$  the criterial equation (5), derived from limiting current measurements on a ED unit of the same geometry [4,7], is recommended:

$$Sh = K Re^{0.13} Sc^{1/3} \quad (5)$$

where  $K$  is a constant including the characteristic dimensions of the cell; while  $Sh$ ,  $Re$ ,  $Sc$  are the Sherwood, Reynolds, and Schmidt number, respectively. By combining (4) and (5), for a given system, results:

$$\eta = \beta Q_D^{0.13} \quad (6)$$

with  $Q_D$ , the dilute flow rate ( $m^3/s$ ).

In the constant voltage operation, the current intensity can be replaced by  $U$ , using the Ohm's law:

$$I = U/(N R_{cp}) \quad (7)$$

where  $N$  is the number of cell pairs and  $R_{cp}$  the electrical resistance of a cell pair ( $\Omega$ ). The calculations done have shown that the membrane resistance was negligible compared to the solution resistance. As a result,  $R_{cp}$  can be reduced to  $R_{sol}$  which is a linear function of concentration in the investigated range, at constant temperature [6]:

$$R_{cp} = R_{sol} = 1/\Lambda = p/C_i + q \quad (8)$$

By combining the above relations, the homogeneous differential equation was obtained:

$$d\tau = (z F V_D / U Q_D) (a/C_i + b) dC_i \quad (9)$$

where  $a = p/\alpha$ , and  $b = q/\alpha$  are constant amounts for a given system. By integrating the equation (9) with the initial condition (10) the expression of ED time (11) was obtained:

$$\tau = 0, C_i = C_i^0 \quad (10)$$

$$\tau = (z F V_D / U Q_D^{0.13}) [\ln(C_i^0/C_i) + b(C_i^0 - C_i)] \quad (11)$$

By introducing the removal degree ( $X_D = 1 - C_i/C_i^0$ ) instead of  $C_i$  as separation performance, the expression of the ED time becomes:

$$\tau = (z F V_D / U Q_D^{0.13}) [b C_i^0 X_D - \ln(1 - X_D)] \quad (12)$$

where  $V_D$  is the volume of the dilute tank ( $m^3$ ), and  $U$  the stack voltage (V). The constants  $a$  and  $b$  have been identified by confronting the equation with the experimental data. The average values of the constants for the investigated parameters are presented in Table 3. The performance ( $C_i$ , and  $X_D$ ) were recalculated with the model including the constants in the Table 3. The agreement between the experiments and computed values was over 98% in each point, as illustrated in Fig.2.

The validated model was then used to extrapolate the process to longer times. The results are presented in Fig. 3. The necessary ED time to remove over 98 % of ammonium sulfate, at a flow rate of  $2.78 \times 10^{-5} m^3/s$ , according to the data in Fig. 3, decreases from 3.9 hours at 5 V to 1.1 hours at 12 V.

Table 3. The average values of the constants  $a$  and  $b$  of the model.

$Q_D, m^3/s$	$2.78 \times 10^{-5} m^3/s$		$3.89 \times 10^{-5} m^3/s$	
$U, V$	$a$	$b \times 10^2$	$a$	$b \times 10^2$
5	0.1622	1.954	1.4693	0.741
7.5	0.6158	0.842	0.4531	1.169
10	0.5549	0.708	0.1731	1.243
12	0.1579	1.147	0.0746	1.316

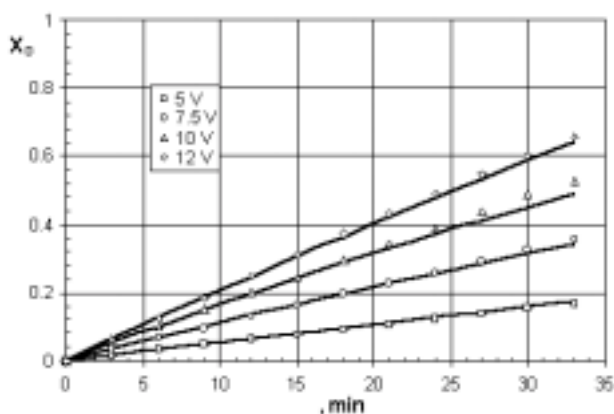


Figure 2. Evolution of the separation degree with time at constant voltage ( $Q_D = 2.78 \times 10^{-5} \text{ m}^3/\text{s}$ ,  $T = 303 \text{ K}$ )

## CONCLUSIONS

An experimental investigation has been performed on a laboratory-scale ED unit at 303 K, operated at a constant voltage in a batch recirculation mode, in order to find the influence of the three main operating parameters: ED time (0 to 33 minutes), stack voltage (5, 7.5, 10, and 12 V), and feed flow rate ( $2.78 \times 10^{-5} \text{ m}^3/\text{s}$ , and  $3.89 \times 10^{-5} \text{ m}^3/\text{s}$ ).

The results were confronted with a mathematical model derived on phenomenological basis. The two empirical constants of the model were identified. The validated model has been employed to extrapolate the process to "extra times" in order to obtain the desired removal degree of ammonium sulfate from a given diluted solution.

These experimental and theoretical studies have shown that electrodialysis (ED) could be a practically efficient process for ammonium sulfate recovery from aqueous solutions resulting in several new biotechnologies.

## IZVOD

### MATEMATIČKO MODELOVANJE ELEKTRODIJALIZE VODENOG RASTVORA AMONIJUM SULFATA

(Naučni rad)

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Definisana je matematički model kojim je opisana promena koncentracije sa vremenom u šaržnom (reaktoru) elektrodijalizatoru sa recirkulacijom reakcione smeše. Model uključuje dve konstante koje su određene upoređivanjem eksperimentalno određenih i izračunatih vrednosti koncentracije amonijum sulfata sa vremenom trajanja elektrodijalize rastvora. U radu je definisana relativna greška izračunavanja koncentracije amonijum sulfata na osnovu definisanog modela, kao i srednje vrednosti izračunatih parametara modela. Ovako potvrđen model je iskorišćen u cilju ekstrapolacije i definisanja neophodnog vremena za uklanjanje amonijum sulfata iz rastvora primenom elektrodijalize do konačnog dostizanja koncentracije u rastvoru koja je manja od  $1.5 \text{ mol}/\text{m}^3$ .

Ključne reči: Elektrodijaliza, Amonijum sulfat, Matematički model, Povećanje razmere.

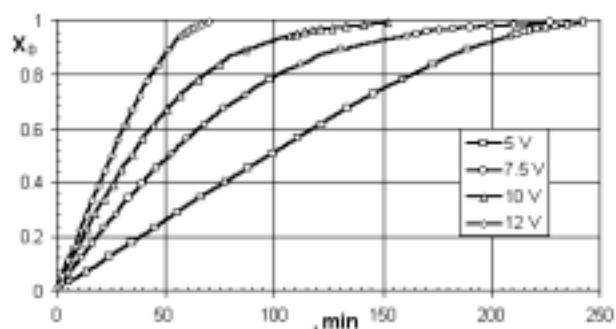


Figure 3. Simulation and extrapolation of the process to longer times, at  $Q_D = 2.78 \times 10^{-5} \text{ m}^3/\text{s}$

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