

## ELECTRODIALYSIS OF AMMONIUM SULFATE SOLUTIONS: EXPERIMENTAL STUDY AND MATHEMATICAL MODELLING

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**Abstract:** The kinetic experimental study was carried out on a laboratory-scale electro dialysis (ED) unit of TS2-5 type from Eurodia-Tokuyama equipped with five cell pairs. The membranes used were the AMX type anion exchange membranes (AEM) and CMS type cation exchange membranes (CEM), each of 0.02 m<sup>2</sup> surface area. The feed was an aqueous ammonium sulfate solution with molar concentrations of 88 to 92 mol/m<sup>3</sup>. The evolution with time of the solution concentration in both dilute and concentrate compartments has been determined for two feed rates and four voltages, at a 303 K constant temperature. A mathematical model has been derived to describe the concentration evolution with time. The model includes two empirical constants *a* and *b*. The constants have been identified by confronting the computed data with the experimental ones. The validated model has been finally used to extrapolate the ED process in order to determine the necessary time for a practically maximal removal of ammonium sulfate. This is equivalent to a final dilute concentration of less than 1.5 mol/m<sup>3</sup>.

**Keywords:** *electrodialysis, ammonium sulfate, experiments, modeling, extrapolation.*

## INTRODUCTION

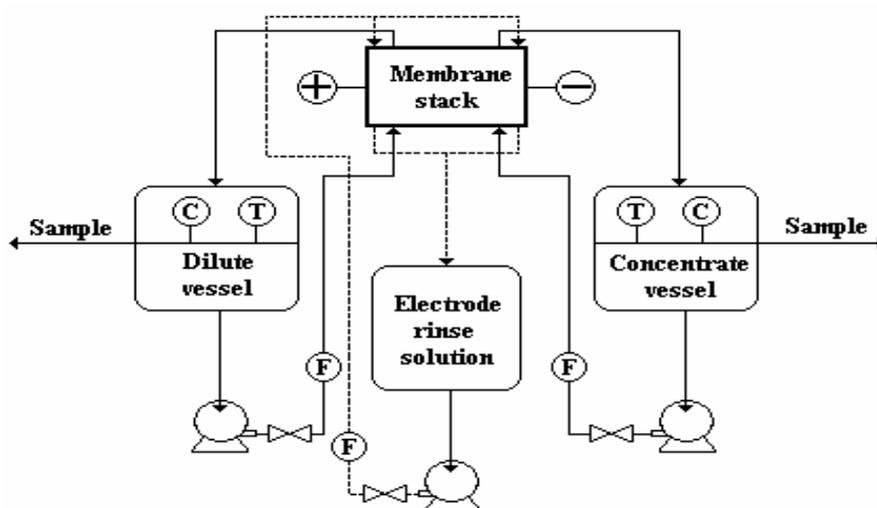
Electrodialysis (ED) is an electrically driven membrane separation process which is capable of separating, concentrating, and purifying selected ions from aqueous solutions (as well as some organic solvents). The process is based on the property of ion exchange membranes to selectively reject anions 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. The second major use of ED was envisaged in Japan where the ED was used to concentrate NaCl from seawater to produce table salt. The use of ED in food, drug and chemical industry has been studied extensively in recent years [3 - 9]. Several applications have great economic significance and are already well established today. The most important are by far the 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 [10]. This paper is devoted to the study of the ED of such diluted solutions in order to recover ammonium sulfate – a valuable fertilizer.

## EXPERIMENTAL

The objective of this study was to determine the ammonium sulfate concentration in the two main streams (dilute and concentrate) versus the ED time 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). 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. The cell was calibrated with the commonly used standard solution of 0.01 M KCl (1.412 μS/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.

*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 [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 meters

## RESULTS AND DISCUSSION

The experimental results at 303 K for a total flow rate of  $2.78 \cdot 10^{-5} \text{ m}^3/\text{s}$ , and for a total flow rate ( $Q_D$ ) of  $3.89 \cdot 10^{-5} \text{ m}^3/\text{s}$  have been tabulated in a previous work [5]. Each table included the measured dilute concentrations at four different voltages, and twelve times of electrodialysis, as well as the removal degree ( $X_D = 1 - C_D/C_D^0$ ) of ammonium sulfate from the feed stream. The results have shown a slight influence of the flow rate increasing from 100 L/h to 140 L/h. The greatest removal degree after 33 minutes ED time at 12 V was 63.71% working with a flow rate of 100 L/h, and 66.25% with a flow rate of 140 L/h. 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? From here, the second question: what is the maximum removal degree 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. This is equivalent to an ammonium sulfate concentration of 1.5 mmol/L at 303 K [3]. 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 has been derived, based on the following assumptions: (1) constant mass transfer flux, and constant current efficiency in the cell bulk, (2) constant ratio  $I/A_m$  along membranes in each cell due to the very short residence time of the solution in the dilute and concentrate compartments, (3) the electrical resistance of the membranes can be neglected, and the cell resistance equals the solution resistance, (4) the solution resistance is a linear function of concentration. Starting from the mass balance of the ion transfer through membranes, with the above hypothesis, the following equation was obtained:

$$\tau = A [a \ln (C^0/C) + b (C^0 - C)] \quad (1)$$

with:

$$A = (z F V_D) / (U Q_D^{0.13}) \quad (2)$$

where:

$\tau$  = ED time (s),

$C^0$  = initial feed concentration (mol/m<sup>3</sup>),

$C$  = dilute concentration at the time  $\tau$ ,

$F$  = Faraday constant (96 500 C/Eq),

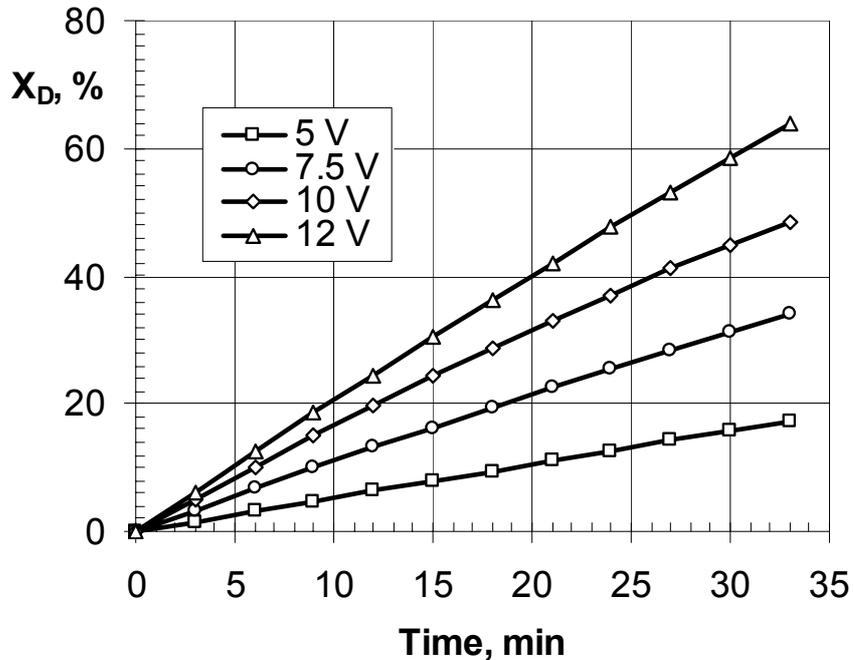
$V_D$  = volume of the dilute tank (m<sup>3</sup>),

$Q_D$  = flow rate of dilute solution (m<sup>3</sup>/s),

$U$  = stack voltage (V),

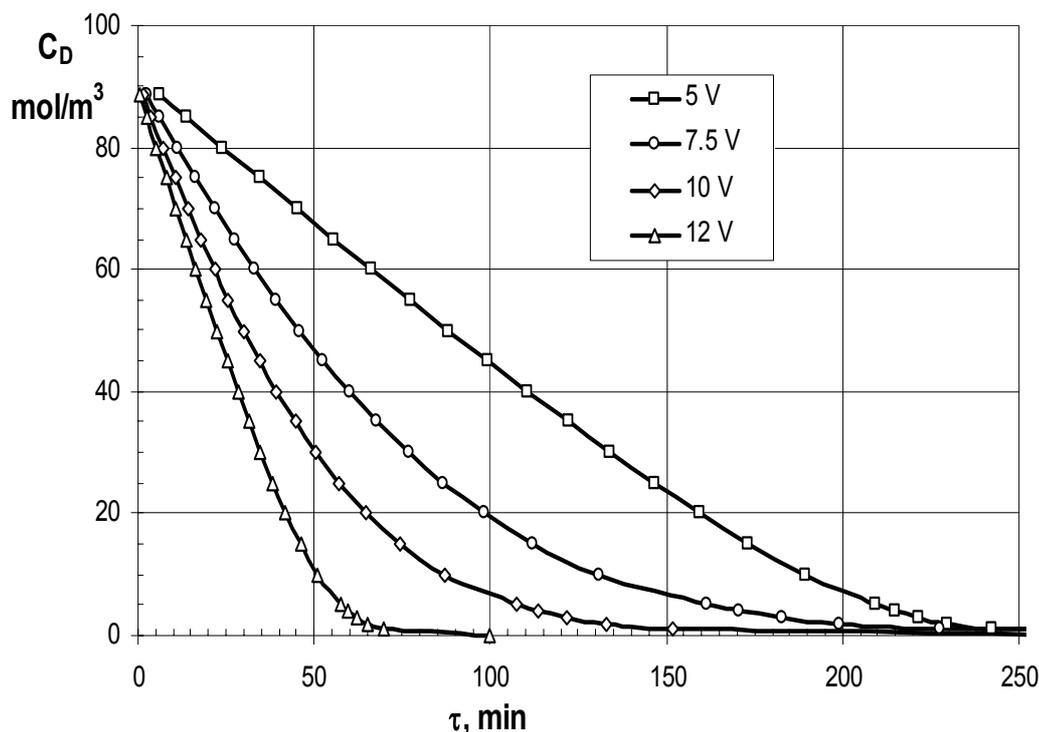
$a$  and  $b$  = constants to be identified.

The constants  $a$  and  $b$  have been identified by confronting the equation with the experimental data (Figure 2). At a voltage of 10 V and a flow rate of 100 L/h, for example, the average values of  $a$  and  $b$  were 4.68 and 0.06 respectively.



**Figure 2.** Evolution of separation degree with time at constant voltage ( $Q_D = 100$  L/h,  $T = 303$  K).

The validated model was then used to extrapolate the process to longer times. The results are presented in Figure 3.



**Figure 3.** Simulation and extrapolation of the process to longer times, at  $Q_D = 100$  L/h.

## 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 (100 L/h, and 140 L/h).

The results have been confronted with a mathematical model derived on phenomenological basis. The two empirical constants of the model have been 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 electro dialysis (ED) could be a practically efficient process for ammonium sulfate recovery from aqueous solutions resulting in several new biotechnologies.

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