Time-Optimal Control of Diafiltration Processes in the Presence of Membrane Fouling

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Abstract

This paper deals with time-optimal operation of batch diafiltration processes in the presence of membrane fouling. Fouling causes a decrease in membrane area and, hence, an increase in processing time. In this work we study a time-optimal operation with several fouling models available in literature. Pontryagin’s minimum principle is applied to characterize the structure of the optimal operation. Due to the specific structure of the problem, it is possible, in several problem setups, to derive and verify an explicit analytic solution. Obtained results are applied in case studies where we provide a comparison between traditional operation and the proposed time-optimal operation. In cases, where the optimal operation cannot be identified analytically, we analyze the performance of sub-optimal control derived from neighboring analytical solution and compare it to optimal operation found via numerical-optimization techniques.

Keywords: optimal control, membrane fouling, Pontryagin’s minimum

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1. Introduction

Diafiltration (DF) membrane processes separate solutes in a solution based on molecular size differences. Thus, membranes retain high molecular weight components and let low molecular weight components pass through. These processes have found a wide range of applications. In food industry it is used for fruit juice clarification [1]. In pharmaceutical industry the membrane separation processes are used for different aims like albumin production from human blood [2] and antibody preparation [3]. Biotechnological industries use membrane processes for enzyme concentration and the removal of impurities like peptides and salts [4]. Diafiltration membrane processes use a solute-free solvent (e.g. water) to control the membrane process and to influence concentrations of solutes.

One of main issues in membrane separation is membrane fouling. It decreases effective membrane area due to the deposit of the solutes in or on the membrane pores. Moreover, the fouled membrane needs to be cleaned or replaced [5]. This results in an increase of the processing time to reach the desired purification and in an increase of processing and operational costs. For this reason modeling of the fouling behavior has gained importance. The pioneering work of [6] presented a unified fouling model describing this behavior from which four standard fouling models can be derived and are expressed in terms of decrease in effective membrane area [7] or the permeate flux [8]. Recently, [9] showed that numerical optimization techniques can be employed to predict types of the fouling mechanism using experimental data.
Optimal operation of diafiltration processes has attracted a lot of attention. [10] derived conditions of optimal switching concentration for a simple membrane process. [11] proposed to optimize switching times between the traditional control modes. Procedures based on numerical optimization have been investigated in [12, 13]. In our previous works [14, 15] we have provided a fully analytical solution for optimal membrane operation without fouling.

The aim of this paper is to study the time-optimal operation of a diafiltration process in the presence of membrane fouling. Preliminary results have been published in [16] and in [17]. Pontryagin’s minimum principle is applied to deduce the structure of the optimal solution. We assume an explicit dependency of permeate flux on processing time as proposed by [8]. The main novelty of this paper is the complete characterization of the time-optimal operation of a diafiltration process in the presence of membrane fouling with no restriction to the specific form of a fouling model or mechanism as we only assume the functional dependency of fouling on the operation time. The resulting optimal operation derived in this paper is given by simple rules and avoids any on-line optimization.

The paper is organized as follows. In the next section, the process description and modeling are presented. In section 3 detailed analysis of membrane fouling and modeling of fouling behavior is described. Section 4.1 defines the overall optimization problem. Section 4.2 forms the main theoretical contribution of the paper. Optimal operation of diafiltration processes in the presence of membrane fouling is derived. Finally, simulation studies are provided in Section 5 to discuss and analyze the proposed solution.
2. Process Description and Modeling

We study a generalized batch diafiltration process shown in Fig. 1. The process operates under constant pressure and temperature. The batch diafiltration process consists of a feed tank and a membrane. The process solution containing a solvent and two solutes (macro and micro-solutes) is brought from the feed tank to the membrane. The stream which is rejected by the membrane (retentate) is taken back into the feed tank. The permeate stream leaves the system at a given flow-rate \( q = AJ \), where \( A \) represents the membrane area and \( J \) is the permeate flux subjected to unit membrane area. The permeate stream is often a function of both concentrations. In addition, it also decreases in time if fouling occurs.

Process control is achieved by adjusting the flow-rate of the solute-free solvent (diluant) into the feed tank. The control variable is denoted by \( \alpha \) and it is defined as a ratio between the inflow of the diluant and the permeate flow-rate \( q \). There are several commonly used control modes such as concentration
mode (C) with $\alpha = 0$, constant-volume diafiltration (CVD) with $\alpha = 1$, and dilution (D) where $\alpha = \infty$. The dilution mode is characterized by a certain amount of diluant added instantaneously into the feed tank. Traditional operation strategies used in the industry then consist of sequences of the individual control modes (e.g. C-CVD).

Mass balances can be used to obtain the process model. The balance of each solute can be written as [18]

$$\frac{dc_i}{dt} = \frac{c_i q}{V} (R_i - \alpha), \quad c_i(0) = c_{i,0}, \quad i = 1, 2,$$

where $V$ is the retentate volume at time $t$ and $i = 1, 2$ denotes the macro-solute and micro-solute, respectively. $R_i$ is the so-called rejection coefficient. The rejection coefficient is a dimensionless number between 0 and 1 that measures the ability of the membrane to retain the $i$th species. It is defined as

$$R_i = 1 - \frac{c_{p,i}}{c_i},$$

where $c_{p,i}$ stands for the concentration of the $i$th species in the permeate.

The total mass balance can be written as

$$\frac{dV}{dt} = u - q = (\alpha - 1)AJ, \quad V(0) = V_0,$$

with $V_0$ being the initial volume of the processed solution.

2.1. Modeling with Perfect Macro-solute Rejection

Rejection coefficients $R_i$ can be functions of both concentrations. The special, yet industrially relevant case assumes that $R_1 = 1$ and $R_2 = R_2(c_1, c_2)$. This means that the membrane is absolutely impermeable for the macro-solute and permeability of micro-solute is a function of both concentrations.
Therefore, the macro-solute will be completely rejected by the membrane and concentrated in the feed tank.

As the rejection of the macro-solute is perfect, its total mass in the system is constant. Thus, \( c_1(t)V(t) = c_{1,0}V_0 \) and the differential equation (3) can be omitted. The model is then of the form

\[
\frac{dc_1}{dt} = c_1^2 \frac{AJ}{c_{1,0}V_0} (1 - \alpha), \quad c_1(0) = c_{1,0}, \quad (4)
\]

\[
\frac{dc_2}{dt} = c_1c_2 \frac{AJ}{c_{1,0}V_0} (R_2 - \alpha), \quad c_2(0) = c_{2,0}. \quad (5)
\]

3. Membrane Fouling

Membrane fouling belongs to one of the main obstacles in the membrane separation processes. The main cause of the membrane fouling is the decrease of the effective membrane area due to the deposit of the solutes in/on the membrane pores. The membrane fouling depends on several properties such as feed properties, membrane material, temperature, and pressure. As the result of the decrease of the membrane area the permeate flow decreases as well. As the consequence to membrane fouling and the decrease of the permeate flow the overall processing time increases. Moreover, once the membrane becomes significantly fouled cleaning has to be performed. Also if the cleaning is insufficient the membrane has to be replaced. This all leads to an increase of operational costs.

Modeling of fouling became highly important in the past years. In [6] a unified fouling model for dead-end filtration systems was derived in terms of total permeate flux and time and reads as

\[
\frac{d^2t}{dV_p^2} = K \left( \frac{dt}{dV_p} \right)^n, \quad (6)
\]
where \( V_p \) represents the permeate volume, \( t \) is time, and \( K \) is the fouling rate constant. Four classical fouling models are characterized by different values of \( n \). We recognize cake (\( n = 0 \)), intermediate (\( n = 1 \)), standard (internal) (\( n = 3/2 \)), and complete fouling (\( n = 2 \)) model. The corresponding differential equation for permeate flux can then be derived as [7, 8]

\[
\frac{dJ}{dt} = -KA^{2-n}J^{3-n}.
\]  

If \( n, K, A \) are considered constant, this differential equation can be solved to give an explicit solution \( J(t, n, K, A, J_0) \) where \( J_0 \) represents initial flux at time \( t = 0 \).

To apply this model to cross-flow systems considered in this study, we propose to substitute the initial flux \( J_0(t = 0) \) by the unfouled flux \( J_0(c_1, c_2) \) that depends on actual concentrations. This change will make possible to unify procedures and results for systems with and without fouling.

Fig. 2 shows graphical representation of the individual fouling mechanisms. These models differ in the way the molecules deposit in/on the membrane.

3.1. Complete Pore Blocking Model

Complete pore blocking model considers that solutes which are brought to the membrane surface will seal the membrane pores (Fig. 2(a)). Flow through such pores is no longer possible. The molecules which deposit on the membrane surface are larger then the membrane pores. The model can be derived from (6) after setting the parameter \( n \) equal to 2. The model is expressed in terms of permeate flux versus time and is of the form

\[
\ln J = \ln J_0 - K_c t,
\]  

7
where $J$ is the permeate flux in m/s, $J_0$ is the permeate flux of unfouled membrane and $K_c$ represents the fouling rate constant in 1/s.

### 3.2. Intermediate Blocking Model

The intermediate pore blocking model again assumes that all solutes brought to the membrane surface will block the membrane pores. However, in this case the solutes can deposit on each others as illustrated in Fig. 2(d). The parameter $n$ is equal to 1 and the permeate flux is of the form

$$\frac{1}{J} = \frac{1}{J_0} + K_i t,$$

with $K_i$ being the fouling rate constant in 1/m.

### 3.3. Cake Filtration Model

The fouling according to this model is caused by deposition of solutes on the surface of membrane. The process repeats itself, that is with each cycle the solutes keep depositing over the previously deposited solutes and this results in forming of a multi-layered cake of solutes, as it is shown in
Fig. 2(c). The parameter \( n \) in this case is equal to 0 and the permeate flux is of the form

\[
\frac{1}{J^2} = \frac{1}{J_0^2} + K_g t,
\]

where \( K_g \) is the fouling constant with the following unit in \( \text{s/m}^2 \).

### 3.4. Internal Blocking Model

On the contrary to previous fouling models discussed, this model defines fouling internally. The model describes that the solutes instead of depositing on the surface of the membrane, are small enough to clog the pores of the membrane. The phenomenon results in the reduction of pore diameter and hence decrease of the permeate flux. The parameter \( n \) is equal to 3/2 and the flux is of the form

\[
\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + K_s t
\]

where \( K_s \) is the fouling rate constant in \( 1/\text{m}^{1/2}/\text{s}^{1/2} \).

### 4. Optimal Operation

#### 4.1. Problem Definition

The optimization goal is to find such time-dependent function \( \alpha(t) \) which guarantees the transition from given initial to final concentrations in minimum time. We assume that the membrane is absolutely impermeable to macro-solute \( (R_1 = 1) \), the permeability of micro-solute changes as a function of concentrations, and is expressed using rejection coefficient \( R_2 = R_2(c_1, c_2) \). Finally, we assume that the unfouled flux is a known function of both concentrations \( J_0(c_1, c_2) \) and the fouling model of the flux \( J \) is given. The opti-
The optimization problem then reads as:

\[ J^* = \min_{\alpha(t)} \int_0^{t_f} 1 \, dt, \]  
\[ \text{s.t.} \]

\[ \dot{c}_1 = c_1^2 \frac{AJ}{c_{1,0}V_0}(1 - \alpha), \quad c_1(0) = c_{1,0}, \]  
\[ \dot{c}_2 = c_1c_2 \frac{AJ}{c_{1,0}V_0}(R_2 - \alpha), \quad c_2(0) = c_{2,0}, \]

\[ c_1(t_f) = c_{1,f}, \]  
\[ c_2(t_f) = c_{2,f}, \]

\[ J = J(t, J_0(c_1, c_2), K, n), \]  
\[ \alpha \in [0, \infty). \]

We note that the optimization problem for a generalized diafiltration setup \((R_1 = R_1(c_1, c_2))\) possesses a similar structure where the equations (12b) and (12c) are replaced with (1) for \(i = 1, 2\) and (3).

### 4.2. Characterization of the Optimal Operation

We use Pontryagin’s minimum principle (PMP) [19, 20, 21] to identify the candidates for optimal control of problem (12). A care has to be taken as the process model depends explicitly on time, thus the problem is non-autonomous. There are two possible approaches to handle optimal control of non-autonomous systems. The first approach considers time explicitly in the process model. Then, the optimal Hamiltonian function is zero only at final time. Therefore, there are two variables (concentrations) and PMP has to supply two equations for optimality. The second approach adds an additional state variable \(\dot{x}_a = 1\) with initial condition \(x_a(0) = 0\) and replaces
t with \( x_a \). Therefore, the new problem is autonomous with increased number of variables. In this case, Hamiltonian function is zero along the optimal trajectory and this fact can be used to provide additional conditions for finding an optimal solution.

Our derivation will use the first approach. Let us define the state vector \( \mathbf{x} = (c_1, c_2)^T \) and rewrite the process differential equations as affine functions of control \( \alpha \)

\[
\dot{\mathbf{x}} = \mathbf{f}(t, \mathbf{x}) + \mathbf{g}(t, \mathbf{x})\alpha, \tag{13}
\]

The Hamiltonian function can then be constructed as

\[
H(t, \mathbf{x}, \lambda, \alpha) = 1 + \mathbf{f}^T(t, \mathbf{x})\lambda + \mathbf{g}^T(t, \mathbf{x})\lambda\alpha = H_0(t, \mathbf{x}, \lambda) + H_\alpha(t, \mathbf{x}, \lambda)\alpha, \tag{14}
\]

where \( \lambda = (\lambda_1, \lambda_2)^T \) is the vector of adjoint variables defined from

\[
\dot{\lambda} = -\frac{\partial H}{\partial \mathbf{x}} = -(\mathbf{f}_x + \mathbf{g}_x\alpha)\lambda, \tag{15}
\]

where

\[
\mathbf{f}_x(t, \mathbf{x}) = \frac{\partial \mathbf{f}^T(t, \mathbf{x})}{\partial \mathbf{x}}, \quad \mathbf{g}_x(t, \mathbf{x}) = \frac{\partial \mathbf{g}^T(t, \mathbf{x})}{\partial \mathbf{x}}. \tag{16}
\]

Since the Hamiltonian is affine in \( \alpha \), its minimum is attained with \( \alpha \) on its boundaries as follows

\[
\alpha = \begin{cases} 
0 & \text{if } H_\alpha > 0, \\
\infty & \text{if } H_\alpha < 0.
\end{cases} \tag{17}
\]

If the Hamiltonian is singular in \( \alpha \), the singular case is characterized by equations \( H_\alpha = 0, \dot{H}_\alpha = 0 \). This gives a set of equations which are linear in adjoint variables

\[
H_\alpha(t, \mathbf{x}, \lambda) = \mathbf{g}^T\lambda = 0, \tag{18}
\]

\[
\dot{H}_\alpha(t, \mathbf{x}, \lambda) = \mathbf{h}^T\lambda = \left(\mathbf{g}_x\mathbf{f} - \mathbf{f}_x\mathbf{g} + \frac{\partial H_\alpha}{\partial t}\right)^T\lambda = 0. \tag{19}
\]
Elimination of $\lambda$ from (18) and (19) results in characterization of the singular surface:

$$S(t, c_1, c_2) = (R_2 - 1) \left( J + c_1 \frac{\partial J}{\partial c_1} + c_2 \frac{\partial J}{\partial c_2} \right) + J \left( c_1 \frac{\partial R_2}{\partial c_1} + c_2 \frac{\partial R_2}{\partial c_2} \right) = 0.$$

(20)

Note that the expression (20) is formally identical to the one without fouling, as derived in [14]. The only difference lies in the fact that $J$ (and thus $S$) is not only a function of concentrations but also of time. For example, an expression for the singular surface in case of $R_2 = 0$ and the intermediate blocking model boils down to

$$S(t, c_1, c_2) = J_0 + c_1 \frac{\partial J_0}{\partial c_1} + c_2 \frac{\partial J_0}{\partial c_2} + K_i J_0^2 t = 0.$$

(21)

The above relation clearly shows the shift in the optimal operation with fouling ($K_i \neq 0$) and without fouling ($K_i = 0$).

To obtain the control which keeps the states on the singular surface, we differentiate the singular surface (20) w.r.t. to time. The obtained singular control is:

$$\alpha(t, c_1, c_2) = \frac{\partial S}{\partial c_1} c_1 + \frac{\partial S}{\partial c_2} c_2 + \frac{\partial S}{\partial t} + c_1 J A \frac{c_1}{c_0 V_0} \left( \frac{\partial S}{\partial c_1} c_1 + \frac{\partial S}{\partial c_2} c_2 \right).$$

(22)

This can be again formally separated into two parts: the first one corresponding to the unfouled singular control and the second one handling the influence of fouling on the optimal operation.

Following the analysis of the unfouled case derived in [14], the optimal operation consists of the following three steps:
1. In the first step we use either concentration mode or pure dilution mode (see equation (17)) until the condition \( S(t, c_1, c_2) = 0 \) is met. The appropriate mode choice depends on initial conditions.

2. During the second step we stay on singular surface where the singular control (22) is used.

3. The last step is again the operation with either concentration mode or pure dilution until the final conditions for concentrations are met.

Note that any step can be missing from the optimal operation. This depends solely on the initial and final conditions. For instance, if there does not exist any three-step strategy fulfilling the final conditions, the middle step is skipped, and the optimal control is saturated on constraints.

5. Case Studies

We will discuss three case studies where we consider that the fouling is described by intermediate pore blocking model described by equation (9). We will compare the proposed control strategy with the traditional control strategy (C-CVD).

5.1. Case Study 1

In this case study we use a classical setup of the separation of two solutes by diafiltration with constant rejection coefficients. The permeate flux is the simplest possible derivative of mass-transfer theory (Fick’s law) and is of the form

\[ J_0(c_1) = k \ln \frac{c_{\lim}}{c_1}, \]

(23)
where \( c_{\text{lim}} \) is the limiting concentration of the product and \( k \) is the mass transfer coefficient.

The goal is to drive the concentrations from the initial point \([c_{1,0}, c_{2,0}] = [3.3 \text{ g/dL}, 5.5 \text{ g/dL}]\) to the final point \([c_{1,f}, c_{2,f}] = [9.04 \text{ g/dL}, 0.64 \text{ g/dL}]\) for 100 dL of solution and for the employed membrane area of 1 m\(^2\). The limiting concentration of the product is 56 g/dL and the mass transfer coefficient is \( k = 12.439 \text{ m/h} \). The singular surface can be derived from (20) and is of the form

\[
S(t, c_1) = \left( \ln \frac{c_{\text{lim}}}{c_1} - 1 \right) + 2tkK_i \ln \frac{c_{\text{lim}}}{c_1} = 0.
\] (24)

If we differentiate the singular surface with respect to time we obtain the singular surface

\[
\alpha(t, c_1) = 1 + \frac{K_i c_{10} V_0 (K_i J_0 t + 1) \left( \ln \left( \frac{c_{\text{lim}}}{c_1} \right) (K_i J_0 t + 1) - 2 \right)}{A c_1 (K_i t (2k + J_0) + 1)},
\] (25)

where \( V_0 \) stands for the initial volume. We can observe that besides concentrations, singular surface and control also depend on fouling rate and time. Note that when no fouling is present, the optimal operation boils down to the classical result that the CVD step should be commenced when \( c_1 = c_{\text{lim}} / e \).

Using the presented theoretical results and knowledge on initial and final conditions, the time-optimal operation in the presence of fouling comprises a sequence of following three steps:

1. The first step is the concentration mode \( \alpha = 0 \) till the singular surface (24) is reached.
2. Then, in the second step, the states reside on the singular surface with
Table 1: Time-optimal operation compared to traditional operation for different fouling rates.

<table>
<thead>
<tr>
<th>$K_i [10^{-3} \text{ m}^{-1}]$</th>
<th>minimum time $t_f$ [h]</th>
<th>C-CVD $t_f$ [h]</th>
<th>$\Delta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.01</td>
<td>5.61</td>
<td>11.97</td>
</tr>
<tr>
<td>10</td>
<td>7.68</td>
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</tr>
<tr>
<td>20</td>
<td>12.44</td>
<td>28.37</td>
<td>128.05</td>
</tr>
<tr>
<td>30</td>
<td>21.67</td>
<td>78.02</td>
<td>260.04</td>
</tr>
</tbody>
</table>

the singular control (25). This step is performed until the condition $c_1(t)/c_2(t) = c_{1,f}/c_{2,f}$ is satisfied.

3. In the last step we perform pure dilution mode with $\alpha = \infty$ until the final concentrations are reached.

Figure 3 depicts the optimal control strategy (states and control) for the minimum-time operation for different fouling rates. The control structure in all the cases is the three-step strategy described above. The circle in the state diagram represents the initial concentrations and the cross depicts the final ones. We can observe that the switching concentration to singular surface (24) changes with different fouling rates $K_i$. Furthermore we can observe that the increase of these values translates to longer processing time, as expected.

Table 1 presents a comparison of the final processing times in case of the proposed minimum-time operation and the traditionally used operation (C-CVD). The traditional mode of operation consists of two steps. It starts with the same concentration mode as the proposed approach. However, its second step is constant volume diafiltration ($\alpha = 1$) and it is switched on at
Figure 3: Comparison of different control strategies (top – state space, bottom – control profiles).
Clearly, as fouling pronounces, this diafiltration step is suboptimal causing overall increase of processing time. For the highest rate of fouling considered here, the savings in terms of processing time are almost threefold.

A care must be taken when applying this optimal operation on a real process. The traditional C-CVD operation and model (23) operate with concentration $c_1 < 10$ g/dL. The proposed optimal operation uses much higher concentrations of macro-solute up to 40 g/dL. Therefore, a new model has to be estimated that also covers this area. Such high concentration can cause strong polarization effects and necessity to move the operation in lower-concentration region. In that case, the singular surface would not be attained and constraint-based operation would be applied, as shown in [17].

5.2. Case Study 2

We study separation of lactose (with concentration $c_2$) from proteins (with concentration $c_1$). The separation problem was originally formulated in [22] and its optimal unfouled control was derived in [14]. The experimentally verified model for the permeate flux is given as

$$J_0(c_1, c_2) = b_0 + b_1 \ln c_1 + b_2 \ln c_2 = 63.42 - 12.439 \ln c_1 - 7.836 \ln c_2.$$  \hspace{1cm} (26)

The permeate flux model can be alternatively rewritten into the form

$$J_0(c_1, c_2) = -b_1 \left( \ln e^{-\frac{b_0}{c_1}} - \ln c_1 + \ln c_2 \right) = -b_1 \ln \frac{e^{-\frac{b_0}{c_1}} c_2}{c_1}.$$  \hspace{1cm} (27)

which resembles the expression for limiting flux. However, compared to the previous case study, in this case the limiting macro-solute concentration depends on the concentration of $c_2$. We will consider the same initial, final
concentrations, the membrane area, and the initial volume as in the previous case study.

The singular surface is of the following form

$$S(t, c_1, c_2) = b_0 + b_1(\ln c_1 + 1) + b_2(\ln c_2 + 1) + K_i t J_0^2 t = 0,$$  \hfill (28)

and singular control is as follows

$$\alpha(t, c_1, c_2) = \frac{b_1}{b_1 + b_2} + \frac{K_i c_1 0 V_0 (K_i J_0 t + 1) (2b_1 + 2b_2 + J_0 (K_i J_0 t + 1))}{K_i t A c_1 (b_1 + b_2) (2b_1 + 2b_2 - J_0 - 1)}.$$  \hfill (29)

Here we can easily distinguish the contribution of the fouling to the optimal operation of unfouled membrane system.

The time-optimal operation in the presence of membrane fouling consist of the same three steps as presented in the previous case study.

Figure 4 depicts the optimal control strategy (states and control) for the minimum-time operation for different fouling rates. Compared to the previous case study, the unfouled singular control mode is no longer the constant volume diafiltration but the variable volume diafiltration ($\alpha = 0.61$) that changes slightly with increasing fouling. As before, the macro-solute concentration that switches to singular mode increases with the fouling rate and the total processing time increases as well.

Table 2 presents a comparison of the final processing time in case of proposed minimum-time operation and the traditionally used operation (C-CVD). The differences in the duration of the respective operations get more significant as the fouling rate increases. For the highest rate of fouling considered here, the savings in terms of processing time are more than threefold.
Figure 4: Comparison of different control strategies (top – state space, bottom – control profiles).
Table 2: Time-optimal operation compared to traditional operation for different fouling rates.

<table>
<thead>
<tr>
<th>$K_i [10^{-3} \text{ m}^{-1}]$</th>
<th>minimum time $t_f$ [h]</th>
<th>C-CVD $t_f$ [h]</th>
<th>$\Delta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.49</td>
<td>4.74</td>
<td>5.57</td>
</tr>
<tr>
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<td>7.24</td>
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<tr>
<td>20</td>
<td>12.02</td>
<td>26.70</td>
<td>122.13</td>
</tr>
<tr>
<td>30</td>
<td>21.27</td>
<td>75.57</td>
<td>255.29</td>
</tr>
</tbody>
</table>

5.3. Case Study 3

The purpose of this study is to show the properties of the proposed approach if some of the assumptions are not satisfied. Namely, we will study a membrane separation process where the rejection of the macro-solute by the membrane is not complete, and varies according to the concentrations of both solutes. As it was pointed out in [15], analytical expressions of singular surface are no longer possible for such a case and the resulting optimal control problem needs to be solved numerically.

The process model is taken from [13] and deals with the separation of sucrose with concentration $c_1$ and sodium chloride with concentration $c_2$. This case of diafiltration presents both rejections, i.e. $R_1$ and $R_2$ as functions of component concentrations, and hence both vary with time during the separation. The empirical relations for $J_0$, $R_1$ and $R_2$ as functions of component
concentrations are as follows:

\[ J_0 = S_1 (c_2) e^{S_2(c_2)c_1}, \]  
(30a)

\[ R_1 = (z_1 c_2 + z_2)c_1 + (z_3 c_2 + z_4), \]  
(30b)

\[ R_2 = W_1 (c_2) e^{W_2(c_2)c_1}, \]  
(30c)

where \( S_1, S_2, W_1, W_2 \) are

\[ S_1 = s_1 c_2^2 + s_2 c_2 + s_3, \]  
(31a)

\[ S_2 = s_4 c_2^2 + s_5 c_2 + s_6, \]  
(31b)

\[ W_1 = w_1 c_2^2 + w_2 c_2 + w_3, \]  
(31c)

\[ W_2 = w_4 c_2^2 + w_5 c_2 + w_6, \]  
(31d)

and \( s_{1-6}, z_{1-4} \) and \( w_{1-6} \) are experimentally evaluated coefficients from [13].

The intermediate fouling model is considered with values of \( K_i \) up to 5 m\(^{-1}\). The maximum value of \( \alpha \) is constrained by 1.

Numerical method of orthogonal collocations [23] with 3–7 time intervals, 5 collocation points on states and 3 collocation points on control was applied to find the optimal separation strategy. Differences in final processing times between 3 and 7 time intervals were not significant.

Fig. 5 depicts the optimal trajectory of concentration of sucrose and sodium chloride to drive from initial states (green circle) to final states (red cross). The figure compares optimal trajectories of sucrose and sodium chloride for both analytical and numerical control approaches with maximum membrane fouling studied (\( K_i = 5 \)). The state trajectory consists of three steps, i.e. concentration mode, diafiltration with time-varying profile of \( \alpha \), and constant volume diafiltration mode. Thus, the control variable \( \alpha \) is equal
Figure 5: Comparison of different control strategies (top – state space, bottom – control profiles).
to 0 in the first step to increase the concentration of both product and impurity. In the second part the control varies in a mid range, and that highly contributes to the concentration increase in our product. The final step is constant volume diafiltration mode with $\alpha = 1$ and directly translates to reduction in impurity to achieve the final product and impurity concentration. The optimal control trajectory obtained numerically shows some typical oscillations in singular mode due to a low sensitivity of the cost function to this part of the control trajectory. In fact, the second step could be replaced, for practical purposes, with a constant $\alpha$ (variable volume diafiltration mode) without a major change in the duration of the operation.

Simulations with other values of the fouling parameter $K_i$ showed the same behavior. Even if assumptions for the proposed method are not valid, the resulting state and control trajectories are almost optimal and the final processing times practically the same as those with numerical optimization. This is due to the fact that the rejection coefficient is close to 1 for the entire operation. Note that the analytical approach is not able to reach final concentrations perfectly due to mismatch between assumed ($R_1 = 1$) and real rejection of the macro-solute, but the differences are negligible (less than $1\%_{\infty}$).

6. Conclusions

In this paper we studied the time-optimal control of a batch diafiltration process in the presence of fouling. The fouling behavior was described by the reduction of the permeate flux caused by the deposit of the solutes on the membrane. Using Pontryagin’s minimum principle we derived candidates
for optimal control. The derived optimal operation is completely analytic, and consists of three steps with singular control being the second one. The developed theory was applied on three case studies. The first two of them with different membrane models showed possible improvements over existing membrane operations. The last case study demonstrated that the proposed approach can also be applied if varying solute rejections are considered with only slight suboptimality loss compared to time-optimal operation. The obtained results indicate that by using advanced control strategy we can reduce the production costs compared to traditionally used membrane operations and avoid any numerical optimization. Thus, the proposed method can be applied to existing plants and hardware.

**List of Symbols**

- $A$ membrane area (m$^2$)
- $c_1$ concentration of macro-solute — product (mol/m$^3$)
- $c_2$ concentration of the first micro-solute — impurity (mol/m$^3$)
- $H$ Hamiltonian function
- $J$ permeate flux (m/h)
- $J_0$ permeate flux of unfouled membrane (m/s)
- $k$ mass transfer coefficient (m/h)
- $K_g$ cake-layer formation constant (s/m$^2$)
- $K_i$ intermediate fouling constant (1/s)
- $K_s$ standard (internal) fouling constant (1/m$^{1/2}$/s$^{1/2}$)
- $K_c$ complete fouling constant (1/s)
- $q$ permeate flow (m$^3$/h)
operation time (h)

$t_f$  processing time (h)

$V$  volume in feed tank ($m^3$)

$R$  rejection coefficient

$S$  singular surface

Greek symbols

$\alpha$  proportionality factor of diluant flow to permeate flow

$\lambda_i$  $i$th adjoint variable

Subscripts

0  initial

f  final

Abbreviations

C  concentration (mode)

CVD  constant-volume diafiltration

D  dilution (mode)

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