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The required membrane length in electrodialytic desalination of river water

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ABSTRACT

A method for estimation of the required membrane length in a single-pass, counter-current electrodialysis was proposed. The limiting current density was determined in a membrane module consisting of four PC-Cell PC-SK/PC-SA membrane pairs and three different intermembrane spacers (0.26, 0.35, and 0.40 mm). The effect of the spacer thickness on a pressure drop was determined. The required membrane length was calculated for electrodialytic desalination of river water as a pretreatment before the electrodeionization. Based on the calculations, desalination costs were estimated and the effect of intermembrane spacer thickness and linear flow velocity was discussed.

Keywords: Electrodialysis; River water; Desalination costs

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1. Introduction

Energy industry needs vast amounts of demineralized water for the water-steam cycle of the power plants. Demineralized water must meet high requirements, especially in the case of high-pressure boilers. Typically, electrodeionization (EDI) or ion exchange is utilized in the production of ultra-pure water for the power industry. EDI requires high-quality feed water, typically of total dissolved salts content below 25 mg dm^{-3}; thus, pretreatment of the feed water is required. There is a set of criteria, which should be met by the EDI feed: free chlorine <0.1, 0.05, and 0.025 mg dm^{-3} for a 80%, 85%, and 95% conversion, respectively; iron, manganese, and sulfates <0.01 mg dm^{-3}; pH 4–11; TOC < 0.5 mg dm^{-3}; and hardness <1.0 mg $CaCO_3$ dm^{-3} [1]. Typically, reverse osmosis (RO) is used as a pretreatment before the EDI. For instance, RO-EDI systems have been successfully implemented in Krasnodar [2] and Putilovo [3] power plants, with water production capacity of 33 and 40 m^3 h^{-1}, respectively.

In Poland, one of the largest power company is TAURON Wytwarzanie. Among its power plants, the "Łagisza" power plant in Będzin has a modern water treatment system, consisting of microfiltration, RO, CO_2 desorption, and ion-exchange. The plant plans are to intake water from Czarna Przemsza river (conductivity ca. 450–675 μS cm^{-1}). The "Bielsko Biała" power plant has two small-scale EDI units, 4 m^3 h^{-1} each. The "Stalowa Wola" power plant utilizes electrodialysis reversal (EDR) – RO – EDI (75 m^3 h^{-1}). The remaining TAURON power plants use several ion exchangers operated in series. The typical feed water conductivity, 200–600 μS cm^{-1}, causes the necessity for frequent resin regeneration, high chemicals consumption, and high volume of postregeneration lyes.

In the previous work, we have proposed electrodialysis (ED) as an EDI pretreatment instead of traditionally used

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RO [4]. There are several reasons why the ED can outperform RO in brackish water desalination. ED shows less maintenance and cleaning downtime than RO and NF units [5]. The ion-exchange membranes are more resistant to biofouling than RO membranes, less sensitive to chlorine, able to operate at higher feed SDI values and are easier to clean up. The basis of the process is different: in RO and nanofiltration, the energy is proportional to the amount of solvent that needs to be transported across the membrane; in ED, the required energy is proportional to the amount of ions that need to be transferred. Because brackish water desalination requires the removal of relatively small amount of salt, the ED can be economically competitive.

The problem with ED, though, is that high electric resistance of diluted solutions dramatically increases the process costs, when a high degree of desalination is to be reached. Previous research [6,7] showed that due to thin intermembrane spacers during electrodialytic boron removal, the treated water was at the same time deionized to approximately distilled water level. Currently, the ED-EDI system is tested as an alternative for the existing RO-ion exchange technology in "Łagisza" power plant.

In order to properly design the pilot-scale electrodialyzer, one has to predict the required membrane length of the electrodialyzer [8]. The optimization of the membrane length is crucial in the case of low salinity water desalination, where equipment costs are the majority of overall desalination costs, with pumping and energy costs being less important.

2. Experimental

The goal was to simulate two edges of the hypothetical membrane mounted in counter-current single pass electrodialyzer: on the one edge, the feed (800 μS cm^{-1}) enters the diluate compartment while the concentrate (3,000 μS cm^{-1}) leaves the concentrate compartment; on the second edge, the diluate (35 μS cm^{-1}) leaves the diluate compartment, while the feed enters the concentrate compartment. The proposed procedure for estimating the membrane length is as follows:

(1) determination of the voltage drop, U, on the electrodialyzer at 80% of limiting current density as measured in the 35–800 μS cm^{-1} arrangement, (2) assuming the constant voltage drop along the electrodialyzer and based on current-voltage characteristic determined in the 800–3,000 μS cm^{-1} arrangement, calculate the current density at voltage U, and (3) assuming a known current density distribution between those two ends, calculate the required membrane length.

Experiments were performed using a bench-scale electrodialyzer of effective membrane length of 3 cm and effective membrane area of 4.5 cm^2, equipped with four pairs of membranes. The cathode and the anode of electrodialyzer were made of platinized titanium. Every solution was recirculated by Masterflex L/S peristaltic pump. All experiments were conducted at 25°C. The limiting current density was determined using the Cowan–Brown method [9] at the set linear flow velocity in the range of 0.5–4.0 cm s^{-1}. Three intermembrane spacers were tested with PC-Cell PC-SK/PC-SA membranes (see Table 1): 0.26 mm woven spacer, 0.35 mm and 0.40 mm nonwoven spacers.

Table 1
Manufacturer data on the membranes used

Membrane	PC-SK	PC-SA
Type	Cation-exchange	Anion-exchange
Electric resistance (Ω cm^2)	1.8	2.5
Water content (%)	14	9
Tensile strength (kg cm^2)	4–5	4–5
Maximum working temperature (°C)	60	50
Thickness (μm)	180–220	160–200

In order to estimate the energy required for pumping solutions through the electrodialyzer, the pressure drop for each of the used spacers was measured using a single-channel module of 19 cm channel length and 90 cm^2 channel area, connected to a U-tube filled with mercury (precision: 1 mmHg). The linear flow velocity was set using Masterflex L/S peristaltic pump.

Finally, the desalination costs were estimated, taking into account the equipment costs, pumping costs, and costs of DC energy required for desalination.

3. Results and discussion

Exemplary current-voltage curves measured in the system are presented in Fig. 1. The results of the limiting current density determination are presented in Table 2. Despite the fact that pressure drop on 0.26 mm spacer was possible to measure even at very high flow velocities, it was not possible to make the measurement at 4 cm s^{-1} for 0.26 mm spacer due to problems with leakage between the concentrate and diluate compartments. This may be explained by a different experimental setup. Single-channel with PMMA walls, without membranes, was used in the case of pressure drop measurements, while a complete ED stack, in which the membrane bulging and deformation could cause leakage problems, was used in the case of limiting current density measurements. Surprisingly, although 0.26 mm spacer showed higher limiting current density at low salinity than the 0.35 mm spacer at

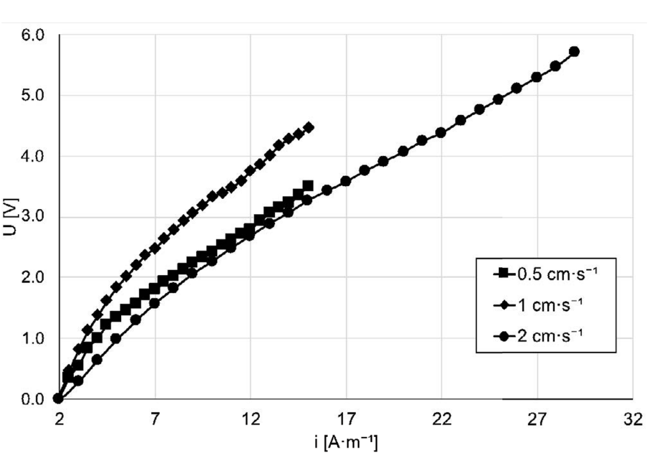

Fig. 1. Exemplary current-voltage curves measured using 0.26 mm spacers.

Table 2
The effect of spacer thickness, *s*, and linear flow velocity, *u*, on the limiting current density, i_{lim}, and working current density of 80% of i_{lim}, i_0, as measured in the 35–800 μS cm^{-1} arrangement; on the voltage drop, *U*, at 80% of the determined limiting current density, and on the current density, i_L, as measured in the 800–3,000 μS cm^{-1} arrangement at given voltage drop *U*, and on the required membrane length

s (mm)	0.26			0.35				0.40			
u (cm·s^{-1})	0.5	1.0	2.0	0.5	1.0	2.0	4.0	0.5	1.0	2.0	4.0
i_{lim} (A m^{-2})	1.22	1.84	2.07	0.84	1.22	1.55	2.60	1.00	1.22	1.60	2.49
i_0 (A m^{-2})	0.98	1.47	1.66	0.67	0.98	1.24	2.08	0.80	0.98	1.28	1.99
U (V)	3.8	4.2	4.2	3.2	4.1	5.1	5.6	4.0	4.0	4.1	4.8
i_L (A m^{-2})	7.08	11.1	15.0	3.30	9.67	19.0	25.6	5.91	6.53	9.20	16.5
L (m)	0.27	0.34	0.54	0.67	0.58	0.68	0.94	0.49	0.86	1.26	1.47

the same linear flow velocity. 0.35 mm spacer showed higher limiting current density at higher salinity.

Using the determined limiting current densities, the required membrane length of a hypothetical single-pass counter-current electrodialyzer was calculated. The current density distribution along the membrane is not linear [10–14], and in this case, it was assumed that it resembled the first-order kinetic equation with the position along the electrodialyzer equivalent to time:

$$i = i_0 e^{-kl} \tag{1}$$

where i_0 is the current density at one end the electrodialyzer, *i* is the current density at membrane length *l*, and *k* is the distribution constant, given as:

$$k = \frac{1}{L}\ln\left(\frac{i_0}{i_L}\right) \tag{2}$$

where *L* is the required length of the electrodialyzer, i_0 is the 80% of the limiting current density at one end of the electrodialyzer (l = 0, where the diluate conductivity is 35 μS cm^{-1} and the concentrate conductivity is 800 μS cm^{-1}), and i_L is 80% of the limiting current density at the second end of the electrodialyzer (l = L, where the diluate conductivity is 800 μS cm^{-1} and the concentrate conductivity is 3,000 μS cm^{-1}). In the literature, a polynomial with empirically-determined coefficients is usually assumed [10,14], however, this assumption would be impractical for the interpolation between two points. The use of first-order model was based on the assumptions that: the voltage drop along the membrane was constant, the stack resistance was proportional only to the diluate concentration with the negligible influence of concentrate salinity, the electromigration being the only transport phenomena responsible for the concentration change, the constant current efficiency along the membrane and the lack of a back-diffusion, a convection, a concentration polarization and water transport across the membranes. These assumptions should be mostly fulfilled in the electrodialyzer operated on low salinity solutions. In such conditions, the rate of concentration change at a given point along the membrane would only be proportional to the current passing through the system at given point, with current/concentration directly proportional to each other. Such behavior resembles the first-order kinetic equation with the position along the membrane being equivalent to time.

The mean value of the function *i*(*l*) over the interval <0,*L*> is given as:

$$\bar{i} = \frac{1}{L}\int_0^L i(l)\,dl = -\frac{1}{L}\times\frac{i_0}{k}\left[e^{-kL}-1\right] \tag{3}$$

Taking into account Eq. (2), Eq. (3) can be rearranged into:

$$\bar{i} = \frac{i_0 - i_L}{\ln\left(\frac{i_0}{i_L}\right)} \tag{4}$$

The charge *q*, required for desalination is:

$$q = \left(C_L - C_0\right) hsLz_+v_+F \tag{5}$$

where z_+ is the valence of the ion (assumed as 1), *s* is the inter-membrane distance, *F* is the Faraday's constant, C_L and C_0 are molar concentrations at the inlet and the outlet of the diluate compartment, respectively, and *h* is the channel height. Assuming the plug flow in the electrodialyzer, the mean residence time can be calculated as:

$$\tau = \frac{L}{u} \tag{6}$$

where *u* is the linear flow velocity, cm s^{-1}.

The required current *I*, assuming 100% current efficiency, is then:

$$I = \frac{q}{\tau} = \left(C_L - C_0\right) hsuzF \tag{7}$$

Taking into account the current density, Eq. (7) becomes:

$$\bar{i} = \frac{I}{Lh} = \frac{C_L - C_0}{L} suzF \tag{8}$$

and the required membrane length is:

$$L = \frac{\left(C_L - C_0\right)}{i_0 - i_L} suzF \ln\left(\frac{i_0}{i_L}\right) \tag{9}$$

The results of calculation are presented in Table 2. The spacer thickness directly influenced on the mass transfer in the diffusion boundary layer adjacent to the membrane and thus, to the limiting current density and the degree of the desalination (analogous to the conversion of the chemical reactor). The results showed this effect as well, showing that smaller membrane length would be required when the smaller intermembrane distance was used.

The pressure drop, measured on a 0.19 m long channel with the tested spacers, is presented in. 2. The 0.35 mm spacer showed very high-pressure drop, which was the result of the low spacer porosity. In all cases, a linear dependence of pressure drop, ΔP, on linear flow velocity, u, could be observed, as presented in Fig. 2. The values of a coefficient are presented in Table 3:

$$\Delta P = a \times u \times \frac{L}{0.19} \tag{10}$$

where L is the membrane length, 0.19 m is the length of the channel in testing device.

3.1. The estimation of desalination costs

To show the effect of intermembrane spacer thickness, the costs of desalination of river water from 800 to 35 μS cm^{-1}, K, were estimated as:

$$K = K_{\mathrm{DC}} + K_{\mathrm{AC}} + K_E \tag{11}$$

where K_{DC} means costs of DC energy required for ED, K_{AC} means costs of pumping, and K_E is costs of equipment, membranes, etc., K_{DC} was calculated as:

$$K_{\mathrm{DC}} = \frac{K_c U A \bar{i}}{\eta_{\mathrm{AC/DC}} \dot{V}} \tag{12}$$

where K_c is the costs of electric energy (assumed as 0.06 € kWh^{-1}), U is the voltage drop on the module (assumed as mean value from voltage drops on both ends of the electrodialyzer plus additional 4 V for electrode rinse compartments), A is the required membrane area, $\dot{V}$ is the volumetric flow of the diluate, and $\eta_{\mathrm{AC/DC}}$ is the rectifier efficiency (assumed as 95%). The assumed electrodialyzer diluate volumetric flow, given for the known required membrane length, is:

$$\dot{V} = uhs = us\frac{A}{L} \tag{13}$$

K_{DC} is then equal to:

$$K_{DC} = \frac{K_c U L \bar{i}}{\eta_{\mathrm{AC/DC}} us} \tag{14}$$

Costs of pumping were calculated as:

$$K_{\mathrm{AC}} = \frac{2.1 K_C \Delta P}{\eta_p} \tag{15}$$

where ΔP is the pressure drop on the electrodialyzer, η_p is the pump efficiency (assumed as 85%). For the sake of simplicity, costs of pumping of fluid through diluate and concentrate compartment were assumed to be equal and the costs of pumping through both electrode rinse compartments were 10% of diluate pumping costs, hence 2.1 modifier in Eq. (15). K_E was calculated as:

Table 3
Empirical coefficients a of Eq. (10)

Spacer	a (bar s cm^{-1})	R^2
0.26 mm, woven	0.0194	0.998
0.35 mm, nonwoven	0.0317	0.997
0.40 mm, nonwoven	0.0166	0.996

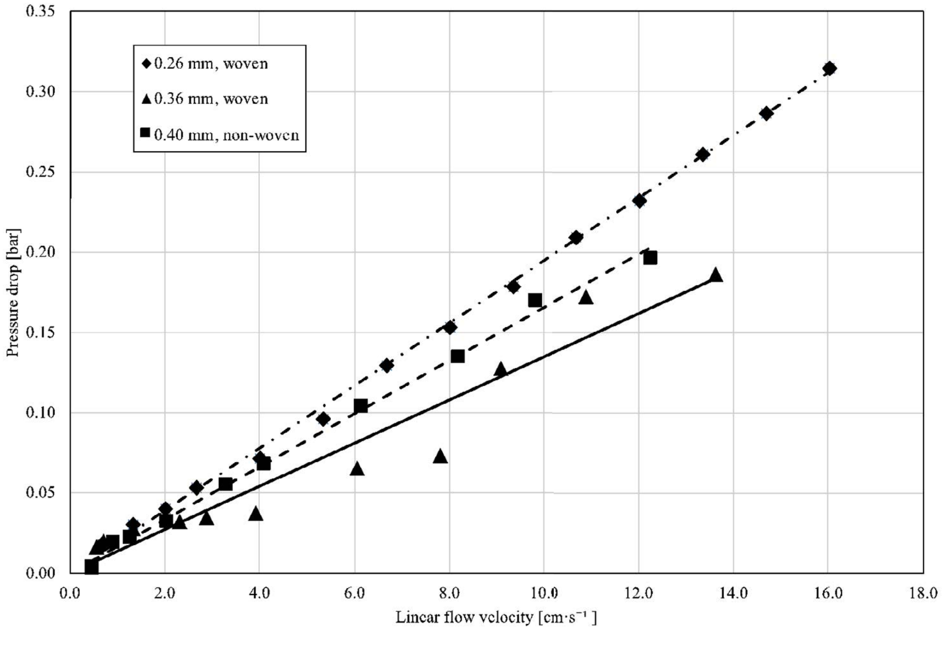

Fig. 2. The effect of the linear flow velocity and the spacer thickness on the pressure drop measured on 0.19 m channel.

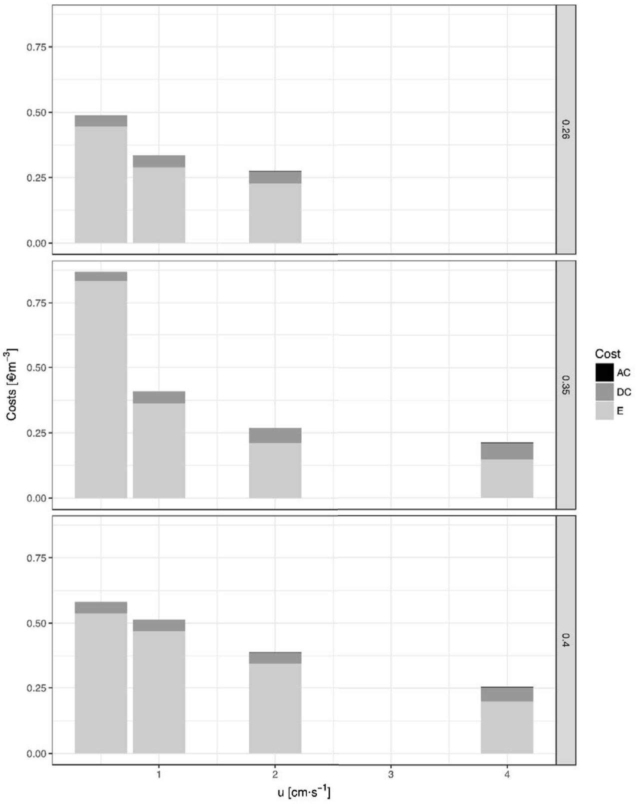

Fig. 3. The dependence of pumping costs (AC), energy costs (DC), and equipment costs (*E*) on spacer thickness and linear flow velocity, assuming desalination of 800 μS cm^{-1} water down to 35 μS cm^{-1}.

$$K_E = \frac{K_m A}{0.3Vt} = \frac{K_m L}{0.3tus} \tag{16}$$

where K_m is the membrane cost (assumed as 200 € m^{-2}), t is the lifetime of membranes (assumed as 85,000 h). It was assumed that the membrane costs were 30% of all equipment costs.

The results are presented in Fig. 3. Depending on the linear flow velocity, equipment costs were projected to be from 78% to 96% of overall ED costs, whereas the pumping costs were negligible. The results suggested that it would be desirable to work at the high linear flow velocity, as this resulted in the decrease of the required membrane area (due to the decreased concentration polarization and enhanced mass transfer, higher current densities were possible). The 0.35 mm and 0.26 mm spacers showed similar overall desalination costs – differences were too small to clearly indicate on the better spacer. They both, however, outperformed 0.40 mm spacer, which suggested that decreasing the intermembrane distance was beneficial for electrodialytic desalination of low salinity waters.

4. Conclusions

The results showed that the required membrane length could be estimated based on the batch-mode limiting current density measurements simulating two ends of an electrodialyzer and assuming current density distribution along the electrodialyzer. The 0.26 and 0.35 mm thin intermembrane spacers were shown to give similar performance, whereas 0.40 mm exhibited higher overall desalination costs. The majority (74%–90%) of overall desalination costs in the tested case of low salinity water desalination were shown to be the equipment (membranes, electrodes, casing, controllers, etc.), whereas the pumping costs were negligible. Applying higher linear flow velocity, despite increasing the required membrane length due to the lower mean residence time, decreased the overall desalination costs.

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Symbols

a — Empirical parameter of Eq. (10), bar s cm^{-1}
A — Membrane area, m^2
C — Molar concentration, mol m^3
η — Efficiency, %
F — Faraday constant, C
h — Channel height, m
i — Current density, A m^{-2}
I — Current, A
k — Current density distribution constant
K — Costs, € m^{-3}
l — Position along the membrane, m
L — Required membrane length, m
ΔP — Pressure drop, bar
q — Charge, C
s — Spacer thickness, mm
t — Membrane life-time, h
τ — Space-time, s
u — Linear flow velocity, cm s^{-1}
U — Voltage, V
V — Volumetric flow, m^3 s^{-1}
z — Valence of ion

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