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Modeling of a monopolar ion-exchange membrane for nutrient salts removal

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ABSTRACT

Mathematical model was developed to determine reliable design conditions of electrodialysis (ED) system with a monopolar ion-exchange membrane and assess its performance. Good agreement was obtained between the simulated results of the mathematical model and the measured data. Removal of nitrogenous ions of NH_4^+-N was easier than that of PO_4^{3-}-P ions because of high mobility due to the small molecular weight. The supplied voltage (E) and the concentration ratio of concentrate to dilute (k) were important controlling factors for the removal rate of nutrient salts (S_i). From the experimental and simulated results, it is believed that the developed model is applicable to the flow analysis of ED system.

Keywords: Modeling; Ion-exchange membrane; Electrodialysis; Nutrients; Concentration ratio

1. Introduction

The development of synthetic ion-exchange membrane stimulated both commercial and academic interests in such membranes and the related processes. Nowadays, synthetic ion-exchange membranes have been improved by various methods and have many practical uses. The most important industrial applications using electrodialysis (ED) were the production of fresh water from brackish water and brine solutions of seawater. With the development of reverse osmosis (RO), the employing of ED has been rapidly decreased for desalination [1,2]. Hence, an alternative application for ED other than desalination has been developed where RO or other membrane processes cannot be applied. Compared to RO, ED has the advantage of being able to utilize more thermally and chemically stable membrane, so that the processes can be run at elevated temperatures and in solutions of very low or high pH values [3]. ED can be used for purification by demineralization of solutions of widely varying industrial fluids found in food, chemical, and

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pharmaceutical industries, namely, separation of inorganic salts from cheese whey containing organics such as proteins and sugars, deacidification of fruit juices, etc. Also, ED technology can be effectively applied for the removal of nitrate in ground and surface water. Pollution of drinking water with nitrate presents a serious health hazard to infants and lead to acute asphyxiation, a syndrome known as methemoglobinemia. This research proposes ED as a better approach to nutrient salts removal in water treatment. ED as post treatment unit is believed to be an applicable technology for nutrient salts removal in the process. This study focused on the development of mathematical model for the evaluation of mass flux of ions and the effect of operational parameters in a monopolar ion-exchange membrane system.

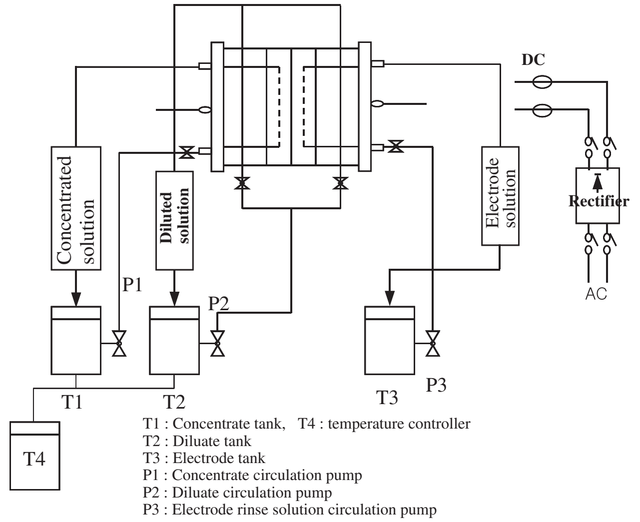


Fig. 1. Schematic diagram of ED process.

2. Materials and methods

2.1. ED system

TS-1-10 type ED equipment (Tokuyama Soda Co., Japan) was employed in this experiment. It is a batch type dialysis unit fitted with 10 pairs of anion- and cation-exchange membranes. The design characteristics and specification of the system are given in Table 1. A solution of 0.1 M Na_2SO_4 with a flow rate of 120 (L/h) was used as an electrode rinse. Schematic diagram of the ED process is shown in Fig. 1.

A cell consists of a volume with two adjacent membranes. If an ionic solution such as an aqueous salt solution is pumped through these cells and an electrical potential established between the anode and cathode, the positively charged cations migrate towards the cathode and the negatively charged anions towards the anode. The cations pass easily through the negatively charged cation-exchange membrane but are retained by the positively charged anion-exchange membrane. Likewise, the negatively charged anions pass through the anion-exchange membrane but are retained by the cation-exchange membrane. The overall result is an increase in the ion concentration in alternate compartments, while simultaneously ions become depleted in the other compartments. Volume of each

Table 1
Design characteristics and specification

Description of equipment	
Cation-exchange membrane	CMX (polypropylene woven fabric) Resistant to chemicals and alkali
Anion-exchange membrane	AMX (polypropylene woven fabric) Resistant to chemicals and alkali
Transport number	>0.99
Membrane active area, cm^2	200
Electric resistance[a], $\Omega\,cm^2$	2.3–3
Number of cell pairs	10
Material of anode	Platinum plated titanium
Material of cathode	Stainless steel 316
Magnetic drive pump (Iwaki, Japan)	Three units
Solution tank	Three sets
Rectifier (Kikuchi, Japan)	DC power 9 (A) × 18 (V)
Size, mm	500W × 400D × 700(H)
Thickness of membrane, mm	0.18
Electric capacity	0.2 kW, 100 V (50/60 Hz)

[a] Equilibrated with 0.5 N NaCl solution at 25°C.

tank is 3.5 L and the retention time was kept 1.8 min at 120 L/h of flow rate. Samples of 50 mL were collected from the dilution tank and the concentration tank with 10 min interval for water quality analysis.

2.2. Preparation of feed solution

Synthetic feed solution was prepared for nutrients desalination. It is a mixture of sodium chloride, with calcium chloride ($CaCl_2$, anhydrous), NH_4Cl, and K_2HPO_4. The characteristics of feed solution are revealed in Table 2.

2.3. Analysis

Using an orion pH meter (model 250A) and conductivity meter (Cole-parmer, model 124), the pH and conductivity of the feed and dilute solution were measured as a function of time. Ca^{2+}, K^+, and Na^+ were measured with an atomic analyzer (AA-11, NJA Co., Japan) and Cl^- was measured by an ion chromatograph (IC-14A, Dionex, USA). NH_4^+-N was measured by the indophenols method with Shimadzu UV-1200, Japan. Measurements of other items were conducted by standard methods [4].

3. Results and discussion

3.1. Estimation of mass flux of ions

If it is assumed that the concentration of dilution and concentration tank, mass balance of ions in ED system can be expressed as shown in Fig. 2.

From Fig. 2, mass balances in dilution tank and dilution chamber are as follows:

$$Q_1(C_1 - C_1') = W_1 \frac{dC_1'}{dt} \tag{1}$$

$$Q_2(C_2 - C_2') = W_2 \frac{dC_2'}{dt} \tag{2}$$

Table 2
Characteristics of feed solution

pH	6.8
Conductivity, μs/cm	3,210
Ca^{2+}	330
Na^+	450
Cl^-	1,050
K^+	35
NH_4^+-N, mgN/L	12.5
PO_4^{3-}-P, mgP/L	1.9

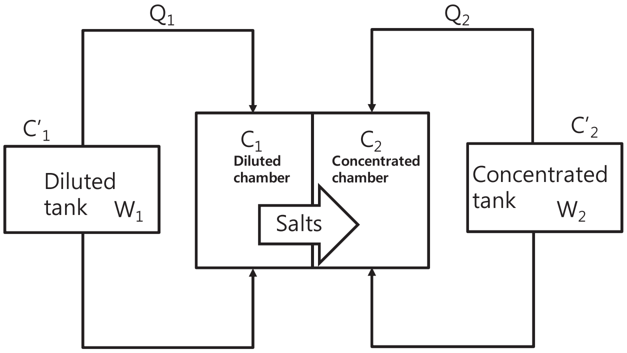


Fig. 2. Mass balance in ED system [5,6].

where C_1 is concentration of diluted chamber (mol/cm^3); C_2 is concentration of concentrated chamber (mol/cm^3); C_1' is concentration of diluted tank (mol/cm^3); C_2' is concentration of concentrated tank (mol/cm^3); Q_1 is flow rate of dilute (cm^3/s); Q_2 is flow rate of concentrate (cm^3/s); W_1 is volume of dilute (cm^3); W_2 is volume of concentrate (cm^3).

From Eqs. (1) and (2), the concentration of the diluted tank and the concentrated tank can be rearranged to Eqs. (3) and (4).

$$C_1 = C_1' + \frac{W_1}{Q_1}\frac{dC_1'}{dt} \tag{3}$$

$$C_2 = C_2' + \frac{W_2}{Q_2}\frac{dC_2'}{dt} \tag{4}$$

In ED, anions pass through anion-exchange membranes from dilution chambers to concentrate chambers by electric potential gradient and cations also move from dilution chambers to concentrate chambers through cation-exchange membranes. Mass flux through the membranes is controlled by electric current that is driven by electric potential gradient, and diffusion driven by concentration gradient between dilution and concentrate. The concept of ion flux through the ion-exchange membrane is shown in Fig. 3. If the yield, film thickness, and diffusion coefficient of salts in each ionexchange membrane is identical, mass flux in ED can be expressed as follows:

$$S = \frac{n}{F} I - D\frac{C_2 - C_1}{2\delta} \tag{5}$$

where S is mass flux of ion (mol/cm^2/s); n is film yield; I is electric current caused by the transfer of ion (A/cm^2); F is Faraday's constant (96,500 C); D is

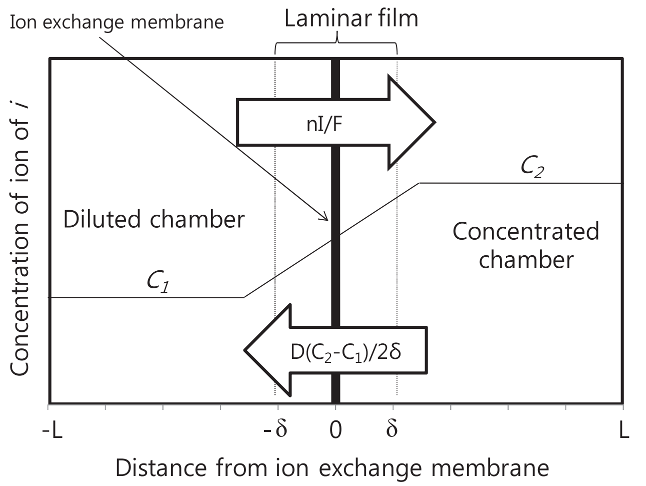


Fig. 3. Concept of ion flux through the ion-exchange membrane.

diffusion coefficient (cm^2/s); δ is thickness of laminar film (cm).

I value is related to supplied voltage and ohmic resistance, which consists of the resistances of anolyte, catholyte, dilution, concentrate and ion-exchange membranes. However, ohmic resistances of aquatic solution by ion is inversely proportional to the concentration of the ion, I can be expressed as in Eq. (6)

$$I \approx \frac{V}{R_a + R_b} = \frac{V}{\frac{L}{\beta C_2} + \frac{L}{\beta C_1}} = \frac{\beta V C_2 C_1}{L(C_2 + C_1)} \tag{6}$$

where R_a is ohmic resistance of dilution in a dilution chamber by ion (Ω/cm^2). R_b is ohmic resistance of concentrate in a concentrate chamber by ion (Ω/cm^2), V is supplied voltage to the ion-exchange membranes (volt), L is thickness of a chamber (cm), and β is a constant (cm/M/Ω). Consequently, S is estimated by the following equation;

$$S = \frac{\beta V}{FL}\frac{C_2 C_1}{C_2 + C_1} - D'(C_2 - C_1) \tag{7}$$

where $D' = D/2\delta$.

β and D' are calculated from Eq. (7) by the least-square method. The prediction of mass flux at time t in the ED system can be expressed to the following relation;

$$S_t = \frac{C_{2,t-\Delta t} - C_{1,t+\Delta t}}{2\Delta t} \tag{8}$$

In the batch and continuous experiment, C_1 and C_2 are described in Eqs. (9) and (10), respectively;

$$V_D\frac{\mathrm{d}C_1}{\mathrm{d}t} = -SA, \quad V_C\frac{\mathrm{d}C_2}{\mathrm{d}t} = SA \tag{9}$$

$$\begin{aligned} V_D\frac{\mathrm{d}C_1}{\mathrm{d}t} &= Q_D C_i + Q_D C_1 - SA \\ V_C\frac{\mathrm{d}C_2}{\mathrm{d}t} &= Q_C C_i + Q_C C_2 + SA \end{aligned} \tag{10}$$

where V_D is the volume of diluted tank (L); V_C is the volume of concentrated tank (L); A is effective filtration area of anion- or cation-exchange membrane.

3.2. Salts removal

Fig. 4 shows the observed data and the calculated data of ammonia nitrogen and phosphate as a function of time. Using Eq. (8), we estimate the S_t and then the Runge–Kutta method with a time step of 20 s was applied to solve Eq. (9) to each ion. The calculated results showed a good agreement with the observed data. Ammonia nitrogen and phosphate decreased in dilution, however increased in concentrate. The established model and the assumptions are believed to be applicable for the analysis of ED system. Removal of ammonia nitrogen was easier than that of phosphate due to its mobility in water. Table 3 shows the estimated values of β and D'. Ammonia nitrogen shows high removal ratio and large values of β and D' that represents the mobility of ion in water by electrical potential gradient.

3.3. Factors affecting mass flux

If the value of C_2/C_1 is k, Eq. (7) can be transformed into Eq. (11).

$$S = \left(\frac{\beta V}{FL}\frac{k}{k+1} - D(k-1)\right)C_1 \tag{11}$$

Table 3
Removal ratio of NH_4^+-N and PO_4^{3-}-P after 30 min operation and values of β and D'

	NH_4^+-N	PO_4^{3-}-P
Thickness of chamber, L (mm)	0.88	0.88
Supplied voltage, V (V)	10	10
Removal ratio (%)	78	61
β (cm/M/Ω)	0.79	0.61
D' (10^{-8} cm/s)	5.84	8.29
Concentration at $t = 0$ (min)	12.5	1.9
Concentration at $t = 30$ (min)	2.8	0.75

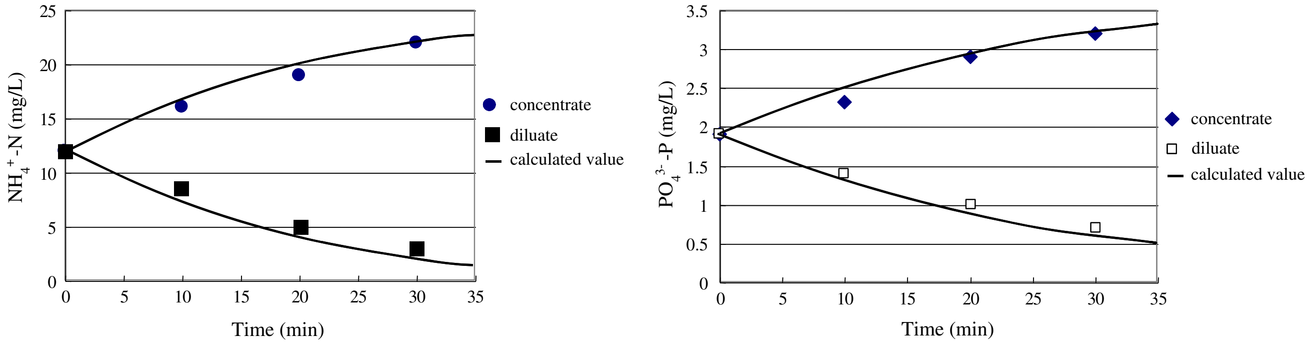
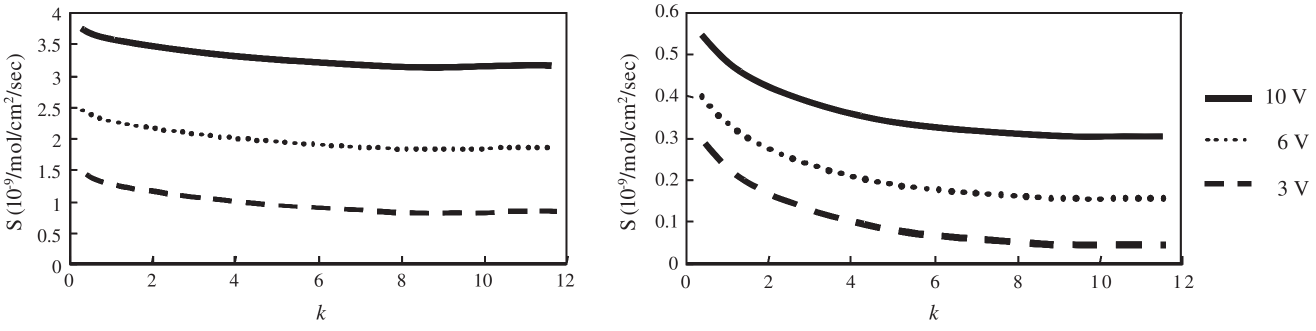


Fig. 4. The variations of nutrient salts concentration in a dilute and a concentrate chamber as a function of time.



(a) Ammonia nitrogen (NH_4^+-N) **(b)** Phosphate (PO_4^{3-}P)

Fig. 5. The variation of mass flux (*S*) as a function of voltage and $C_2/C_1 = k$ value.

In Eq. (11), we can understand that the values of V (voltage) and *k* are easily controllable parameter for mass flux, which is high voltage gives favorable effect on mass flux enhancement when voltage is less than the critical electric current. Fig. 5 shows the effect of *k* on mass flux (*S*) of ammonia nitrogen and phosphate estimated from Eq. (11). Mass flux increased with the increase in voltage and showed higher value in lower concentration ratio (*k*).

Among the parameters affecting modeling results, the control of voltage is more important and an effective parameter for nutrients removal and flux enhancement. Appropriate mathematical model was developed to find reliable design conditions of ED for nutrients removal and assess its performance. However, there may be a limitation of model particularly to predict nutrients removal in real wastewater containing suspended and dissolved solids affecting model estimation.

Conclusions

A developed mathematical model well predicted the observed data. It is believed to be applicable to the analysis of mass flux in ED. Removal of ammonia nitrogen was easier than that of phosphate due to its mobility by the difference of molecular weight in water. High voltage gives favorable effect on mass flux enhancement when voltage is less than the critical electric current especially in the case of ammonia nitrogen removal. From the experimental and simulated results, it is believed that developed model is to be applicable to the flow analysis of ED system.

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