Korean J. Chem. Eng., **21**(3), 629-634 (2004)

Fouling Mitigation in the Repeated Batch Runs of Electrodialysis with Humate Foulant

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(*Received 17 February 2003 • accepted 26 December 2003*)

Abstract−Since membrane fouling is one of the important considerations in electrodialysis, many approaches have been considered in order to minimize fouling of the process. In this study, square wave powers having pulsing effects were employed to investigate the effects of the frequencies on the fouling mitigation during fouling experiments of humate, forming a loosely packed fouling layer on the anion exchange membrane surface. It was shown that a pulsing electric field with determined optimal frequency reduced the fouling potential of an already fouled system in repeated batch runs at a significant level. It was suggested through electrodialysis experiments of humate that the pulsation of the electric field affected the electromigration of the charged particles deposited in the fouling layer, thus decreasing fouling potentials.

Key words: Electrodialysis, Humate, Fouling, Fouling Mitigation, Pulsing Electric Field

INTRODUCTION

Applications of electrodialysis (ED), which uses the electrical potential as a driving force with ion exchange membranes, can be found in the environmental and biotechnological industries as well as in conventional fields, such as production of table salt and desalination of seawater [Kang et al., 2002; Choi and Jeong, 2002]. In spite of the perspectives of ED, fouling of ion exchange membranes is one of the most significant considerations in the design and operation of the electrodialysis process. It is known that most foulants (humate, biomass, proteins, surfactants and others) existing in many streams have negative charges, and thus anion exchange membranes are fouled by chemical adsorption of foulants, followed by deposition on the surfaces [Linstrand et al., 2000].

Many approaches, including pretreatment of the feed solution, increase in the flow rate, and optimization of process conditions, have been considered to minimize membrane fouling during electrodialysis [Lee et al., 2002b; Park et al., 2003a; Lee, 2002; Sheikholeslami, 1999]. The approaches reduce fouling during electrodialysis to some extent. However, cleaning-in-place (CIP) is still needed in practical membrane processes in order to recover process performances especially during the extended period. Chemical cleaning is one of the most important and extensively used methods, which requires additional chemicals and has difficulty in applications during ED operation [Scott, 1995].

Of methods to reduce fouling potential in pressure-driven membrane processes, it was reported that the application of electric fields could be a very effective means to remove deposits from membrane surfaces [Huotari et al., 1999; Bowen et al., 1997]. Also, the DC (direct current) electric fields created a higher filtrate flux even in the presence of bovine serum albumin during ultrafiltration, the gel layer on the membrane surface being completely removed [Zumbush et al., 1998]. However, the process performance was decreased due to reactions on the electrode surface. As one of the methods to overcome the problem, the pulsing DC electric field was examined with process variables such as the applied electric field, the pulse interval, the pulse duration and the feed solutions [Bowen et al., 1992; Oussedik et al., 2000].

In the case of electrodialysis, the electrodialysis reversal (EDR) has been used to prevent inorganic fouling (scale) in desalination of brackish water with the cathode and anode being changed periodically, thus the diluate and concentrate compartments being changed. Therefore, the material of the electrodes and the period to change the polarity should be carefully considered in the EDR system [Scott, 1995]. It was reported that fouling of the process could be mitigated without change of the polarity of the electrodes in ED by using the half-wave power, generated from AC (alternating current) using one diode allowing current to flow in only one direction. It was observed that the half-wave power could reduce the fouling potentials and improve the desalting performances of the solutions containing foulants [Lee et al., 2002c, 2003]. However, it was difficult to investigate the influence of frequency on fouling mitigation since the half-wave power used only a frequency of 60 Hz from AC.

In the previous results, square wave powers were supplied, which is a modified DC power source with a function generator and a power transistor to give pulsation effects on the DC electric field. The results of fouling experiments of humate showed that the square wave powers reduced membrane fouling with an optimal frequency due to different properties of foulants and membranes [Lee et al., 2002b; Park et al., 2003b]. However, the previous electrodialysis experiments in the presence of humate were performed during a somewhat short period. In this study, the effect of frequency on fouling mitigation was further examined in extended long-term operation and repeated batch runs.

The objectives of this study are (i) to investigate the frequency influence of the square wave powers on fouling mitigation during an extended period (over 10 hours), and (ii) to observe fouling mitigation in the pulsing electric field having an optimal frequency dur-

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ing three consecutive batch runs.

EXPERIMENTAL

Humate having highly negative charges and a high molecular weight was used as a synthetic foulant in electrodialysis of NaCl solution [Lee et al., 2002a]. The apparent molecular weight distribution of humate was measured with a size exclusion method in high performance liquid chromatography (HPLC-SEC), which larger molecules pass quickly through a column and smaller molecules proceed through longer pathways. Using a column Protein Pak 125 (Waters, USA), a buffer solution with $NaHPO_4$ and NaH_2PO_4 (pH 6.8) was pumped at a flow rate of 0.7 ml/min from Waters 510 (Waters, USA). Molecular weights were calibrated with PSS (polystyrene sulfonates) standards of MW 4,000, 6,000, 18,000, and 80,000 daltons (Polyscience, USA) by using a UV detector, M 720 (Young-Lin, Korea) at 254 nm [Lee et al., 2002d].

The two-cell pair unit consisting of CMX and AMX (NEOSEPTA, Tokuyama Corp., Japan) with an effective area of 100 cm^2 each was assembled in a TS-1 electrodialysis stack with flow-sheet spacers (Tokuyama Corp., Japan). Table 1 shows the properties of the ion exchange membranes [Strathmann, 1990; Tokuyama Corp., 1995]. The initial diluate solution in each experiment was 5.0 L of 0.1 M NaCl containing 100 mg/L of sodium humate (Aldrich, USA). Five liters of 0.05 M NaCl was used as an initial concentrate solution. The flow rates of the diluate and concentrate solutions were maintained as 0.2-0.3 L/min. As an electrode rinse solution, 800 mL of 3% Na_2SO_4 was used. The electrodialysis experiments were performed for 10 hours or longer, and the end point of each experiment was determined as the time when the desalting rate reached at a steady state.

DC power with a constant current of 0.6 A (current density: 6.0 mA/cm^2) was supplied during electrodialysis experiments as a reference experiment. The frequencies were varied with various frequencies (10 Hz, 25 Hz, 50 Hz, 100 Hz and 200 Hz) for the square wave powers in order to observe the influences of the frequencies in the pulsing electric field on the fouling in the presence of humate. After the optimal frequency for the square wave power was determined in the 2 cell pair unit of CMX and AMX, batch runs were repeated without cleaning procedures to investigate the effects of electric pulses on already fouled membranes. The anion exchange membranes were fouled at the first and second batches using the DC power. Then the square wave pulse power of the determined optimal frequency was supplied to the fouled system.

RESULTS AND DISCUSSION

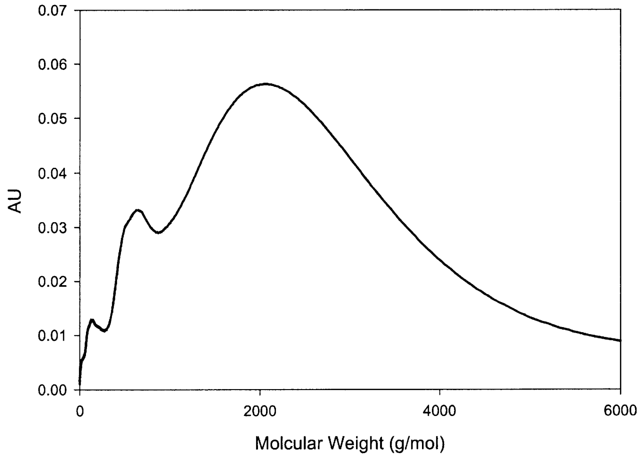

Fig. 1. Molecular weight distribution of humate in the feed solution.

1. Determination of the Optimum Frequency for the Pulsing Electric Field

The molecular weight (MW) distribution of humate in the initial diluate solution (feed solution) was measured by using the HPLC-SEC method, and the result is shown in Fig. 1. As shown in the figure, the average molecular weight of humate in the feed solution was about 3,400 g/mol. In the previous result, the electrokinectic property (the zeta potential) was measured to be within −18 and −25 mV over the measured pH range (pH 3 to 8). The fouling effects on the anion exchange membranes are assumed to be due to the negative charge density and the high molecular weight [Lee et al., 2002a].

The results of electrodialysis experiments during the extended operation time using the square wave powers with various frequencies are presented in Figs. 2 and 3. In a constant current mode, little difference was observed in the time course of NaCl concentration in diluate solutions even when experiments were carried out during enough time for humate to deposit on the membrane surface during electrodialysis (Fig. 2). Fig. 3 shows the cell resistance change of the stack according to NaCl concentration in diluate solution. As shown in the figure, the square wave powers having pulsation effects on the electric field for all examined frequencies represented lower values than those of the DC power especially at low NaCl concentrations. In the electrodialysis experiments in the presence of humate, it was reported that the humate fouled membranes through deposition, followed by formation of the loosely packed fouling layer rather than the fouling gel layer [Lee et al., 2002a; Song, 1998]. Also, it was observed that the pulsation of the electric field

Table 1. Characteristics of commerial ion exchange membranes

	CMX	AMX
Specific properties	High mechanical strength	High chemical resistance
Type	Strong cation-permeable (Na-form)	Strong anion-permeable (Cl-form)
Electric resistance (Ohm cm^2)	2.5-3.5	3.5[a]
Water content (gH_2O/g-dried membrane)	0.25-0.30	0.25-0.30
Exchange capacity (meq/g-dried membrane)	1.5-1.8	2.5[a]
Thickness (mm)	0.17-0.19	0.16-0.18

[a]Data were referred in the reference of Lee et al., 2002a.

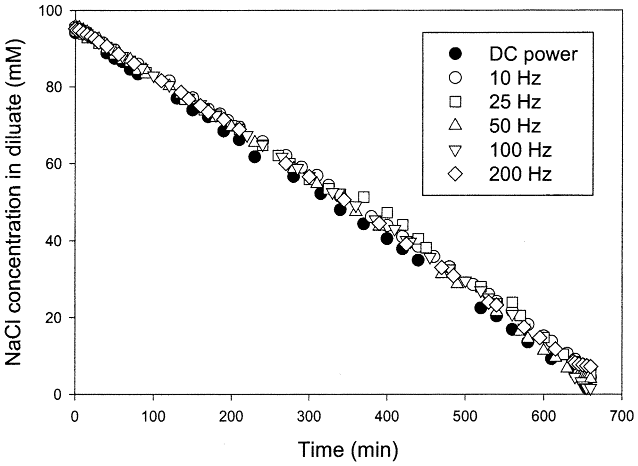

Fig. 2. Changes of NaCl concentration in diluate solutions for various frequencies.

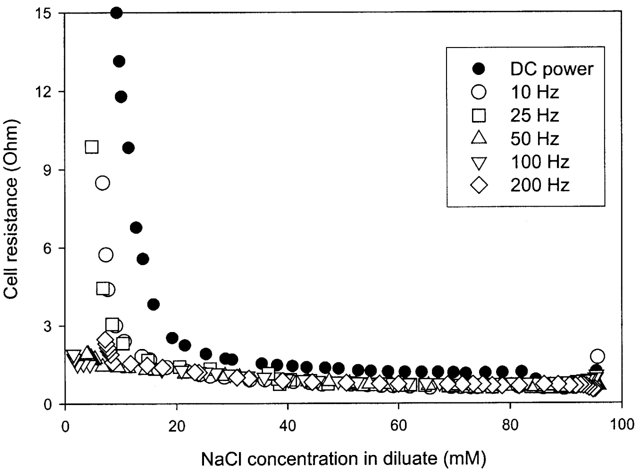

Fig. 3. Changes of cell resistance for various frequencies.

gave electromigration of the foulant deposited on the anion exchange membrane surface, thus decreasing fouling potential. Considering the cell resistance changes with the frequencies, the low frequencies (10 Hz and 25 Hz) and the highest frequency (200 Hz) showed higher resistances than the other frequencies. The frequencies of 50 Hz and 100 Hz showed the least values, assuming that there existed an optimal frequency for fouling mitigation.

The electrodialysis performance for various frequencies was compared with those of the DC power in terms of resulting parameters (NaCl flux, current efficiency and power consumption), and the results are summarized in Table 2. The current efficiency (CE) shown in the table was estimated by NaCl molecules transported per accumulated electrical charges during electrodialysis:

$$CE = 100x\frac{zF(N^fV^f - N^iV^i)}{itA} \tag{1}$$

where z is the electrical valence, F the Faraday constant, N the normal concentration of electrolyte, i the current density, and t the operation time, V the operation volume, and A membrane area. The superscripts, f and i, denote final and initial state, respectively. The characteristic values in the transport rates of NaCl for the pulsing electric field with different frequencies and the DC power were found as 2.0 mol/m^2·hr or higher. It is assumed that the flux of NaCl through ion exchange membranes is independent of the pulsation effects on the electric field, only depending on the accumulation of electrical charges [Lee, 2002].

The results of the power consumption and the current efficiency, however, showed notably different values between different frequencies and the DC power in Table 2. Considering the current efficiency as a function of frequency, the current efficiencies for the frequencies of 100 Hz, 200 Hz and the DC power showed below 90%, while those for lower frequencies (10 Hz, 25 Hz, and 50 Hz) showed higher than 90%. In particular, the current efficiency for 50 Hz showed the highest value among the examined frequencies. It is noted that pulse powers with high frequencies (100 Hz and 200 Hz) showed lower current efficiencies than the DC power. The high frequency seemed to have a rather compacting effect on the fouling layer. The power consumption for the different power sources showed significantly different results, including that the pulsing electric fields led to a lower power consumption compared to the characteristic value of the DC power (16.42 wh/mol NaCl). Also, the square wave power of 50 Hz showed the least value, disturbing formation of the fouling layer. It is considered through the experimental results that the pulsing electric field reduced the fouling rate in electrodialysis of solution containing humate and that the optimal frequency was determined as 50 Hz to minimize fouling potential in the fouling experiments.

2. Enhancement of ED Performance in Repeated Batch Runs

In the repeated batch runs, the DC power was supplied at the first and second batches; then a square wave pulse power of 50 Hz was supplied to the already fouled system. The results were compared in terms of conductivity changes, cell resistance changes, and the fouling index. In Fig. 4, the conductivity in diluate at the second batch shows the values of 1.8 mS/cm, greater than the first batch due to humate deposition. Then, that of the third batch decreased to 0.9 mS/cm, the similar level of the first batch (See Table 3). Fur-

Table 2. Performance with different frequencies in electrodialysis of humate

Power source		Flux of NaCl (mol/m^2·hr)	Current efficiency (%)	Power consumption (wh/mol NaCl)
Frequency of	10	2.02	92.1	8.66
the square	25	2.04	93.2	9.00
wave pulse	50	2.09	94.5	7.35
power	100	2.13	87.5	10.14
	200	2.00	88.3	9.20
DC power		2.04	90.5	16.42

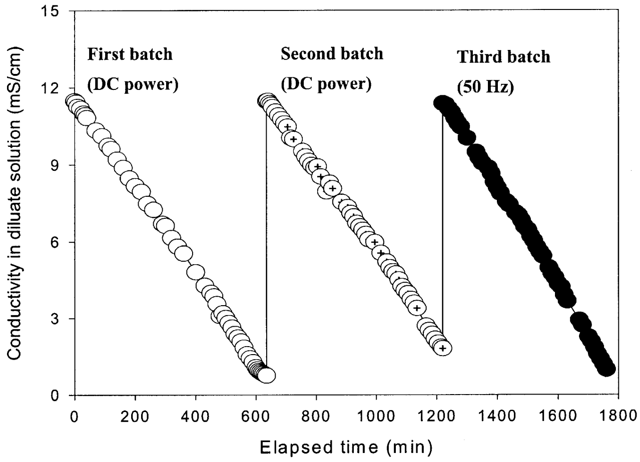

Fig. 4. Conductivity changes in diluate solution in the repeated batch runs.

Table 3. Summary of repeated batch runs in electrodialysis of humate

Batch runs	Value at the final of each batch run		Fouling index (Ohm/A·min) (Fig. 6)
	Conductivity in diluate (mS/cm) (Fig. 4)	Cell resistance (Ohm) (Fig. 5)	
First batch (DC power)	0.8	19.0	0.0006
Second batch (DC power)	1.8	21.9	0.0041
Third batch (50 Hz)	0.9	7.1	0.0014

ther, notable differences in the cell resistances were observed between the DC powers (at the first and second batches) and the pulsing electric field at 50 Hz (at the third batch). The cell resistance increased up to 19.0 Ohm at the first batch and showed a higher value at the second batch due to humate deposition. However, the cell resistance at the third batch using the square wave power increased only to 7.1 Ohm (one third of the second batch), demonstrating that the pulsing power reduced fouling potential in the fouling experiments of humate (See Fig. 5 and Table 3).

The membrane fouling index for electrodialysis (EDMFI) was used in this study for the quantitative analysis of the fouling mitigation during electrodialysis, which was defined previously [Lee et al., 2002d]. Under a constant current condition, the fouling index is obtained between the elapsed time and E/I^2:

$$\frac{E(t)}{I^2}=\frac{R_m}{I}+EDMFI*t. \tag{2}$$

Here, EDMFI can be defined as follows:

$$EDMFI=K\frac{C_b r_b}{C_g A^2} \tag{3}$$

where, E(t) is the cell voltage drop, I the operating current, R_m the intrinsic membrane resistance, K the constant related to the stack design, hydrodynamic conditions, species, and foulant concentration, C_b the foulant concentration in the bulk solution, C_g the foulant concentration in the gel layer, A the effective membrane area, and t the elapsed time. A higher value of the EDMFI, estimated in the relationship between the elapsed time and E/I^2, indicates a higher fouling tendency. Changes in fouling potentials were compared by using the membrane fouling indices in Fig. 6. The EDMFI of the second batch in the repeated batch runs showed a much higher value (about 7 times) than that of the first batch due to increasing amount of the deposited foulant on the membrane surface (See Table 3). Using the square wave power with an optimal frequency of 50 Hz, the fouling index of the third batch decreased to 0.0014 Ohm/A·min, which is one-third of the value for the second batch. During fouling mitigation with a pulsing electric field, one cycle of pulsing may be divided into three stages [Czekaj et al., 2000]: (i) formation of the fouling layer on the membrane surface due to electromigration of foulants, (ii) movement of the charged foulant in the pulsing electric field with the opposite direction, and (iii) movement of the particles dispersed in the boundary layer near the membrane surface and the fouling layer formation of a layer on the membrane

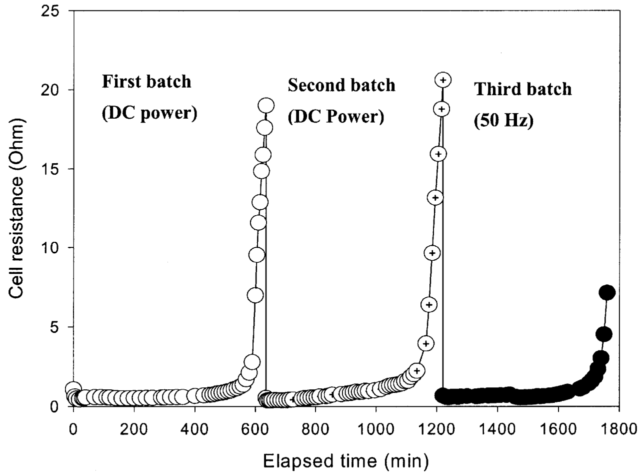

Fig. 5. Cell resistance changes in the repeated batch runs.

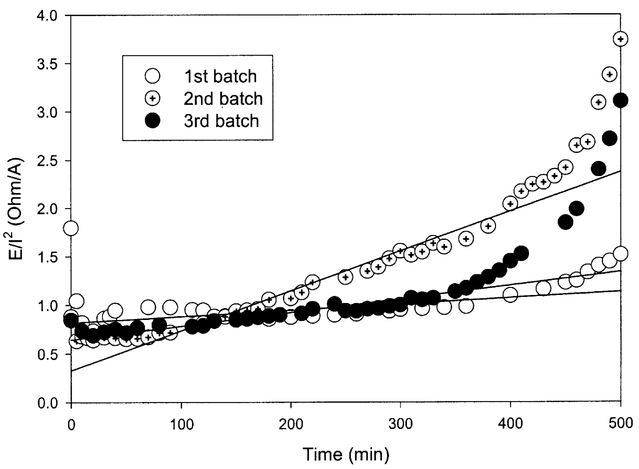

Fig. 6. Changes of foluling potentials in the repeated batch runs using the fouling index (the lines in the graph were calculated from Eq. (2)).

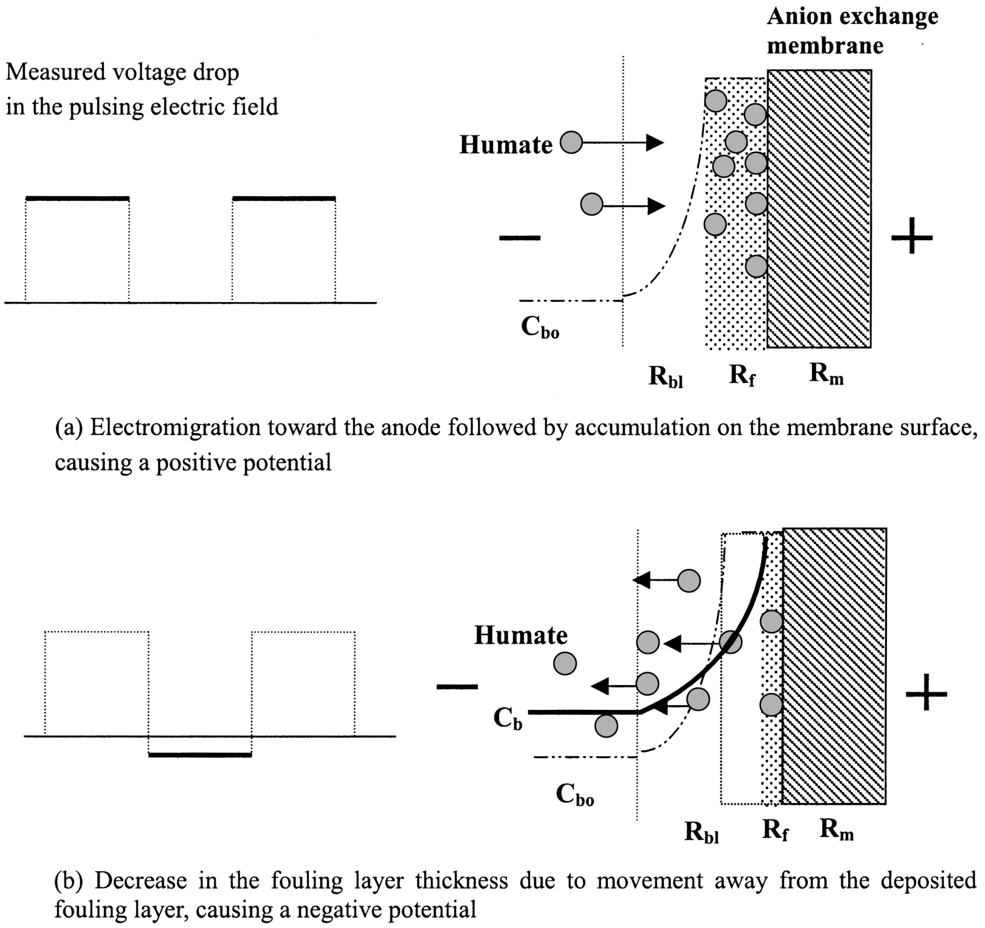

Fig. 7. Illustration showing the influence of the pulsing electric field on the movement of humate.

surface again, which depends on the pulse period and the electric field.

The fouling mitigation effects may be understood by the second and the third stages during electrodialysis under the pulsing electric fields [Lee et al., 2002d]. It was assumed to be due to the movement of the charged foulants away from the membrane surface during electrodialysis. When the constant current is supplied with a square wave profile having positive potential, the charged particles move toward the anode resulting in the positive potential (See Fig. 7a). Meanwhile, the charged particles move away from the membrane surface when the current is shut-off in the pulsing electric field, showing negative potential (See Fig. 7b) [Czekaj et al., 2000; Rogers and Sparks, 1992]. The pulsation effect on the electromigration of the foulant will be small at high frequencies (100 Hz and 200 Hz in this study) due to short periods as shown in the results [Zumbush et al., 1998].

CONCLUSION

In this study, square wave powers having different frequencies in electric fields were employed to investigate the effects of the frequencies on fouling mitigation during extended operation of fouling experiments. The optimal frequency to minimize fouling potential was determined as 50 Hz after the resulting parameters relating to the electrodialysis performances were compared. Also, it was clearly shown in the repeated batch runs that a pulsing electric field with the optimal frequency reduced the fouling potential. Through electrodialysis experiments of humate, it was suggested hat the pulsation on the electric field using the square wave powers enhanced the mobility of the charged foulants away from the fouling layer on the membrane surface, decreasing the electric resistance of the electrodialysis cell. The use of the pulsing electric field showed the feasibility of removal of the foulant as a cleaning-in-place method to enhance the ED performance even in an already fouled system.

ACKNOWLEDGEMENT

This work was supported by the National Research Laboratory (NRL) Program of Korean Institute of Science and Technology Evaluation and Planning (KISTEP) (Project No. 2000-N-NL-01-C-185).

NOMENCLATURE

A : effective membrane area [m^2]
C_b : humate concentration due to pulsing effect in Fig. 7 [mol/L]
C_{bo} : humate concentration without pulsing effect in Fig. 7 [mol/L]
E : cell voltage drop [V]
F : Faraday constant [96500 C/eq]

I : operating current [A]
K : constant used in Eq. (3) [m^3/Coulomb]
N : normal concentration [eq/L]
R_{bl} : boundary layer resistance [ohm]
R_f : fouling layer resistance [ohm]
R_m : membrane resistance [ohm]
V : operation volume [L]
i : current density [A/m^2]
t : elapsed time [min]
z : electrical valence [-]

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