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Highlights

- Model-based design of experiments is proposed for electro dialysis modelling.
- A dramatic reduction of the experimentation time is obtained.
- This approach can be used for development and assessment of electro dialysis models.

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Optimal design of experiments for parameter identification in electro dialysis models

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electric resistance.

Abstract

The Nernst-Planck approach, previously used to model the electro-dialytic recovery of uni-, di or tri-valent electrolytes, was used to accomplish the desalination of concentrated brines with an initial NaCl concentration up to 4.6 kmol m^{-3} . The complexity of the proposed model is such that an extensive experimentation is required for a statistically sound estimation of the relevant model parameters, including solute (t_B) and water (t_W) transport numbers through the ion-selective membranes; solute (L_B) and water (L_W) transport rate by diffusion; average electro-membrane resistance (R). A model-based design of experiments (MBDoe) approach is proposed in this paper to minimise the number of trials and resources required for model identification. The use of this approach in an experimental case study allowed for a dramatic reduction of the experimentation time from 1080 min (corresponding to a classical experimentation with multiple batch desalination trials) to 30-60 min corresponding to a single optimal batch desalination experiment. The results obtained show the potential of MBDoe for quick development and assessment of electro-dialysis models, where highly predictive capability can be achieved with the minimum experimental time and waste of resources.

1. Introduction

Electrodialysis (ED) is a unit operation for the separation or concentration of electrolytes in solutions based on the selective electro-migration of ions through semipermeable anionic and cationic membranes forced by a direct electric voltage applied to the electrodes [1,2].

Its main area of application is the desalination of brackish water [2,3] and de-ashing of milk whey to obtain valuable raw materials for baby-foods [4]. In the food

industry, ED is gaining growing importance with large-scale industrial installations for the tartaric stabilization of wine, fruit juice de-acidification, and molasses desalting [5]. A sector where the application of ED is potentially interesting is that of the fermentation industry, especially when the main product of the microbial metabolism is an electrolyte [5].

In a previous study [6], a mathematical model for ED, derived from the Nernst-Planck equation for ion electro-migration, was used in combination with an experimental procedure to determine all the independent ED process and design parameters. The procedure consisted of five sets of experiments: (i) zero-current leaching, osmosis, and dialysis; (ii) electro-osmosis; (iii) desalination; (iv) current–voltage with the stack installed with either cationic or anionic membranes only; and (v) validation tests. This allowed us reconstructing accurately the performance of an ED stack during the recovery of a target strong electrolyte (i.e., sodium chloride) up to a salt concentration of about 1.7 kmol m^{-3} when two identical model solutions were initially used to fill the concentrating and diluting compartments [6].

In a more recent work [7], the above experimental procedure was simplified to assess only the engineering parameters (e.g., the transport numbers and rates, as well as the membrane resistances) that control ED desalination of concentrated brines having a higher initial NaCl content of $1.44\text{-}3.00 \text{ kmol m}^{-3}$ when using a concentrating stream at about 0.40 kmol m^{-3} of initial NaCl. The experimental procedure was simplified to three sets of experiments: *i*) desalination according to a 2×2 factorial experiment added with a replicated centre point with electric current and initial NaCl concentration in the diluting stream in the intervals of $2.5\text{-}6.5 \text{ A}$ and $1.5\text{-}3.0 \text{ kmol m}^{-3}$, respectively; *ii*) current–voltage with the stack equipped with cationic and anionic membranes installed in

alternating fashion; and (iii) validation tests. However, a clear drawback of the above approach is that a significant number of experiments is required for achieving a statistically sound estimation of the model parameters. Furthermore, the definition of the electric current profiles to be used in the identification experiments is experience-driven and this occurrence may lead to sub-optimal and/or poorly informative experiments for the identification of ED models.

In the field of process systems engineering, model-based design of experiments (MBD_{oE}) techniques have been developed to maximize the amount of information from dynamic experiments to the purpose of discriminating between rival model structures [8] and/or for estimating the model parameters with the greatest possible precision [9]. According to MBD_{oE}, the experiment design problem is formulated as an optimal control problem where the experiment decision variables (time varying and/or time invariant inputs, sampling times on measured responses, experiment initial conditions and duration) can be designed optimally. This allows minimising the number of trials, with great benefit in terms of time and cost required for model development. The effectiveness of MBD_{oE} was demonstrated in several case studies (also in electrochemistry for creating optimal test sequences for the identification of battery cell models [10-11]) as discussed, for instance, in the review by Franceschini and Macchietto [12]. In general, over the last years, several studies have appeared to improve numerical robustness [13], to exploit parallel equipment [14], to adapt the experiment design online [15], to incorporate uncertainty effects [16,17], to choose among different design criteria [18], and to optimize sampling decisions [19].

Just to consider few recent applications, MBD_{oE} was successfully exploited for the optimal design of drug delivery profiles for the identification of pharmacokinetic-

pharmacodynamic (PK-PD) models [20], and the development of models for the description of liquid-liquid equilibria [21].

The aim of this paper is to show how the experimental effort to estimate the engineering parameters needed to design ED systems can be dramatically reduced by using an MBDoE approach, according to which experiments are dynamically excited so that measurements can provide the maximum amount of information for model parameter estimation. Thanks to the application of optimal experiment design methodologies, a single optimally informative batch desalination experiment can be designed for the efficient estimation of all the relevant parameters of a detailed ED model. Optimally designed experiments involve the determination of an appropriate time profile for the current intensity and of initial concentrations and volumes, as well as the minimisation of the experiment duration.

The effectiveness of the proposed methodology is demonstrated in the parameter identification of an improved ED model based on the original model by Fidaleo and Moresi [7], where the differential water mass balance was modified to account for the variation of the density of the solution as a function of NaCl concentration.

2. Materials and Methods

2.1. Preparation of feed solutions

The feed solutions were prepared by dissolving analytical grade sodium chloride in de-ionised water.

2.2. Analytical Methods

During the ED experiments, the NaCl concentration was indirectly estimated from electric conductivity data.

2.3. Equipment

ED experiments were carried out by using a laboratory-scale electrolysers (model EUR2, Eurodia Industrie SA, Wissous, France) previously described (Fidaleo and Moresi, 2011) whose scheme is shown in Figure 1. The ED stack consisted of 9 cation- (Neosepta CMX-Sb) and 8 anion- (Neosepta AMX-Sb) exchange membranes (Tokuyama Soda Co, Tokyo, Japan), separated by sheet flow spacers and gaskets and assembled in parallel in alternate fashion between platinum (anode) and titanium (cathode) electrodes. The mesh of the net-type spacers could be approximated with a rhombus (diagonal lines 3 and 6 mm, wire diameter 0.3 mm). Each electrode was separated from the membrane pack by a 9.7-mm thick plastic base with 89 circular openings (diameter of 11.9 mm), resulting in overall exposed surface areas of electrodes (a_E) of about 99 cm², while the geometrical surface area of any membrane (a_{mg}) was 200 cm². The main characteristics of the electro-membranes used and ED stack are reported in Table 1.

The direct current (D.C.) generator Mod. N5767A (Agilent Technologies Inc., Santa Clara, CA, USA) could supply voltage (E) and current (I) in the ranges of 0-60 V and 0-25 A, respectively. A Visual Basic based Excel macro (Microsoft Excel 2003, Microsoft Visual Basic 6.3, Microsoft Corporation, Redmond, WA, USA) was developed to control the generator connected to a computer through USB connection and allowed also recording of time, electric current and voltage on an Excel spreadsheet.

The dilute (D), concentrate (C) and electrode rinsing solution (ERS) were recirculated through the ED stack by means of 3 polypropylene centrifugal pumps and were stocked into three 1.6-dm³ PVC tanks. Both C and D tanks were equipped with a 2-m high Plexiglas tube provided with a millimetre scale to assess precisely any volume variation in the C and D tanks.

The electric conductivity (κ_B) of the solutions flowing out of D and C compartments was measured on-line using two continuous cell flow units (model Tetracon DU/T, WTW, Germany) connected to a WTW Inolab Cond Level 1 conductivity meter or to a WTW multi-parameter instrument model Inolab pH/Cond 740, respectively. The latter instrument was connected to a computer and allowed the electric conductivity and temperature of C stream as a function of time to be recorded by using the Multilab pilot software (WTW, Germany). The conductivity of the solution flowing out of the electrode rinsing compartments was measured using a discontinuous WTW cell model Tetracon 325, fitted on-line and connected to a WTW Inolab Cond Level 1 instrument.

The membranes were routinely cleaned-in-place by performing a series of recirculation cycles with de-ionised water. The stack was filled with NaCl 0.5 kmol m⁻³ when not operated.

2.4. Experimental procedure and operating conditions

All the experiments were operated in a batch mode at 20 °C by recycling continuously both the dilute (D) and concentrate (C) at a flow rate of 148.2 dm³ h⁻¹ and the electrode rinsing solution (ERS) at a nominal flow rate of 300 dm³ h⁻¹.

Before the start of each experiment, the ED membrane pack was equilibrated with a 0.5-kmol m^{-3} NaCl solution for at least 12 h. This solution was then discarded and the apparatus rinsed with deionised water. The hold-up of the C and D compartments was estimated to about 0.17 ± 0.07 and 0.24 ± 0.09 dm^3 , respectively, in all experiments. Electrode rinsing was carried out by recirculating an aqueous solution containing 0.32 ± 0.01 kmol m^{-3} of NaCl for all the experiments.

A slight difference is present between the actual and desired (target) values of liquid volumes in D and C due to the different liquid hold-ups, given by the water retained in D or C circuit after cleaning of the plant. After re-circulating such solutions through the ED stack and corresponding reservoir under a constant flow of about 148.2 $\text{dm}^3 \text{h}^{-1}$ (this involving a superficial feed velocity in each compartment of 6.07 cm s^{-1}) until a constant electric conductivity was monitored in both tanks, the Excel macro for the control of the DC generator was run allowing regulation of the current as a function of time and data recording (current, voltage, time). At the same time, the software for recording conductivity and temperature of the C stream was started. The experiment duration varied with the chosen operating conditions and ranged from 0.50 h to 2 h .

2.5 Data analysis

A preliminary data analysis has been carried out to screen out potential outliers in the available measurements and to define the measurements errors through the use of appropriate variance models (see Section 4.2). Process simulation, optimal design of experiment and parameters estimation tasks were carried out by using the software gPROMS[®] (PSE Ltd., London, UK) [22].

3. Modelling of the ED desalting process

The ED model used in this study was previously presented and described in detail by Fidaleo and Moresi [7]. A modification was introduced here to take into account the dependency of the solution density on salt concentration (see Section 3.2 for further details).

3.1 Physical properties of water-NaCl solutions

Density (ρ), osmotic pressure (π), and electric conductivity (κ_B) of sodium chloride solutions were extracted from technical handbooks and correlated as a function of solute molar concentration by Fidaleo and Moresi [7]. The regression equations obtained by the abovementioned authors together with the regression coefficient estimates were used in this work to predict density, osmotic pressure and electric conductivity in a larger range of salt concentration compared to the original one, the difference between the data extracted from literature [23] and predicted by the regression equations being less than 0.24%, 5.20% or 0.78%, respectively.

3.2. Salt and water mass balances in an ED system

By assuming pseudo-steady state conditions in any compartment, the differential solute and water mass balances in the diluted (D) and concentrated (C) reservoirs of an ED system can be written as follows [7]:

$$\frac{d(n_{BC})}{dt} = -\frac{d(n_{BD})}{dt} = \frac{t_B}{F} I N_{\text{cell}} + L_B \Delta c_B a_{\text{mg}} N_{\text{cell}} = W_B \quad (1)$$

$$\frac{d(n_{WC})}{dt} = -\frac{d(n_{WD})}{dt} = \frac{t_W}{F} I N_{\text{cell}} - L_W \Delta \pi a_{\text{mg}} N_{\text{cell}} = W_W \quad (2)$$

where n_{Bk} and n_{Wk} are the instantaneous amounts of solute and water in the k -th reservoir; t is the process time; F is the Faraday constant; t_B is the effective cation- ($= t_{+c} - t_{+a}$) or anion- ($= t_{-a} - t_{-c}$) transport number; L_B is the membrane constant for solute transport by diffusion; t_W is the water transport number; L_W is the membrane constant for water transport by diffusion; $\Delta c_B (= c_{BD} - c_{BC})$ and $\Delta \pi (= \pi_D - \pi_C)$ is the difference in solute concentrations and osmotic pressure, respectively, in compartments D and C provided that the polarisation effect is negligible; N_{cell} the overall number of cell pairs; a_{mg} the geometric membrane surface; I is the electric current intensity ($= j a_{me}$); j the electric current density; a_{me} the effective membrane surface area as viewed by the electrodes themselves; W_B and W_W the overall molar flow rate of solute and water, respectively.

In a previous work [7], integral forms of Eqs. (1) and (2) were used to fit the experimental net increment (or decrement) in the k -th reservoir of solute (Δn_{Bk}) or water (Δn_{Wk}) masses as a function of time. In particular Δn_{Wk} was estimated from the variation of the liquid volume in the k -th reservoir (V_k) on the assumption that its density was constant and corresponding to that of water. In this study we did not make use of this simplifying assumption, considering the wider salt concentration range investigated.

By expressing the instantaneous amounts of solute and water in the k -th reservoir as $n_{Bk} = c_{Bk} V_k$ and $n_{Wk} = c_{Wk} V_k$, where c_{Bk} and c_{Wk} are the molar solute and water concentration in the k -th reservoir, Eq.s (1-2) can be rearranged as a system of four differential equations:

$$\frac{dc_{BC}}{dt} = \frac{\left(W_B - c_{BC} \frac{dV_C}{dt} \right)}{V_C} \quad (3)$$

$$\frac{dc_{BD}}{dt} = \frac{\left(-W_B - c_{BD} \frac{dV_D}{dt}\right)}{V_D} \quad (4)$$

$$\frac{dV_C}{dt} = \frac{\left(M_W W_W + (W_B - c_{BC} \frac{dV_C}{dt})(M_B - \frac{d\rho_C}{dt})\right)}{\rho_C - M_B c_{BC}} \quad (5)$$

$$\frac{dV_D}{dt} = \frac{\left(-M_W W_W + (-W_B - c_{BD} \frac{dV_D}{dt})(M_B - \frac{d\rho_D}{dt})\right)}{\rho_D - M_B c_{BD}} \quad (6)$$

where M_W and M_B are the water and solute molar mass, respectively, and ρ_k is the density of the solution in the k -th reservoir. In particular, the first derivative of the density was obtained by differentiating the corresponding regression equation in order to include the effect solution density on the volume expressions.

Eq.s (3-6) can be solved numerically once the initial conditions $c_{BC}(t=0) = c_{BC}^0$, $c_{BD}(t=0) = c_{BD}^0$; $V_C(t=0) = V_C^0$; $V_D(t=0) = V_D^0$ are known.

3.3. Overall potential drop across an ED stack

The overall voltage applied to the ED stack (D), in the absence of any polarisation effect, can be calculated from the following equation [6]:

$$E - E_{el} + E_D N_{cell} = \left(\frac{2h_{ERS}}{zE\kappa_{ERS}} + R_c N_c + R_a N_a + \frac{h(N_a + N_c - 1)}{2z_m e} \left(\frac{1}{\kappa_{BC}} + \frac{1}{\kappa_{BD}} \right) \right) I \quad (7)$$

with

$$E_D = 2t_B \frac{R_g T}{F} \ln \left(\frac{c_{BD}}{c_{BC}} \right) \quad (8)$$

where all symbols are defined in the Nomenclature section.

It is worth noting that a_{me} , the effective membrane surface area as viewed by the electrodes themselves, depends on the stack and spacer geometry. For the stack under

use, Fidaleo and Moresi [7] estimated a value of a_{me} equal to 106.7 cm^2 , just 8% greater than the exposed surface area of the electrodes ($a_E=99 \text{ cm}^2$) and about half of the geometrical membrane surface area ($a_{mg}=200 \text{ cm}^2$). This discrepancy can be attributed partly to the so called shadow effect of the spacers and partly to the fact that the bases separating the electrode chambers from the membrane pack have a small degree of open area ($a_E=99 \text{ cm}^2$).

The electric resistances of the cationic (R_c) and anionic (R_a) electromembrane under use in contact with sodium chloride solutions can be assumed approximately equal ($R_a \approx R_c$), in line with the manufactures' data, and practically independent of solute concentration [7]. Thus we used the symbol R to refer to the electric resistance of both the cationic and anionic electromembrane resistance. In general, when the two resistances differ in magnitudes, only the equivalent resistance $R_c N_c + R_a N_a$ can be determined from experiments carried out with the ED stack equipped with cationic and anionic membranes installed in alternated fashion.

3.4 Limiting current intensity in an ED stack

The limiting current density (j_{lim}) is the first value at which current density is diffusion limited [24], that is the current density associated with an electrolyte concentration at the anion- ($j_{lim,a}$) or cation-exchange membrane surface ($j_{lim,c}$) falling to zero.

In the industrial practice, ED stacks are operated at current intensities ($I=a_{me} j$) lower than 2/3 of the limiting one (the smallest value between $I_{lim,c}$ and $I_{lim,a}$). In this case, any polarization effect can be neglected and the current–voltage relationship of the ED stack is practically linear (the stack operates in the ohmic region) [6, 7].

4. Model-based design of experiments

The set θ of parameters to be estimated for model identification is summarized in Table 2. Note that it is assumed that all model parameters are independent of solute concentration, electric current, voltage and time (additionally, the temperature does not change during the experiment). In fact, previous studies demonstrated that, under this assumption, the model can successfully represent the ED recovery of the sodium salts of some weak mono-, di- or tri-protic acids of microbial origin (e.g., acetic [25], propionic [26], lactic [27], itaconic [28] and citric acid [29]).

Ideally, experiments to collect data for model identification should be as informative as possible, i.e. vector $y(t)$ of the measured variables of the outputs should be maximally sensitive to the model parameter values. However, in the experimental practice this issue is often neglected, and experiments are typically designed to only explore the operability of the specific piece of equipment, and process dynamics is poorly exploited. For example, in continuous systems, experiments are carried out at a few different steady-state conditions, whereas in batch system only initial conditions are assigned and the system is left to evolve dynamically at fixed operating conditions. Stated differently, the experimental trials are not designed taking into account the relationship between y and θ so as to excite the system effectively and to collect the measurements where they are most informative. On the other hand, MBDoE techniques are conceived to specifically achieve this goal: namely, they find the optimal initial conditions, the optimal profile of manipulated inputs and the optimal measurement sampling instants that maximize the sensitivity of all measurements to the set of model parameters to be estimated, thus making the parameter estimation job much more

effective. This is achieved by exploiting the dynamic Fisher information matrix [30], which is calculated from the sensitivity matrix of the system; see also Appendix A).

Note that a necessary prerequisite to the applicability of MBDoE techniques is parameter identifiability. In this study parameter identifiability and estimability have been assessed using the formal approach described in [20]. Additional details on the procedure used for testing parametric identifiability are given in Appendix B. MBDoE involves the sequential interaction between three key activities: *i*) design of the dynamic experiment; *ii*) experiment execution; *iii*) parameter estimation. The theoretical framework of MBDoE can be found elsewhere [12,14]. Figure 2 illustrates the procedure. Here it is important to describe how the technique is applied practically in the specific case study. The electro dialysis model (Eq.s 3-8) is described by a set of differential and algebraic equations (DAEs) of the following general form:

$$\begin{aligned} \mathbf{f}(\hat{\mathbf{x}}(t), \mathbf{x}(t), \mathbf{u}(t), \boldsymbol{\theta}, t) &= 0 \\ \hat{\mathbf{y}}(t) &= \mathbf{g}(\mathbf{x}(t)) \end{aligned} \quad (9)$$

where $\mathbf{f}(\cdot)$ and $\mathbf{g}(\cdot)$ are nonlinear vector functions, \mathbf{x} is the vector of states, \mathbf{u} is the vector of inputs that can be manipulated (dynamically) by the experimenter. Note that in Eq. (9) the symbol $\hat{\cdot}$ is used to indicate the estimate of a variable (or of a set of variables): thus, $\mathbf{y}(t)$ is the vector of measured values of the outputs, while $\hat{\mathbf{y}}$ is the vector of the corresponding values estimated by the model. In the current ED study, the vector of measured outputs \mathbf{y} includes concentration (c_{BD} , c_{BC}), volume (V_D , V_C) and voltage (E) measurements.

The experiment design optimisation for estimating the set of unknown model parameters $\boldsymbol{\theta}$ is carried out by acting on the experiment design vector $\boldsymbol{\varphi}$:

$$\boldsymbol{\varphi} = [\mathbf{y}_0, \mathbf{u}(t), \mathbf{t}^{sp}, \tau]^T \quad (10)$$

in order to minimise some metrics of the expected variance-covariance matrix of model parameters (see Appendix A). The suitable metrics are represented by the so-called alphabetical design criteria, A-, D-, E-optimal criteria (minimising, respectively, the trace, the determinant and the maximum eigenvalue of the variance-covariance matrix) [30] or criteria based on singular value decomposition [14].

The optimal experiment (i.e. the dynamic experiment returning the most informative outputs for the estimation of θ) is given by:

- a set of initial conditions \mathbf{y}_0 on the measured variables. In the current study they are the concentration of salt (c_{BD}^0 and c_{BC}^0) and the volume (V_D^0 and V_C^0) in the diluted and in the concentrated reservoirs;
- a vector of time dependent manipulated inputs $\mathbf{u}(t)$, which is here constituted by the electric current intensity profile I , modelled as a piecewise constant input variable characterised by five switching times and six switching levels (i.e. we assume that, after its initial setting, the current intensity profile may be changed five times so as to obtain six constant levels). Note that the intensity current dynamics is much faster than the dominant system dynamics. Therefore, perfect control of the manipulated inputs can be assumed during the experiment design activity;
- the set of time instants t^{sp} at which the output variables are sampled. Thus, in general the optimal experimental design also comprises the measurement optimal allocation in time. However, since here volume, concentration and overall voltage measurements are available very frequently, it is assumed that 120 samples, equally distributed along the experiment duration, are used;

- the duration of the experiment τ ; here the impact of the experimental duration τ is evaluated by fixing an upper bound (τ^{MAX}) for this design variable in each proposed MBDoe configuration.

The measurement readings are affected by noise, which is assumed to be Gaussian (zero mean and a constant standard deviation). Standard deviations were estimated from the replicated centre point of Fidaleo and Moresi [7]:

$$\sigma_{c_{BC}} = \sigma_{c_{BD}} = 0.07 \frac{\text{kmol}}{\text{m}^3}, \sigma_{V_C} = \sigma_{V_D} = 5 \cdot 10^{-6} \text{m}^3, \sigma_{E_V} = 0.2 \text{V}.$$

Note that experiments can be designed so as to account for some constraints on design variables. In this case, constraints involve bounds on E , V_D and V_C , c_{BD} and c_{BC} and I . The maximum voltage supplied by the DC generator was 60 V ($E^{\text{max}} \leq 60 \text{ V}$); the volume of solution in each tank had to be in a range that allowed correct pump working and reading of solution volumes ($1.0 \text{ dm}^3 \leq V_C \leq 2.5 \text{ dm}^3$; $2.1 \text{ dm}^3 \leq V_D \leq 2.5 \text{ dm}^3$); the solute concentration had to be less than the solubility value of NaCl (c_{BC} , $c_{BD} \leq 5.30 \text{ kmol m}^{-3}$ at 20°C). In order to assure operating at a current intensity lower than the limiting one, Fidaleo and Moresi [7] performed current-voltage studies for the system under investigation by using the stack equipped with anionic and cationic membranes installed in alternating fashion. From their data a region of the electric current – electrolyte concentration plane can be established in which the stack works in the absence of polarization, that is at $I < I_{\text{lim}}$. This allowed to set an upper bound on the applied electric current intensity (I^{max}) as a function of electrolyte concentration in the diluting stream (c_{BD}) to be used in experiment designing:

$$I^{\text{max}} = \frac{k_1 c_{BD}}{k_2 + c_{BD}} \quad (11)$$

The initial guesses θ^0 of the parameter vector $\theta = [L_B \quad t_B \quad L_W \quad t_W \quad E_{cl} \quad R]$ is given by $\theta^0 = [1.38 \cdot 10^{-8} \quad 0.969 \quad 1.43 \cdot 10^{-7} \quad 10.08 \quad 2.0 \quad 0.026]$, where the initial guesses (with appropriate units) are derived from literature values [7].

5. Results and discussion

Two different design approaches are compared for the estimation of the model parameters:

1. A standard DoE approach following extensive experimentation (7 batch desalination experiments);
2. An MBDoE approach, where a single experiment is designed according to the following design configurations:
 - O1: optimally designed experiment with $\tau = \tau^{\text{MAX}} = 120$ min (2 h);
 - O1*: optimally designed experiment with $\tau = \tau^{\text{MAX}} = 60$ min (1 h);
 - O2: an MBDoE with an additional objective function including the minimisation of the amount of salt used (n_B [mol]), evaluated from the following expression:

$$n_B = c_{BC} V_C + c_{BD} V_D \quad (12)$$

The duration was fixed to $\tau = \tau^{\text{MAX}} = 30$ min (shorter duration).

An A-optimal design criterion was applied in all the MBDoE configurations, given the fact that a limited correlation is present between the model parameters (see Section 5.1 for further details). Results for each design approach are compared in terms of estimated value and related statistics obtained after a maximum likelihood parameter estimation [31] is carried out. Further details on the parameter estimation technique used in this paper are given in Appendix C. In particular, the precision of the estimate is assessed by

evaluating for each parameter the interval of estimation confidence and the t -value statistic:

$$t_i = \frac{\hat{\theta}_i}{\sqrt{v_{ii}}} \quad i = 1 \dots N_\theta, \quad (13)$$

where v_{ii} is the i -th diagonal element of \mathbf{V}_θ . For a reliable parameter estimation the t -value of each parameter must be greater than ξ , the computed reference value derived from a Student t -distribution with $n_{sp} - N_\theta$ degrees of freedom (reference t -value).

5.1. Parameter estimation under extensive experimentation

Fidaleo and Moresi [7] used a 2^2 factorial design with replicated centre points to assess the effect of the electric current and initial NaCl concentration in the diluting stream in the range of 2.5-6.5 A and 1.5-3.0 kmol m⁻³, respectively, on water and solute fluxes. A total of seven batch desalination experiments carried out at constant electric current were run (four factorial runs and three replicated centre runs). By using an integrated and simplified form of Eq.s (1-2), the authors fitted the predicted decrement in the amount of electrolyte in tank D (Δn_{BD}) and the increment in the amount of water in tank C (Δn_{WC}) to the data from the designed experiments and estimated the parameters L_B , t_B , L_W , t_W .

In this study, a modified form of the differential mass balance equation for water was used to take into account density variation with solute concentration, the concentration of solute in the diluting stream being higher. Thus the abovementioned parameters were re-estimated by using Eq.s (5-8) on the experiment set of Fidaleo and

Moresi [7] (all the experiments were used, except trial D5). Results obtained after parameter estimation are shown in Table 3. They show that some parameters (t_B , t_W) are estimated with great precision, but the design configuration fails on estimating the membrane constant L_B in a statistically sound way, as underlined by the low t-value achieved.

Table 4 reports the correlation matrix of the parameters associated with the model and the experimental design, as obtained by the software gPROMS[®]. It can be observed that the degree of correlation among parameter estimates is low ($|r| \leq 0.7$), thus confirming that the model parameters can in principle be identified from the experimental data. However, the design is not robust because, as a result of the uncertainty on volume measurements, the parameter estimation obtained (together with the estimate of E_{el} , R and a_{me} obtained by Fidaleo and Moresi [7] from independent current-voltage experiments) is such that information appears to be oriented to the estimation of a specific subset of model parameters. More importantly, the experiment execution is rather demanding in terms of both time (the overall time dedicated to the experiments is approximately 18 h) and experimental effort (experiments must be performed sequentially and the apparatus has to be re-set for each new experiment).

5.2. *Parameter estimation under optimal experimental designs*

Optimal experiment design results are summarised in Table 5 in terms of optimal design vector ϕ , while the actual experimental conditions realised in the ED equipment are shown in Table 6. According to O1, a sudden increment of the electric current intensity after 45 min is scheduled in order to optimise the information content of the experiment. After 60 min the current intensity is decreased and suddenly increased after

89 min. In optimal experiment O1* the same excitation pattern of O1 for the electric current intensity is maintained by MBDoe optimisation, but the experiment duration is shorter and set to $\tau = \tau^{\text{MAX}} = 60$ min.

A similar excitation pattern with a sudden increment in the electric current after 10 min is obtained for design configuration O2. In both design settings, the initial concentration of solute in the concentrate tank is practically set to zero, while in the dilute one it is close to its upper bound, i.e. the salt solubility limit (about 5.3 kmol m^{-3} at $20 \text{ }^\circ\text{C}$). Intuitively, it seems that the optimal design settings are such that the system is controlled by the maximum allowable diffusion driving force in the first part of the experiment, before switching to high current intensity when the maximum allowable electro-migration driving force predominates (corresponding to the upper bound of the electric current predicted by Eq. (11)).

Figures 3 and 4 report the time course of the input variable (I) and the experimental and simulated outputs (c_{BD} , c_{BC} , V_{D} , V_{C} , E) for optimal experiments O1 and O2, respectively. In particular, it can be noted that the water flux changes direction when the electric current is increased: in the first part of the experiment the osmosis contribution predominates, while in the second part electromigration gives the larger contribution to the flux. It is evident that the mathematical model fits the data accurately. Note that the continuous lines plotted in Figure 3 were obtained by using the parameters set estimated from the data of the first hour (according to optimally designed experiment O1*), but provide excellent predictions also in the second part of the experiment (experiment O1), after the vertical grey line time point, thus validating the model. Results after parameter estimation from optimally designed experiments O1, O1* and O2 are given in Table 3. The results in terms of parameter estimation precision

are quite interesting. The experimental conditions and optimal excitation pattern on the manipulated input I provided by $O1^*$ provide a statistically sound estimation of the full set of model parameters after a single trial, lasting only 1 h. If the experiment is prolonged to 2 h (configuration $O1$), the parameter estimation precision is improved significantly, in particular for the estimation of t_w , which is the critical parameter to be estimated.

Both $O1$ and $O1^*$ require to use a significant amount of salt in order to be able to identify the full set of model parameters. This problem can be overcome by minimising the amount of salt by optimal design according to Eq. (12). The significant result in this case is that it is possible to reduce the experiment duration to only $\tau = 30$ min, achieving at the same time a statistically sound parameter estimation of the full set of model parameters, as underlined by the t -values in Table 3.

From an engineering point of view, the parameter estimates obtained from the optimal designs practically match the values estimated from the thorough experimental study. The estimates of t_B , L_w , t_w , E_{el} or R obtained from the two optimal designs $O1$ and $O2$ differed from the true values by 2.5 and 11.3%, 0.9 and 2.8%, 10.1 and 3.2%, 18.3 and 5.7% or 7.7 and 3.8%, respectively. Furthermore, the parameter confidence intervals estimated from the two optimal experiments include in many cases the estimate obtained from the thorough experimentation, thus showing that there is no evidence of significant differences among estimates.

Thus, the significant achievement of these experiments designed by MBDoE is that they allow for a precise estimation of the full set of parameters with a single trial, and the duration of this trial can be reduced to $\tau = 30$ minutes (against at least 18 h required by a standard DoE).

A validation test (trial V1 whose experimental conditions are reported in Table 6), was carried out to check for the accuracy of the model parameters estimated from optimally designed experiments (in particular, we used the parameter values as estimated after experiment O1 and reported in Table 3). Figure 5 shows a substantially good agreement between the time profiles of the experimental and calculated values of the solute molar concentrations (c_{BD} and c_{BC}), volumes of concentrate (V_C) and dilute (V_D), and voltage applied to the electrodes (E), thus demonstrating the effectiveness of the experimental design approach.

We believe that the case study shows how MBDoE techniques can be successfully applied for identifying models in ED applications. They allow reducing the overall experimental effort in terms of time and materials. On the other hand, they require the availability of an experimental equipment where dynamic experiments can be handled quite accurately. In fact, it is essential to guarantee that the designed initial conditions and input profile can be actually reproduced in the experimental apparatus. Similarly, the prescribed sampling schedule should be achievable practically. Although the experiment design problem can be formulated in such a way as to account for the actual characteristics of the experimental and measurement, it is clear that advanced design techniques are most effective within a properly instrumented and controlled experimental environment. For instance, uncertainty in initial conditions, imprecise (noisy) measurements, (auto-) correlation effects may hinder the MBDoE efficacy [32] and make it equivalent to more traditional experimental design approaches.

6. Conclusions

A model-based design of experiments (MBDoe) approach was proposed to minimise the number of trials and resources required for identification of electro dialysis models. As a case study, an ED model previously developed for the desalting of highly concentrated NaCl brines [7], based on Nernst-Planck derived equations, was improved to extend its validity to initial NaCl concentration (c_{BD0}) up to 4.6 kmol m^{-3} , close to the solubility limit. The model was fit to a large literature data set from several batch desalinations carried out according to a standard 2×2 factorial with added centre point [7] and all the relevant model parameters including solute (t_B) and water (t_W) transport numbers through the ion-selective membranes; solute (L_B) and water (L_W) transport rate by diffusion; and the cationic and anionic electro-membrane resistance (R) was estimated. As a comparison, two single batch desalination experiments were designed by using the MBDoe approach. Both experiments resulted in a statistically sound estimation of the model parameters matching the estimates obtained from standard (but much more demanding) experimental practice. This approach allowed for a dramatic reduction of the experimental time corresponding to the overall duration of the batch desalination experiments from 1080 minutes (without considering the time needed to reset the ED system for each trial) for the extensive experimentation, to 60 and 30 minutes for the two design configurations examined. The results achieved confirm the high potential of MBDoe for quick development and assessment of electro dialysis models describing both mass transfer and electric current – voltage relationship, where highly predictive capability can be achieved with the minimum experimental time and waste of resources. Future work will include the application of the MBDoe approach to

the ED recovery of the sodium salts of weak monocarboxylic acids, such as acetic, lactic and propionic acid (some preliminary tests show very promising results).

Appendix A: Mathematical formulation of MBD_oE

MBD_oE techniques aim at decreasing the model parameter uncertainty region by identifying the optimal experiment design vector (Eq. (10)) as the solution of the optimisation problem:

$$\boldsymbol{\varphi}^{\text{opt}} = \arg \min_{\boldsymbol{\varphi}} \left\{ \psi \left[\mathbf{V}_\theta(\boldsymbol{\theta}, \boldsymbol{\varphi}) \right] \right\} = \arg \min_{\boldsymbol{\varphi}} \left\{ \psi \left[\mathbf{H}_\theta^{-1}(\boldsymbol{\theta}, \boldsymbol{\varphi}) \right] \right\} \quad (\text{A.1})$$

subject to the model equations (Eq. (9)) and to a n_φ -dimensional set of constraints on design variables, usually expressed as:

$$\varphi_i^l \leq \varphi_i \leq \varphi_i^u \quad i = 1 \dots n_\varphi \quad (\text{A.2})$$

with lower (superscript l) and upper (superscript u) bounds on the elements of $\boldsymbol{\varphi}$. In general, the experiment design procedure needs to take into account also the existence set of equality and inequality constraints on state variables in the form:

$$\mathbf{C} = \{ \boldsymbol{\varphi} : \mathbf{x}(\boldsymbol{\theta}, \boldsymbol{\varphi}, t) - \mathbf{G}(t) \leq \mathbf{0} \} \quad (\text{A.3})$$

where \mathbf{C} is an admissible set of design vectors satisfying the set of constraint conditions expressed through the vector $\mathbf{G}(t)$ of (possibly time-varying) active constraints on the state variables $\mathbf{x}(t)$. \mathbf{V}_θ and \mathbf{H}_θ are the variance-covariance matrix of model parameters and the dynamic Fisher information matrix, respectively, defined by

$$\mathbf{H}_\theta(\boldsymbol{\theta}, \boldsymbol{\varphi}) = \mathbf{H}_\theta^0 + \sum_{k=1}^{n_{\text{sp}}} \sum_{i=1}^{N_y} \sum_{j=1}^{N_y} s_{ij} \left[\frac{\partial \hat{y}_i(t_k)}{\partial \theta_1} \frac{\partial \hat{y}_j(t_k)}{\partial \theta_m} \right]_{1,m=1 \dots N_\theta} \quad (\text{A.4})$$

In Eq. (A.4), s_{ij} is the ij -th element of the $N_y \times N_y$ inverse matrix of measurements error and \mathbf{H}_θ^0 is the prior dynamic information matrix, taking into account the preliminary

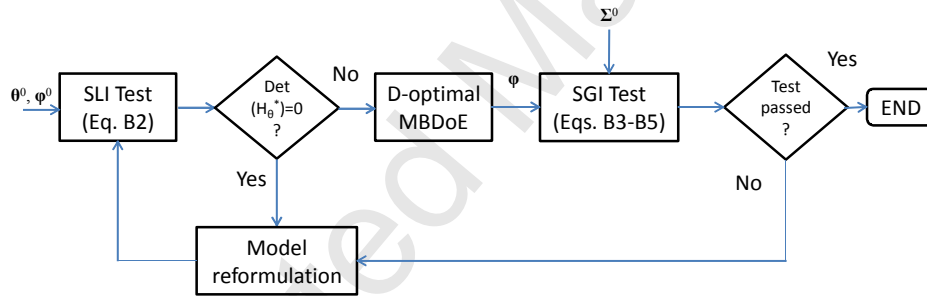
statistical information about the parametric system before each trial is carried out. For more information see, for instance [9,31].

Appendix B: Procedure for testing parametric identifiability

A three-step procedure [20] coupling structural local identifiability (SLI) and structural global identifiability (SGI) analysis was used in this paper for testing the parametric identifiability of the proposed ED model. The scheme of the proposed procedure is shown in Figure B1.

Figure B1

Procedure used for testing parametric identifiability.



The procedure started given the model equations (Eqs. 3-8 in the main text) and prior knowledge on the parametric set in terms of initial guesses (θ^0), preliminary variance-covariance matrix of model parameters (Σ^0) and experimental conditions (φ^0) as derived from literature [7].

In the first step of the procedure, a SLI test was carried out. The SLI test is based on the definition of local identifiability proposed by Shaw [33]:

Definition (local identifiability, SLI test): the model \mathbf{M} with output trajectory \mathbf{y} is locally identifiable if, in an open neighborhood of $\boldsymbol{\theta} \in \Theta$, for the set of system inputs \mathbf{u} and the initial conditions \mathbf{y}_0 , the $N_y N_{sp} \times N_\theta$ estimability matrix \mathbf{P}_E

$$\mathbf{P}_E = \begin{bmatrix} \mathbf{S}_y(t_0) \\ \vdots \\ \mathbf{S}_y(t_{N_{sp}}) \end{bmatrix} = \begin{bmatrix} \left. \frac{dy_1}{d\theta_1} \right|_{t_0} & \dots & \left. \frac{dy_1}{d\theta_{N_\theta}} \right|_{t_0} \\ \dots & \ddots & \dots \\ \left. \frac{dy_{N_y}}{d\theta_1} \right|_{t_0} & \dots & \left. \frac{dy_{N_y}}{d\theta_{N_\theta}} \right|_{t_0} \\ \vdots & & \vdots \\ \left. \frac{dy_1}{d\theta_1} \right|_{t_{N_{sp}}} & \dots & \left. \frac{dy_1}{d\theta_{N_\theta}} \right|_{t_{N_{sp}}} \\ \dots & \ddots & \dots \\ \left. \frac{dy_{N_y}}{d\theta_1} \right|_{t_{N_{sp}}} & \dots & \left. \frac{dy_{N_y}}{d\theta_{N_\theta}} \right|_{t_{N_{sp}}} \end{bmatrix}$$

(B1)

has full rank. In (B1) $\mathbf{S}_y(t_i)$ is the $N_y \times N_\theta$ sensitivity matrix evaluated at the sampling time t_i .

The SLI test performed in this paper is based on the evaluation of the Fisher information matrix: if the Fisher information matrix is non-singular, the model is deemed locally identifiable [34]. In fact, under the hypothesis of constant measurement errors

$$\mathbf{H}_\theta^* = \sum_{i=1}^{N_y} \sum_{j=1}^{N_y} s_{ij} \mathbf{Q}_i^T \mathbf{Q}_j \propto \mathbf{P}_E^T \cdot \mathbf{P}_E \quad (\text{B2})$$

and a D-optimal MBDoe can be carried out where the experimental conditions aiming at maximising the determinant of \mathbf{H}_θ^* are the ones producing the lowest correlation for \mathbf{P}_E . Conversely, experimental conditions providing high correlation among \mathbf{P}_E columns

leads to singularity of \mathbf{H}_θ matrix with the information related to specific subsets of model parameters becoming close to zero [34]. The SLI test is used to test the applicability of a D-optimal MBDoE acting on (B2) where the maximisation of the expected information is realised by maximising the determinant of \mathbf{H}_θ^* . In this phase, if the determinant is null, the model is locally not identifiable and its structure has to be modified before a suitable design vector can be determined adopting MBDoE techniques. For the ED model, the proposed structure was SLI for all the set of experimental conditions investigated in [7], thanks to the high sampling frequency realised in the experiments. However, the relatively small values of the determinant realised in these experiments (ranging from 10^{-6} to 10^{-5}) was such that the practical identifiability of the model parameters (i.e. the precise estimation of the model parameters) was not possible with the preliminary experimental design.

In the second step, after the SLI test was performed, a D-optimal MBDoE was carried out where a set of optimal experimental settings ($\boldsymbol{\varphi}$) was evaluated ensuring the local identifiability of the model at the currently available information on the parametric set ($\boldsymbol{\theta}^0$). This MBDoE optimisation provided the same results in terms of manipulated inputs of the O1 design (A-optimal MBDoE) described in the main text.

In the final step, once $\boldsymbol{\varphi}$ was determined, the global identifiability of the model was tested by performing a SGI test on the variability domain of model parameters (Θ), identified by $\boldsymbol{\theta}^0$ and by the preliminary variance-covariance matrix of model parameters ($\boldsymbol{\Sigma}_0$). In this way the SGI of the ED model was tested at the experimental settings $\boldsymbol{\varphi}$ satisfying the SLI conditions. SGI test verifies that different parametric sets do not provide the same model response in the entire variability domain of model parameters.

The SGI test adopted in this paper follows the optimisation-based approach to test global identifiability suggested by Asprey and Macchietto [35]:

Definition (global identifiability, SGI test): the model with structure \mathbf{M} and output trajectory \mathbf{y} is globally identifiable if, for any two parametric sets $\boldsymbol{\theta}, \boldsymbol{\theta}^* \in \Theta$, and a time horizon of interest $t \in [0, \tau]$, for the set of system inputs \mathbf{u}_0 and the same initial conditions \mathbf{y}_0 for the measured outputs, the distance Φ^I between two parameter vectors $\boldsymbol{\theta}$ and $\boldsymbol{\theta}^*$ providing the same model output is such that

$$\Phi^I = \max_{\boldsymbol{\theta}, \boldsymbol{\theta}^*} (\boldsymbol{\theta} - \boldsymbol{\theta}^*)^T \mathbf{W}_\theta (\boldsymbol{\theta} - \boldsymbol{\theta}^*) \leq \varepsilon_\theta \quad (\text{B3})$$

subject to

$$\int_0^\tau (\mathbf{y}(\mathbf{u}_0, \boldsymbol{\theta}) - \mathbf{y}(\mathbf{u}_0, \boldsymbol{\theta}^*))^T \mathbf{W}_y (\mathbf{y}(\mathbf{u}_0, \boldsymbol{\theta}) - \mathbf{y}(\mathbf{u}_0, \boldsymbol{\theta}^*)) dt < \varepsilon_y \quad (\text{B4})$$

$$\mathbf{f}(\dot{\mathbf{x}}, \mathbf{x}, \mathbf{u}_0, \boldsymbol{\theta}, t) = 0 \quad (\text{B5})$$

where $\mathbf{W}_\theta \in \mathfrak{R}^{N_\theta \times N_\theta}$ and $\mathbf{W}_y \in \mathfrak{R}^{N_y \times N_y}$ are two proper weighting matrices and ε_θ and ε_y are arbitrarily small numbers.

The test (B3-B5) implies the direct numerical evaluation of SGI over the entire variability domain of model parameters Θ for the set of manipulated inputs provided by MBDoE ($\mathbf{u}, \mathbf{y}_0 \in \varphi$) as determined from SLI test, stating that the SGI of the ED model can be guaranteed if the distance between two parameters vectors providing the same model response is arbitrarily small. The optimisation problem (B3-B5) was solved using the SQP-based dynamic optimisation solver available in the gPROMS[®] environment.

Appendix C: Parameter estimation

The estimation of model parameters was carried out adopting a maximum likelihood parameter estimation approach. The benefit of using such an approach is that it allows using the existing information on the variability of measurements in terms of standard deviation for each measured response providing a-posteriori statistics on model parameters in terms of variance-covariance matrix \mathbf{V}_θ . The objective function Φ being optimised during the parameter estimation is the log-likelihood function as proposed by Bard [31]:

$$\Phi = \frac{N}{2} \ln(2\pi) + \frac{1}{2} \min_{\theta \in \Theta} \left\{ \sum_{i=1}^{N_{\text{exp}}} \sum_{j=1}^{N_y} \sum_{k=1}^{N_{\text{sp}}} \left[\ln(\sigma_{ijk}^2) + \frac{(y_{ijk} - \hat{y}_{ijk})^2}{\sigma_{ijk}^2} \right] \right\}. \quad (\text{C1})$$

In (C1) N is the total number of experimental points, N_{exp} is the number of experiments, N_y is the number of measured responses and N_{sp} is the number of sampling points in each performed experiment; y_{ijk} and σ_{ijk}^2 represent, respectively, the measured value and the variance of the k -th measurement related to the j -th response in the i -th experiment, while \hat{y}_{ijk} is the corresponding model response. Note that in the current study the values of standard deviation for the j -th measured response were known from preliminary experiments performed in the ED system [7] ($\sigma_{c_{BC}} = \sigma_{c_{BD}} = 0.07 \text{ kmol/m}^3$; $\sigma_{V_c} = \sigma_{V_d} = 5 \cdot 10^{-5} \text{ m}^3$; $\sigma_{E_v} = 0.2 \text{ V}$) and for this reason were kept constant during the

parameter estimation activities (i.e. a constant variance model was used). The parameter estimation tool of gPROMS[®] ModelBuilder [22], exploiting a modified SQP routine for

the optimisation of (C1), was used in all the activities related to the estimation of model parameters, as well as for the analysis of statistics obtained after each parameter estimation session has been carried out.

Nomenclature

Model-based design of experiments

f	differential and algebraic system implicit function
g	measurements selection function
n_{sp}	number of samples
N_u	number of manipulated inputs
N_x	number of state variables
N_y	number of measured variables
N_θ	number of model parameters
N_c	number of constraints
n_φ	number of design variables
s_{ij}	ij th element of the inverse matrix of measurements errors
t	time
t_i	i th t value
x	generic state variable
y	generic measured output

Greek Symbols

φ_i	i th element of the design vector
θ_i	i th model parameter

τ	experiment duration
τ^{MAX}	experiment duration upper bound
ψ	measurement function of V_θ
σ_i	standard deviation of i th measurement
ξ	reference value of t-distribution with $n_{\text{sp}}-N_\theta$ degrees of freedom

Vectors and Matrices [dimension]

C	set of constraint functions [N_c]
G	set of active constraints [N_c]
H_θ	dynamic information matrix [$N_\theta \times N_\theta$]
H_θ^0	preliminary information matrix [$N_\theta \times N_\theta$]
y_0	vector of initial conditions [N_y]
y	measurements vector [N_y]
\hat{y}	vector of estimated responses [N_y]
t_{sp}	vector of sampling points [n_{sp}]
u	vector of manipulated inputs [N_u]
V_θ	variance-covariance matrix of model parameters [$N_\theta \times N_\theta$]
x	vector of state variables [N_x]
x_0	vector of initial states [N_x]
\dot{x}	vector of derivatives on state variables [N_x]
ϕ	design vector [n_ϕ]
θ	vector of values of true model parameters for the system [N_θ]
$\hat{\theta}$	vector of estimated values of model parameters [N_θ]
θ_0	vector of initial guesses of model parameters [N_θ]

Modelling of the ED desalting process

A_{me}	overall effective membrane surface area ($=a_{me} N_{cell}$, m^2)
A_{mg}	overall geometric membrane surface area ($=a_{mg} N_{cell}$, m^2)
a_E	exposed surface area of the electrodes (cm^2)
a_{me}	effective membrane surface area (m^2)
a_{mg}	geometrical membrane surface area (cm^2)
c	molar concentration ($kmol m^{-3}$)
c_{ERS}	solute molar concentration in the electrode rinsing solution ($kmol m^{-3}$)
E	voltage applied to the ED electrodes (V)
E_D	Donnan potential difference across membranes of any ED cell (V)
E_{el}	thermodynamic potential and overpotential of electrodes (V)
F	Faraday's constant ($96,486 C mol^{-1}$)
h	channel interval or membrane gap (m)
h_{ERS}	thickness of the electrode compartment (m)
I	electric current (A)
I_{lim}	limiting electric current (A)
j	electric current density ($A m^{-2}$)
L_B	membrane constant for solute transport by diffusion ($m s^{-1}$)
L_W	membrane constant for water transport by diffusion ($mol m^{-2} s^{-1} bar^{-1}$)
M_B	solute molar mass ($kg kmol^{-1}$)
M_W	water molar mass ($kg kmol^{-1}$)
N_{cell}	overall number of cell pairs (dimensionless)
N_k	overall number of the k-th electro-membrane (dimensionless)
n	number of moles (mol)

R	average electric resistance of any electro-membrane (Ω)
R_G	gas-law constant ($= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
R_k	electric resistance of the k-th electro-membrane (Ω)
T	absolute temperature (K)
t	process time (s or h)
$t_{\pm k}$	cation or anion transport number in the k-th electro-membrane (dimensionless)
t_B	effective solute transport number ($=t_c^+ - t_a^+ = t_a^- - t_c^-$; dimensionless)
t_W	water transport number (dimensionless)
V_k	volume solution in the generic k-th tank (m^3)
W_B	solute molar flow rate (kmol s^{-1})
W_W	water molar flow rate (kmol s^{-1})

Greek Symbols

Δc_B	difference in solute concentration in compartment D and C ($=c_{BD}-c_{BC}$, kmol m^{-3})
Δt	duration of batch mode experiments (h)
$\Delta \pi$	trans-membrane osmotic pressure difference ($=\pi_D-\pi_C$, bar)
κ_B	electric conductivity (S m^{-1})
π	osmotic pressure of solution (bar)
ρ	density of solution (kg m^{-3})

Subscripts

a	referred to the anion-exchange membrane
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B	referred to solute
C	referred to the concentrate
c	referred to the cation-exchange membrane
D	referred to the dilute
ERS	referred to the electrode rinsing solution
f	referred to the boundary layer
k	referred to the generic k-th membrane or solute
W	referred to water
0	initial

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Figure 1

Scheme of the electrolysers.

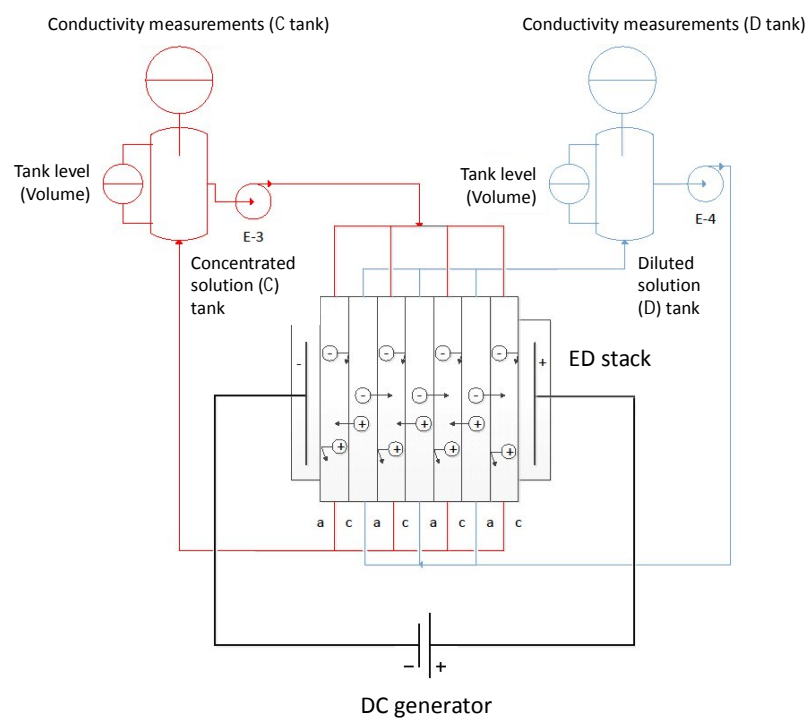


Figure 2

MBDoe procedure and information flux.

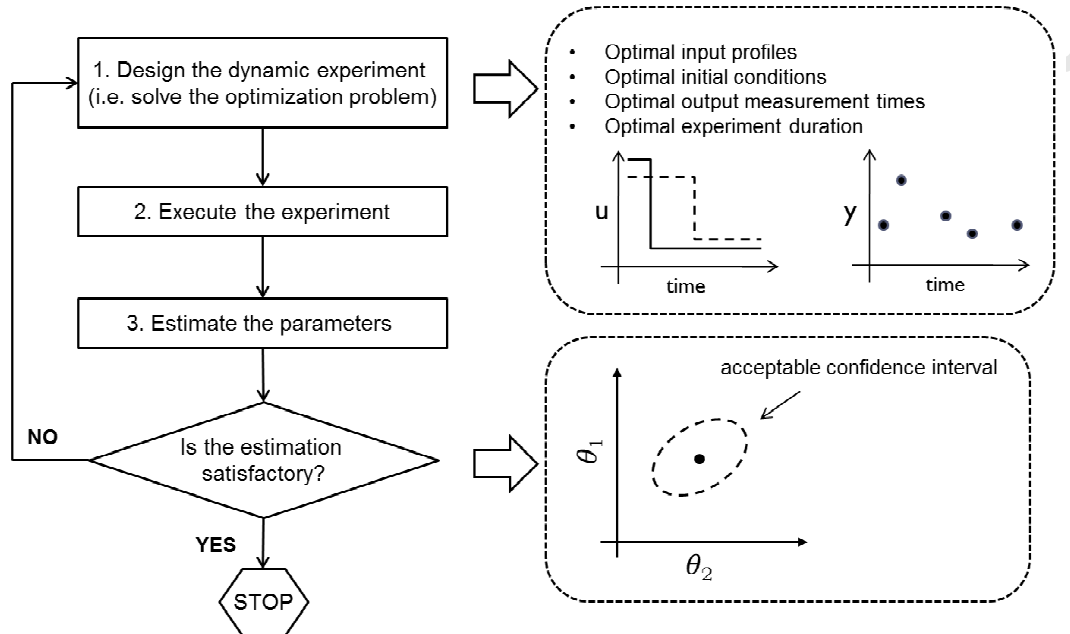


Figure 3

Time course of trial O1 carried out using the operating conditions listed in Table 6: **a)** electric current (I : dashed line) and voltage applied to the ED stack (E : \circ) as a function of time (t); **b)** solute concentration in the concentrate (c_{BC} : \circ) and dilute (c_{BD} : \square) and their corresponding volumes (V_C : Δ ; V_D : \diamond) vs. t . All the continuous lines (---) were calculated using the mathematical model and the engineering parameters determined by fitting the data corresponding to the first 60 minutes and reported in Table 3 (optimal design O1*). All the data points used in the fitting procedure are reported on the plot.

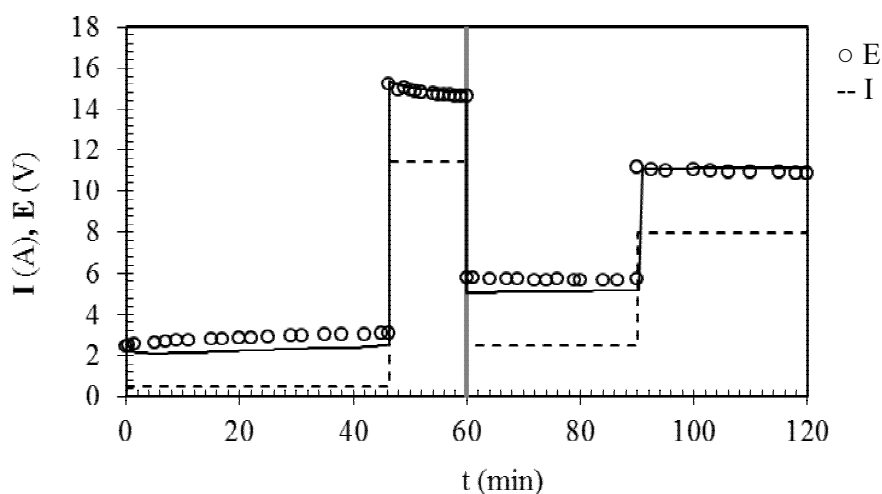
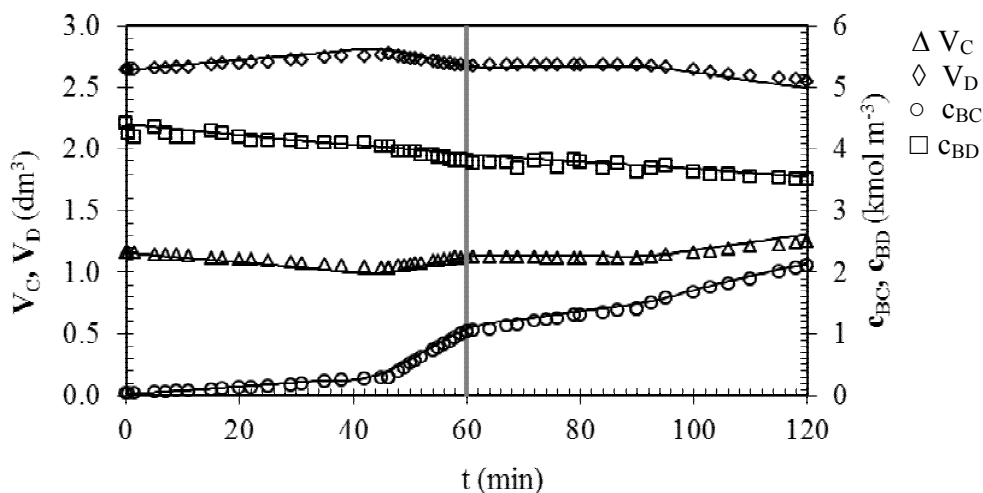
a)**b)**

Figure 4

Time course of trial O2 carried out using the operating conditions listed in Table 6: **a)** electric current (I : dashed line) and voltage applied to the ED stack (E : \circ) as a function of time (t); **b)** solute concentration in the concentrate (c_{BC} : \circ) and dilute (c_{BD} : \square) and their corresponding volumes (V_C : Δ ; V_D : \diamond) vs. t . All the continuous lines (—) were calculated using the mathematical model and the engineering parameters determined from experiment O2 (Table 3). Fewer points than used for fitting are shown for a better visualization.

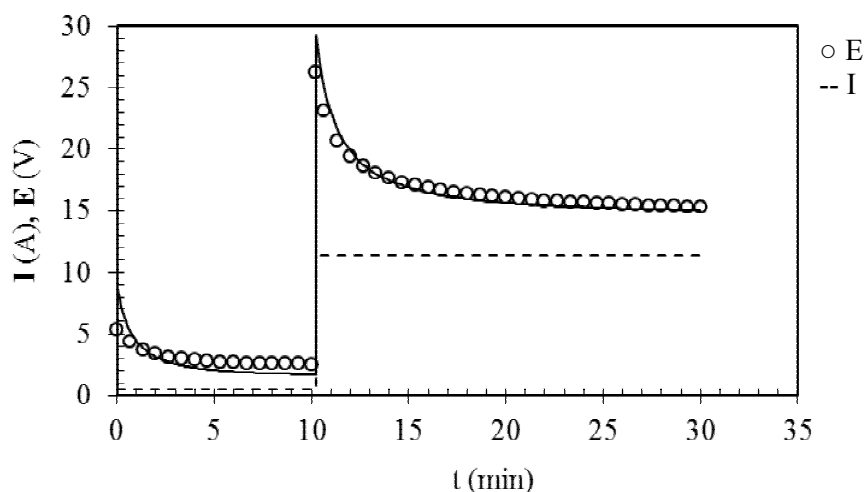
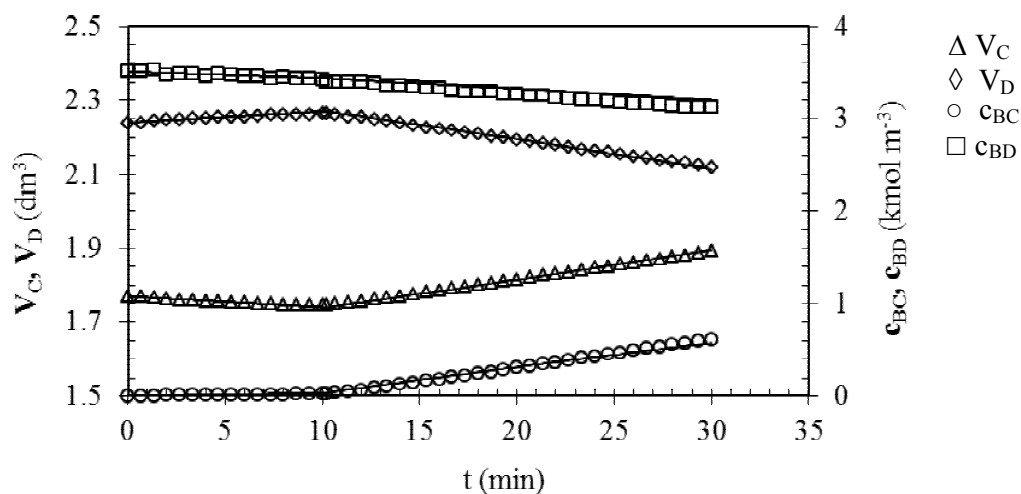
a)**b)**

Figure 5

Time course of trial V1 carried out using the operating conditions listed in Table 6: **a)** electric current (I : dashed line) and voltage applied to the ED stack (E : \circ) as a function of time (t); **b)** solute concentration in the concentrate (c_{BC} : \circ) and dilute (c_{BD} : \square) and their corresponding volumes (V_C : Δ ; V_D : \diamond) vs. t . All the continuous lines (—) were calculated using the mathematical model and the engineering parameters determined from experiment O1 (Table 3).

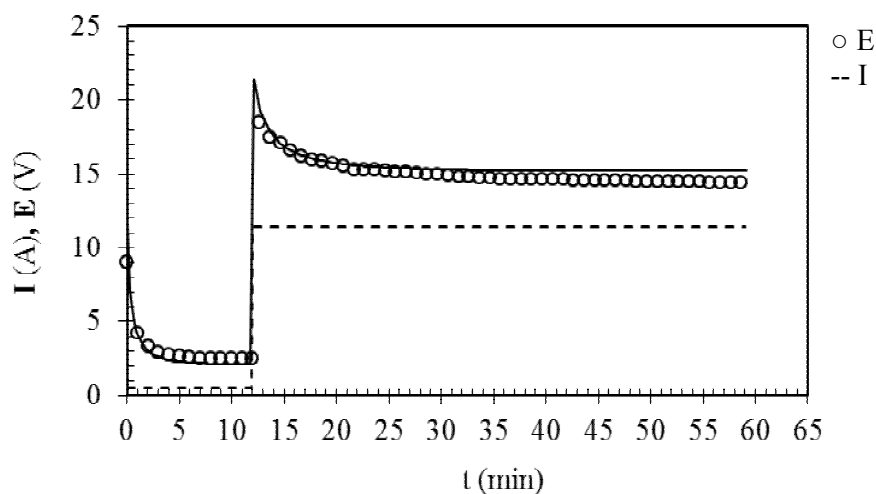
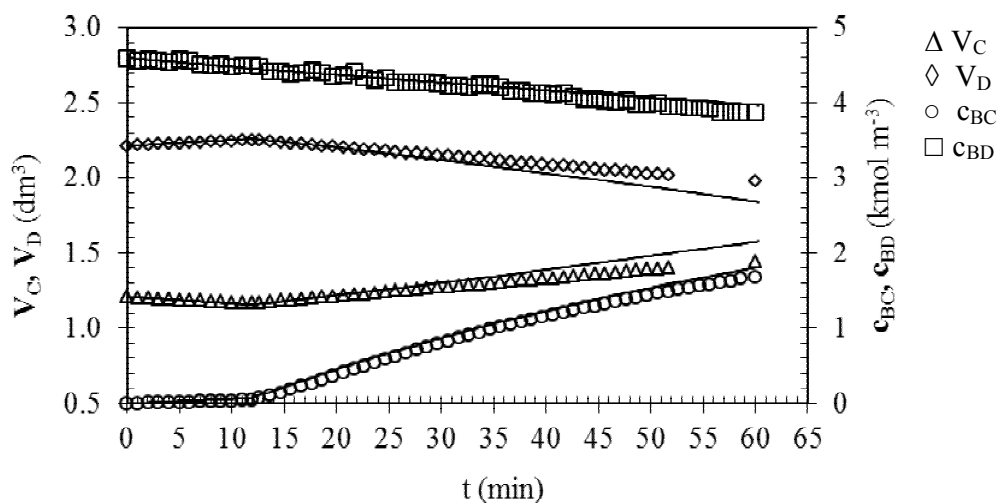
a)**b)**

Table 1 Specifications of the ED stack used in this work (model EUR2, Eurodia Industrie SA, Wissous, France) and manufacturer's data on membrane properties.

Membrane type	Cationic	Anionic	Unit
	Neosepta	Neosepta	
	CMX-Sb	AMX-Sb	
Thickness	0.14-0.20	0.12-0.18	(mm)
Burst Strength	≥ 0.40	≥ 0.25	(MPa)
Electric resistance at 0.5 M NaCl and 25°C	2.0~3.5	2.0~3.5	(Ω cm ²)
Perselectivity 1.0/0.5 M KCl	92	95	(%)
Electrode Dimensions	117 x 177.2		(mm x mm)
Membrane overall size	148 x 280		(mm x mm)
Geometric membrane surface area (a_{mg})	200		(cm ²)
Number of membranes (N_c or N_a)	9	8	-
Number of cell pairs (N_{cell})	8		-
Overall membrane surface area (A_{mg})	0.16		(m ²)
Intermembrane channel (h)	0.7		(mm)
Electrode compartment thickness (h_{ERS})	9.7		mm

Table 2 Vector of model parameters estimated in this work.

Parameter	Description	Unit
L_B	membrane constant for solute transport by diffusion	m s^{-1}
t_B	effective solute transport number ($=t_c^+ - t_a^+ = t_a^- - t_c^-$)	dimensionless
L_W	membrane constant for water transport by diffusion	$\text{mol m}^{-2} \text{s}^{-1} \text{bar}^{-1}$
t_W	water transport number	dimensionless
E_{el}	thermodynamic potential and overpotential of electrodes	V
R	average electric resistance of k-th electro-membrane ($= (N_a R_a + N_c R_c) / (N_a + N_c)$)	Ω

Table 3 Results obtained after parameter estimation. Estimated values ($\hat{\theta}_i$) including 95% confidence interval semi-widths ($sw_{95\%}$) and t-values (parameters failing the t-test are shown in boldface) from standard DoE following extensive experimentation (data of batch desalination experiments reported in reference [7]) and obtained from optimally designed experiment O1, O1* and O2 (see Table 5 for optimal experimental conditions).

Parameter	Parameter estimation results								Unit
	Experiments from [7]		Optimal design O1		Optimal design O1*		Optimal design O2		
	$\hat{\theta}_i \pm sw_{95\%}$	t-value	$\hat{\theta}_i \pm sw_{95\%}$	t-value	$\hat{\theta}_i \pm sw_{95\%}$	t-value	$\hat{\theta}_i \pm sw_{95\%}$	t-value	
L_B	$2.32 \cdot 10^{-8}$ $\pm 3.80 \cdot 10^{-8}$	0.6	$9.81 \cdot 10^{-8} \pm 2.76 \cdot 10^{-8}$	3.6	$1.00 \cdot 10^{-7}$ $\pm 0.40 \cdot 10^{-7}$	2.5	$9.81 \cdot 10^{-8}$ $\pm 1.38 \cdot 10^{-8}$	7.1	$m s^{-1}$
t_B	0.98 ± 0.01	98.3	0.92 ± 0.06	15.2	0.96 ± 0.15	6.3	0.87 ± 0.04	20.7	dimensionless
L_W	$1.06 \cdot 10^{-7}$ $\pm 0.12 \cdot 10^{-7}$	8.8	$1.04 \cdot 10^{-7}$ $\pm 0.12 \cdot 10^{-7}$	9.0	$1.05 \cdot 10^{-7}$ $\pm 0.18 \cdot 10^{-7}$	6.0	$1.03 \cdot 10^{-7}$ $\pm 0.37 \cdot 10^{-7}$	2.8	$mol m^{-2} s^{-1} bar^{-1}$
t_W	8.08 ± 0.25	32.3	8.54 ± 1.21	7.1	8.89 ± 3.29	2.7	7.82 ± 1.89	4.1	dimensionless
E_{el}	2.4 ± 0.3	12.0	2.99 ± 0.09	33.4	2.84 ± 0.15	18.8	2.26 ± 0.09	25.7	V
R	$2.6 \cdot 10^{-2} \pm 0.8 \cdot 10^{-2}$	3.3	$2.3 \cdot 10^{-2} \pm 0.07 \cdot 10^{-2}$	30.5	$2.4 \cdot 10^{-2} \pm 0.09 \cdot 10^{-2}$	27.2	$2.5 \cdot 10^{-2} \pm 0.05 \cdot 10^{-2}$	48.2	Ω
t^{rif}		1.65		1.66		1.66		1.60	
Tot. duration [min]		1080		120		60		30	

Table 4 Correlation matrix of parameters L_B , t_B , L_W and t_W estimated from experiments labeled D1-D7 (excluding trial D5) of Fidaleo and Moresi [7] by using Eq.s (5-8).

	L_B	L_W	t_B	t_W
L_B	1.000			
L_W	-0.187	1.000		
t_B	-0.700	0.111	1.000	
t_W	-0.202	0.684	0.179	1.000

Table 5 Results from model-based design of experiment (O1, O1* and O2 optimal design configurations) in terms of optimal design vector (elements y_0 , \mathbf{u} and τ) and total amount of salt (n_B) used for each designed experiment.

Design vector elements		Optimal design O1		Optimal design O1*		Optimal design O2	
		Switching time [min]	Current intensity [A]	Switching time [min]	Current intensity [A]	Switching time [min]	Current intensity [A]
\mathbf{u}	I	0	0.5				
		46	11.5	0	0.5	0	0.5
		60	2.5	46	11.5	10	11.4
		89	8.0				
y_0	c_{BC}^0 [kmol m ⁻³]	0.01		0.01		0.01	
	c_{BD}^0 [kmol m ⁻³]	5		5		3.8	
	V_C^0 [dm ³]	1		1		1.5	
	V_D^0 [dm ³]	2.46		2.46		2.1	
τ	[min]	120		60		30	
n_B	[mol]	12.3		12.3		8.0	

Table 6 Outline of the actual ED experimental conditions used for parameter identification and validation: I , range of direct electric current applied; c_{BD0} and c_{BC0} , initial solute molar concentration (in tank D and C respectively); V_{C0} and V_{D0} , initial solution volume in tank C and D, respectively; c_{ERS} , solute molar concentration in the electrode rinsing solution. The design values are indicated in brackets.

Experimental conditions						
	I (A)	c_{BD0} (kmol m^{-3})	c_{BC0} (kmol m^{-3})	V_{D0} (dm^3)	V_{C0} (dm^3)	c_{ERS} (kmol m^{-3})
Optimal design (O1)	0.5-11.46	4.40 (5.00)	0.03 (0.01)	2.64 (2.46)	1.16 (1.00)	0.34
Optimal design (O2)	0.5-11.40	3.51 (3.80)	0.00 (0.01)	2.24 (2.10)	1.77 (1.50)	0.32
Validation (V1)	0.5-11.45	4.60	0.00	2.21	1.21	0.31