

## 이온교환막의 막오염 및 오염저감

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## Fouling of Ion Exchange Membranes and Their Fouling Mitigation

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**요 약 :** 본 총설에서는 전기투석 공정의 운전과 설계 능력 향상을 위해 이온교환막의 막오염현상에 관한 연구를 조사하였다. 이온교환막의 막오염현상을 정량적으로 평가하기 위해 압력차를 구동력으로 하는 막공정의 막오염지수와 유사한 전기투석 막오염지수(EDMFI)를 정의하였다. 막오염현상은 무기오염원인 실리카졸과 유기 오염원인 휴믹산과 BSA를 함유한 전기 투석 실험 결과를 비교하여 연구되었다. 이 비교에서 EDMFI는 전기투석 공정의 막오염경향을 정량적인 척도로 유용하게 이용될 수 있음을 보여주었다.

새로운 오염저감 기술로 사각파 전원이 유효함이 유기 오염물을 포함한 전기투석 실험결과에서 보고되었다. 이 펄스 형태의 사각파 전원은 최적주파수에서 막오염현상을 현저하게 감소시킬 수 있었다.

**Abstract :** Fouling phenomena of ion exchange membranes were reviewed for improved design and operation of electrodialysis. The membrane fouling index for electrodialysis (EDMFI) was defined for the quantitative analysis of fouling potential as an analogy to the pressure-driven membrane process. Fouling phenomena were compared in the electrodialysis experiments with inorganic foulant (silica sol) and organic foulants (humate and bovine serum albumin (BSA)), and their fouling potentials were analyzed using the fouling index. The comparison showed that the EDMFI could be used as a quantitative measure of the fouling tendency in electrodialysis processes.

As a novel fouling mitigation method, square wave power was reported to be effective in electrodialysis with organic foulants. The square wave powers having the pulsed electric field enabled to reduce the membrane fouling significantly at an optimal frequency.

**Keywords :** fouling, foulant, fouling index, electrodialysis, fouling mitigation

### 1. Introduction

Electrodialysis (ED) is an ion exchange membrane separation process using an electrical potential as a driving force. Applications of ED can be found in the envi-

ronmental and biochemical industries as well as in the production of table salt and the desalination of seawater[1-3]. Typical industrial applications of electrodialysis are summarized in Table 1[2]. In spite of the perspectives on ED, fouling of ion exchange membranes is one of the most important limitations in the design and operation of an electrodialysis process.

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**Table 1.** Industrial Applications of Electrodialysis and Related Processes[2]

| Application                                 | Membranes   | Stack design                 | Key problems                   |
|---|---|------------------------------|--------------------------------|
| Brackish water desalination                 | Anion and cation exchange membranes                             | Tortuous path and sheet flow | -                              |
| Boiler feed water, industrial process water | Anion and cation exchange membranes                             | Tortuous path and sheet flow | Scaling costs                  |
| Production of table salt                    | Anion and cation exchange membranes                             | Sheet flow                   | Costs                          |
| Industrial effluent                         | Anion and cation exchange membranes                             | Tortuous path and sheet flow | Costs                          |
| Food and pharmaceutical industries          | Anion and cation exchange membranes                             | Tortuous path and sheet flow | Membrane fouling, product loss |
| Diffusion dialysis of acids                 | Cation exchange membranes                                       | Sheet flow                   | Costs                          |
| Ultrapure water                             | Ion exchange resins and anion and/ or cation exchange membranes | Filled cell stack            | Process reliability            |
| Water dissociation                          | Bipolar membranes   | Tortuous path and sheet flow | Membrane performance           |

**Table 2.** Foulants in Electrodialysis[12]

| Foulant Category | Description   | Foulants   | Charge properties | Methods of fouling prevention and/or cleaning   |
|------------------|---|--|-------------------|---|
| Scale            | Precipitates of sparingly soluble salts in solution     | CaCO <sub>3</sub> , SiO <sub>2</sub> , CaSO <sub>4</sub> ·2H <sub>2</sub> O, BaSO <sub>4</sub> , SrSO <sub>4</sub> , | Non-charged       | <ul style="list-style-type: none"> <li>• Lower recovery</li> <li>• Adjust pH</li> <li>• Clean with citric acid or EDTA based solution</li> </ul>                |
| Colloids         | Agglomeration of suspended matters on membrane surfaces | SiO <sub>2</sub> , Fe(OH) <sub>3</sub> , Al(OH) <sub>3</sub> , FeSiO <sub>3</sub> , Cr(OH) <sub>3</sub>              | Negative          | <ul style="list-style-type: none"> <li>• Pretreatment with MF or UF</li> <li>• Charge stabilization</li> <li>• Higher flow rate Adjust</li> <li>• pH</li> </ul> |
| Organics         | Attachment of organic species to membrane surfaces      | Macromolecules, Proteins, Whey, Polyelectrolytes, Humate, SDS, Alginate  | Negative          | <ul style="list-style-type: none"> <li>• Pretreatment with MF or UF</li> <li>• Pretreatment with activated carbon</li> <li>• Clean with NaOH</li> </ul>         |

Fouling is essentially caused by deposition of foulants such as scale, colloids, and organics on the membrane surface, causing deterioration in the membrane performance in terms of the flux decline and/or the resistance increase[4].

Many approaches have been examined to minimize fouling potentials during electrodialysis. They include pretreatment of the feed solution, the turbulence in the compartments, the optimization of process conditions, and the modification of the membrane properties. Although all the methods reduce fouling to some extent, cleaning-in-place (CIP) is still needed in practical processes. Chemical cleaning can not be applied during processes although chemical cleaning is the most extensively used methods for CIP (cleaning-in-place) and fouling control in membrane processes[5,6].

The application of electric fields has been found to

be an effective method to remove deposits from membrane surfaces in pressure-driven membrane processes [7,8]. It was reported that the DC electric field created a high filtration flux in a system fouled with BSA (bovine serum albumin), the gel layer on the membrane surface being completely removed[9]. Also, the DC electric field has been studied with process variables such as the applied electric field, the pulse interval, the pulse duration and the feed solutions in the pressure-driven membrane processes[10,11].

Recently, the pulsed electric fields with different frequencies demonstrated an ability to minimize membrane fouling as both a fouling mitigation method and a CIP method in electrodialysis[4], while other methods are considered for various foulants as shown in Table 2 [12]. The application of pulsed electric fields was assumed to provide turbulence effects, resulting in the

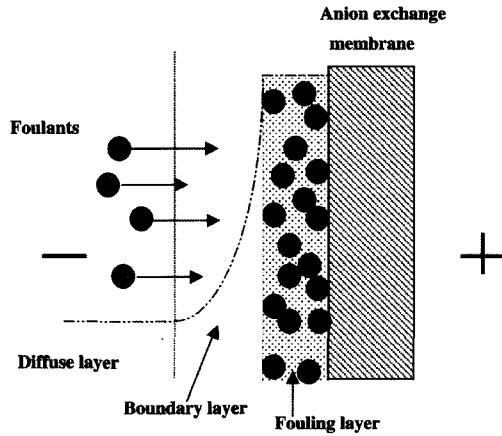


Fig. 1. Membrane fouling mechanism of negatively charged organic foulants in electro dialysis.

movement of charged species away from the membrane surface and improving the permeability through the ion exchange membranes.

## 2. Definition of the Membrane Fouling Index for Electro dialysis (EDMFI)

Several membrane fouling indices have been used to describe fouling phenomena such as the silt density index (SDI), the modified fouling index (MFI), and the multi-plugging factor index (MPFI) in microfiltration, ultrafiltration, nanofiltration and reverse osmosis[13,14]. To predict the quantitative fouling phenomena, different fouling behaviors are compared under various conditions with the membrane fouling indices. In electro dialysis process, some physical parameters were considered to describe the membrane fouling, which caused difficulty in applying to practical processes[15,16].

The membrane fouling index for electro dialysis (EDMFI) was derived based on a fouling layer formation on the surface of ion exchange membranes during electro dialysis[4,17]. The rate of ion transport through an ion exchange membrane increases with the electrical charge, while non-permeable foulants are rejected by the selectivity of the membrane as illustrated in Fig. 1. While the electrical charges accumulate, the amount of foulants on the membrane surface increases

and the fouling layer become thicker and more compact. Once the fouling layer forms, the resistance of the layer to ion transport increases an additional electric resistance.

Amount of a foulant deposited on the membrane,  $m_f$ , is assumed to be proportional to the time-integrated electrical charge,  $Q$ , and the foulant concentration in the bulk solution,  $C_b$ . The gel volume,  $V_{gel}$ , can be expressed as the ratio of the bulk volume losing the foulants ( $m_f/C_b$ ) and the concentration factor ( $C_g/C_b$ ), i.e.:

$$V_{gel} = \frac{m_f/C_b}{C_g/C_b} = \frac{KQC_b}{C_g} \quad (\text{Eq. 1})$$

where  $K$  is a constant that is related with the stack design, hydrodynamic conditions and concentration of foulants and species of foulants, and  $C_g$  the foulant concentration in the fouling layer. Therefore, the gel thickness,  $\delta_{gel}$ , is expressed as follows:

$$\delta_{gel} = \frac{KQC_b}{C_g A} \quad (\text{Eq. 2})$$

The resistance of a fouling gel layer of an effective membrane area,  $R_f$ , can be rewritten as the product of the gel thickness and specific resistance of the fouling layer,  $r_c$ [18], i.e.:

$$R_f = K \frac{C_b r_c}{C_g A^2} Q \quad (\text{Eq. 3})$$

The resistance of the fouling layer on ion exchange membranes in electro dialysis is inversely proportional to the square effective membrane area[4].

The total resistance of the cell is the sum of the intrinsic membrane resistance,  $R_m$ , considered to be constant during the electro dialysis, the resistance of the boundary layer,  $R_{bl}$ , related to the concentration polarization of dilute solution, and the resistance of the fouling gel layer,  $R_f$ , in Eqs. 4 and 5, i.e.:

$$\frac{E(t)}{I(t)} = R_m + R_{bl} + R_f \quad (\text{Eq. 4})$$

$$\text{or } \frac{E(t)}{I(t)} = R_m + R_{bl} + K \frac{C_b r_c}{C_g A^2} Q(t) \quad (\text{Eq. 5})$$

**Table 3.** Illustration of Analogies between the MFI and the EDMFI

|                                 | MFI<br>(Membrane fouling index)  | EDMFI<br>(membrane fouling index for electro dialysis)               |
|---------------------------------|--|--|
| Applied membrane processes      | Pressure-driven membrane processes   | Mainly electro dialysis  |
| Equation                        | $\frac{t}{V} = \frac{\eta R_m}{\Delta P A} + \frac{\eta I}{2 \Delta P A^2} V$  | $\frac{E(t)}{I(t)} = R_m + K \frac{C_b r_c}{C_g A^2} Q(t)$           |
| Fouling mechanism               | Cake filtration theory   | Gel layer formation  |
| Definition of the fouling index | $I \frac{\eta}{2 \Delta P A^2}$<br>Gradient in the plot of $t/V$ vs. $V$   | $K \frac{C_b r_c}{C_g A^2}$<br>Gradient in the plot of $E/I$ vs. $Q$ |
| Analogous parameters            | $t$ (the elapsed time)   | $E$ (electrical voltage drop)  |
|                                 | $V$ (filtration volume)  | $Q$ (accumulated charges)  |
| Similarities                    | <ul style="list-style-type: none"> <li>• The fouling indices are inversely proportional to the square of membrane area.</li> <li>• The fouling indices are related to the retention of the particles and then formation of layer on the membrane surface.</li> <li>• The fouling indices are obtained the filtration behaviors with time during membrane processes.</li> </ul> |  |

When movable ions exist in the boundary layer facing the dilute solution, the concentration polarization does not occur and then  $R_f$  is negligible. The fouling index for electro dialysis (EDMFI) under the constant voltage mode is defined as the coefficient of  $Q(t)$  in Eq. 5. Actually this fouling index can be used under any operating conditions theoretically if hydrodynamic conditions remain nearly constant. A greater fouling tendency is to be indicated by a higher value of EDMFI.

The EDMFI in Eq. 5 is analogous with the membrane fouling index (MFI) used in pressure-driven membrane processes as follows[19,20]:

$$\frac{t}{V} = \frac{\eta R_m}{\Delta P A} + \frac{\eta I}{2 \Delta P A^2} V \quad (\text{Eq. 6})$$

where  $t$  is the elapsed time,  $V$  the filtration volume,  $I$  the constant taken to be the product the specific resistance of the cake and concentration of the particles,  $\eta$  the viscosity of the feed solution,  $\Delta P$  the transmembrane pressure, and  $A$  the cross-sectional area of a membrane. The MFI of the pressure-driven membrane processes is based on the cake filtration theory, where the colloidal particles deposit on the membrane surface during filtration. The MFI is defined as the gradient of the linear region found in

the plot of  $t/V$  vs.  $V$  from Eq. 6 for the constant pressure mode. Table 3 illustrates analogies between the MFI and the EDMFI.

For the constant current operation Eq. 5 can be rewritten as following:

$$\frac{E(t)}{I^2} = \frac{R_m}{I} + \frac{K C_b r_c}{C_g A^2} t. \quad (\text{Eq. 7})$$

The EDMFI is the coefficient of time in Eq. 7 under the constant current mode, and can be obtained from the slope of the plot of  $E(t)/I^2$  vs. time[4,9]. The resistances can be estimated in the plot of the EDMFI. The membrane resistance,  $R_m$ , is determined by the intercept at y axis. Also the resistance of the fouling layer,  $R_f$ , is calculated by substitution of the index in Eq. 7 into Eq. 3, i.e.:

$$R_f = K \frac{C_b r_c}{C_g A^2} Q = \text{EDMFI} * Q. \quad (\text{Eq. 8})$$

It is known that the pulsed electric fields mitigates fouling effects on the membrane surface by decreasing the fouling layer thickness as a fouling mitigation method. However, it is difficult to estimate the fouling layer thickness directly. In the expression of the layer thickness based on the fouling gel layer model in Eq.

2, the values of  $K$  and  $C_g$  are assumed to depend on the operating conditions. The ratio of the fouling layer thickness between the DC power and the pulsed electric field is written in Eq. 9. The resulting equation is same as the ratio of the EDMFI in Eq. 10, i.e.:

$$\frac{\delta_p}{\delta_{DC}} = \frac{\left( \frac{K_{pulse} QC_b}{C_{g,pulse} A} \right)}{\left( \frac{K_{DC} QC_b}{C_{g,DC} A} \right)} = \frac{K_{pulse} C_{g,DC}}{K_{DC} C_{g,pulse}} \quad (\text{Eq. 9})$$

$$\frac{EDMFI_p}{EDMFI_{DC}} = \frac{\left( \frac{K_{pulse} C_b r_c}{C_{g,pulse} A^2} \right)}{\left( \frac{K_{DC} C_b r_c}{C_{g,DC} A^2} \right)} = \frac{K_{pulse} C_{g,DC}}{K_{DC} C_{g,pulse}} \quad (\text{Eq. 10})$$

where the subscripts, *pulse* and *DC*, mean the pulsed electric field and the DC power, respectively. The equation implies that differences in the fouling index directly represent the thickness of the fouling layer [21].

### 3. Quantitative Analysis of the Fouling Potentials

#### 3.1. Fouling Potentials in Electrodialysis of Solution Containing Silica Sol

Among common foulants, colloidal particles exist in natural waters and many effluent streams in forms of clay minerals, colloidal silica, iron oxide, aluminum oxide, and manganese oxide. Colloidal fouling is caused by accumulation of colloidal particles on the membrane surface and/or a cake layer formation [22,23]. Particularly silica sol is often found in wastewater streams generated in semiconductor industries. Negatively charged silica sols move toward an anion exchange membrane in the electric field and deposit on the membrane surface due to their electrostatic attraction to the membrane[24]. The deposit of colloids on the membrane surface in electrodialysis depends on the properties of colloidal particles such as the zeta potential and critical coagulation concentration. It is also related to the

properties of the anion exchange membrane, such as hydrophobicity, exchange capacity, surface charge and so on.

The performances were compared in terms of the removal rate of conductivity in dilute solution and the time course of cell resistances in the electrodialysis of solution containing 0.4 wt.% of silica sol. It was observed that the silica sol deposited on the membrane surface facing the dilute compartment in the electrodialysis experiments[21]. Notable differences in the cell resistance, however, were not observed between electrodialysis experiments with different anion exchange membranes. The results indicate that the deposited silica sol might improve the chemical property of anion exchange membranes to some extent[21]. The electrodialysis of silica sol showed the similar performances with 2.1 mol/m<sup>2</sup>hr of flux and 95-96% of current efficiency for all cell structures. Even deposition of silica sol did not affect on the performance of anion exchange membranes significantly. In addition, fouling potentials in electrodialysis of NaCl with silica sol were observed using the membrane fouling index. The EDMFIs of the cell structures showed similar values, indicating that silica sol deposited on the membrane surface, then forming a cake layer with the porosity with small fouling effects on the surface during electrodialysis.

#### 3.2. Fouling Potentials in Electrodialysis of Solution Containing Humate

Fouling due to negatively charged organics occurs in many streams of electrodialysis application, some of the foulants being fermentation broth[12,25], sodium dodecylbenzene sulfonate[26], sulfonated lignin[27], sodium humate[28,29], grape must[30], and milk whey [31] as well as the Kraft pulping process[32]. Negatively charged organic foulants move toward anion exchange membranes under an electric field and then deposit on the surface of membranes due to electrical interactions between membrane surface and the foulant, increasing the electric resistance of membranes.

Through the electrodialysis of NaCl containing humate the performances of the cell structures having different anion exchange membranes were compared in terms of the cell resistance and the removal rate of NaCl in the dilute solution. The cell resistance of

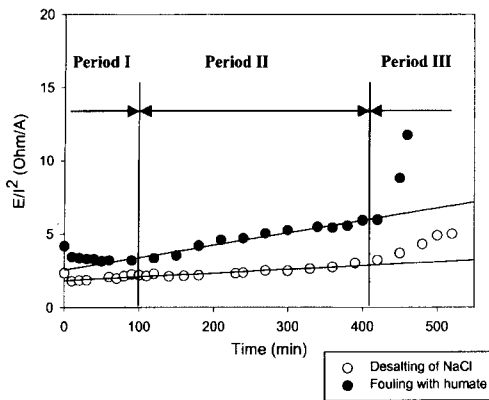


Fig. 2. EDMFI plot in electro dialysis of humate (Period I: the period for the acclimation of foulant, period II: the period for the fouling gel layer formation, and period III: the period for the concentration polarization).

AMX and AM-1 membranes showed little change until NaCl in the feed was depleted[29]. However, the resistance increasing rate of the ACM membrane was the highest, even at the beginning of the experiment. The cell resistance increased due to the formation of a fouling layer on the ACM membrane surface, assuming that the hydrophobicity of ACM membrane leads to accumulation of hydrophobic humate substances more easily[29]. It is thought that humate with its large molecular weight increased the resistance and power consumption due to its accumulation on the membrane surface during electro dialysis[24,28]. Considering current efficiency and power consumption, cell structure of the ACM membrane showed the lowest current efficiency and the highest power consumption.

For the quantitative analysis of the fouling potentials, the EDMFIs of fouling experiments containing humate were obtained graphically from experimental data under a constant current condition. Like membrane fouling indices in pressure-driven membrane processes, the plot of the EDMFI also can typically be seen in three distinct regions as shown in Fig. 2[13,14,20]: (i) the acclimation period, where resistance decreases and the foulants migrate to the boundary layer, (ii) the period for the fouling layer formation, where the fouling layer resistance increases due to foulant deposition, where the fouling index is determined, and (iii) the period where the resistance increases very

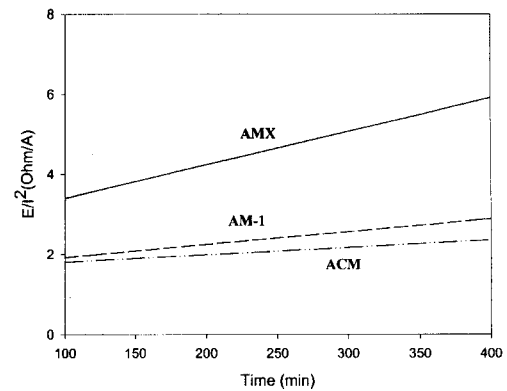


Fig. 3. Fouling potentials of cell structures in terms of EDMFI in the presence of humate.

sharply due to the depletion of mobile ion in the boundary layer.

As electrical charges accumulate in the first period, humate with large molecular weight moves to the surface of an anion exchange membrane with a low electric mobility, increasing the concentration of humate near the membrane surface[33]. The slight decrease in the resistance in the first period is attributed by the transport of  $\text{Na}^+$  and  $\text{Cl}^-$  through ion exchange membranes in the electric field. A fouling layer forms on the membrane surface as the concentration of humate increases and then the resistance of the fouling layer increases with time at the second period, where the fouling index is determined[34]. The rapid increase in the resistance due to the concentration polarization is not considered in the EDMFI plot.

Fig. 3 shows the EDMFI plots in the cell configuration of three anion exchange membranes. Of the membranes, the cell of the ACM membrane showed the highest fouling index. Meanwhile, the cell of the AMX membrane showed the least value of the fouling index, indicating the least fouling potential with respect to humate. The EDMFI of each cell structure was compared between different cell configurations and changes of fouling effects due to humate fouling were investigated using the ratio of the index of desalting to that of fouling experiments. The cell pairs of the ACM membrane showed the highest fouling potential and that of AMX the lowest fouling potential[29].

**Table 4.** Electrodialysis Performance in the Presence of BSA

|  | Flux of Lactate<br>(mol/m <sup>2</sup> hr) | Current efficiency of<br>lactate (%) | Power consumption (Wh/mol<br>lactate) |
|--|--|--------------------------------------|---------------------------------------|
| Electrodialysis of lactate<br>(Before fouling) | 1.81                                       | 86.7                                 | 4.87                                  |
| Fouling experiment with BSA                    | 1.89                                       | 84.7                                 | 6.89                                  |
| Electrodialysis of lactate<br>(After fouling)  | 1.81                                       | 77.5                                 | 6.96                                  |

**Table 5.** Fouling Indices and Related Parameters for BSA Fouling

|                                | EDMFI<br>(Ohm/Amin) | Membrane resistance,<br>$R_m$ (Ohm) | Fouling layer resistance,<br>$R_f$ (Ohm) |
|--------------------------------|---------------------|-------------------------------------|--|
| ED of lactate (before fouling) | 0.00038             | 0.431                               | 0.165                                    |
| Fouling experiment With BSA    | 0.00081             | 0.559                               | 0.348                                    |
| ED of lactate (after fouling)  | 0.00028             | 0.616                               | 0.111                                    |

### 3.3. Quantitative Fouling Potentials in Electrodialysis of Lactate Containing BSA

Fouling proceeds in two consecutive steps during a membrane process of solution containing BSA. The pre-adsorption of BSA results in a flux decline with only a minimal effect over the initial stage of filtration due to the absence of any protein retention in the first step [35, 36]. In the second step, fouling occurs due to cake filtration, which is believed to be the result of protein deposition leading to the formation of a compressible protein deposit (or cake) on the surface of the membrane. The transition between these two steps depends on the membrane structure and bulk protein concentration[37-39].

The electrodialysis experiments of lactate containing BSA were performed in an electrodialysis cell[21]. Little difference was observed in the conductivity removal rate in the dilute solution and the lactate transport rate into the concentrate solution even in the presence of BSA. The cell resistance, however, increased significantly in the presence of BSA, showing that adsorption of BSA on the anion exchange membrane surface fouled the membrane during electrodialysis. Table 4 summarizes the electrodialysis performances in terms of lactate flux, current efficiency and power consumption. The flux of lactate, the first column, was nearly unchanged, even in the presence of BSA. In the following electrodialysis of

lactate, however, the performances of the already fouled membrane did not recover due to the deposition of BSA. In particular, the power consumption during the fouling experiment with BSA increased by 41%, implying that the BSA fouled the anion exchange membrane irreversibly. It was found that the performances did not recover with respect to the current efficiency and the power consumption during the second experiment even without BSA.

The fouling effect of BSA on the anion exchange membrane was investigated using difference of membrane resistance and the fouling layer resistance, and the results are shown in Table 5. It was found that fouling increased the membrane resistance as well as the resistance of the fouling layer in the fouling experiment. The increased membrane resistance decreased the electrodialysis performance. Electrodialysis of lactate after fouling experiment in the third row showed large increase in the membrane resistance, implying that the AMX membrane was fouled irreversibly. The fouling index of this experiment was the double of the previous experiment without BSA.

## 4. Consideration of Fouling Potentials with Different Foulants

Fouling potentials were compared in electrodialysis of silica sol, humate and BSA. Table 6 summarizes the characteristics of the foulant and the anion

**Table 6.** Fouling Characteristics with the Properties of Foulants and Membranes

| Foulant   |       | Inorganic  | Organic   |  |
|---|-------|--|---|--|
|   |       | Silica sol   | Humate  | BSA (Protein)  |
| Concentration in feed solution  |       | 0.4 wt% of silica sol, Ludox, HS-40  | 100 mg/L of sodium humate (Aldrich)                                 | Heat-shocked Fraction V (Sigma)  |
| Characteristics of the foulant  |       |  |   |  |
| Charge density (meq/g)  | Total | 0.72   | 34.5  | 1.49   |
|   | -COOH | 0.02 (3.2 %)   | 9.4 (27.2 %)  | 1.14 (76.5 %)  |
|   | -OH   | 0.70 (96.8 %)  | 25.1 (72.8 %)   | 0.35 (23.5 %)  |
| Hydrophobicity  |       | Hydrophilic  | Hydrophobic   | Hydrophilic  |
| Zeta potential (EP <sup>a</sup> ) (mV)                                |       | -21 mV (pH 9)  | -35 mV (pH 8)   | -25 mV (pH 8)  |
| Molecular weight  |       | 1,340 K (Referred)   | 5,000 (Measured)  | 68,000 (Referred)  |
| Size (nm)   |       | 12   | 550   | 12   |
| Fouling characteristics of the virgin and the fouled AMX membranes    |       |  |   |  |
| Change in exchange capacity (meq/g mem)                               |       | Increased  | Decreased   | Decreased  |
| Change in electrical resistance (Ohm cm <sup>2</sup> )                |       | Decreased  | Increased   | Decreased  |
| Change in the zeta potential (SP <sup>b</sup> ) (mV)                  |       | More negative  | More positive   | More positive  |
| Fouling phenomena in electrodialysis and suggested fouling mechanisms |       |  |   |  |
| Resistance change in the presence of foulant                          |       | Little difference  | Notable difference  | Notable difference   |
| Conductivity change in presence of foulant                            |       | Little difference  | Little difference   | Notable difference   |
| Suggested fouling mechanism   |       | Cake layer with low charge density (Mostly reversible fouling and increased performance) | Loosely packed layer with high charge density (Partly irreversible) | Partly gel layer with slightly high charge density (Mostly irreversible) |
| Fouling index in the cell of AMX                                      |       |  |   |  |
| EDMFI (Ohm/A min)   |       | 0.0016   | 0.0019  | 0.0008   |

<sup>a</sup>EP: Electrophoretic mobility measurement and <sup>b</sup>SP: streaming potential measurement.

exchange membrane, the fouling phenomena in terms of cell resistance and conductivity changes and suggested fouling mechanisms. Also the membrane fouling indices for electrodialysis were compared for different foulants in the Table 6[21].

The properties of the representative foulants were characterized with the charge properties (the acidities measurement and the zeta potential by electrophoretic mobility measurement), the physical properties (molecular weight, molecular size) and the constituents (the

hydrophilic and the hydrophobic fraction). The charge properties were found to give fouling effects by interaction between foulant and membrane. The properties of the fouled anion exchange membranes were characterized and compared with those of the virgin anion exchange membranes to predict the fouling potentials. In the presence of the organic foulants, it was found that exchange capacity and the zeta potential decreased after the AMX membrane was fouled. Of the properties, fouling is mainly related to



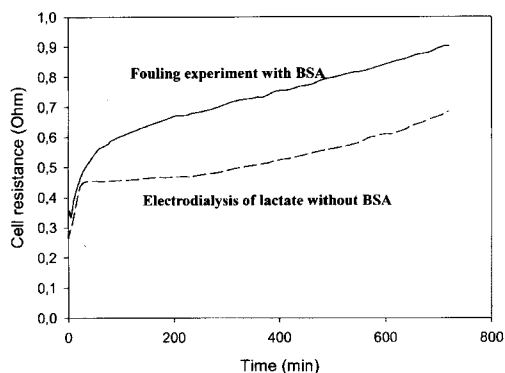


Fig. 4. Influence of BSA on cell resistances according to time (Dilute solution: 0.1 M NaCl containing 1.0 wt.% of BSA, operating current density: 6 mA/cm<sup>2</sup>).

an electrochemical property (exchange capacity) and an electrokinetic property (zeta potential). It is interesting that the silica sol improved the membrane properties to some extent, different from the results for the organic foulants (*e.g.* humate and BSA). It is suggested that it is related to the changes of the hydrodynamic conditions on the surface and the electrochemical properties[21].

The BSA fouling increased the cell resistance and reduced the conductivity, resulting in the reduced electrodialysis performances. It is suggested that the BSA fouled anion exchange membrane after the slightly packed gel layer formed on the surface due to deposition of the protein having a low charge density, which is considered as an irreversible fouling. In the case of the silica sol the colloidal particles formed a loose cake layer on the surface, resulting in the reversible fouling. The humate fouled anion exchange membranes by formation of loosely packed cake layer due to high molecular size and the high molecular weight. However, the humate with high charge density fouled membranes partly irreversibly.

The humate fouling showed the highest fouling index as the highest fouling potential mainly due to highly negatively charges. The EDMFI in the electrodialysis of lactate containing BSA was much lower than that of humate due to low charge properties. It is considered that the EDMFI is mainly related to the properties of foulant rather than those of membranes.

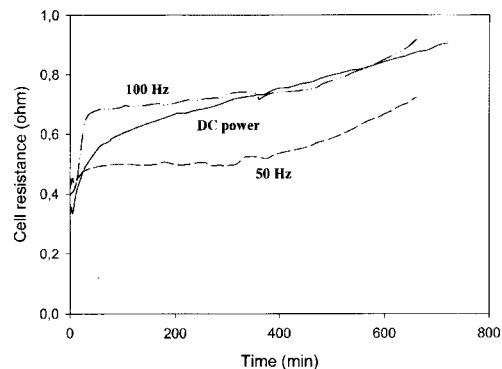


Fig. 5. Time course of the cell resistances for square wave powers at different frequencies.

## 5. Fouling Mitigation in the Electrodialysis of Lactate Containing BSA

The square wave powers having pulsing effects were used for fouling mitigation of ion exchange membranes in comparison with the DC power. The square wave powers with different frequencies were supplied to observe the effects on the membrane fouling, which were generated by modification of the DC power with a function generator and a dual type power supplier connected to an amplifier[4].

The fouling potentials of the square wave powers having different frequencies were compared in Fig. 5 in the electrodialysis of lactate containing BSA. It was clearly observed that the frequency of 50 Hz reduced the fouling potential compared with the DC power experiment. Meanwhile, the frequency of 100 Hz did not reduce the fouling potential, suggesting that the higher frequency caused a close packing of the foulants in the fouling layer, resulting in a reduced fouling mitigation during electrodialysis[4,40].

Table 7 summarizes the electrodialysis performances of the different power sources during BSA fouling experiments in terms of the current efficiency, flux of lactate and the power consumption. Irrespective of frequencies, the square wave powers increased the current efficiency and the flux of lactate increased, reducing the power consumption. In particular, a frequency of 50 Hz showed the least power consumption by 68% compared with that of the DC power.

**Table 7.** Performances with Different Frequencies during the Electrodialysis of Lactate Containing BSA

|                       |        | Current efficiency of lactate (%) | Flux of lactate (mol/m <sup>2</sup> .hr) | Power consumption (wh/mol lactate) |
|-----------------------|--------|-----------------------------------|--|------------------------------------|
| Square wave powers    | 50 Hz  | 93.7                              | 2.57                                     | 4.67                               |
|                       | 100 Hz | 95.2                              | 2.32                                     | 6.09                               |
| DC power ( $\infty$ ) |        | 84.7                              | 1.89                                     | 6.89                               |

**Table 8.** Investigation of Reduced Fouling Potentials According to the Frequencies in the Electrodialysis of Lactate Containing BSA

|                      |        | EDMFI (Ohm/Amin) | $\delta_{pulse}/\delta_{DC}$ | $R_m$ (Ohm) | $R_f$ (Ohm) |
|----------------------|--------|------------------|------------------------------|-------------|-------------|
| Square wave powers   | 50 Hz  | 0.00033          | 0.41                         | 0.458       | 0.132       |
|                      | 100 Hz | 0.00052          | 0.65                         | 0.644       | 0.208       |
| DC power( $\infty$ ) |        | 0.00080          | -                            | 0.559       | 0.348       |

Electrodialysis performances showed that the frequency of 50 Hz was an optimum frequency for the fouling mitigation in the fouling system among examined pulsed electric fields.

For the quantitative analysis of the fouling mitigation effects due to the pulsed electric fields, the fouling indices, the fouling layer thickness, the membrane resistances and the fouling layer resistances were investigated using experiments for both the square wave powers and the DC power. The results are listed in Table 8. Estimation of the fouling layer thickness in Eqs. 9 and 10 showed that the pulsed electric fields decreased the thickness. It is assumed that the square wave powers having the pulsing effect caused turbulence on the fouling layer, decreasing the fouling layer thickness near the anion exchange membrane surface.

It is noted that the 50 Hz of the square wave power reduced the fouling layer thickness by about 40% compared with the DC power experiment. It was found that the pulsed electric fields at the low frequency (50 Hz) reduced the membrane resistance compared with the DC power. Slight increases in the membrane resistance were observed for the high frequency (100 Hz) during the fouling experiments. Considering the differences in the fouling layer resistance, as shown the fourth column of Table 8, it was clearly observed that the pulsed electric fields reduced the resistance, the fouling mitigation occurring on the surface[9].

## 6. Concluding remarks

Fouling of ion exchange membranes is an important consideration in the design and the operation of membrane systems including electrodialysis process. For the prediction and the quantitative analysis of the fouling potentials, reliable values of fouling tendencies are necessary in electrodialysis. The membrane fouling index for electrodialysis (EDMFI) was derived based on a gel layer formation on the surface of an ion exchange membrane during electrodialysis process.

The electrodialysis performances were considered with inorganic foulant (silica sol) and organic foulants (humate and BSA). And their fouling potentials were analyzed using the fouling index in the plot of  $E/I^2$  and time. The membrane fouling index for electrodialysis was used as a quantitative measure of the membrane fouling tendency of electrodialysis processes. Also the pulsed power was effectively utilized in electrodialysis to control fouling of ion exchange membranes.

## Nomenclature

- $A$  the effective membrane area,
- $C_b$  the concentration of the foulant,
- $C_g$  the foulant concentration in the fouling layer,
- $E$  the voltage,
- $I$  the operating current,
- $I$  a constant in Eq. 6,

- $K$  a constant,  
 $Q$  the accumulated electrical charge,  
 $R_f$  the fouling layer resistance,  
 $R_m$  the membrane resistance,  
 $r_c$  the specific resistance,  
 $t$  the elapsed time,  
 $V$  the filtration volume,  
 $\eta$  the viscosity of the feed solution,  
 $\Delta P$  the transmembrane pressure,  
 $\delta$  the fouling layer thickness

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