

MATHEMATICAL MODELING OF DIAFILTRATION

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The main objective of this study is to provide a general mathematical model in a compact form for batch diafiltration techniques. The presented mathematical framework gives a rich representation of diafiltration processes due to the employment of concentration-dependent solute rejections. It unifies the existing models for constant-volume dilution mode, variable-volume dilution mode, and concentration mode operations. The use of such a mathematical framework allows the optimization of the overall diafiltration process. The provided methodology is particularly applicable for decision makers to choose an appropriate diafiltration technique for the given separation design problem.

Keywords: membrane separations, diafiltration, mathematical modeling, optimization

Introduction

The objective of industrial purification processes is usually dual: (1) to separate certain solutes from the process liquor and (2) to concentrate the purified solution in order to obtain a final product. In this work we examine a batch diafiltration process that is designed to fulfill these objectives simultaneously.

In the following we consider a binary aqueous solution consisting of two solutes, namely a macrosolute and a microsolute. Diafiltration is known as a conventional process technique to achieve high purification of macrosolutes with an economically acceptable flux [1]. The requirement for an effective separation is the utilization of a membrane which has a high rejection for the macrosolute and a low rejection for the microsolute. The terms *macrosolute* and *microsolute* are widely-used in the literature dealing with membrane diafiltration. In order to eliminate ambiguity, we would like to point out, that the separation is not necessarily based on solely size exclusion as it might be suggested by this nomenclature. Membrane filtration also allows separation of solutes of similar molecular weights but having different charges as reported in many studies, for example in [2, 3].

There have been many published works on batch diafiltration. However, there is no exact and uniform definition for the term *diafiltration*. Indeed, the terminology currently being used is somewhat conflicting. In this paper, we use the term *diafiltration* in its broad sense referring to the actual technological goal. Thus, *diafiltration* is a membrane-assisted process that can be used to achieve the twin-objectives of concentrating a solution of a macrosolute, and removing a microsolute

by the utilization of a diluant. In this context, batch *diafiltration* is a complex process that may involve a sequence of consecutive operational steps. We consider three frequently used operational modes. These are the *concentration mode* (C), the *constant-volume dilution mode* (CVD), and the *variable-volume dilution mode* (VVD). They differ from each other in the utilization of wash-water as it is discussed in more details later in this paper. Note that an operation mode does operate with fixed operational settings. A *diafiltration* process, in contrast, is usually constructed by changing the settings of wash-water addition (i.e. switching to another operational mode) according to a pre-defined schedule. In the following, we examine two frequently used diafiltration techniques: the *traditional diafiltration* (TD) and the *pre-concentration combined with variable-volume dilution* (PVVD).

The most commonly used concept of diafiltration is the TD process that involves three consecutive steps (i.e. operational modes). First, a pre-concentration is used to reduce the fluid volume and remove some of the microsolute. Then, a constant-volume dilution step is employed to “wash out” the micro-solute by adding a washing solution (e.g. diluant) into the system at a rate equal to the permeate flow rate. Thus, the volume of the solution in the feed tank is kept constant during this operational mode. Finally, a post-concentration is used to obtain the final volume and concentrate the macrosolute to the final concentration due to the specific technological demands.

The VVD is an operation mode in which fresh water is continuously added to the feed tank at a rate that is proportional but less than the permeate flow. This causes a simultaneous concentration of macrosolute and removal

of microsolite. This operation has been proposed by Jaffrin and Charrier [4], analyzed in some detail by Tekić et. al and Krstić et. al [5, 6], and recently revised by Foley [7]. A modification of VVD is PVVD, i.e., a two step process in which the solution is first pre-concentrated to an intermediate macrosolute concentration and then subjected to VVD to reach the final desired concentrations of both solutes. This concept is credited to Foley [8].

Several studies have examined the different types of diafiltration techniques in terms of process time and wash-water requirement [1, 4-11]. However, only a few works have considered concentration-dependent rejections in the optimization procedure [12]. Assuming constant rejections might lead to inaccurate simulation and subsequent optimization results under conditions where the rejections of solutes are strongly vary depending on their feed concentrations and a considerably interdependence in their permeation occurs.

In this work, we attempt to enlarge our perspective on how engineers in general should cope with the complexity of a diafiltration design problem. We present a general mathematical model in a compact form for batch diafiltration techniques. From this perspective we discuss the model limitations when simplifying assumptions on solute rejections are being used. We consider a common separation objective and through a specific example we demonstrate the power of the presented modeling methodology. Finally, we present some specific ideas of how optimization should support decision makers in finding the best wash-water utilizing profile for the given engineering design problem.

Theory

Configuration of diafiltration

The schematic representation of membrane diafiltration setting is shown in Fig. 1.

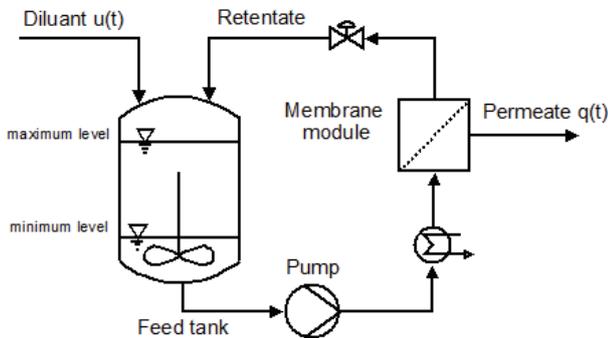


Figure 1: Schematic representation of diafiltration settings

In a batch operation, the retentate stream is recirculated to the feed tank, and the permeate stream $q(t)$ is collected separately. During the operation, fresh solute-free diluant stream $u(t)$ (i.e. wash-water) can be added into the feed tank to replace solvent losses.

General mathematical framework

In this section we derive the governing differential equations for diafiltration. The proportionality factor $\alpha(t)$ is defined as the ratio of diluant flow $u(t)$ to permeate flow $q(t)$:

$$\alpha(t) = \frac{u(t)}{q(t)} \quad (1)$$

where the diluant flow $u(t)$ is given as a product of the membrane area A and the permeate flux $J(t)$. The change in the volume in the permeate tank V_p is given by the permeate volumetric flow-rate q :

$$\frac{dV_p(t)}{dt} = q(t) \quad (2)$$

The change in the feed volume during the operation is given as

$$\frac{dV_f(t)}{dt} = u(t) - q(t) \quad (3)$$

Considering two solutes and assuming that the diluant consists of no solutes, the mass balance for the solute concentrations yields

$$\frac{d}{dt} V_f(t) c_{f,i}(t) = -q(t) c_{p,i}(t) \quad i=1, 2 \quad (4)$$

where $c_{p,i}(t)$ denotes the permeate concentration of solute i at time t . Equation (4) can be rewritten in the following way:

$$\frac{dV_f(t)}{dt} c_{f,i}(t) + V_f(t) \frac{dc_{f,i}(t)}{dt} = -q(t) c_{p,i}(t) \quad i=1, 2$$

Using Eq.(3) and recalling that $c_{p,i}(t) = c_{f,i}(t)(1-R_i(t))$, where $R_i(t)$ is the rejection of solute i at time t , we obtain, for $i = 1, 2, \dots$

$$V_f(t) \frac{dc_{f,i}(t)}{dt} = c_{f,i}(t) [q(t) R_i(t) - u(t)]$$

Thus, we have the following initial-value problems:

$$\begin{cases} \frac{dV_f}{dt} = u(t) - q(t) \\ V_f(0) = V_f^0 \end{cases} \quad (5)$$

and, for $i = 1, 2, \dots$

$$\begin{cases} V_f(t) \frac{dc_{f,i}(t)}{dt} = c_{f,i}(t) [q(t) R_i(t) - u(t)] \\ c_{f,i}(0) = c_{f,i}^0 \end{cases} \quad (6)$$

which describe the evolution in time of the volume in the feed tank V_f and of the feed concentration $c_{f,i}$. V_f^0 and $c_{f,i}^0$ denote respectively the initial feed volume and the initial feed concentration of the solute i .

In the next two sections, we briefly describe discuss the possible strategies to determine flux and rejection.

Later we formulate an optimization problem that represents a frequent industrial separation flask. Then, to examine and compare the TD and PVVD processes, we make a use of the filtration data from our earlier work [14].

Rejection and permeate flow

The separation behaviour of the membrane can be characterized in terms of permeate flux and solute rejections. The estimation of the flow $q(t)$ and of the rejection $R_i(t)$ can be carried out separately using the most convenient approach for the problem at hand. Possible strategies to determine flux and rejection are presented in our previous study [13]. In brief, either mechanism-driven or data-driven models can be employed. Mechanism-driven models are based on a physical understanding of the transport phenomenon. In contrast with that, data-driven models make a direct use of the experimental data obtained from filtration tests with the process liquor. The main challenges in employing a data-driven model are the minimization of necessary a-priori experiments and the conversion of raw data into useful information. In this study, we consider the following empirical relations which were reported earlier in [14]:

$$q = (s_1 c_{f,2}^2 + s_2 c_{f,2} + s_3) e^{(s_4 c_{f,2}^2 + s_5 c_{f,2} + s_6) c_{f,1}} \quad (7)$$

$$R_1 = (z_1 c_{f,2} + z_2) c_{f,1} + (z_3 c_{f,2} + z_4) \quad (8)$$

$$R_2 = (w_1 c_{f,2}^2 + w_2 c_{f,2} + w_3) e^{(w_4 c_{f,2}^2 + w_5 c_{f,2} + w_6) c_{f,1}} \quad (9)$$

where $s_1, \dots, s_6, z_1, \dots, z_4, w_1, \dots, w_6$ are suitable coefficients that were previously determined from laboratory experiments with the test solution as described later.

Special cases and analytical solutions

The complexity of the modelling problem originates from the fact that in most of the membrane filtration processes the solute rejections are concentration-dependent quantities. Since the concentrations are due to change while processing the feed, the rejections of both microsolite and macrosolute are affected by the extent to which the microsolite concentration is reduced and also to which the macrosolute is concentrated. Analogously, the permeate flux also depends on the actual feed concentration of both components. In general, the model equations require numerical techniques to solve them, since no closed form solutions exist. However, when the effect of the feed concentrations on the rejections is neglected, then a constant rejection coefficient σ can be introduced such that $R_i(t) = \sigma_i = \text{constant}$ for $i = 1, 2$. When introducing this simplifying assumption on the rejections, the differential equations

can be reduced to simple algebraic equations, The resulting exact solutions are reviewed below:

1. Concentration mode: Since no diluant is applied, $u(t) = 0$ and $c_{d,i} = 0$. The concentration of component i at the end of the operation is given by

$$(10)$$

where the expression $\frac{V_f(0)}{V_f(t_f)}$ is by definition the concentration factor n .

2. Constant-volume dilution mode: The solute free-diluant is continuously added to the feed tank in a rate equal to the permeate flow. Thus, $c_{d,i} = 0$ and $u(t) = q(t)$. The component concentration is related to the total volume of wash-water V_w can be written as

$$c_{f,i}(t_f) = c_{f,i}(0) e^{\frac{V_w(\sigma_i-1)}{V_f(t_f)}} \quad i = 1, 2, \dots \quad (11)$$

where the expression $\frac{V_w}{V_f(t_f)}$ is by definition the dilution factor D .

3. Variable-volume dilution mode: Solute-free wash-water is added at a rate $\alpha q(t)$, where α is a parameter with value $0 \leq \alpha \leq 1$. Assuming that the permeate flux remains unchanged during the process, Krstić et al. [6] gave the expression for the component balance:

$$c_{f,i}(t_f) = \frac{c_{f,i}(0)}{\left(1 - \frac{(1-\alpha)V_p(t_f)}{V_f(0)}\right)^{\frac{\sigma_i-\alpha}{1-\alpha}}} \quad i = 1, 2, \dots \quad (12)$$

Note, that the main pitfall of the commonly used modelling approaches is often the assumption of constant rejection coefficients. These simplifying assumptions can easily be misused when their appropriateness is not carefully checked for the given separation process. For instance, a typical rejection profile of an inorganic salt nanofiltration is illustrated in Fig. 2.

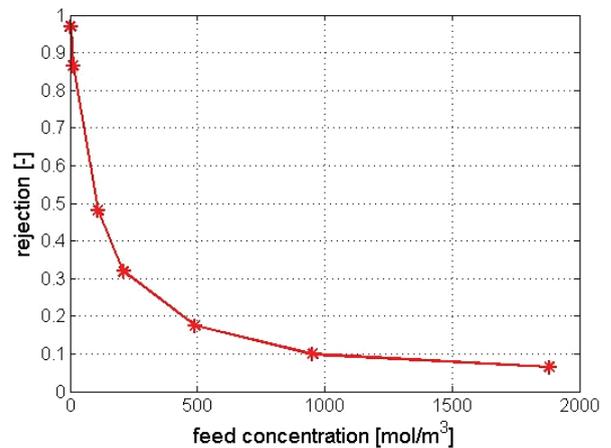


Figure 2: Rejection of the membrane Desal-DK5 for NaCl as a function of feed concentration (30 bar, 25 °C, 0.55 m² spiral-wound element, 1.0 m³h⁻¹ recirculation flow-rate). Solid line is for eye guidance

The complexity of the problem further increases in the presence of more than one solute, due to their interdependent permeation.

Optimization problem formulation

We define the optimization problem as follows:

$$\text{minimize } (J = c_{f,2}(t_f)) \quad (13)$$

such that

$$t_f \leq 6 \quad (14)$$

$$n = 3. \quad (15)$$

Thus, the objective of the separation is to reduce the concentration of component 2 in the final product as much as possible with the restriction that the total operation time should not exceed 6 hours and a total concentration factor 3 is achieved.

In the case of TD, the objective is to find the optimal set of variables of pre-concentration factor n_1 , dilution factor D , and post-concentration factor n_2 . In the case of PVVD, the optimal set of variables n_1 and α is to be determined.

Note that the numerical values of the constraints in Eqs. (14) and (15) are chosen according to the processing conditions and the specifications of our laboratory system. However, the concept itself can find a general interest. Industrial problems can be handled in an analogous way, when the optimal operational parameters of an existing membrane plant with a defined membrane area are to be found.

Experimental

In this study we use the filtration data from our earlier work [13]. These data serve as input for the mathematical analysis. The laboratory apparatus, applied chemicals, and sample analysis have been described in details earlier. In brief, nanofiltration experiments were carried out with the membrane Desal-DK5 separating a binary aqueous solution at constant temperature and pressure. The process liquor was a test system consisting of sucrose (hereafter called component 1) and sodium chloride (component 2). A limited number of a-priori experiments were used to determine the dependence of R and q on concentration. The resulting functions are reported in section "Rejection and permeate flow".

Results

The dynamics of a diafiltration process can be evaluated by simultaneous solving of Eqs. (5) and (6). Considering a TD process with a fixed pre-concentration factor n_1 , the post-concentration factor n_2 is readily given with the

use of the constraint on the total concentration factor as $n_2 = n/n_1$. It is evident that longer dilution results in lower final microsolute concentration. Thus, for each pre-concentration factor, a maximal dilution factor can be found so that the given constraint on the total operation time is still satisfied. For instance, when the initial solution is pre-concentrated with a factor 2, then a maximal operational time for CVD can be calculated so that the total operation time including the post-concentration step does not exceed the given 6 hours. This example is illustrated in Figs. 3a and 3b.

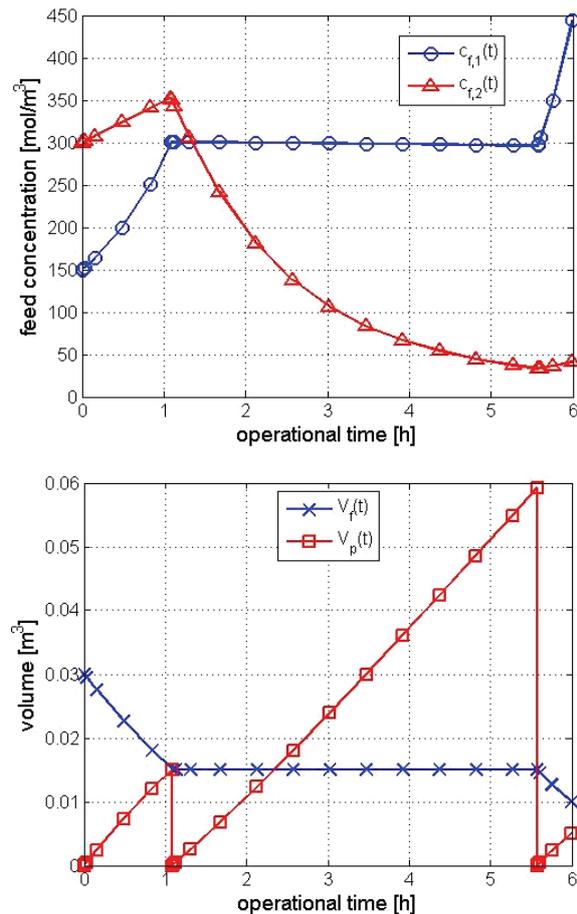


Figure 3: The estimated 6-hour time-course of the concentrations and the volumes of feed and permeate for a traditional diafiltration process with a pre-concentration-factor of 2

The optimization problem of PVVD is analogous to TD. Here, an optimal α has to be found for each fixed n_1 so that the objective function is minimized while satisfying the constraints. Fig. 4 shows the calculated values of α for fixed n_1 values. Obviously, when $n_1 = n$, α must be 1 in order to satisfy the constraint on n .

In both cases of TD and PVVD, the respective operation parameters of D and α for a fixed n_1 were found by applying iterative methods similar to as reported in [13]. The optimization results obtained by varying n_1 stepwise from 1 to n are illustrated in Figs. 5 and 6.

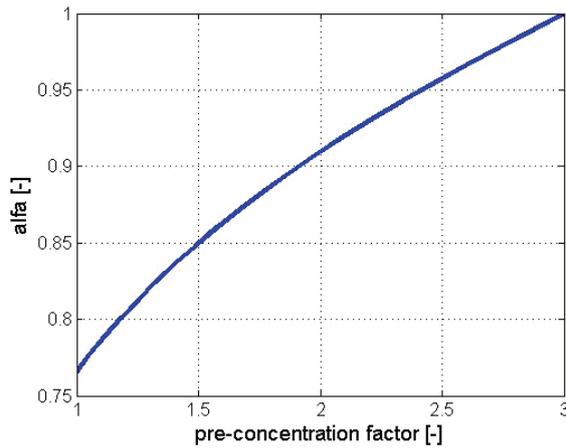


Figure 4: Optimized α values as a function of pre-concentration factor for the PVVD process

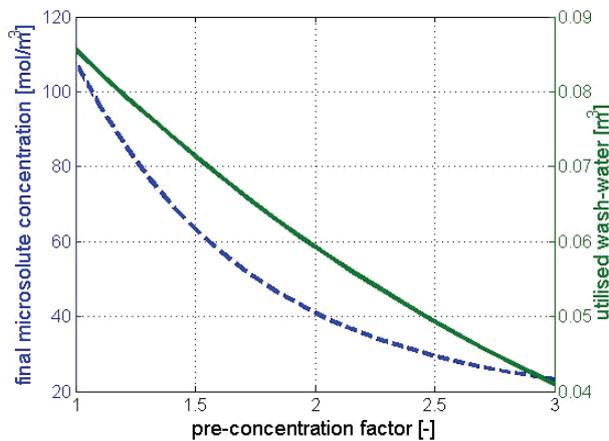


Figure 5: Optimization diagram for traditional diafiltration. Final microsolute concentration (dashed line) and required wash-water volume (continuous line) are plotted versus pre-concentration factor

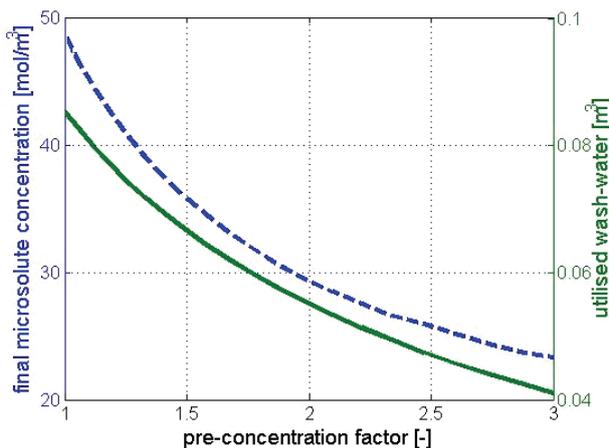


Figure 6: Optimization diagram for diafiltration involving pre-concentration combined variable-volume dilution. Final microsolute concentration (dashed line) and required wash-water volume (continuous line) are plotted versus pre-concentration factor

When comparing the TD and the PVVD processes, from the optimization diagrams shown in Figs. 5 and 6,

we can conclude that the best diafiltration strategy is a specific case when $n_1 = n$ and $\alpha = 1$. In other words, the optimal strategy is to pre-concentrate the process liquor to its minimum volume and then to apply a constant-volume dilution without a post-concentration step. We would like to draw attention to the fact that a great care is needed when interpreting and generalizing such finding. The here presented methodology for choosing an appropriate diafiltration technique is general in the sense that it can be readily adopted for different solute/membrane systems without the need of major changes in the provided procedure. However, the output of the optimization is unique for each application. The choice of TD versus PVVD depends primarily on

1. the response of the particular membrane to the specific solution that is expressed in terms of rejection R_i and permeate flow q ,
2. the terms involved in the objective function (i.e. the definition of the separation goal),
3. the involved constraints (technological demands) and their numerical values that need to be satisfied.

Any changes in these above listed specifications may modify the output of the optimization, and lead to a different optimal strategy of diafiltration.

Further optimization aspects

It should be pointed out that the main difference between the various types of operational modes is due to the quantity and the duration of the diluant stream introduced in the feed tank during the entire operation. In this context, diafiltration techniques differ in their strategies for controlling the introduction of the diluant stream $u(t)$. In the widely applied conventional diafiltration processes, such as TD or PVVD, the trajectory of the control variable $u(t)$ is arbitrarily pre-defined for the entire operational time. However, it may happen that the optimal time-dependent profile of the diluant flow is not among these arbitrarily constructed scenarios. The optimal control trajectory can be determined by formulating an optimization problem subject to process model described by differential equations. Using a dynamic optimization solver called *Dynopt* developed by Čížniar et. al [15], we are currently developing a unified technology for water utilization control that addresses generality versus special cases. This approach is currently under investigation and will be published soon.

Conclusions

We provide a methodology that is useful for the design of batch diafiltration processes. A general mathematical model in a compact form is presented. It unifies the existing models for constant-volume dilution mode, variable-volume dilution mode, and concentration mode operations. A rich representation of the separation process is given due to the employment of concentration-

dependent solute rejections in the design equations. Thus, a formal tool is provided for describing the engineering design that supports the disciplined use of data-driven and mechanism-driven permeation models. The use of such a mathematical framework allows the optimization of the overall diafiltration process. The provided methodology is particularly applicable for decision makers to choose an appropriate diafiltration technique for a given separation design problem. Further research effort is directed at the dynamic optimization of diafiltration processes.

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LIST OF SYMBOLS

A	– membrane area (m^2)
c	– concentration ($mol\ m^{-3}$)
D	– dilution factor
J	– permeate flux ($m\ h^{-1}$)
n	– concentration factor
q	– permeate flow-rate
R	– rejection
t	– operation time (h)
u	– diluant flow-rate ($m^3\ h^{-1}$)
x	– state variables ($mol\ m^{-3}$)
V	– volume

GREEK SYMBOLS

α	– proportionality factor of diluant flow to permeate flow
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SUBSCRIPTS

d	– diluant
f	– feed
i	– component ($i = 1$ macro-solute, and $i = 2$ micro-solute)
p	– permeate
w	– wash-water

ABBREVIATIONS

C	– concentration mode
CVD	– constant-volume dilution mode
VVD	– variable-volume dilution mode
PVVD	– diafiltration involving pre-concentration and variable-volume dilution mode
TD	– traditional diafiltration

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