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# Evaluation of variable volume diafiltration processes using the Logarithmic Integral

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**ABSTRACT**

The minimum process times for ultrafiltration with constant volume diafiltration (UFCVD) and ultrafiltration with variable volume diafiltration (UFVVD) are compared for limiting flux conditions. Using the series definition of the Logarithmic Integral, the optimum concentration to begin VVD is found by numerical solution of a non-linear algebraic equation. This equation is used to establish a criterion for UFVVD to be faster than UFCVD. Calculations indicate that this criterion is never satisfied and thus UFVVD can never be done more rapidly than UFCVD.

*Keywords*: Ultrafiltration; Constant volume diafiltration; Variable volume diafiltration; Modelling; Optimisation; Logarithmic Integral

## 1. Introduction

The processes of ultrafiltration and diafiltration can be used to concentrate a solution of a macrosolute such as a protein, and remove a microsolute such as a salt impurity. The standard way of achieving the objectives of macrosolute concentration and microsolute diafiltration has been to use batch ultrafiltration combined with constant volume diafiltration, a process denoted here as UFCVD [1]. The typical process involves concentrating the macrosolute to an intermediate concentration, $c_i$, diafiltering at constant volume and further concentrating to the final desired concentration.

The last few years has seen a number of alternative strategies proposed for ultrafiltration-diafiltration processes. Foremost of these have been processes based on variable volume diafiltration (VVD). In VVD, water is added continuously to the retentate tank at a rate that is less than the permeate flowrate. In its simplest form, the water flowrate is kept at a constant fraction, $\alpha$, of the permeate flowrate, where the appropriate value of $\alpha$ can be determined from component balances [2–4]. VVD allows one to perform ultrafiltration and diafiltration simultaneously without the need for switching between the two processes. While VVD is an elegant process, it has been shown to use substantially more water and take significantly longer than an optimally run UFCVD process [5]. Recently Foley has suggested that VVD can be improved by including a pre-concentration step, defining a new process named ultrafiltration with variable volume diafiltration or UFVVD [6]. Preliminary work suggested that this process could offer substantial advantages over UFCVD in terms of water usage but, based on very limited calculations, the minimum process time achievable with UFVVD appeared to be greater than the minimum achievable with UFCVD.

This study has two objectives. The first is to determine whether, for any given process specification, a UFVVD process can be devised that is faster than an optimally run UFCVD process. The analysis we present and the conclusions we reach will of course be valid only within the limitations of the assumptions we make regarding solute rejection coefficients and the relationship between flux and macrosolute concentration. The second objective is to show how the series solution of the Logarithmic Integral (which arises naturally in batch ultrafiltration problems) can be used to effect practical calculations without the need for large numbers of numerical integrations.

## 2. Model development

A schematic diagram of a generalised ultrafiltration-diafiltration process is shown in Fig. 1. We consider a process where a macrosolute is to be increased in concentration from $c_0$ to $c_f$ and a microsolute reduced in concentration from $c_{s0}$ to $c_{sf}$.

The macrosolute balance can be written

$$\frac{d(Vc)}{dt} = 0 \text{ with } c = c_0 \text{ @ } t = 0 \tag{1}$$

where $V$ is the retentate volume at time, $t$, and $c$ is the macrosolute concentration. The rejection coefficient of the macrosolute is assumed to be equal to 1.0, i.e., no macrosolute passes through the membrane. Throughout this paper, the permeate flowrate $Q_p$ is assumed to be given by the gel polarization model as [1]

$$Q_p = kA\ln\left(c_g / c\right) \tag{2}$$

where $k$ is the mass transfer coefficient, $A$ is the membrane area and $c_g$ is the gel concentration. The microsolute balance can be written

$$\frac{d(Vc_s)}{dt} = -Q_p c_s \text{ with } c_s = c_{s0} \text{ @ } t = 0 \tag{3}$$

where $c_s$ is the microsolute concentration and its rejection coefficient is assumed to be zero. The volume balance can be written

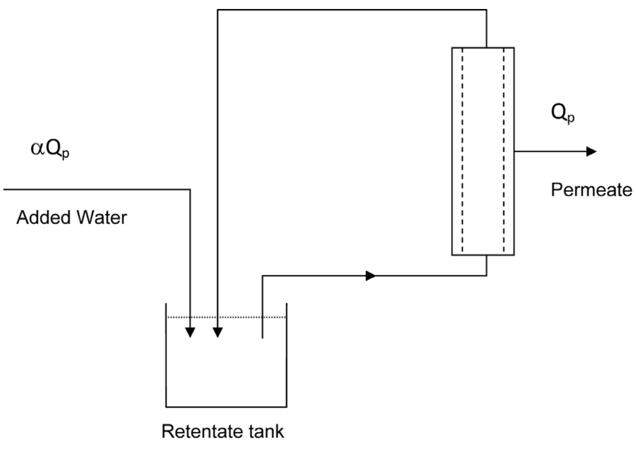


Fig. 1. Schematic representation of a generalised ultrafiltration diafiltration process.

$$\frac{dV}{dt} = (\alpha - 1)Q_p \text{ with } V = V_0 \text{ @ } t = 0 \tag{4}$$

UFCVD, VVD and UFVVD are all special cases of this generalised process and are defined in Table 1 and shown schematically in Fig. 2.

In Table 1, $c_i$ is the intermediate macrosolute concentration ($c_0 < c_i < c_f$) at which diafiltration is commenced. The equations for $\alpha$ in VVD and UFVVD are due to Jaffrin et al. [2] and Foley [6] respectively. Thus, UFCVD is a three step process composed of an initial macrosolute concentration step, in which the microsolute concentration remains constant, a constant volume diafiltration step in which the microsolute concentration is reduced while the macrosolute concentration remains constant, followed by a final macrosolute concentration step. UFVVD is a two-step process composed of an initial macrosolute concentration step followed by a variable volume diafiltration step during which the macrosolute concentration increases and the microsolute concentration decreases and both concentrations reach their required targets simultaneously.

### 2.1. Minimum process time for UFCVD

In the case of UFCVD, the process time is easily shown to be given by [1]

$$t_{ufcvd} = \frac{1}{kA}\int_{V_i}^{V_0} \frac{dV}{\ln\left(c_g / c\right)} + \frac{V_i \ln\left(c_{s0} / c_{sf}\right)}{kA\ln\left(c_g / c_i\right)} + \frac{1}{kA}\int_{V_f}^{V_i} \frac{dV}{\ln\left(c_g / c\right)} \tag{5}$$

Table 1
Definition of $\alpha$ for various ultrafiltration–diafiltration processes

| | |
|---|---|
| UFCVD: | IF $c \geq c_i$ and $c_s > c_{sf}$ THEN $\alpha = 1$ ELSE $\alpha = 0$ |
| VVD: | $\alpha = \ln\left(c_{s0} / c_{sf}\right) / \left[\ln\left(c_f / c_0\right) + \ln\left(c_{s0} / c_{sf}\right)\right]$ |
| UFVVD: | IF $c < c_i$ THEN $\alpha = 0$ ELSE $\alpha = \ln\left(c_{s0} / c_{sf}\right) / \left[\ln\left(c_f / c_i\right) + \ln\left(c_{s0} / c_{sf}\right)\right]$ |

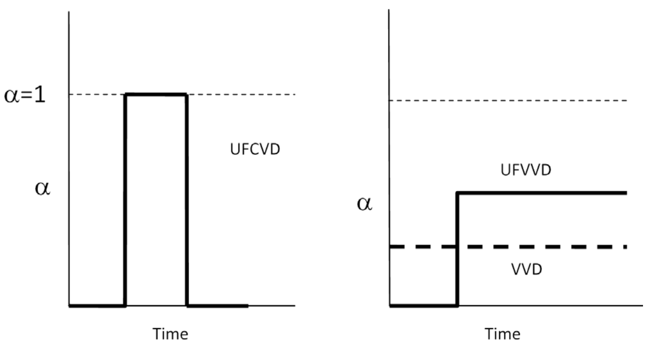


Fig. 2. Representation of UFCVD, VVD and UFVVD in terms of the α function.

where $V_f$ is the final retentate volume and $V_i$ is the retentate volume when diafiltration begins. The integral terms represent the ultrafiltration steps and the middle term represents the constant volume diafiltration step during which the flux is constant. If we recognize that Eq. (1) implies

$$c_0 V_0 = c_i V_i = c_f V_f \tag{6}$$

and define the dimensionless time by

$$t^*_{ucvd} = \frac{t_{ufcvd} kA}{V_0} \tag{7}$$

we can combine the two integral terms and ultimately rewrite Eq. (5) in the following more compact form:

$$t^*_{ufcvd} = \frac{c_0}{c_g}\int_{c_g/c_f}^{c_g/c_0} \frac{dx}{\ln x} + \frac{c_0 \ln\left(c_{s0}/c_{sf}\right)}{c_i \ln\left(c_g/c_i\right)} \tag{8}$$

where $x$ is defined here as $c_g/c$. Since the integral in the above equation (which represents the total ultrafiltration time) is independent of $c_i$, minimization of the process time in this case simply involves finding the value $c_i$ that minimizes the second term, i.e., the diafiltration time. Thus, the following well known result is obtained [7]

$$c_i^{opt} = c_g / e \tag{9}$$

where $e$ is the base of the natural logarithm. Thus the minimum dimensionless time in a UFCVD process is given by

$$\left(t^*_{ufcvd}\right)_{\min} = \frac{c_0}{c_g}\left[\int_{c_g/c_f}^{c_g/c_0} \frac{dx}{\ln x} + e\ln\left(c_{s0}/c_{sf}\right)\right] \tag{10}$$

It is important to note however that this is only meaningful if the final concentration $c_f$, is greater than $c_g/e$. If $c_f$ is less than $c_g/e$, the optimum concentration for a UFCVD process is simply $c_f$ and the minimum process time in that case is given by

$$\left(t^*_{ufcvd}\right)_{\min} = \frac{c_0}{c_g}\left[\int_{c_g/c_f}^{c_g/c_0} \frac{dx}{\ln x} + \frac{c_g}{c_f}\frac{\ln\left(c_{s0}/c_{sf}\right)}{\ln\left(c_g/c_f\right)}\right] \tag{11}$$

## 2.2. *Minimum process time for UFVVD*

Again using Eqs. (1)–(4), the process time in UFVVD can be written

$$t_{ufvvd} = \frac{1}{kA}\int_{V_i}^{V_0} \frac{dV}{\ln\left(c_g/c\right)} + \frac{1}{1-\alpha}\int_{V_f}^{V_i} \frac{dV}{\ln\left(c_g/c\right)} \tag{12}$$

In dimensionless notation, we have after a little rearranging

$$t^*_{ufvvd} = \frac{c_0}{c_g}\int_{c_g/c_i}^{c_g/c_0} \frac{dx}{\ln x} + \frac{1}{1-\alpha}\frac{c_0}{c_g}\int_{c_g/c_f}^{c_g/c_i} \frac{dx}{\ln x} \tag{13}$$

which can be written

$$t^*_{ufvvd} = \frac{c_0}{c_g}\int_{c_g/c_f}^{c_g/c_0} \frac{dx}{\ln x} + \frac{\alpha}{1-\alpha}\frac{c_0}{c_g}\int_{c_g/c_f}^{c_g/c_i} \frac{dx}{\ln x} \tag{14}$$

An obvious way to find the minimum process time in this case would be to employ numerical integration to compute $t^*_{\text{ufvvd}}$ for a range of values of $c_i$ and determine the optimum by inspection. Such an approach has been used previously in a slightly different context [8]. Here, however, we adopt a more precise approach. The minimum of this expression is found by differentiating, giving the following criterion to be satisfied at the optimum:

$$\frac{\alpha}{1-\alpha}\left(\frac{-c_g}{c_i^2}\frac{1}{\ln\left(c_g/c_i\right)}\right) + \frac{1}{(1-\alpha)^2}\frac{d\alpha}{dc_i}\int_{c_g/c_f}^{c_g/c_i} \frac{dx}{\ln x} = 0 \tag{15}$$

Using the appropriate expression for $\alpha$ from Table 1, rearranging and simplifying gives the following equation which must be solved to determine the optimum value of $c_i$ in a UFVVD process

$$\int_{c_g/c_f}^{c_g/c_i^{opt}} \frac{dx}{\ln x} - \frac{c_g}{c_i^{opt}}\left(1 - \frac{\ln\left(c_g/c_f\right)}{\ln\left(c_g/c_i^{opt}\right)}\right) = 0 \tag{16}$$

## 2.3. *Comparison of minimum process times*

Noting the common integral in the expressions for process time in UFCVD and UFVVD, Eqs. (10) and (14), and using the expression for $\alpha$ in Table 1, the minimum process time for UFVVD will be less than the minimum process time for UFCVD (for $c_f > c_g/e$) when

$$\frac{1}{\ln\left(c_g/c_i^{opt}\right) - \ln\left(c_g/c_f\right)}\int_{c_g/c_f}^{c_g/c_i^{opt}} \frac{dx}{\ln x} < e \tag{17}$$

When $c_f < c_g/e$, it will be shown later that the optimum UFVVD process become a UFCVD process by default (i.e. diafiltration is best done at the final concentration where $\alpha = 1$ and the volume is constant) and no separate criterion needs to be established in this case.

Combining Eqs. (16) and (17) leads to the following criterion for an optimised UFVVD process to be faster than an optimised UFCVD process:

$$\lambda < 1 \tag{18}$$

where

$$\lambda = \frac{c_g/c_i^{opt}}{e\ln\left(c_g/c_i^{opt}\right)} \tag{19}$$

## 2.3. *Formulation in terms of the Logarithmic Integral*

It is normal practice to compute the integral that arises frequently in this analysis with numerical integration techniques. In this work, however we note that solution to this integral can be written in terms of the Logarithmic Integral, a special function denoted *Li*, where $Li(y)$ is defined by [9]

$$Li(y) = \int_0^y \frac{ds}{\ln s} \tag{20}$$

The practical significance of adopting this notation is that the Logarithmic Integral has the following series definition

$$Li(y) = \gamma + \ln(\ln y) + \sum_{k=1}^{\infty} \frac{(\ln y)^k}{k\,k!} \tag{21}$$

where $\gamma$ is the Euler constant = 0.5772157 to seven decimal places. Thus the optimum concentration for UFVVD can be computed by rewriting Eq. (16) as

$$Li\left(c_g / c_i^{opt}\right) - Li\left(c_g / c_f\right) - \frac{c_g}{c_i^{opt}}\left(1 - \frac{\ln\left(c_g / c_f\right)}{\ln\left(c_g / c_i^{opt}\right)}\right) = 0 \tag{22}$$

As long as an accurate, truncated form of the series for the *Li* function can be used, this equation is now a relatively straightforward non-linear algebraic equation that can be solved using standard methods. This means that a trial and error approach to finding the optimum, involving numerous numerical integrations, can be avoided.

## 3. Results and discussion

Eq. (22) was solved using the Solver utility within Microsoft Excel. When solving, a constraint to the effect that $c_i^{opt} \le c_f$ was included to ensure physically meaningful results. Ten terms of the *Li* series were used, although seven would generally have been enough to give results that were accurate to three decimal places.

### *3.1. Calculation of optimum concentration for UFVVD*

Fig. 3 is a plot of the optimum concentration for both UFCVD and UFVVD as a function of final concentration. As in all subsequent graphs, the symbols denote the point at which computations were performed.

In the case of UFCVD, the optimum is identical to the final concentration when $c_f < c_g/e$ and equals $c_g/e$ when $c_f \ge c_g/e$. The optimum concentration for UFVVD is also the final concentration when $c_f < c_g/e$. In that case VVD defaults to CVD as $\alpha = 1$. When $c_f > c_g/e$ we find that the optimum concentration for UFVVD shows a significant dependence on $c_f/c_g$ in contrast to UFCVD.

### *3.2. Validation of optimum concentration calculation*

In order to check the above calculations, the optimum concentration was computed using a cruder method for two scenarios, one where $c_f < c_g/e$ and one where $c_f > c_g/e$. The goal here was to find the minimum of Eq. (14) by inspection. Since the value of the first integral is fixed, this means finding

$$\min\left\{\frac{\alpha}{1-\alpha}\int_{c_g/c_f}^{c_g/c_i} \frac{dx}{\ln x}\right\} \tag{23}$$

Using the Logarithmic Integral and the definition of $\alpha$ in Table 1, it is easily shown that this means finding min $\{\varphi\}$ where

$$\varphi = \frac{1}{\ln\left(c_g / c_i\right) - \ln\left(c_g / c_f\right)}\left[Li\left(c_g / c_i\right) - Li\left(c_g / c_f\right)\right] \tag{24}$$

Fig. 4 is a plot of $\varphi$ vs. $c_i/c_g$ for $c_f/c_g = 0.8$, i.e., $c_f > c_g/e$. By inspection, we see that the minimum occurs at $c_i/c_g = 0.2$ which is in very good agreement with Fig. 3.

Fig. 5 is a plot $\varphi$ vs. $c_i/c_g$ for $c_f/c_g = 0.3$, i.e., $c_f < c_g/e$. We see that in this case, no true minimum is found and the

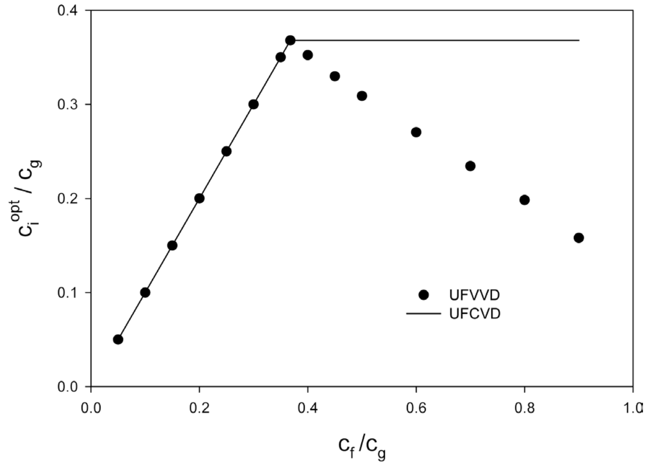


Fig. 3. Optimum concentrations vs. $c_f/c_g$ for UFCVD and UFVVD.

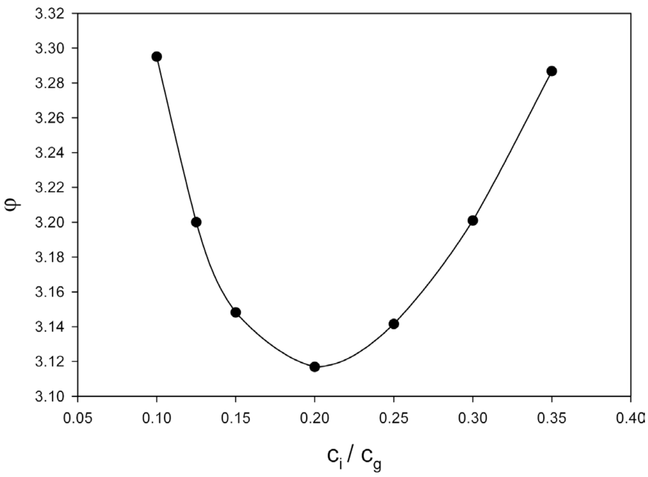


Fig. 4. Locating the optimum diafiltration concentration in UFVVD for $c_f/c_g = 0.8$. $\varphi$ defined by Eq. (24).

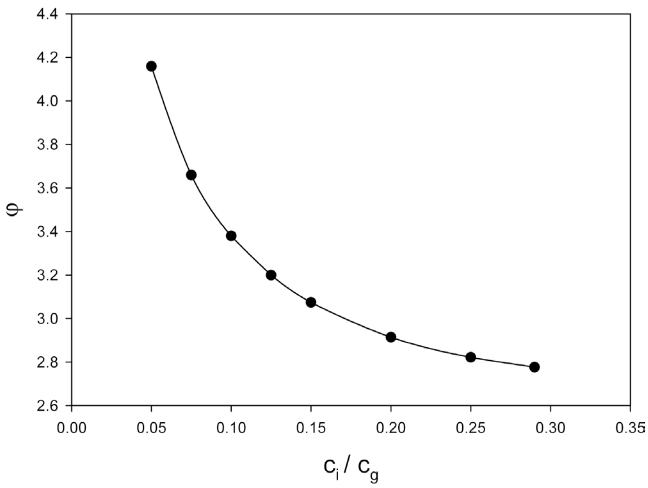


Fig. 5. Locating the optimum diafiltration concentration in UFVVD for $c_f/c_g = 0.3$. φ defined by Eq. (24).

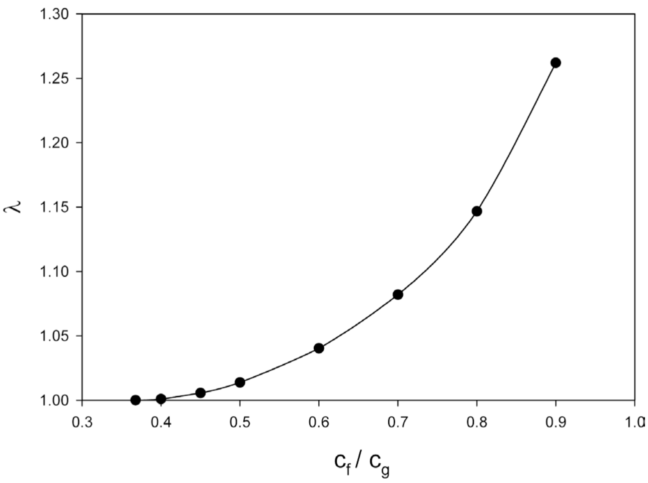


Fig. 6. Test of criterion for UFVVD to be faster than UFCVD. λ defined by Eq. (19).

best way to perform diafiltration is when $c_i = c_f$ where a UFVVD process becomes a UFCVD process.

### *3.3. Can UFVVD ever be faster than UFCVD?*

Fig. 6 is a plot of λ, defined by Eq. (19), as a function of $c_f/c_g$ where $c_f/c_g \geq e$. It is clear that $\lambda > 1$ in all calculations showing that a UFVVD process can never be faster than a UFCVD process.

The value of a UFVVD process can probably only be seen therefore if one were to conduct a full economic comparison of the two processes, where, for example, process time and water usage are taken into account. Reduced water usage has previously been shown to be a characteristic of UFVVD [6]. Economic optimisation of UFVVD is the subject of current work in our laboratory where we are employing a similar technique to that outlined here.

A more general problem would be to determine if there is any generalised VVD process, including those with time-dependent $\alpha$ [10] that can be faster or more economical than UFCVD. To answer that problem, more powerful techniques based on optimal control theory are required, as described recently by Fikar et al. [11].

## 4. Conclusions

The series definition of the Logarithmic Integral has provided a simple computational tool to (i) precisely determine the optimum concentration to begin diafiltration in a UFVVD process and (ii) show that for the assumed flux model and rejection coefficients, no UFVVD process can be designed that is faster than an optimally run UFCVD process.

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