Separation of Macromolecules by Dynamic Ultrafiltration

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Abstract
Ultrafiltration is mainly used to concentrate macromolecules and removing salts and smaller molecules through the membrane. Sharp separation is rarely seen which is partly due to the coupling of solute and water transport and the concentration polarization at the membrane surface. In case of real fractionation of macromolecules a decoupling of the solute transport from the water transfer together with a minimization of the concentration polarization of the larger molecules have to take place. Using hollow fiber membranes under high-frequency backflushing the concentration polarization can be minimized due to the non-steady state operation. The build-up of the polarized highly concentrated layer at the membrane surface takes typically 10-30 seconds why it is possible to obtain a dynamic layer with a substantially reduced surface concentration thereby increasing the selectivity of the membrane.The paper describes the modeling of the dynamics of the concentration polarization and how it influences the membrane selectivity and productivity. The modeling is further supported by experiments fractionating dextrans and proteins on a hollow fiber system using backflushing intervals from 1 to 30 seconds and backflushing times from 0,1 to 5 seconds.

Introduction

The modeling of ultrafiltration is often done by either the gel model or by the osmotic pressure model. The gel model can often describe the permeate flux as a function of pressure and concentration reasonably well. However, the assumption of a constant concentration of the macromolecules at the membrane surface equal to the gel concentration and with a varying thickness depending of the pressure would be expected to result in a constant retention of the macromolecules independent of the flux rate which are rarely seen. The osmotic pressure model on the other hand can explain such variations and it has further been shown, that it can also explain the limiting flux with increasing pressure, due to an exponential increase in the osmotic pressure of the macromolecules at the concentrations, which are observed at the membrane surface. The background for description of the concentration polarization in ultrafiltration are usually the film model which assumes a steady-state concentration profile between the bulk solution and the membrane surface. Since the concentration at the membrane surface might well be one to two orders of magnitude higher than in the bulk solution, a certain amount of permeate is needed before steady-state is obtained.

In the present work some earlier findings (1) of the relation between the measured osmotic pressure of dextrans and their concentration is used to model the dynamics of the concentration polarization build-up at the membrane surface and how this influences the permeate flux and observed retention, assuming the true membrane retention to be constant and the permeate flux to depend on the water permeability with the difference in

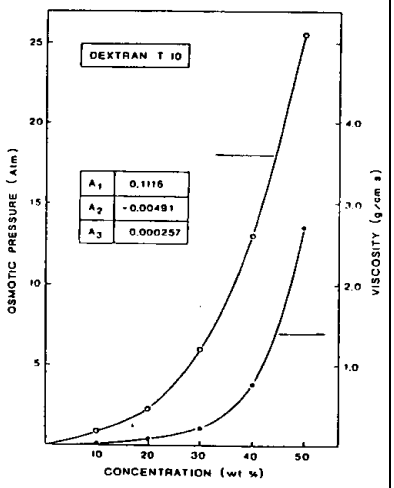
pressure and osmotic pressure gradient to be the driving force. This is illustrated in Fig.1 together with the experimental relation for the osmotic pressure.

Osmotic pressure model

$$J_v = L_p \cdot (\Delta P - \Delta \pi)$$

$$\Delta \pi = A_1 \cdot (c_m) + A_2 \cdot (c_m)^2 + A_3 \cdot (c_m)^3$$

$$\frac{C_m - C_p}{C_b - C_p} = \exp\left(\frac{J_v}{k}\right)$$



Figur 1. Osmotic pressure model.

To model the the concentration build-up a differential mass balance in the boundary layer is set up with the boundary conditions shown in Fig. 2:

Non-steady-state transport model

Differential mass balance for the solute:

$$\frac{\partial c}{\partial t} = -\frac{\partial J_s}{\partial x} = D \cdot \frac{\partial^2 c}{\partial x^2} - J_v \cdot \frac{\partial c}{\partial x}$$

For $x \in [0; \delta]$, $t = 0$ then $c = c_b$

For $x = 0$, $t \in [0; +\infty[$ then $c = c_b$

For $x = \delta$, $t \in [0; +\infty[$ then $J_s = J_v \cdot (1 - R_{int}) \cdot c_m$

Figure 2

The differential equation is solved as a difference equation in a work sheet assuming a constant boundary layer thickness and a constant retention of the membrane, R_{int}, in which case the permeate concentration is related to the concentration at the membrane surface as shown in Fig. 3. Further the average permeate concentration and average permeate flux are calculated by a summation from time zero to the actual time before an eventual backflux is started.

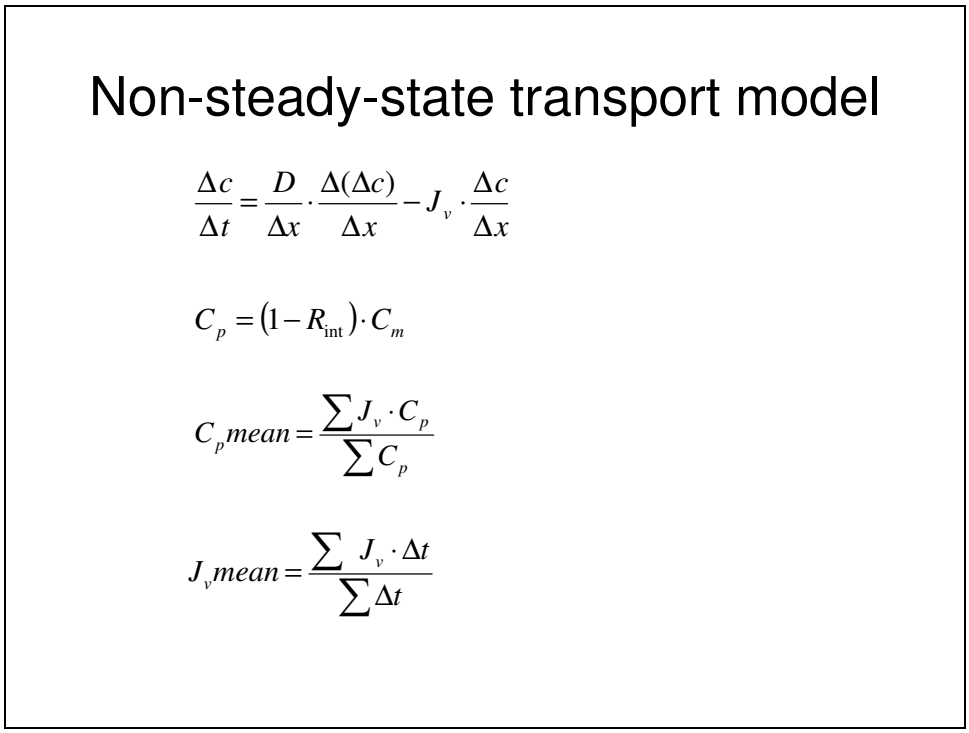


Figure 3.

Fig. 4 shows the calculated concentration at the membrane surface versus the time since the starting of the process for a given set of parameters represented by the diffusion coefficient of the dextran, the water permeability and the pressure difference, the bulk concentration and the intrinsic retention of the membrane. In this example the concentration at the membrane surface increases from 1,5 to 26 g/l which are the steady-state value reached after about 10 seconds.

Fig.5 shows the calculated values for the actual flux as well as the average flux from time zero to the given time before backflushing. This shows that with the given parameters a substantial increase in the average flux (35 l/m^{2}h at time 10 seconds) is seen in comparison to the steady-state flux which are close to 18 l/m^{2}h.

Fig. 6 shows the calculated values for the actual retention as well as the average retention from time zero to the given time before backflushing. Again a marked increase in the average retention can be seen compared to the steady-state value which is around 31% in this example.

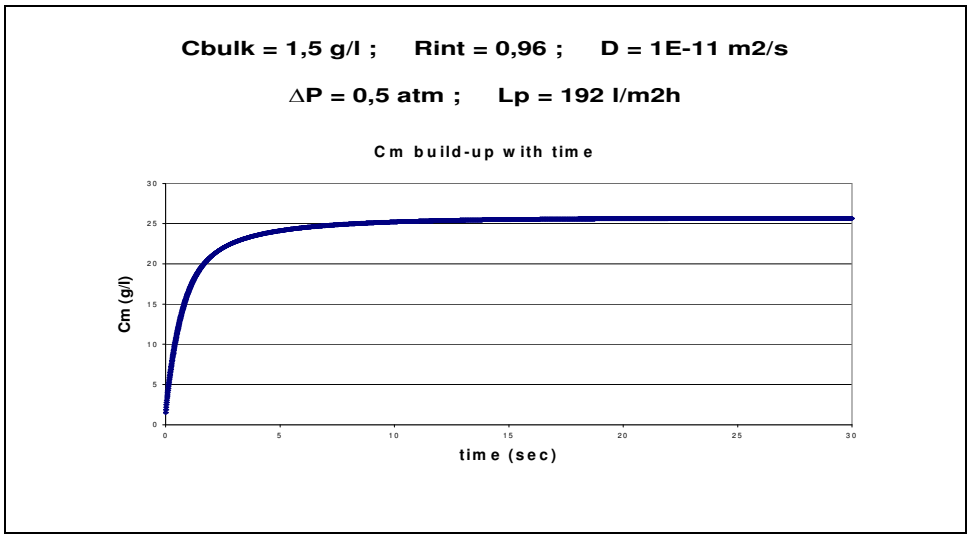
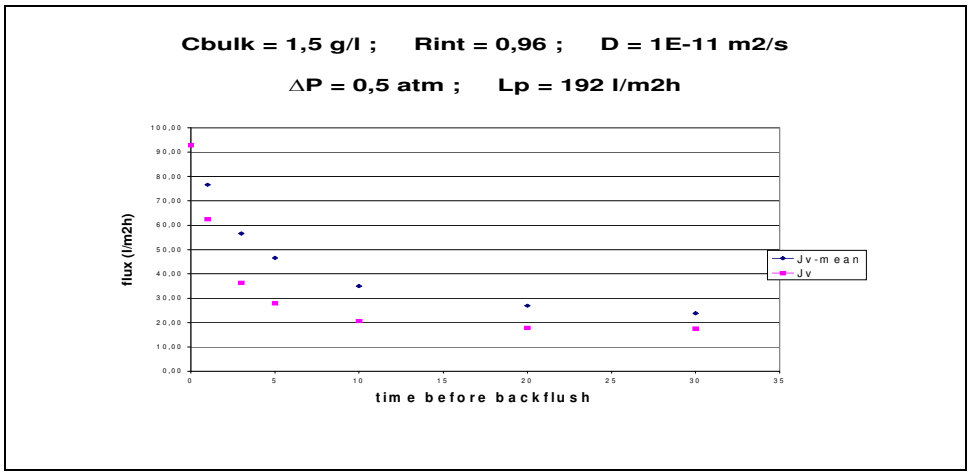


Figure 4.



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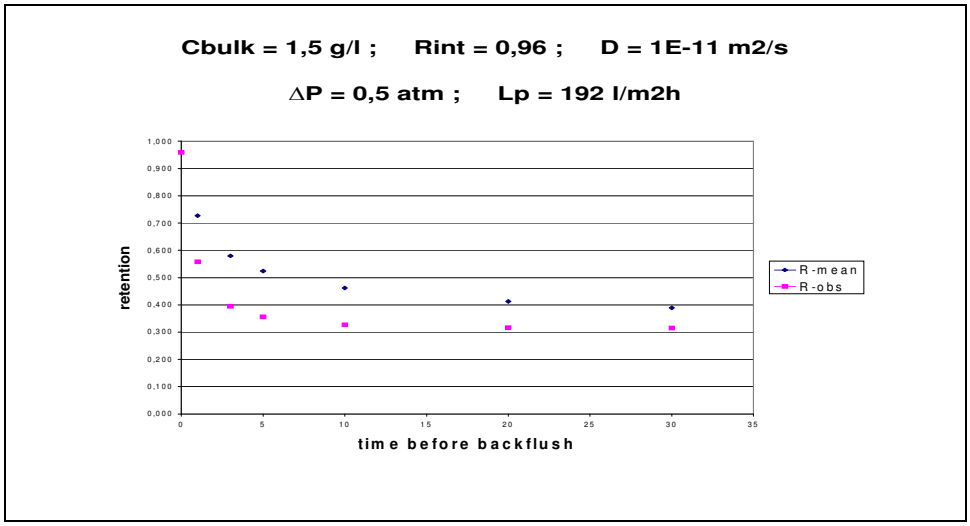

Figure 6.

Experimental evidence

Experiments with high frequency backflushing have been made using a hollow fibre membrane module consisting of 50 fibres in parallel with an effective length of 44 cm, inner diameter of 0,15 cm potted together into a module having 0,1 m^2 effective membrane area. Backflushing were performed using an on-off valve connected to the permeate outlet and a home made backflush valve connected to the other end of the permeate outlet. The backflush valve consists of a stainless steel housing with an inner rubber tube which are connected to an air source operated by an on-off valve. Both valves are operated and controlled by a computer so that at given times the permeate valve are closed and at the same time the air valve to the backflush housing is opened thereby setting a high pressure on the permeate inside the membrane module. The bulk solution used are a 1,5 g/l dextran T110 from Pharmacia with an average molecular weight of about 110 kDa.

Fig. 7 shows the measured flux and retention at varying pressure difference without using any backflushing. This shows the typical situation mostly seen in ultrafiltration, namely an initial increase in flux which levels out at higher pressures and a strong decrease in retention with increasing flux due to the increase in concentration polarization.

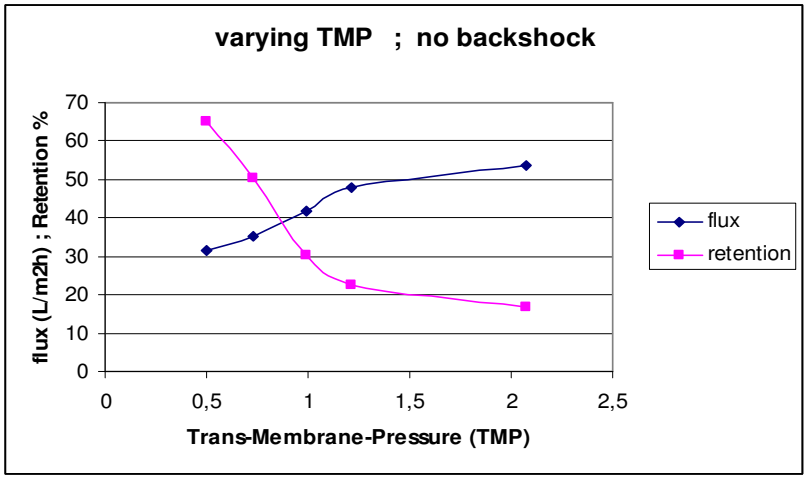

Figure 7.

Fig.8 shows an example of the effect of using backflushing every 5 seconds with increasing backflushing times from 0,1 to 0,8 seconds. This shows that the average flux obtained are increasing until 0,4 seconds of backflushing even that this time are lost for forward filtration and that further some permeate are returned back into the feed solution during the backflushing. Further a strong increase in the retention of the dextran is seen in the whole range of backflushing times (from 52% to 97%).

Fig.9 shows in similar way data for the experiment operated at a higher pressure difference, a longer time between backflushing and longer times during the backflushing itself. Again a maximum in the average permeate flux is seen whereas the retention increases continuously as before. The main difference is seen by the fact that at longer backflushing times the average permeate flux decreases substantially due to the lack of operating time and permeate which are returned during the backflushing.

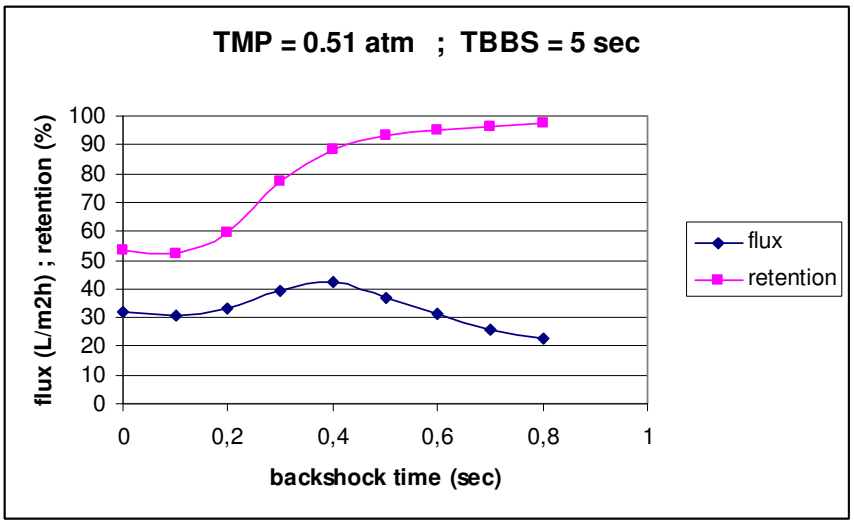

Figure 8.

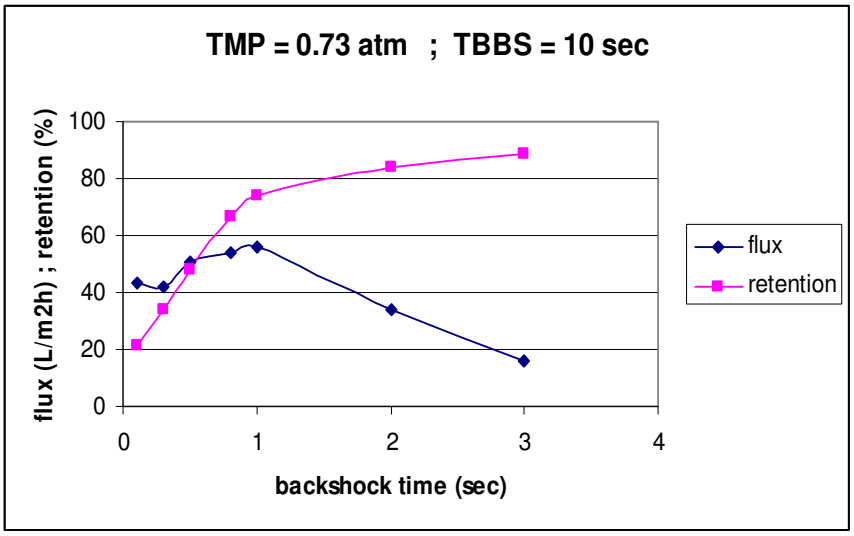

Figure 9.

Since dextrans have a rather broad molecular weight distribution even that this sample is a fractionated one, the permeate have been analyzed by Size Exclusion Chromatography and compared with the bulk solution. Fig. 10 shows such an example where the chromatograms of the different permeate samples taken at varying backflushing times keeping the time between backflushing constant at 10 seconds and operating at a pressure difference of 0,38 atm. The figure further shows the chromatograms of the bulk solution before and after the experiment. This shows that the bulk solution has increased slightly in concentration during the experiment because of the permeate samples taken out of the system but no change in the MW distribution can be seen because of the small volume changes. However, a substantial change in the MW distribution to lower molecular weights can be seen for the permeate samples with increasing backflushing time. Further the total permeate concentrations are decreasing as well.

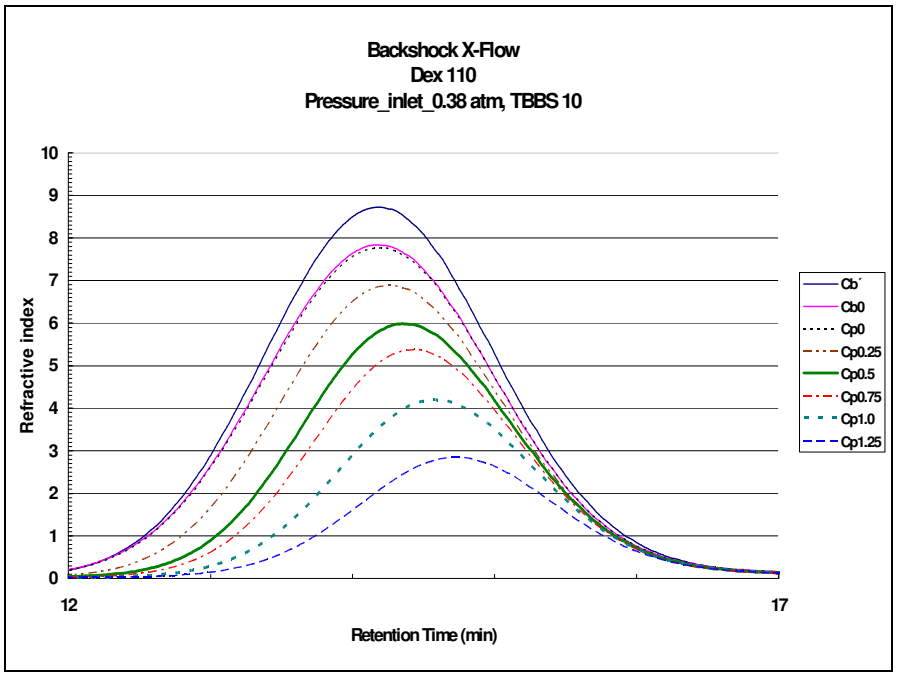

Figure 10.

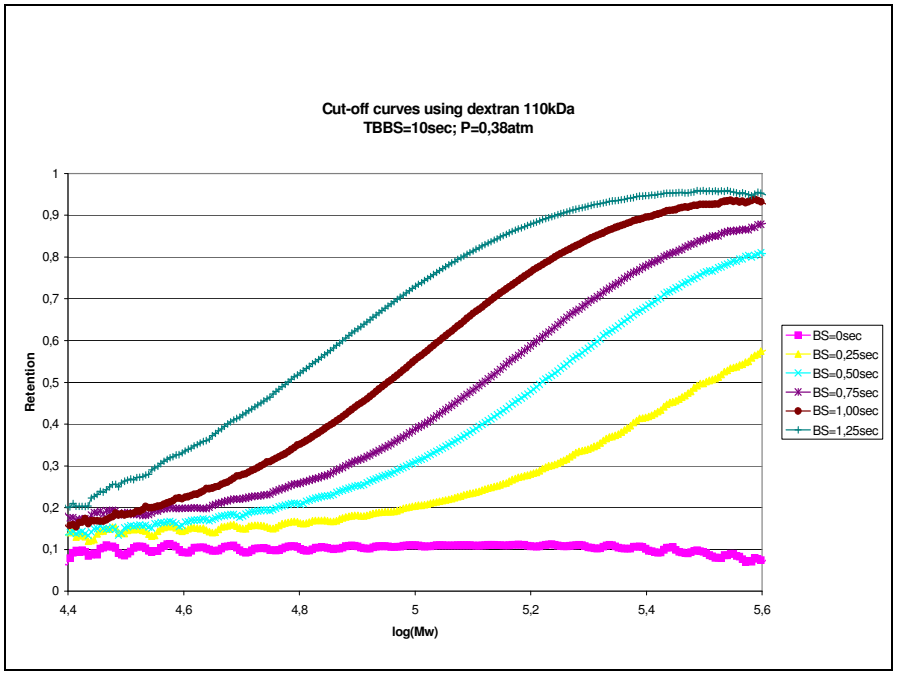

Figure 11.

From the relation between the retention time in the SEC and the molecular weight of the dextrans, a cut-off curve for the membrane system depending on the operating conditions can be calculated. This is seen in Fig. 11 which shows a dramatic increase in retention with increasing backflushing times, especially for the larger sized macromolecules. Without any backflushing no separation between the different molecular sizes are seen at

all, whereas the steepness of the cut-off curve increases with increasing backflushing times and shifts to lower molecular weights at even longer backflushing times.
In this way high frequency backflushing gives an opportunity for fractionating larger macromolecules from smaller ones and makes it further possible to tune the separation performance of a certain membrane system to optimize a given type of separation.

Conclusions

- Membrane selectivity of ultrafiltration membranes are strongly dependent on the operating parameters. Normally concentration polarisation are reduced by operating at high cross-flow velocities but in most ultrafiltration modules such high velocities are not possible due to pressure losses which further gives problems with uneven trans-membrane-pressure variations inside the membrane module.

- High frequency backflushing is very effective in reducing the average concentration polarization and can further be used to tune the membrane selectivity (cut-off curve) thereby making a fractionation of macromolecules due to size more realizable. Further it has been shown that the average permeate flux can be significantly increased and has a maximum at a certain ratio between the time between backflushing and the backflushing time itself, due to the much lower average osmotic pressure exerted of the macromolecule at the surface of the membrane.

- It is further expected that a high frequency backflushing will have a beneficial effect on the fouling tendency of the membrane surface itself.

References

G. Jonsson, “Boundary layer phenomena during ultrafiltration of dextran and whey protein solutions”, Desalination 51 (1984) 61-77.