



Simultaneous rational design of ion separation membranes and processes

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Abstract

Economically viable water treatment process plants for drinking water purification are a prerequisite for sustainable supply of safe drinking water in the future. However, modern membrane process development experiences a disconnect in this domain: the synthesis of the membrane and the design of the process are decoupled. We propose an optimization strategy to simultaneously design the performance of layer-by-layer nanofiltration membrane modules and the separation process. This approach achieves overall optimal performance by extending the search space and thus exploiting synergies. Better separation performances at a lower cost as compared to conventional optimization strategies can be achieved. The key feature of this optimization framework is the integration of artificial neural networks. This machine-learning technique describes membrane performance as a function of its synthesis protocol. We optimize the design problem rigorously by a deterministic global nonlinear optimization method. Thus, this framework yields membrane synthesis protocols and membrane processes that are optimally tailored to the desired separation task. In a showcase, the simultaneous membrane synthesis and process optimization design achieve immediately favorable results with lower impurities at comparable costs. The process investment and operation costs are compared to a state of the art commercially available membrane for nanofiltration.

Keywords: Layer-by-layer, Nanofiltration, Deterministic global optimization, Artificial neural network, Hybrid modeling

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1. Introduction

In conventional development of membrane process plants, the modification of membranes and the design of membrane processes are decoupled [1]. On the one hand, process design of water treatment plants uses numerical optimization methods to find the right connectivity of membranes, pumps, and mixers [2–11]. On the other hand, recent developments in membrane science deliver better performance, balancing the delicate trade-off between permeability and selectivity in membrane design [1, 12] by changing the material systems, using composite membranes or modifying the membrane surface [13–18]. However, the simultaneous design of membranes and processes may offer opportunities for synergies, as the development of the membrane and the process takes place concurrently. In this study, we propose a methodology which simultaneously performs the optimization of membrane synthesis protocol and process design.

The major difficulty for the simultaneous optimal design of membranes and processes has been the lack of a model describing the influence of the synthesis protocol on the membrane performance. Additionally, optimizing mechanistic models across multiple scales is challenging. Previous efforts by Bowen et al. (2002), for instance, describe the membrane transport phenomena by a simplified differential-algebraic model based on membrane-specific fitting parameters, i.e., the model-based membrane properties pore radius and fixed charge density [19]. However, inferring pore radius and fixed charge density directly from synthesis protocols is currently not possible with phenomenological models. For layer-by-layer (LbL) nanofiltration membranes, we demonstrated in our recent work that an artificial neural network (ANN) approach can predict ion separation properties and pure water flux directly based on synthesis protocols, i.e., the fabrication parameters of the membrane [20]. Contrary to conventional screening procedures or educated guess experimental design, we developed a deterministic global optimization method [20, 21] that is applied in this work to enable optimal tailoring of synthesis protocols towards desired membrane retention and permeability in process optimization. Moreover, this framework is versatile enough to compute the resulting trade-off boundary (Pareto front) between permeability and retention.

In membrane science, there exist a variety of publications describing process-related modeling using ANNs [22, 23]. For instance, ANNs enable empirical predictions of fouling behavior [24–27], process parameters [28–30], and salt retention for nanofiltration systems [31–33]. ANNs have also been used in various disciplines for process modeling with subsequent optimization with ANNs embedded [34–36]. To the best of our knowledge, there are no publications integrating membrane performance optimization and simultaneous membrane synthesis. Here, we present simultaneous membrane synthesis for a given synthesis platform (LbL membranes) in process optimization for a given application (water desalination). We integrate the previously developed ANNs [20] in a hybrid mechanistic/data-driven process model. Multi-objective optimization reveals optimal membrane synthesis protocols and process operations that provide the optimal trade-off for the two conflicting objectives of (a) minimal annual operation costs and (b) minimal permeate impurity.

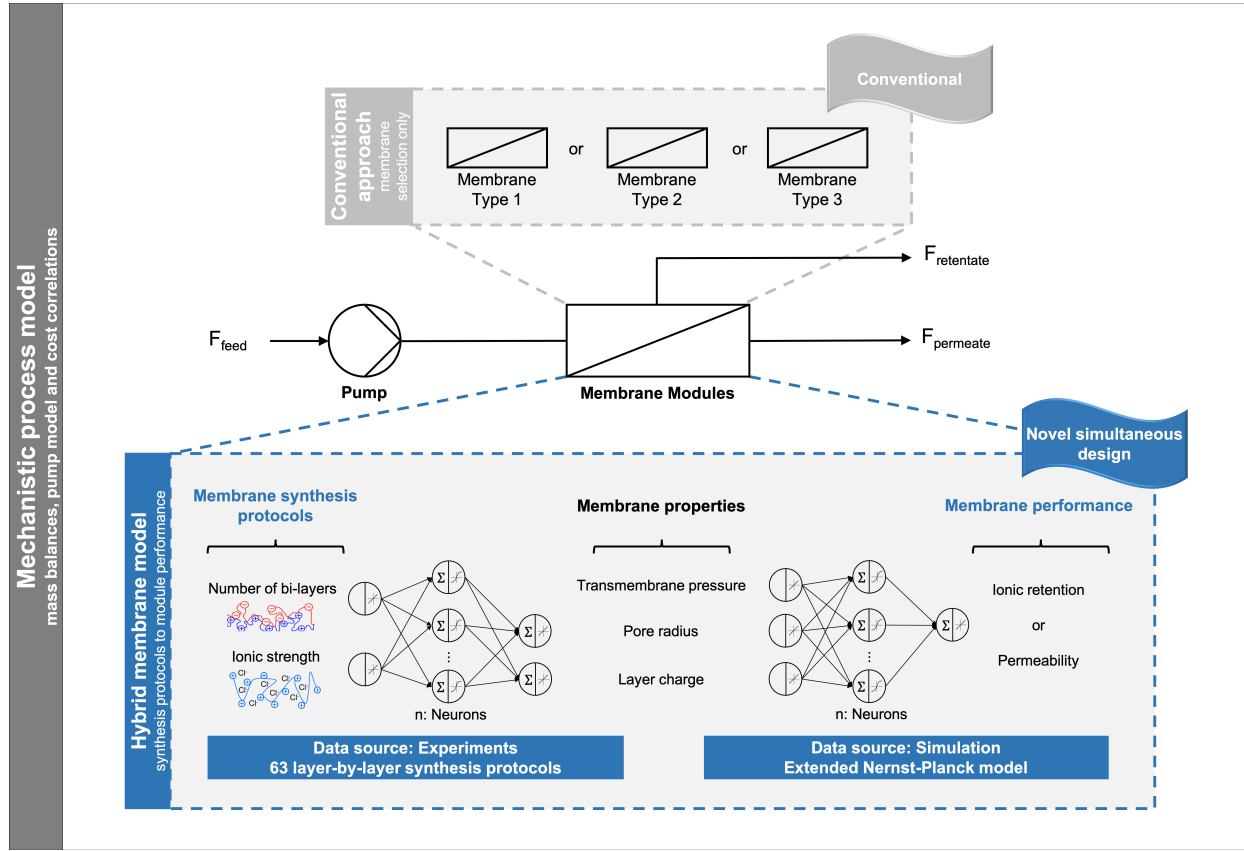


Figure 1. Overview of the scope of the manuscript: A **mechanistic process model** is used to optimize the membrane process plant in a MINLP optimization. The **conventional approach** is an optimization strategy where a membrane process is optimized, and the corresponding membrane is selected from a pool of known membranes (index (CA) - conventional approach). The novel simultaneous design presented in this paper uses a **novel hybrid membrane model** [20] where the performance of layer-by-layer membrane modules is simultaneously designed along with the process (index (SD) - simultaneous design).

First, we optimize the process model and select a membrane from an existing set of three different membrane modules (c.f., Figure 1 Conventional approach, index (CA)). A single-stage system without recirculation is considered. Both the operational variables and the membrane selection variable are degrees of freedom optimized by the deterministic global optimization solver MAiNGO [37]. This algorithm is well-suited for optimization problems with ANNs embedded [21] and flowsheet optimization problems [38]. Second, this conventional optimization strategy is extended by the simultaneous design of the LbL membrane modules (c.f., Figure 1 Novel hybrid membrane model, index (SD)) with the synthesis protocol of the membrane being a new and important degree of freedom of the optimization problem.

The optimization of process scale problems using data at a lab-scale is possible because the optimization framework addressed here uses LbL nanofiltration membranes, which are molecularly modular, easy-to-scale, and fabricated by dynamic coating inside an existing module housing with different support membranes [39]. The availability

of this modular fabrication method - with many degrees of freedom to yield tailored membrane synthesis protocols and properties - next to a methodology to optimize a membrane process - under very specific boundary conditions to achieve the desired separation task- would be a dream methodology for the inverse design paradigm: from the individual problem to the tailored membrane.

2. Material and methods

We now provide a brief overview of the LbL nanofiltration membranes we use (Subsection 2.1). Then, we describe the overall process model, including cost correlations (Subsection 2.2). The description of the membrane performance via ANNs is described in Subsection 2.3. Then, we describe the two optimization approaches: (CA) Conventional Approach of process design based on a pool of known membranes (Subsection 2.4) and the (SD) Simultaneous Design of membrane synthesis protocols (Subsection 2.5). Finally, numerical optimization methods are briefly described (Subsection 2.6).

2.1. Layer-by-layer nanofiltration membranes

All LbL nanofiltration membrane synthesis protocols and resulting membrane module separation performances used are based on our extensive data set [39]. Therein, we fabricated 63 LbL-based membrane modules, each housing ten polyethersulfone-based ultrafiltration hollow fiber support membranes with a dynamic coating procedure in a dead-end mode with constant flux. The resulting polyelectrolyte bi-layers consist of alternating polycation polydimethylammonium chloride (PDADMAC) and polyanion polystyrene sulfonate (PSS) layers prepared at different conditions, i.e., salt concentration in the coating solution, amount of permeated solution, and the number of polyelectrolyte layers coated.

The module separation performance is characterized by the uncharged retention of polyethyleneglycol (PEG) with various molecular weights using size exclusion chromatography. The retention of charged components (i.e., salt retention R_j) is measured for single salt solutions with a feed concentration of 5 mmol L^{-1} . All membrane modules are characterized for the salts MgSO_4 , Na_2SO_4 , MgCl_2 , and NaCl . All measurements are performed at cross-flow at turbulent conditions. Furthermore, the pure water permeability is measured for all membrane modules. All relevant information on this dynamic coating procedure as well as its characterization can be found in [39].

Tailoring the membrane module separation performances can be achieved by altering the membrane synthesis protocols of the dynamic coating procedure. The synthesis protocols, i.e., fabrication parameters of the membrane, are (1) the NaCl concentration in the polyelectrolyte coating solution (c_{NaCl}), (2) the number of polyelectrolyte bi-layers applied ($N_{\text{bi-layers}}$), (3) the deposition flux (J_{coating}), and (4) the deposition time (t_{coating}). ANNs can predict the modules' separation performance from the aforementioned membrane synthesis protocols and model-based membrane properties as we presented in [20]. A list of membrane synthesis protocols that are considered in this study and their range can be found in Table 1. Therein, we distinguish between variables, which are degrees of freedom of

the optimization, and parameters, which are held constant throughout the optimizations. In the context of this paper, only the number of polyelectrolyte bi-layers applied (N_{layer}) and the NaCl concentration in the polyelectrolyte coating solution (c_{NaCl}) are selected as degrees of freedom to reduce the uncertainty and complexity of the optimization.

LbL-based nanofiltration membranes and their performance to reject ions depend on the transmembrane flux. As our measurements are available at a constant transmembrane flux, we use a mechanistic model to extend the validity of the data-driven ANN. Therefore, the data on measured retention at a given flux is extended by the two-parameter model proposed by Bowen et al. [19]. This model can describe the transport of ions based on a two-staged fitting procedure using the Extended Nernst-Planck equation. First, a theoretical pore radius r_p is derived in an uncharged fit of the uncharged solute retention. Second, a fixed charge density X_j for the salts $MgSO_4$, Na_2SO_4 , $MgCl_2$, and $NaCl$ is determined by the charged solute retention. In our previous study [20], this hybrid model is used to describe the 63 different LbL-based membrane modules.

Variable name & range	Unit	Description	Data type
$N_{bi-layers} \in \{1, 2, 3, 4, 5, 6\}$	[–]	Number of bi-layers	Integer variable
$t_{coating} = \{10\}$	[min]	Deposition time	Constant parameter
$J_{coating} = \{30\}$	[LMH]	Deposition flux	Constant parameter
$c_{NaCl} \in [0, 0.5] \subset \mathbb{R}$	[g L ⁻¹]	NaCl coating concentration	Continuous variable

Table 1. Membrane synthesis protocols of LbL membrane modules and their valid ranges used for the optimization studies. As observed from the measured data, variation in the given ranges results in a retention $R_{Na_2SO_4}$ in the range of $0.5 \leq R_{Na_2SO_4} \leq 99.8\%$ and in the permeability Q in the range of $8.2 \leq Q \leq 49.9$ LMH bar⁻¹. Constant parameters are not altered in the optimization, while the variables are degrees of freedom of the optimization. For a full description, please refer to [20] and [39].

2.2. Mechanistic process model to describe the process plant

The membrane process plant is described by a standard state of the art mechanistic process model, consisting of mass and concentration balances, a pump model, and cost correlations. As shown in Figure 2, the membrane process is based on a single nanofiltration unit. A pump is installed on the feed side of each membrane as the main driving force of the separation process. The process can be adapted to a two-stage nanofiltration process. However, the membranes' retention data is only valid for a feed concentration of 5 mmol L⁻¹. Therefore, the mixing of streams at different concentrations cannot be considered in this study.

The nanofiltration unit is fed with a feed stream F_{feed} which is pressurized in a pump. The nanofiltration unit has two outputs: (1) The purified permeate stream $F_{permeate}$, and (2) the waste stream which is retentate stream of the membrane unit $F_{retentate}$.

The membrane itself and the separation process are described by a mechanistic model for the permeate stream that is based on two governing equations. The performance of the membrane module is described by the permeability Q and by the salt retention R_j for salt j . The permeate stream is calculated based on the membrane's permeability Q and

the transmembrane pressure difference across the membrane Δp

$$F_{\text{permeate}} = Q \cdot A_{\text{unit}} \cdot \Delta p \quad (1)$$

where $A_{\text{unit}} = n_{\text{module}} \cdot A_{\text{module}}$ is the total membrane area of the unit and A_{module} is the area of one module.

The separation performance of each nanofiltration unit is described by the salt retention R_j for salt j which is the computed by the salt concentration on the permeate side $c_{\text{permeate},j}$ and the feed sided concentration $c_{\text{feed},j}$.

$$R_j = 1 - \frac{c_{\text{permeate},j}}{c_{\text{feed},j}} \quad (2)$$

Further, mass balances couple the permeate and retentate concentration and flow rates. Additional constitutive equations are listed in the supplementary material.

The Verberne cost model [40–42] is used to calculate the total investment cost $C_{\text{investment}}$ and annual operation cost $C_{\text{operation}}$ for the economic optimization. All parameters of this cost model are listed in the supplementary material. The total investment cost $C_{\text{investment}}$ is calculated based on the sum of the civil C_{civil} , mechanical $C_{\text{mechanical}}$, electromechanical C_{electro} , and membrane C_{membrane} investment cost.

$$C_{\text{investment}} = C_{\text{civil}} + C_{\text{mechanical}} + C_{\text{electro}} + C_{\text{membrane}} \quad (3)$$

The annual operation cost is the sum of the depreciation cost $C_{\text{depreciation}}$, the energy cost C_{energy} , the maintenance cost $C_{\text{maintenance}}$, and specific cost C_{specific} .

$$C_{\text{operation}} = C_{\text{depreciation}} + C_{\text{energy}} + C_{\text{maintenance}} + C_{\text{specific}} \quad (4)$$

Herein, appropriate depreciation periods are accounted for the individual investment cost.

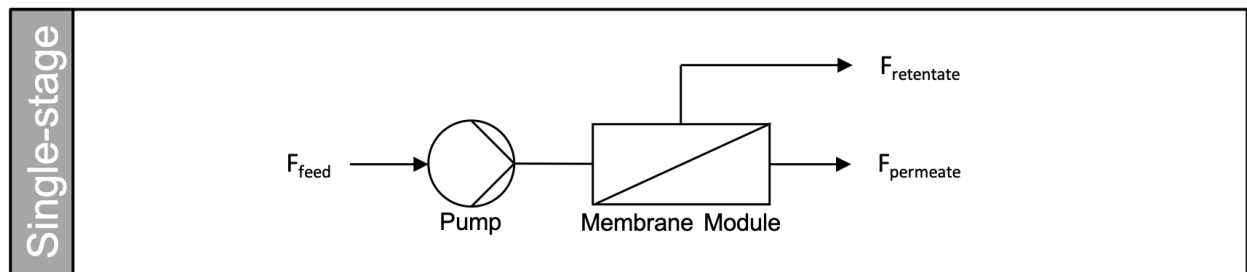


Figure 2. Considered process configuration: Single-stage nanofiltration unit. The membrane unit is equipped with a feed-sided pump. A global feed, and retentate and permeate represent the process input and outputs, respectively.

2.3. Describing ionic transport in membranes with artificial neural networks

The central part of this study is the description of the salt retention R_j and permeability Q of a nanofiltration unit based on the synthesis protocols via ANNs. The salt retention R_j and permeability Q of a nanofiltration unit is the interface to the mechanistic process model. These two variables are necessary for the solution of the governing equations and are each computed by an individual ANN.

We use a shallow feed-forward fully connected architecture, known as a multi-layer perceptron architecture with one hidden layer. The input and outputs are linearly transformed, i.e., scaled, and we apply the hyperbolic tangent transfer function in the hidden layer and a linear transfer function in the output layer.

The data preparation and training procedure is based on our previous work [20] and adapted in order to account for fixed deposition time and flux. The considered data sets for the training of the ANNs are adapted due to the mixed data types. The inputs of the ANNs are partly continuous variables and integer variables, e.g., the number of bi-layers $N_{bi-layers}$ (see Table 1). We represent the integer inputs using a set of binary variables. This means that we introduce one binary input for each feasible integer value. A binary input is set to 1 if the respective integer is selected and is 0 otherwise (so-called SOS-1 set). It should be noted that the consideration of discrete decision variables in surrogate-based optimization was applied in the literature (e.g., [43–45]), but theoretical foundations of these methods are an active field of research [46, 47].

For each ANN, a suitable number of hidden neurons is determined by k -fold cross-validation [48] to avoid over- and under-fitting. Table 2 contains the ANNs used in the optimization framework and their corresponding number of hidden neurons. After the ANN sizes are fixed, a final training of the ANNs is performed. The data is randomly split into 70 % training, 15 % test, and 15 % validation sets. Then, a Levenberg-Marquardt training algorithm [49] is used to minimize the MSE on the training set. In order to avoid overfitting, early stopping is used to terminate the training by checking error on the validation set. The training is repeated multiple times on ANNs with the optimal number of hidden units ± 3 . Then, the ANN with the lowest MSE on the test set is chosen for the process optimization framework. Although this leads to a bias, the selection based on the test set was made due to the relatively sparse data set for training and validation.

	Hidden neurons n	Method	Used in
ANN _{SelectedMembranes}	10	(CA)	Section 2.4
ANN _{MembraneProperties}	15	(SD)	Section 2.5
ANN _{ModelParameter}	35	(SD)	Section 2.5
ANN _{Permeability}	16	(SD)	Section 2.5

Table 2. ANNs used in the process plant optimization framework to describe the performance parameter of LbL membrane modules. For the conventional approach (CA), an ANN is used to describe the membrane performance of the selected membrane from a pool of known membranes. In the novel simultaneous design (SD) strategy, the ANNs link the membrane performance to the membrane synthesis protocols. Given is the number of neurons n used for each ANN.

2.4. Conventional approach of process design based on a pool of known membranes (CA)

In the conventional approach, the process operation of the single-stage process configurations (Figure 2) is optimized, and their membranes are selected by the optimization among an a-priori determined membrane pool consisting of three known membranes (cf. Figure 3). The whole process is optimized for the two objectives - minimal annual operation costs and minimal permeate concentration. To select only one membrane at a time, the constraint Equation (5) is added for the membrane selection variables y_m . It ensures that the sum of the selection variable is equal to one and, hence, exactly one membrane is selected from the membrane pool.

$$\sum_{i=1}^3 y_m = 1 \quad (5)$$

The R_j and Q are linked to the selected membranes via ANNs, i.e., the ANNs take the membrane selection as an input. From a mathematical programming point of view, this is an innovative modeling approach which avoids the use of additional Big-M or convex hull reformulations and thus reduces the problem size in the reduced-space formulation. An in-depth comparison of these methods and their relaxations is a relevant future research.

The three known membranes and their ion separation performance R_j strongly depend on the transmembrane velocity, i.e., flux. The membranes of the membrane pool originate from [20] and [39]. As indicated in Figure 3, the retention of the salt Na_2SO_4 not only depends on the transmembrane velocity but also on the trade-off between retention and permeability of the membranes. For evaluation of the process, the membranes are compared to the commercially available FILMTEC™ NF 270 [50] membrane. The retention of the FILMTEC™ NF 270 is measured for this study at the same flow conditions for comparability.

2.5. Novel simultaneous design of the process and membrane fabrication (SD)

In the novel simultaneous design, the process design optimization of the plant is extended by tailoring the optimal membrane synthesis protocol simultaneously with the entire process (cf. Figure 1). The mechanistic process model is extended by a novel hybrid membrane model [20]. A single-stage nanofiltration unit is considered, as shown in Figure 2. The whole process is optimized for the two objectives - minimal annual operation costs and minimal permeate concentration.

Unlike in the conventional process design, now the membrane synthesis protocol is simultaneously optimized. Therefore, the performance parameters of LbL membrane modules are described by ANNs as shown in Figure 1 “Hybrid membrane model” and enlisted in Table 2.

- The first ANN_{MembraneProperties} is used to link membrane synthesis protocols $N_{bi-layers}$, c_{NaCl} to model-based membrane property fixed charge density X_{Na2SO4} of the membrane that is responsible for Na_2SO_4 retention and the membrane property pore radius r_p . Those model-based membrane properties can fully describe the membranes as proposed by Bowen et al. [19]. The description and range are enlisted in Table 3. Linking those

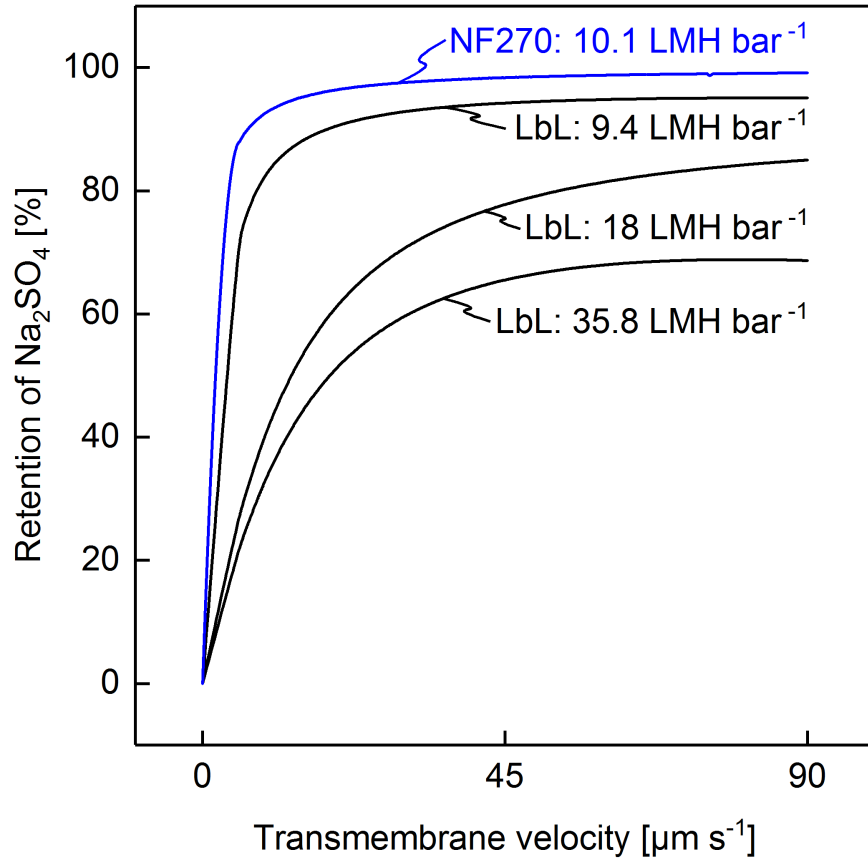


Figure 3. A-priori determined membrane pool for the conventional approach (CA): Retention of Na_2SO_4 of the membrane modules depends on the transmembrane velocity. The pure water permeability is given for each membrane. From membrane pool: Three known LbL nanofiltration membranes [20, 39] in a module. NF270: Comparison to commercially available nanofiltration FILMTEC™ NF 270 [50] membrane.

properties to membrane synthesis protocols is presented in our previous study [20]. The data basis for this ANN is experiments.

- The second $\text{ANN}_{\text{ModelParameter}}$ is used to link the model-based membrane properties, fixed charge density $X_{\text{Na}_2\text{SO}_4}$ of the membrane and the pore radius r_p , with the process properties transmembrane velocity to the separation performance parameter R_j . The data basis for this ANN is simulations.
- The third $\text{ANN}_{\text{Permeability}}$ is used to link the pure water permeation performance parameter Q . The data basis for this ANN is experiments.

As the ANNs are data-driven models, extrapolation capabilities, i.e., predictions outside the training region, are limited. Thus, we allow only membrane synthesis protocols in proximity to an existing training data point. In particular, we allow only 10% relative deviation to an existing membrane (cf. [20]). This reduces the uncertainty of the ANN predictions.

Variable name	Unit	Description	Data type
$X_{Na_2SO_4} \in [-90.47, -28.36] \subset \mathbb{R}$	$[\text{mol m}^{-3}]$	Fixed charge density for Na_2SO_4	Continuous variable
$r_p \in [0.38, 1.33] \subset \mathbb{R}$	$[\text{nm}]$	Pore radius	Continuous variable

Table 3. Model-based variables of LbL membrane modules used as data set for the process plant optimization framework. The range of the variables is given. For a full description, please refer to Rall et al. [20].

2.6. Numerical optimization approach

We formulate the simultaneous design as a bi-objective mixed-integer nonlinear program (MINLP):

$$\begin{aligned}
 \min_{\mathbf{x}, \mathbf{y}} \quad & \begin{pmatrix} f_1(\mathbf{x}, \mathbf{y}) \\ f_2(\mathbf{x}, \mathbf{y}) \end{pmatrix} \\
 \text{s.t.} \quad & g_i(\mathbf{x}, \mathbf{y}) = 0, \quad i = 1, \dots, I \\
 & h_j(\mathbf{x}, \mathbf{y}) \leq 0, \quad j = 1, \dots, J \\
 & \mathbf{x} \in X \subset \mathbb{R}^n, \quad \mathbf{y} \in Y \subset \mathbb{Z}^m
 \end{aligned} \tag{6}$$

where $\mathbf{x}$ are continuous optimization variables, $\mathbf{y}$ are integer optimization variables, $g_i(\mathbf{x}, \mathbf{y})$ are equality constraints, $h_j(\mathbf{x}, \mathbf{y})$ are inequality constraints, and $f_1(\mathbf{x}, \mathbf{y}), f_2(\mathbf{x}, \mathbf{y})^T$ are the objective functions. All optimization variables and model equations are described in Subsection 2.2 and Subsection 2.3 for the two optimization approaches. The objective functions are (1) minimal annual operation costs ($f_1(\mathbf{x}, \mathbf{y}) = C_{\text{operation}}$) and (2) minimal permeate concentration ($f_2(\mathbf{x}, \mathbf{y}) = c_{\text{permeate}}$).

To solve (6), we use the ϵ -constraint method, which solves a sequence of single-objective problems. In particular, one objective is minimized while the other objective enforced to be less or equal to a parameter ϵ of iteratively increasing value. This yields Pareto-optimal points. We impose the annual operation cost $C_{\text{operation}}$ as a constraint and minimize the permeate concentration.

All optimization problems are solved using the recently developed deterministic global solver MAiNGO (v0.1.24) [37] on a single core of an Intel(R) Xeon(R) CPU E5-2630 v2 with 2.60 GHz, 128 GB RAM and Windows 2008 server 64 bit operating system. The solver uses a branch-and-bound algorithm and guarantees to identify global optimal solutions to a given tolerance in finite time. In contrast to other general-purpose global solvers like BARON [51], MAiNGO uses McCormick relaxations provided by MC++ [52–54] to construct lower bounding problems. Moreover, MAiNGO allows the solution of problems in a reduced-space formulation [55] which is favorable for flowsheet problems [38, 56] and optimization problems with ANNs embedded [20, 21, 35, 36, 57]. We also considered a full-space formulation with the solver BARON (version 18.5.8 using default options) [51] in GAMS [58] (version 25.1.1). BARON gave similar optimization results in most cases. However, in some problem instances, BARON did not converge, leading to significantly longer overall CPU times. This observation is in agreement with our previous results showing that the reduced-space formulation in MAiNGO outperforms the full-space formulation in BARON on problems with ANNs embedded [21].

3. Case study & results

In this section, the two proposed optimization strategies are compared for a given case study. First, the conventional approach of process design based on a pool of known membranes (CA) is performed for comparison. Second, the process design of the plant is extended by the novel simultaneous design of the process and membrane fabrication (SD) by tailoring the optimal membrane along with the entire process.

3.1. Case study scenario description

The membrane purification plant is optimized to provide fresh drinking water meeting given quality specifications. The case study aims for water softening by retaining Na_2SO_4 salt in the membrane plant. Here, the process dimensions of the case study are determined by drinking water needs for a small town with 10,000 inhabitants as specified by Rautenberg et al. [59] in 2014. The drinking water demand is approximately $1400 \text{ m}^3 \text{ d}^{-1}$ with a peak demand of $224 \text{ m}^3 \text{ h}^{-1}$ product (or permeate) volume flow. All processes are optimized for the peak demand because demand-side management is not within the scope of this work. The complete listing of all consumers and their needs can be found in the supplementary material.

The process design and membrane development are performed based on our previous laboratory experiments [20, 39] where a 5 mmol L^{-1} feed concentration of a single salt Na_2SO_4 in water is used. Thus, the proposed case study is currently limited to this feed concentration and is not directly applicable to realistic wastewater concentrations. However, the proposed method can be extended in future research studies or corporate membrane development. The size of one module A_{module} is set to 60 m^2 in accordance with multiple membrane modules available on the market [60, 61].

3.2. Conventional approach of process design based on a pool of known membranes (CA)

The conventional approach of process design is optimized with a membrane selection among three candidate membranes. The resulting Pareto front for a single nanofiltration unit (cf. single staged in Figure 2) is shown in Figure 4. Herein, each point on the Pareto front depicts a process in which neither one of the objectives can be improved anymore without worsening the other objective. That means for each Pareto point, one cannot improve purity without spending additional annual operational cost. Thus, the trade-off between the two objectives annual operation costs and permeate concentration is evident. All Pareto optimal points define the boundary of the infeasible region and are called Pareto front.

The process optimization is eventually stopped for a maximum annual operational cost since no better permeate impurity can be achieved. In Table 4, the different choices of the membranes are displayed ordered by their permeability. A table of all process properties is listed in the supplementary material. The curve of the Pareto front shows significant discontinuities. This is attributed to the discrete membrane selection in the MINLP optimization problem. In regions of low annual operational costs, a membrane with the highest permeability is chosen ($35.8 \text{ LMH bar}^{-1}$). Here, the retention of the nanofiltration unit increases with decreasing permeate impurity. Further, with decreasing

permeate impurity, more pump power is required. Contrarily, in regions of high annual operational costs, a membrane with the lowest permeability but high retention is chosen (9.4 LMH bar^{-1}). The size of the membrane module is fixed to 60 m^2 and the membrane itself is fixed with a distinct explicit permeability. Consequently, the minimal permeate concentration depends on the retention of the unit, which is strongly influenced by the transmembrane velocity.

In total, 50 optimization problems are solved to obtain the illustrated approximation of the Pareto front. Each optimization problem has 6 degrees of freedom, 2 equality constraints, and 7 inequality constraints. The equations that describe the ANNs are formulated in a reduced-space formulation and are thus hidden from the branch-and-bound solver [21]. On average, the solution of one problem required 27 CPU seconds with a standard deviation of 11 CPU seconds. The total time of the optimization, including all 50 points, is 22 min. A list of all CPU times is provided in the electronic supplementary material.

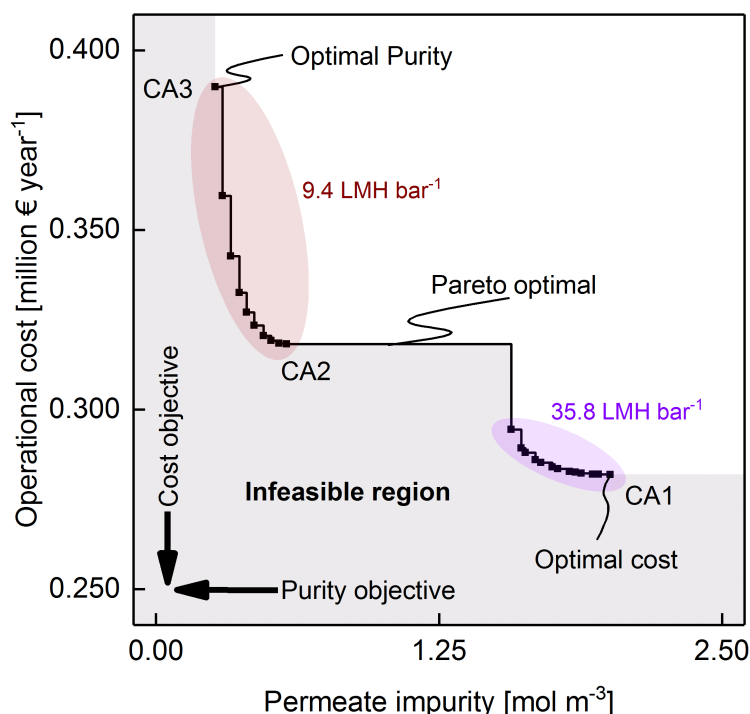


Figure 4. Conventional approach of process design based on a pool of known membranes (CA): Pareto front of a process plant optimized for a previously known selection of LbL membranes. Optimization is performed for the two objectives (1) minimal annual operation costs and (2) minimal permeate concentration. Results shown in are for a process plant having a single nanofiltration unit.

In addition, especially for challenging separation tasks, an interconnection of multiple units is of interest. However, if nanofiltration plants are allowed to intersect and mix streams, the concentration and thus the salt retention of the membrane changes. Higher concentrations lead to decreasing salt retention of the LbL nanofiltration membrane, whereas the decreased concentration in the permeate stream will result in higher salt retention in the subsequent unit. The data considered in this study is limited to a fixed feed concentration. Hence, a two-stage connection of

Table 4. Conventional approach of process design based on a pool of known membranes (CA): Selected membrane and process properties from Figure 4

Case	n_{module} [-]	W_{pump} [kW]	p_{module} [bar]	R [%]	Q [LMH bar ⁻¹]
CA 1	34	20.62	4.07	59.86	35.8
CA 2	18	40.51	6.93	88.45	9.4
CA 3	67	151.90	23.06	94.76	9.4

nanofiltration unit is not optimized at this point. However, we suggest that the presented methodology is directly applicable to multi-unit membrane processes. Connecting streams and considering the change in salt concentration will be addressed in future research.

3.3. Novel simultaneous design of the process and membrane fabrication (SD)

Although the process optimization with a selection of membranes already delivers good results, an extension of the process design to simultaneously optimize the membrane itself offers potential synergies. Again the process plant is optimized for annual operation costs and permeate concentration. A single nanofiltration unit is considered.

The resulting Pareto front of the multi-objective optimization is displayed in Figure 5. Three illustrative Pareto optimal process designs cases are listed in Table 5. The process having the lowest cost Figure 5 (SD 1): This combined optimization achieves lower permeate impurity than before (c.f. Figure 4 (CA 1)) because a membrane is tailored to these exact process conditions. Table 5 demonstrates that the simultaneous optimization of the membrane synthesis protocol can achieve higher separation performance at a lower cost compared to the process designs cases enlisted in Table 4. The process determining parameters, such as the permeability Q , salt retention R_j , and pump power W_{pump} follow the intrinsic trend towards more difficult separation processes.

Table 5. Novel simultaneous design of the process and membrane fabrication (SD): Selected membrane and process properties from Figure 5

Case	n_{module} [-]	W_{pump} [kW]	p_{module} [bar]	c_{NaCl} [g L ⁻¹]	$N_{bi-layers}$ [-]	X_{Na2SO4} [mol m ⁻³]	r_p [nm]	R [%]	Q [LMH bar ⁻¹]
SD 1	33	19.02	3.78	0.473	2	-34.13	0.93	90.03	40.71
SD 2	22	41.20	6.97	0.014	6	-50.42	1.11	97.57	28.40
SD 3	23	117.33	14.22	0.041	2	-72.30	0.41	99.50	12.27
NF270	-	-	-	-	-	-	-	99.08	10.1

Finally, as shown in Figure 6, both process plant optimization frameworks are compared along with a process model of a single nanofiltration unit, including a commercially available FILMTEC™ NF 270 [50] membrane. A simultaneous membrane and process optimization (cf. Figure 6 Novel simultaneous design (SD)) achieves significantly

better results as compared to establishing an existing membrane only (cf. Figure 6 Conventional approach (CA)). The results show that the performance of the conventional approach is limited to the considered membranes and can thus be outperformed by other previously not considered membranes, e.g., the NF 270. Contrary, the simultaneous membrane and process optimization (cf. Figure 6 Novel simultaneous design (SD)) expands the possible solution domain and immediately achieves favorable results. This is not possible compared to establishing an existing membrane only (cf. Figure 6 Conventional approach (CA)) in conventional piloting since many optimal solutions may stay hidden when only relying on known membrane systems. The laboratory-based LbL nanofiltration membranes show comparable results to the commercially available FILMTEC™ NF 270 [50] membrane. A customized adjustment of the membranes for the specific processes with ANNs enlarges the solution space and hence should be considered in future process plant optimization. In addition, the accuracy of the optimization is strongly influenced by the quality of the available data. Therefore, new synthesis protocols may be used as a guideline on how to fabricate the next generation of membranes. This still needs to be verified in laboratory experiments.

Although this cost estimation by the Verberne cost model [40] provides a valid economic basis, reliable information on the pricing of the individual costs and depreciation periods remains a challenge. A comparison with alternative treatment plants is given in the supplementary material. Here, the annual operation cost and the investment cost of this LbL nanofiltration plant are compared to similar water treatment processes (brackish water reverse osmosis (BWRO), ion exchange, and ultrafiltration plants). Reasonable pricing as compared to these processes is estimated. However, this is a qualitative estimation, since the assumed cost parameters of the model are strongly dependent on the technology, the process, and the location of the plant. In total, 50 optimization problems were solved to obtain the illustrated approximation of the Pareto front. Each optimization problem has 5 degrees of freedom, 1 equality constraint, and 11 inequality constraints. The equations that describe the ANNs are formulated in a reduced-space formulation and are thus hidden from the branch-and-bound solver [21]. On average, the solution of one problem required 86 CPU seconds with a standard deviation of 269 CPU seconds. The total time of the optimization, including all 50 points is 71 min. The large standard deviation is mainly due to the long CPU time for computing the edges of the Pareto front. A list of all CPU times is provided in the electronic supplementary material.

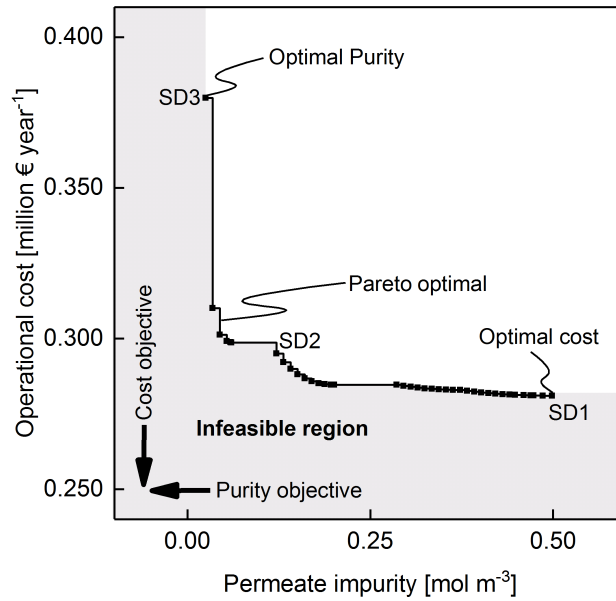


Figure 5. Novel simultaneous design of the process and membrane fabrication (SD): Pareto front of a process plant simultaneously optimized for the membrane itself in addition to the process. Results shown are for a process plant having a single nanofiltration unit. Optimization is performed for the two objectives (1) minimal annual operation costs and (2) minimal permeate concentration (i.e., permeate concentration).

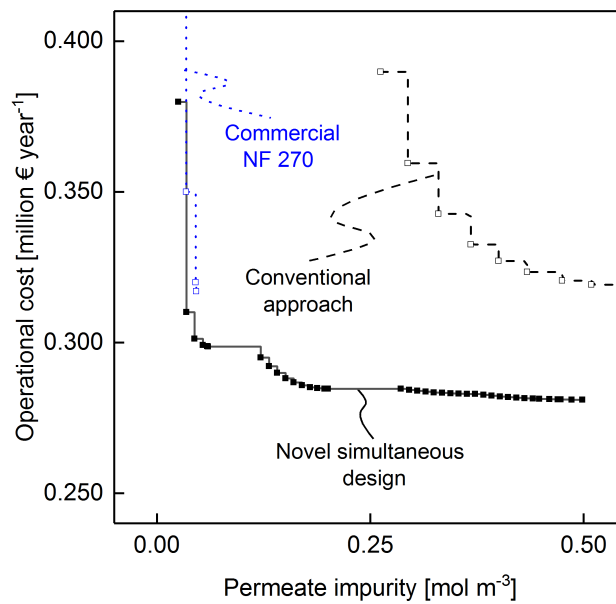


Figure 6. Comparison of development methodologies: (CA) Conventional process optimization with a selection of known membranes only versus (SD) simultaneous membrane and process optimization. (NF270) The results of this optimization framework are compared to a process model of a single nanofiltration unit with a commercially available FILMTEC™ NF 270 [50] membrane. Filled data points are Pareto efficient, and non-filled data points are dominated.

4. Conclusion

In practice, membrane separation plants are often designed by taking a known membrane and optimizing the process operating conditions for this membrane. This has one major disadvantage: The process optimization is limited by fixing the critical component of the plant. Therefore, synergies in development cannot be discovered.

We propose a novel method for the simultaneous membrane and process optimization. The retention and permeability of LbL nanofiltration membrane modules are linked in a hybrid data-driven/mechanistic model to the membranes' synthesis protocols. This integrated design framework provides membrane synthesis protocols tailored to the separation process. In contrast, the performance of the conventional approach is limited to the considered membranes and can thus be outperformed by other previously not considered membranes. The simultaneous membrane and process optimization expands the possible solution domain and immediately achieves favorable results.

This novel data-driven development methodology enables detailed investigations to find non-intuitive solutions of a membrane treatment plant. The ANN optimization framework can potentially improve the first membrane plant development phase (i.e., membrane pre-selection and piloting) and can make it more case-specific. Different membranes can be piloted to find optimal solutions immediately. This is not possible with conventional piloting since many optimal solutions may stay hidden/invisible when only relying on known membrane systems. Adapting this novel data-driven development approach will enable engineers and scientists of water treatment companies to find non-intuitive solutions of membrane treatment plant layouts and thereby improve piloting/plant projecting. Exploiting and expanding existing knowledge by surrogate-based design of experiments will potentially consolidate design knowledge beyond single (lead) engineers' knowledge to make future projecting more efficient.

In future work, this optimization framework should be extended to varying feed concentrations, enabling a comprehensive superstructure optimization including multiple process configurations of membrane modules. The transition to different membrane types and multiple salts can be made to transfer the presented methodology to water treatment applications.

This manuscript serves as a guideline how the methodology can be adapted by other groups to design membrane process plants and membrane materials in a simple fashion, using established software packages for ANN development together with a novel deterministic global optimization algorithm (MAiNGO). Thereby we enable detailed investigations and the development of complex materials systems, incomprehensible for classical analytical model descriptions so far.

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