

Optimal Operational Profiles in an Electrodialysis Unit for Ion Recovery

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Electrodialysis is an efficient process for the cleaning of industrial water effluent streams from toxic ionic substances with the simultaneous recovery of valuable ions for reuse. Energy consumption and waste recovery are the two key goals of the process. A dynamic optimisation program aims to determine the optimal operating conditions in terms of applied voltage and effluent flow rate in a batch operating scheme. A model is developed that accounts for the ion transfer through the ion selective membranes and the dynamics of the system. A combination of three objective functions targeting the minimisation of the overall batch process time, the minimisation of the electrical energy consumption required for the ion transfer, and the maximisation of the overall degree of separation is investigated. The manipulated variables applied voltage and feed stream flow rate are considered as piecewise constant during each time interval, spanning the duration of the entire batch. The dynamic optimisation problem is solved through standard non-linear programming techniques which calculate the optimal batch duration and condition profiles for the system. A multi-objective analysis is presented for various combinations of weight values for the joint objective function through the development of the Pareto optimal front. The current approach has been implemented in the removal and recovery of sulfuric anions from an aqueous solution and resulted in the achievement of a high degree of separation in a shorter period at a much lower energy consumption.

1. Introduction

Electrodialysis is an electrochemical process in which ions are transferred through ion selective membranes under the influence of an externally applied electric field imposed by two electrically charged electrodes. Electrodialysis units enable the separation of anions and cations from waste discharge streams and enable the simultaneous recovery of valuable ions. Extensive research has been carried out on the fundamental principles of the electrolysis system as well as the latest technological developments that have taken place in this process (Al-Amshawee et al., 2018). The complexity of an electrodialysis unit is quite high due to the combined electrochemical and mass transfer phenomena within a complicated geometry of alternating flow channels and membrane modules. The efficient operation of an electrodialysis unit depends on a number of process parameters as stated by Voutetaki et al. (2020).

Electrodialysis units aim to meet stringent quality specifications for the discharged stream while enabling a high degree of recovery for valuable ions from the effluent stream. In order to develop optimal operating policies for the electrodialysis process a model-based optimisation approach is necessary. To this end, Rohman et al. (2010) developed a model of high accuracy for hydrochloric acid recovery. Voutetaki et al. (2020) provided a validated process model with optimally estimated parameters using experimental process data for the recovery of sulfuric acid. Usually, electrodialysis operates in a batch mode and the calculation of optimal operating policies involves the determination of the intensity of the electric field applied to the recirculated effluent stream. Shah et al. (2018) investigated the optimal design of electrodialysis units for the desalination of brackish groundwater and concluded that capital cost dominates over energetic cost and therefore high current density units were preferred. Parulekar (1998) minimised energy consumption using a weighted-average resistance for the electrodialysis stack by obtaining optimal profiles for the electric current and the fluid flow. A more systematic

approach was presented by Rohman and Aziz (2019) where a dynamic optimisation approach was employed for the minimisation of the energy requirements. Orthogonal collocation achieved the lowest energy for the highest hydrochloric acid recovery within manageable computational requirements. Chehayeb and Lienhard (2019) investigated three different modes of operation for optimal brackish water desalination and concluded that constant current operation is energetically superior than constant voltage or constant entropy generation. According to Shah et al. (2018) the optimal operating policies depend on the composition and the concentration of the effluent stream as well as the amount of feed flowrate. In addition, variations in the efficiency of the membranes and disturbances occurring in the quality of the effluent stream are key factors that need to be considered in the operation of an electro dialysis unit.

The objectives of the present work are the development of a dynamic optimisation program using the method of orthogonal collocation on finite elements (OCFE) to determine the optimal operating conditions of a sulphate ion solution cleaning unit. The program seeks to calculate the optimal profile of the applied current voltage and effluent fluid flow in a batch electro dialysis configuration in order to meet desired specifications for the concentration of ions in the output stream of the process. The problem has multiple competing objectives and therefore their balance requires a careful consideration for the specific input stream properties. The present work aims to bring a systematic approach to the online optimisation of a batch electro dialysis plant.

2. Modeling of an electro dialysis system

A schematic of a batch electro dialysis process unit that is based on recirculation of the contaminated effluent is shown in Figure 1 (Voutetaki et al., 2020). The solution that is processed is passed through an electro dialysis cell with the aid of a pump from a feedstock tank (dilute). A specific electric voltage potential is applied at the electrodes in the two sides of the cell stack. Two types of compartments-cells can be distinguished. The compartments that carry the concentrate (indicated as C) solution in which the concentration of the ions increases for possible ion recovery and the compartments that carry the dilute (indicated as D) in which the concentration of the ions decreases and is the effluent product of the electro dialysis process. The cations move towards the negatively charged cathode, and the anions towards the positively charged anode. The cations can selectively permeate through the negatively charged Cation Exchange Membranes (CEM), whereas the anions can permeate through the positively charged Anion Exchange Membranes (AEM) separating C and D successive compartments.

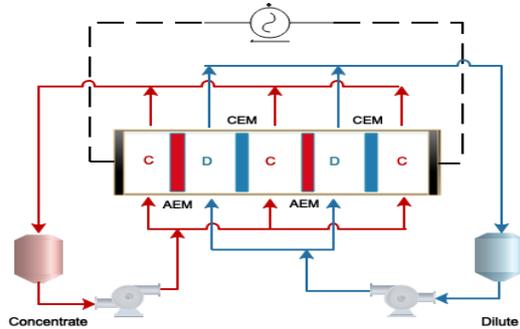


Figure 1: Electro dialysis batch process with recirculation of the concentrate and dilute solutions

The mathematical model that describes the electro dialysis process is taken by Rohman et al. (2011):

$$\frac{dC_{conc}}{dt} = \frac{Q(C_{conc}^{tank} - C_{conc}) + \frac{N\phi jA}{zF} - \frac{NAD_{AEM}(C_{conc}^{AEM} - C_{dil}^{AEM})}{l_{AEM}} - \frac{NAD_{CEM}(C_{conc}^{CEM} - C_{dil}^{CEM})}{l_{CEM}}}{NV_{comp}} \quad (1)$$

$$\frac{dC_{dil}}{dt} = \frac{Q(C_{dil}^{tank} - C_{dil}) - \frac{N\phi jA}{zF} + \frac{NAD_{AEM}(C_{conc}^{AEM} - C_{dil}^{AEM})}{l_{AEM}} + \frac{NAD_{CEM}(C_{conc}^{CEM} - C_{dil}^{CEM})}{l_{CEM}}}{NV_{comp}} \quad (2)$$

$$\frac{dC_{conc}^{tank}}{dt} = \frac{Q(C_{conc} - C_{conc}^{tank})}{V_{conc}^{tank}} \quad (3)$$

$$\frac{dC_{dil}^{tank}}{dt} = \frac{Q(C_{dil} - C_{dil}^{tank})}{V_{dil}^{tank}} \quad (4)$$

The mass balance equations express the ions' transfer between the compartments (Eq(1) and Eq(2)) and the concentrate and dilute tanks (Eq(3) and Eq(4)). C_{conc} , C_{dil} , C_{conc}^{tank} , C_{dil}^{tank} correspond to the ion's concentration in the concentrate and dilute, compartments and tanks, V_{comp} , V_{conc}^{tank} , V_{dil}^{tank} correspond to the volumes of the

solutions. Q is the overall flowrate of the treated solution, j and φ are the current density and efficiency, N is the number of cell pairs, A is the membrane area per cell pair, z is the ion's charge, and F is Faraday's constant. D_{AEM} and D_{CEM} denote the diffusion coefficients through AEM and CEM, l_{AEM} and l_{CEM} denote the membrane thickness. C_{conc}^{AEM} , C_{dil}^{AEM} , C_{conc}^{CEM} , C_{dil}^{CEM} denote the concentration of ions on the surface of the corresponding membranes. The overall energy of the system is the summation of the electrical energy consumed in the stack, in order to achieve the transfer of ions, and the energy required for the pumps used for the recirculation of the solutions, which can be considered negligible due to the absence of significant pressure drop and the low flow rate in the ED stack. Electrical energy consumption ($\frac{kWh}{m^3}$) is calculated by the following formula:

$$E_{des} = U_{st} \int_{t_0}^{t_f} \frac{j_{st} * A_{st}}{V_{dil}^{tank}} dt \quad (5)$$

where U_{st} is the applied potential difference; j_{st} the current density; A_{st} the membrane area.

2.1 Dynamic optimisation of operation

In a batch electro dialysis operation, the factors that can directly affect the process performance are the power source voltage, U_{st} , and the overall flow rate, Q . Ortiz et al. (2005) carried out experiments to test the effect of these variables and proved their dominant impact on the dynamic behaviour of the electro dialysis process. They are selected as control variables. Usually, the control variables are set at an optimal value but remain constant throughout the duration of the batch. However, the optimal values for the source voltage and the circulation rate may change as the concentration of the dilute changes with time. In addition, disturbances associated with the membrane performance and unknown feed concentration may affect the performance of the system. A dynamic optimisation approach enables the calculation of the optimal control profiles in order to ensure the maximum degree of ion recovery at the minimum process time and energy consumption. In the present work, the following optimisation criteria have been selected:

Minimisation of the process batch time:

$$\min_{x,u} t \quad (6)$$

Minimisation of energy consumption (energy for the pumps is considered constant and negligible):

$$\min_{x,u} E_{des} = \min_{x,u} E_{st} \int_{t_0}^{t_f} \frac{j_{st} * A_{st}}{V_{dil}} dt \quad (7)$$

Maximisation of the degree of separation defined as:

$$\max_{x,u} \text{Degree} = \min_{x,u} \left(1 - \frac{C_{dil}^{tank}(t_f)}{C_{dil}^{tank}(1)} \right) \quad (8)$$

In this case, the final dilute tank concentration C_{dil}^{tank} is bounded by an upper limit to ensure a satisfactory level of separation.

In addition to the aforementioned criteria, an extra term is included in the overall goals that accounts for the rate of change for the control variables, $u^T R u$. The symbol u corresponds to either the source voltage or the circulation flowrate variation between two consecutive control intervals whereas R is a weight matrix. The combination of the objective criteria results to the following function:

$$f(x, u) = Q_t * t + Q_E * E_{st} \int_{t_0}^{t_f} \frac{j_{st} * A_{st}}{V_{dil}} dt + \int_{t_0}^{t_f} u^T R u dt - Q_{Deg} \left(1 - \frac{C_{dil}^{tank}(t_f)}{C_{dil}^{tank}(1)} \right) \quad (9)$$

where Q_t , Q_E , R and Q_{Deg} are weighted factors used to normalise the different, usually competing goals of the objective function.

The objective function is minimised subject to the modelling equations Eq(1) to Eq(4). The method of orthogonal collocation on finite elements is employed to discretise the differential equations as implemented in Kiparissides et al. (2002). The time domain, $t \in [t_0, t_f]$, is divided into a number, NE , of equally spaced time intervals, $\Delta \zeta_n$, namely the finite elements, with $\zeta_0 = t_0$ and $\zeta_{n+1} = t_f$. Time within each interval is normalised so that it varies between $\tau \in [0, 1]$. The actual time is then derived by $t = \zeta_{n-1} + \Delta \zeta_n \tau$. The control variables, current voltage and fluid circulation flowrate, are parameterised as piecewise constant variables within each time interval. In each finite element a number of collocation points, NC , is defined as the roots of Legendre orthogonal polynomials,

The state variables, $C_{conc}, C_{dil}, C_{conc}^{tank}, C_{dil}^{tank}$, are approximated within each time interval using Lagrange interpolating polynomials, $\varphi_i(\tau)$.

$$\varphi_i(\tau) = \prod_{\substack{k=0 \\ k \neq j}}^{NC} \frac{\tau - \tau_k}{\tau_i - \tau_k} \quad i = 1, \dots, NC \quad (10)$$

The balance equations, Eq(1) to Eq(4), are assumed to be satisfied exactly only at the collocation points.

$$x_i(\tau) = \sum_{j=0}^{NC} x_{ij}(\tau_j) \varphi_j(\tau) \quad (11)$$

Where $x_i(\tau)$ corresponds to any of the state variables in the i -th finite element and $x_{ij}(\tau_j)$ is the value of the state variable at the j -th collocation point. The adaptive placement of the element boundaries can change the density of the collocation points in the time and the discretisation method can increase its accuracy when steep state profiles are formed during the dynamic transition. Finally, state and control variable bounds are defined along the time domain.

3. Optimisation results and discussion

The selected modelling approach is based on fundamental principles of electrodialysis and consists of a set of general, universal and theoretical steps regardless of the structural and functional details of the stack or the breaks and concentrations used. In the present study, the general mathematical model developed describes the separation of sulfuric acid solution. The model and the parameters used were validated using experimental results (Voutetaki et al., 2020).

The initial control variables are selected as: $E_{stack} = 20 [V]$ and $q = 0.15 [\frac{m^3}{h}]$. The initial conditions of the concentrations are defined by Voutetaki et al. (2020): $C_{conc}(0) = C_{dil}(0) = C_{conc}^{tank}(0) = C_{dil}^{tank}(0) = 2000 * (\frac{1}{98}) [\frac{mol}{m^3}]$. It is considered that the volume of the solution in the concentrate and diluent tanks are equal ($V_{tank}^{conc} = V_{tank}^{dil} = 0.02 [m^3]$) with identical sulfuric acid concentration at the beginning of the batch process. The electrodialysis compartments are considered as flooded with the initial solution. The goal is to achieve a desired final dilution tank concentration which is introduced into the optimisation problem in the form of a constraint: $C_{NE, c_n}^{dil, tank} \leq 600 [\frac{mg}{L}]$. The time domain is divided into 10 finite elements with 4 interior collocation points in each element. Bounds have been set for the control variables: $0 \leq E_{stack} \leq 80 [V]$ and $0 \leq q \leq 0.4 [\frac{m^3}{h}]$.

Several optimisation runs were performed using Eq(9) as the objective function with different sets of values for the weighting factors. The analysis of the converged optimal solutions was utilised in the construction of Pareto optimal fronts for the determination of the non-dominated optimal solutions as shown in Figure 2. In this way, the set of weighting factors that achieved the lowest value in the aggregate objective function, Eq(9), is obtained. The desired point in the Pareto front exhibits relatively low sensitivity (i.e. moderate slope) of the Pareto front. Case 76 is the selected optimal solution. The steady state solution in Figure 2 shows the achieved performance for the case operating at an optimal but constant profile for the control variables.

The optimal current voltage and dilute flow rate profiles are shown in Figure 3. The current voltage reduced at its lower bound for about the first half of the batch as the dilute compartments have a high concentration of sulfuric ions. Gradually the voltage increased in the second half of the batch to push the smaller amount of sulfuric anions to the concentrate side as shown in Figure 4. Regarding the circulation flow rate, the optimal profile started with the lowest possible flow rate when the dilute concentrate was high in sulfuric ions to increase the residence time in the electrodialysis compartments. Progressively as the dilute concentration was dropping (Figure 4), the circulation flow rate was increased which in interaction with the strong applied electric field the degree of separation eventually reached the desired level. The combination of the two profiles enabled the completion of the desired degree of separation at the lowest possible batch time. This is also significant from an economic point of view as the shorter the batch time the greater the amount of processed effluent stream and the greatest the amount of recovered sulfuric ions.

The final concentrations of the concentrate and dilute tanks and compartments achieved at the end of the batch are shown in Table 1. The case is considered acceptable as it achieves the final dilution tank concentration target set. Comparison of the optimal result with the steady state case reveals that the optimised process achieved a 75 % faster separation of the solution, in addition to a lower separation level which was acceptable but closer to the constraints. Finally, a slight decrease by 15 % was observed in the required energy.

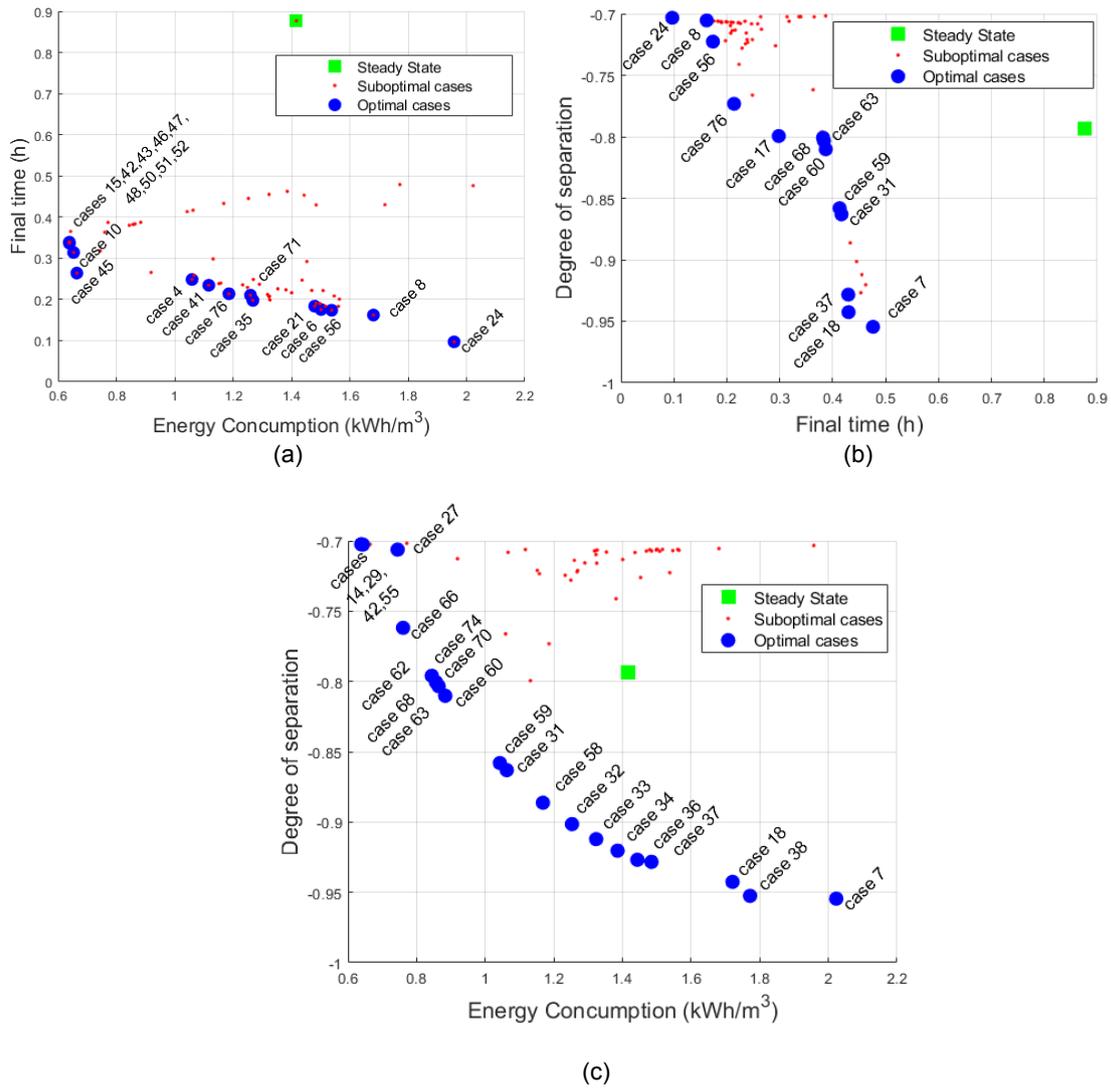


Figure 2: Pareto optimal fronts for the multiple optimisation criteria

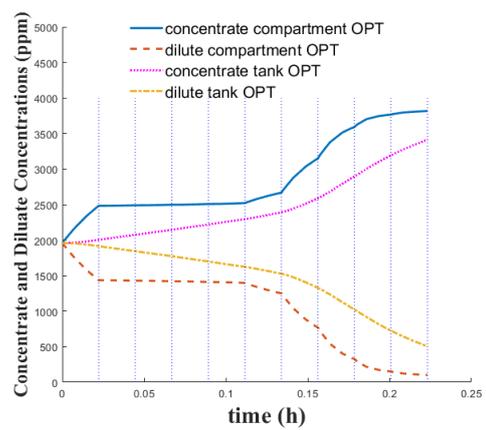
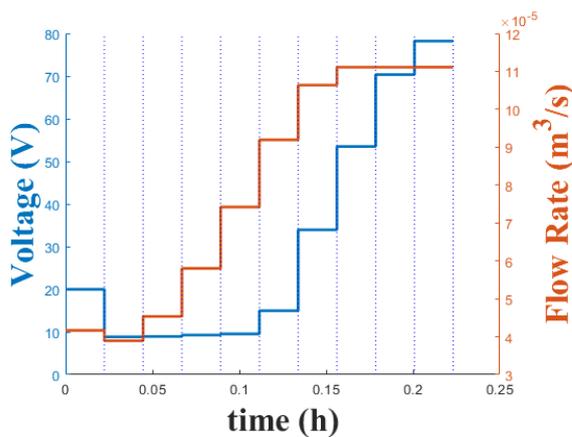


Figure 3: Control actions: Voltage (left-blue) and flowrate (right-red) during the batch duration

Figure 4: Concentrations of solutions in electro dialysis compartments and tanks during the batch duration

Table 1: Final concentration values of the selected case at the end of the batch

Final Time [min]	Final Concentration of Dilute Tank $[\frac{mg}{L}]$	Final Concentration of Concentrate Tank $[\frac{mg}{L}]$	Energy Consumption $[\frac{kWh}{m^3}]$	Degree of Separation
13.5	519	3,481	2.1	0.74

4. Conclusions

The present study investigates the application of dynamic optimisation in a batch electro dialysis system with recirculation. A multi-objective framework was utilised to investigate the behaviour of the optimal control variables with respect to the various performance criteria. The dynamic optimisation enables the optimal adjustment of the control profiles to accommodate the variation in the feed concentration and feed amount in the electro dialysis unit. The optimisation achieves the completion of the batch in a shorter period of time by approximately 50 % while satisfying the effluent quality criteria and achieving a considerable reduction in energy requirements. On the meantime, the concentrated solution enables the recovery of valuable sulphuric ions. In addition, the proposed approach can potentially handle the optimisation of the operating conditions in the case that the performance of the ion exchange membranes changes with time. The incorporation of the proposed optimisation framework in a control scheme that also includes model prediction updates would further enhance the ability of the electro dialysis unit to operate under a wide range of effluent composition and concentration ranges.

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