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Electrodialysis reversal desalination: optimal voltage application rate, linear velocity, and mean ion residence time for maximal ion removal rate

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ABSTRACT

Optimal voltage application rate, linear velocity, and mean ion residence time ($\mathrm{MIRT_d}$) in dilute stream were searched for electrodialysis reversal desalination by using two different feed waters containing TDS 3330 and 7190 mg/L NaCl. Two sets of literature data were used in the analyses. First, the relation among demineralization degree, voltage application rate, and $\mathrm{MIRT_d}$ were derived from theory. Then, the findings were analyzed from the first set of literature data and validated with the second set of data. The analyses show that the maximal demineralization degree does not appear at the highest voltage application alone and that demineralization degree increases with the increasing voltage application rate to a certain critical value only. The maximal demineralization degree occurs at the combination of lower voltage application and longer $\mathrm{MIRT_d}$ or vice versa. Data show the maximal demineralization degree does not always present the maximal ion removal rate per effective area of cell pairs per power. Therefore, both the maximal demineralization degree and maximal ion removal rate per effective area of cell pair per power were used to gauge optimal voltage application, linear velocity, and $\mathrm{MIRT_d}$. Optimal voltage application, linear velocity, and $\mathrm{MIRT_d}$ were found to be 45–70 V, 15.1–12.3 cm/s, and 2.3–2.7 min for feed water 3330–7190 mg/L NaCl in Aquamite I membrane stack with Mark I spacer in 135 different operational conditions.

Keywords: Maximal demineralization; Maximal ion removal rate per effective area of cell per power

1. Introduction

In electrodialysis reversal (EDR) desalination, direct current is supplied to the membrane cell pairs through electrodes. Dissolved ions carry the current through the solution and through the membrane to desalt ions from diluate into concentrate steams. Dissolved ions are built up along the length of concentrate stream, while dissolved ions are diminished from the length of diluate stream. Subsequently, ions tend to scaling on the surface of membranes facing to the concentrate stream if they reach saturated levels. Ions also tend to block the pore space of membrane during facing to the dilute stream their migration through pore. Therefore, EDR was designed by Ionics, to switch polarity (between positive and negative) and hydraulic streams (between diluate and concentrate) regularly (15–30 min) for removing scaling forming substances on the surfaces of membranes facing both concentrate and diluate streams. The quantities of ions present in both diluate and concentrate determine the current carrying capacity that is defined as conductivity. The number of ions in the solution is defined as concentration or normality. The amount of current applied (I), effective area of cell pair (A_π), and normality of solution maintaining between diluate in and diluate out along the diluate stream (N_{diluate}) are the controlling parameters in design and operation of current driven membrane separation systems. These three parameters can be lumped as a current density per normality of diluate (i/N_{diluate}) for the given feed water. If i/N_{diluate} increases, the concentration of ions at the diluate stream decreases. If i/N_{diluate} reaches to a higher value, there will not be enough ions to carry the desired electron current in diluate stream, and a limiting i/N_{diluate} will be reached where film depletion of concentration polarization appears [1,2]. There will be a high-voltage drop and excessive heating and excessive power consumption if i/N_{diluate} approach to $(i/N_{\text{diluate}})_{\text{limiting}}$ [2]. Furthermore, this lumped parameter was defined as polarization parameter. Davis et al. [3] used 200 A cm/mole of i/N for univalent ions to identify a suitable current application rate and the required effective area of cell pairs.

Moreover, i/N was found to be a function of linear velocity of feed solution in different concentrations [4]. Linear velocity of diluate flow rate and geometric shape of the spacers are used to mathematically predict ionic mass permeate rate [3].

If the required degree of demineralization or concentration cannot be achieved in a single path through the stack, several stacks are designed in series [5,6] to extend ions travelling length and mean ion residence time in dilute and/or MIRT_{d}. During the desalination process, some ions are blocked and built up at the surfaces and in pores of the membrane as a boundary layer thickness, and the available area of membrane for ions migrating decreases. One way to prevent the ions from building up and reducing the boundary layer thickness is to promote the turbulence between the surfaces of membrane by increasing the linear velocity of feed water. However, the faster the feed water velocity is, the shorter MIRT_{d} is available for ions to migrate through the ion-exchange membrane [7]. The shorter MIRT_{d} also causes lower desalination efficiency. Lee [8] stated that increasing the flow rate (or velocity) leads to an increase of the removal rate; however, the effect was insignificant when the flow rate is more than 2.4 L/min. Lee [8] and Meng et al. [9] also pointed out the demineralization and efficiency rates increase with the applied voltage (or current) only to a certain critical value. The increment of demineralization rate, however, was decreased as the applied voltage increases beyond a certain critical value. Beyond a certain critical current, efficiency decreases with the increasing current applied [9] due to the total resistance of stack increases. Meng et al. [9] concluded that increasing all of the applied voltage, linear velocity of feed water in diluate steam, and/or MIRT_{d} simultaneously to a certain critical value would achieve superior performance of ED cell.

Faraday's first Law of Electrolysis also stated that the mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred (or electrical charge, expressed in Coulomb) at that electrode (equation derivation in the appendix). The more coulomb applied at the electrode, the higher ion altered in the electrode. Coulomb is defined as the multiplier of current and time duration, and we hypothesize that all of *current, linear velocity, and time duration* are necessary to increase to a certain critical value for achieving superior efficiency in EDR.

The purpose of EDR desalination is to gain a highest efficiency or the highest ion removal rate per an effective area of cell pairs per power in a given stack. The objective of the article is to find the optimal voltage application rate, optimal linear velocity, and optimal MIRT_{d} in the membrane stack to gain the highest efficiency for a one pass-through EDR. GE-Ionics's Aquamite I with Mark I spacer was used as a model membrane stack.

2. Methods

2.1. Fundamental method

Our derivation in the appendix shows that the chemical compositions of water maintained from diluate in to diluate out along the diluate stream, the amount of voltage applied, and the linear velocity and/or MIRT_{d} in the diluate stream are the key factors for the ratio of ions concentrations between feed and product streams as shown in Eq. (1):

$$\ln\left(\frac{N_f}{N_p}\right) = \frac{\xi_I \beta}{F}\,\frac{1}{t k_{\text{spacer}}}\left(\frac{\varepsilon_\pi}{R_\pi\, N_{\text{diluate}}}\,\text{MIRT}_{\text{d}}\right) \tag{1}$$

2.2. Experiment methods

The experiment data used in this article were referred from [10] due to its data availability. A "GE-Ionics Aquamite I" EDR stack containing 100 cell pairs with the cation-, anion-exchange membranes (CATION-CR67-HMR-412 and ANION-204-SXZL-386) and Mark I spacers (1 mm thickness and 348 cm length of the flow path) were used [10]. Current density application rates were 2–9 mA/cm^2 in electrical stage I and 2–5 mA/cm^2 in electrical stage II. The polarity reversal interval cycle was 15 minutes.

The tests from [10] were run with two different feed waters with TDS 3,330 and 7,190 NaCl mg/L to generate two different sets of data. Nine different voltage applications (30, 40, 50, 60, 70, 80, 90, 100, and 110 V) with eight different linear velocities of feed water in diluate stream (4.7, 7.0, 9.1, 11.3, 13.4, 15.5, 17.7, and 19.8 cm/s) in each of voltage application were tested for feed water which has TDS 3,330 mg/L. Seven different voltage applications (30, 40, 50, 60, 70, 80, 90 V) with nine different linear velocities of feed water in diluate stream (4.7, 7.0, 9.1, 11.3, 13.4, 15.5, 17.7, 19.8, and 22.0 cm/s) in each of voltage application were tested for feed water which has TDS 7,190 mg/L.

3. Results and discussion

Results obtained from analyses are summarized in Figs. 1(a–c) and 2(a–c). Figs. 1(a) and 2(a) confirm the degree of ion removal rate per effective area of membrane and power based on the intercorrelated effects of chemical compositions of feed water, voltage applied in the stack, and MIRT$_d$ as stated in [5]. Fig. 1(a)–(c) shows that for feed water (3,330 mg/L NaCl) with the 30, 40, 50, 60, and 70 V of voltage application rates, 2.6 min MIRT$_d$ is required to gain 83.5, 85.3, 87.7, and 91.9% of the maximal demineralization, respectively. Fig. 1(a)–(c) also shows that in the same feed water (TDS 3,330 mg/L NaCl), the higher voltage application rates (80, 90, and 100 V) are required in the higher linear velocity (15.6 cm/s) of feed water in diluate stream and lower MIRT$_d$ 2.2 min to gain the maximal demineralization degrees (89.2, 90.4, and 92.2%) or minimal ions concentration in diluate stream (Fig. 1(b)), respectively, in the same membrane stack with the same type of Mark I spacers. These two statements explain that the maximal demineralization degrees increase from 83.5 to 91.9% and 89.2 to 92.2% by increasing voltage application from 30 to 70 V and 80 to 90 V with the linear velocities of feed waters of 13.4 and 15.6 cm/s (or 2.6 and 2.2 min MIRT$_d$), respectively. This first finding concludes that a combination of lower voltage application and longer MIRT$_d$ or vice versa is required to achieve the maximal demineralization degree. The first finding was verified by the other set of literature data: for the same feed water (TDS 3,330 mg/L NaCl), the combination of the highest voltage application (110 V) and the lowest MIRT$_d$ (1.8 min) is required to gain the highest maximal demineralization degrees of 93.7% in the same of membrane stack with the same type of Mark I spacers. Fig. 1(a) and (b) also shows the maximal demineralization degrees 91.9 and 89.2% resulted from the voltage applications of 70 V (2.6 min MIRT$_d$) and 80 V (MIRT$_d$ 2.2 min) for feed water 3,330 mg/L NaCl. Therefore, the increase in voltage application alone does not always increase the maximal demineralization degree as our second finding. The reason for this is at very high-voltage application, the ions concentration is too low at the end of diluate stream, and current requires these ions (conductivity) to carry out the current electrons from membrane to membrane.

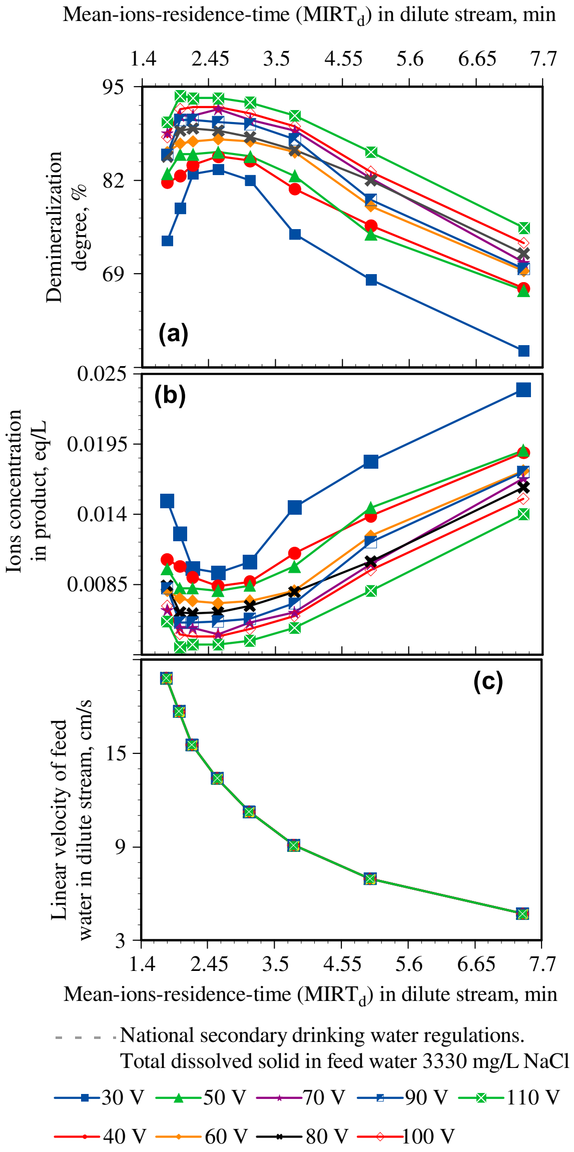

Fig. 1. MIRT$_d$ vs. demineralization (a); MIRT$_d$ vs. ions concentration in product stream of EDR (b); MIRT$_d$ vs. linear velocity of feed water in dilute stream (c).

Near-limiting current density, there are not enough ions to carry current in the diluate stream. This finding concurs with Lee's [8] statement of "the increment of demineralization decreases with the increasing voltage after a certain critical point." The linear velocity only promotes turbulence to increase the mass transfer rate in the membrane cell pair.

Our first and second findings from 3,330 mg/L NaCl feed water were validated by the literature data [10] with 7,190 mg/L NaCl feed water. Fig. 2(a)–(c) shows that for feed water which has 7,190 mg/L NaCl in the 30 V of potential application rate, 11.3 cm/s of linear velocity of feed water in diluate stream (or 3.1 min of MIRT_d) is required to gain 88.9% the maximal demineralization degrees or minimal ions concentration in dilute stream (Fig. 2(b)) in ED Aquamite I (100 cell pairs) with the Mark I spacers. For the same feed water (TDS 7,190 mg/L NaCl), the higher voltage application (40, 50, 60, 70, 80, and 90 V) are required in the higher linear velocity (13.4 cm/s) of feed water in diluate stream (or lower MIRT_d 2.6 min) to gain the maximal demineralization degrees (91.2, 92.6, 96.8, 95.8, 95.6, and 94.9%) in the same membrane stack with the same type of Mark I spacers. This statement explains that the maximal demineralization degrees increase from 91.2 to 96.8, then decrease from 96.8 to 94.9% by the increasing of voltage applications only from 40 to 60 and 60 to 90 V, respectively, with the same linear velocities of feed waters of 13.4 cm/s (or 2.6 min MIRT_d). This validates our first finding which is the combination of the lower voltage application and longer MIRT_d or vice versa is required to achieve the maximal demineralization degree. The maximal demineralization degrees 96.8, 95.8, 95.6, and 94.9% resulted from the voltage applications of 60, 70, 80, and 90 V for feed water with 7,190 mg/L NaCl. The lower voltage application 60 V generates the higher maximal demineralization degree while as the higher voltage application 90 V generates the lower maximal demineralization degree. Therefore, this statement validates our second finding which is that the increase of voltage application alone does not always increase the maximal demineralization degree.

3.1. *Using maximum ion removal rate per effective area of cell pairs and power to locate optimal zones*

The maximal demineralization degrees that correspond to voltage applications (30–110 and 30–90 for 3,330 and 7,190 mg/L of feed waters) were read from Figs. 1(a) and 2(a) and then, plotted in Fig. 3(a). The linear velocity of feed water in diluate stream, ions removal rate per effective area of cell pairs per power, and MIRT_d that correspond to the maximal demineralization degrees were plotted in Fig. 3(b–d). Fig. 3(a) shows two maximal demineralization degrees 91.9 and 93.7% occurring for 70 and 110 V of voltage application, respectively, for feed water with TDS of 3,330 mg/L. About 93.7% of maximal demineralization requires the higher voltage application (110 V) and results lower ion removal rate per effective area of cell pairs per power 0.539 eq/(h m^2 kWh) (Fig. 3(c)). However, the 91.9% of maximal demineralization needs the lower voltage application (70 V) and leads to the higher ion removal rate over effective area of cell pairs

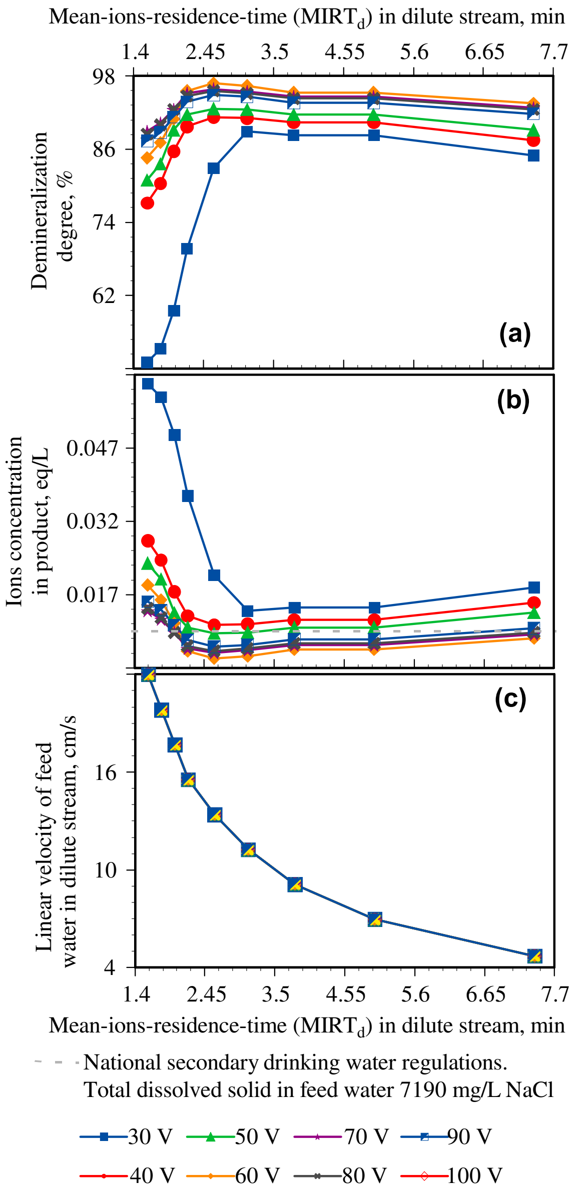

Fig. 2. MIRT_d vs. demineralization (a); MIRT_d vs. ion concentration in product stream (b); MIRT_d vs. linear velocity of feed water in dilute stream (c).

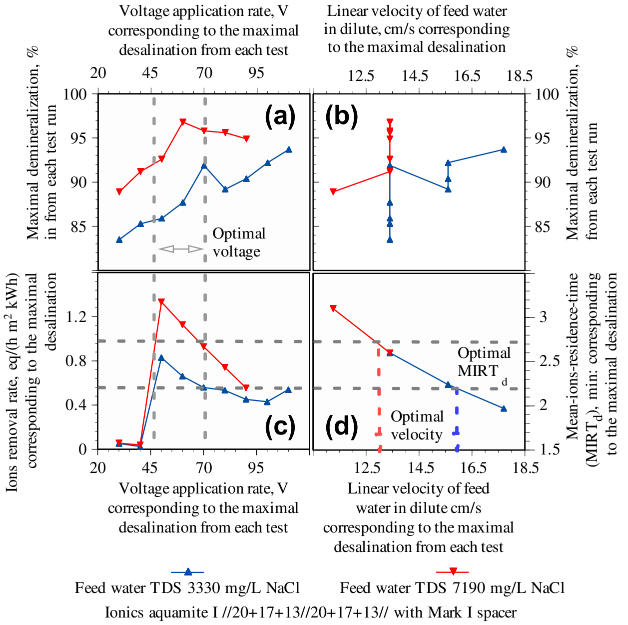

Fig. 3. Optimal potential application rate, linear velocity, and $\mathrm{MIRT_d}$.

and power 0.559 eq/(h m^2 kWh) (Fig. 3(c)). Therefore, both the maximal demineralization and the maximum ion removal rate per effective area of cell pairs and power were used to define the optimal voltage application rate, linear velocity feed water in cell pairs, and $\mathrm{MIRT_d}$ for both feed waters 3,330 and 7,190 mg/L as shown in Fig. 3(a–d).

Fig. 3 explains that to achieve the maximal dissolved ions removal rate per effective area of cell per power 0.56 and 0.94 eq/(h m^2 kWh) (Fig. 3(a)) for 3,330 and 7,190 mg/L of feed waters, the optimal voltage application rates of 45 and 70 V (Fig. 3(c)), respectively are required to inter-correlate with the optimal linear velocity 15.1–12.3 cm/s or $\mathrm{MIRT_d}$ 2.3–2.7 min (Fig. 3(b) and (d)).

4. Conclusion

Our findings in Figs. 1(a), 2(a), and 3 reveal optimal linear velocity is required to gain turbulence in the cell pair to reduce ions scaling on the membrane surface and to enhance ion mass migration rate from dilute to concentrate stream. At the same time, the adequate $\mathrm{MIRT_d}$ (Figs. 1(d) and 2(d)) is required for ion migration, and optimal voltage application (Fig. 3) is required to attract ions to migrate from dilute to concentrate streams. Fig. 3 shows our third findings as optimal voltage application, optimal linear velocity, and optimal $\mathrm{MIRT_d}$ are 45–70 V, 15.1–12.3 cm/s, and 2.3–2.7 min for the feed waters with TDS 3,330–7,901 mg/L NaCl in Aquamite I membrane stack with Mark I spacer desalination.

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Symbols

a — empirical coefficient related between resistance and normality
A_π — effective area of a single membrane cell pairs, m^2
F — Faraday's coefficient = 96485.34 C/eq = 96485.34 A s/eq
L_e — effective length of spacer, cm
L_{eT} — solution traveling length = $nt\ L_e$, cm
I — current, A
$\mathrm{MIRT_d}$ — mean ion residence time in dilute stream, min
nt — number of water flowing path in one cell pair in diluate, no unit
$N_d = N_{\mathrm{diluate}}$ — normality of solution maintaining between diluate in and diluate out along the diluate stream, eq/L. $\mathrm{N_{dilute}}$ was taken as the mean value of the inlet and outlet diluate normality.
Q_d — linear flow rate in one diluate stream = $nt\ tk_{sp}\ w\ vL_d$, cm^3/s
R_π — resistance in a single cell pair, ohm
v_{Ld} — linear velocity of solution in diluate, cm/s
V — voltage potential, V
w — with of diluate water flowing waterway in one cell pair, cm
tk_{sp} — thickness of spacer, cm

Greek

β — the value is affected by the type of electrode, filling materials, configuration of membrane stack, and characteristics of feed water [12]
ε_π — dV/dA_π = potential difference between cation and anion membrane per area of cell pair, V/m^2
ξ_I — mass of ion removed = (constant) (charged coulomb)/F

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Appendix

The relation among the current applied (I), voltage across the unit area of ED, and the resistance is as in Eq. (A1).

$$\mathrm{d}I = \varepsilon_\pi \mathrm{d}A_\pi / R_\pi \tag{A1}$$

Faraday's first Law of Electrolysis stated that the mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred (or charged coulomb) at that electrode. The mass of substance altered (ions removed) is related to the charged coulomb (current second) applied as the following:

Mass of ion removed = (constant)(charged coulomb)/F

Mass of ion removed = (constant)(current)(time duration)/F

Mass of ion removed/time duration = (constant)(current)/F

$$Q_d\,\mathrm{d}N_{\text{diluate}} = \mathrm{d}I\ \xi_I\ \beta/F \tag{A2}$$

(L/s) (eq/L) = A (unitless) (unitless)/{96485.34 A s/(eq)}

(L/s) (eq/L) = A (unitless) (unitless) {eq/(96485.34 A s)}

Eq/s = Eq/s

Insert Eq. (A1) into Eq. (A2)

$$Q_d\,\mathrm{d}N_{\text{diluate}} = (\varepsilon_\pi/R_\pi)\mathrm{d}A_\pi \xi_I \beta/F \tag{A3}$$

where

$$R_\pi = a/N_{\text{diluate}} \tag{A4}$$

Insert Eq. (A4) into Eq. (A3),

$$Q_d\,\mathrm{d}N_{\text{diluate}} = (\varepsilon_\pi N_{\text{diluate}}/a)\mathrm{d}A_\pi \xi_I \beta/F \tag{A5}$$

$$(1/N_{\text{diluate}})\ \mathrm{d}N_{\text{diluate}} = \{\xi_I\ \beta\ \varepsilon_\pi\ /\ (a\ F\ Q_d)\}\ \mathrm{d}A_\pi$$

$$\int_{N_f}^{N_p} \frac{\mathrm{d}N_{\text{diluate}}}{N_{\text{diluate}}} = \frac{\xi_I \beta \varepsilon_\pi}{aFQ_d} \int_0^{A_\pi} \mathrm{d}A$$

$$a \ln\left(\frac{N_f}{N_p}\right) = \xi_I \beta \varepsilon_\pi A_\pi/(FQ_d)$$

where $A_\pi = w\ L_{eT}$

$$R_\pi\, N_{\text{diluate}} \ln\left(\frac{N_f}{N_p}\right) = \frac{\xi_I \beta}{F} \varepsilon_\pi w L_{eT}/(Q_d)$$

$$\ln\left(\frac{N_f}{N_p}\right) = \frac{\xi_I \beta}{F} \frac{\varepsilon_\pi}{R_\pi N_{\text{diluate}}} w L_{eT} \frac{1}{tk_{\text{spacer}}\, w v_{Ld}}$$

$$\ln\left(\frac{N_f}{N_p}\right) = \frac{\xi_I \beta}{F} \frac{L_{eT}}{tk_{sp}} \left(\frac{\varepsilon_\pi}{R_\pi N_{\text{diluate}}} \frac{1}{v_{Ld}}\right) \tag{A6}$$

$$\ln\left(\frac{N_f}{N_p}\right) = \frac{\xi_I \beta}{F} \frac{1}{tk_{sp}} \left(\frac{\varepsilon_\pi}{R_\pi N_{\text{diluate}}} \mathrm{MIRT}_d\right) \tag{A7}$$

Eqs. (A6) and (A7) confirm that the log ratio of ions concentrations between feed to product is a function of voltage applied, linear velocity in dilute stream (or $\mathrm{MIRT_d}$), and concentration in diluate stream. Since, it is mathematically not so 'easy' to enter N_{diluate}, as N was the dependent variable in the differential equation above (Eqs. (A2)–(A7)). In here, N_{diluate} was assumed as a mean and thus constant value throughout the stack in Eqs. (A2)–(A7).

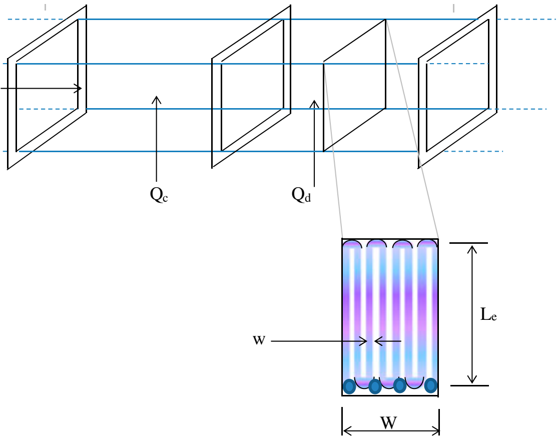

Fig. A. Schematic diagram of current and hydraulic flows in one cell pair of ED.