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Optimal design of experiments for parameter identification in electrodialysis models

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ABSTRACT

The Nernst–Planck approach, previously used to model the electrodialytic 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 electrodialysis 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 (Lacey and Loeb, 1972; Ho and Sirkar, 1992).

Its main area of application is the desalination of brackish water (Ho and Sirkar, 1992; Audinos, 1992) and de-ashing of milk whey to obtain valuable raw materials for baby-foods (Batchelder, 1987). In the food industry, ED is gaining growing importance with large-scale industrial installations for the tartaric stabilisation of wine, fruit juice de-acidification, and molasses desalting (Fidaleo and Moresi, 2006a). 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 (Fidaleo and Moresi, 2006a).

In a previous study (Fidaleo and Moresi, 2005a), a mathematical model for ED, derived from the Nernst–Plank 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)

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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}	ijth element of the inverse matrix of measurements errors
t	time
t_i	ith t value
x	generic state variable
y	generic measured output

Greek symbols

φ_i	ith element of the design vector
θ_i	ith model parameter
τ	experiment duration
τ^{MAX}	experiment duration upper bound
ψ	measurement function of V_θ
σ_i	standard deviation of ith measurement
ξ	reference value of t-distribution with $n_{sp} - N_\theta$ degrees of freedom

Vectors and matrices [dimension]

$\mathbf{C}$	set of constraint functions [N_c]
$\mathbf{G}$	set of active constraints [N_c]
$\mathbf{H}_\theta$	dynamic information matrix [$N_\theta \times N_\theta$]
$\mathbf{H}_\theta^0$	preliminary information matrix [$N_\theta \times N_\theta$]
$\mathbf{y}_0$	vector of initial conditions [N_y]
$\mathbf{y}$	measurements vector [N_y]
$\hat{\mathbf{y}}$	vector of estimated responses [N_y]
$\mathbf{t}_{sp}$	vector of sampling points [n_{sp}]
$\mathbf{u}$	vector of manipulated inputs [N_u]
$\mathbf{V}_\theta$	variance-covariance matrix of model parameters [$N_\theta \times N_\theta$]
$\mathbf{x}$	vector of state variables [N_x]
$\mathbf{x}_0$	vector of initial states [N_x]
$\dot{\mathbf{x}}$	vector of derivatives on state variables [N_x]
$\boldsymbol{\varphi}$	design vector [n_φ]
$\boldsymbol{\theta}$	vector of values of true model parameters for the system [N_θ]
$\hat{\boldsymbol{\theta}}$	vector of estimated values of model parameters [N_θ]
$\boldsymbol{\theta}_0$	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 kth electro-membrane (dimensionless)
n	number of moles (mol)
R	average electric resistance of any electro-membrane (Ω)
R_G	gas-law constant (=8.314 J mol^{-1} K^{-1})
R_k	electric resistance of the kth electro-membrane (Ω)
T	absolute temperature (K)
t	process time (s or h)
$t_{\pm k}$	cation or anion transport number in the kth 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 kth 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
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 kth membrane or solute
W	referred to water
0	initial