Controlled Flux Behaviour of Membrane Processes

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Summary: Controlling ultrafiltration (UF) and microfiltration (MF) membrane fluxes at or around a region where fouling is minimal can provide an interesting and economic operating regime. Selectivity may be enhanced and cleaning may be easier. For a given flux it is sometimes possible to filter a product suspension at the same trans-membrane pressure (TMP) as for pure water (PWP), but this can require a lot of energy input to maintain cross-flow or high shear in other ways if high fluxes are required. The critical flux is the flux above which one starts to observe fouling. By operating at lower cross-flow velocities and just above the critical flux, and thus, with lower TMPs, periodic cleaning can be effected by temporarily stopping permeation. A change in feed rate demands a change in flux which is obtained by temporarily increasing energy inputs.
Controlled flux improves macromolecular fractionation. As flux increases the rejection of high molecular weight materials decreases whilst that of lower molecular weight materials decreases. This paper discusses the causes of fouling and the use controlled flux operation to mitigate its effects.

Introduction

In a membrane filtration under constant pressure conditions a very rapid initial flux decline often occurs when during filtration of a suspension containing particles above a micron in diameter. After some time the filtration seems to reach a steady flux which has been called the *critical flux*. At this point there is an apparent balance between particles arriving and those being removed from the membrane surface.[1]

If the flux is controlled rather than the pressure then one can find a situation in some systems where the transmembrane pressure remains constant and does not rise with time, even from the start of filtration. The flux above which pressure rises with time is the *critical flux*.[2]

Many authors have been interested in the processes which control the removal of particles from the membrane surface and many mechanisms have been suggested. Convective forces can bring a particle towards the membrane surface as described by Stokes law. A shear field provides a force on the particle resulting from the induced

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spin which gives a Magnus effect. This is significant for larger particles such as blood cells in arteries but is unimportant for sub micron particles. If particles interact in a shear field they can create a diffusion effect with a diffusion coefficient given by Leighton and Acrivos.[3]

Sethi and Wiesner[4] have incorporated the above three mechanisms together with the effect of concentrated flowing layers of particles at the membrane surface. The shear-induced diffusion effect was treated and experimentally confirmed by Romero and Davis.[5] These techniques can predict a steady state flux known as the *equilibrium flux*. It is established after a cake layer has formed on the membrane and the innermost flowing layers have stabilised Sethi and Wiesner[4] have shown that combined mechanisms are important except for very small or very large particles. Their results confirm earlier results of Bacchin et al[6] that there is an intermediate particle diameter which leads to the minimum flux with a prolonged cake build-up over several hours.

This mechanism may be expected to be very important when a flowing cake has been formed on the membrane surface either directly above the surface, as reported by Li et al,[7] or above a static cake. It should be less important before particles have reached the surface. This leads directly to attempts to improve the critical flux and hence steady state fluxes under constant pressure, by increasing the shear at the membrane surface. Many attempts have been reported and discussed at length.[8,9,10] Later work has looked at three methods of enhancing shear, the use of vibrating membranes,[11] the use of secondary flows in curved ducts giving rise to Dean vortices,[12,13,14] and the injection of air bubbles.[15] The latter two are more promising as membrane costs reduce and more emphasis is placed on low energy methods of flux enhancement. It is claimed that the replacement cost of membranes in a wastewater treatment application has decreased by a factor of 15 over the last 7 years.[16] This dynamic of economics means that it is unlikely to be economic to use high cross-flow velocities or other high energy flux enhancement systems in the future on large scale plants. The modern tendency is to operate with controlled fluxes which exceed the critical and thus allow fouling, which is then removed fairly frequently by a backflush or backshock or by removing the driving pressure force holding the cake to the membrane surface. Under such dynamic operating conditions the lowering of the flux allows self cleaning of the membrane and an intermittent operation can give stable and sustainable flux patterns.

Complete blocking

Kuiper et al.[17,18] used a low porosity novel Microsieve which has monodisperse pores formed by controlled etching of the membrane surface. That showed that when a particle is blocking a pore it will be held there so long as the TMP exceeds a critical value known as the *critical pressure.* If the critical flux is exceeded a particle is brought to the membrane surface, and if it sticks there it will remain as long as the critical pressure is exceeded. Otherwise it will flow along the membrane surface. Where Kuiper[18] used a high porosity membrane the particles on the surface interacted with each other and prevented complete blocking of every pore. In this situation flux continued to rise once the critical pressure was exceeded, though at a reduced rate. The particles bridge over the pores only partially blocking them and allowing some permeation.

Strong and weak forms of the critical flux

Wu et al.[19]measured the transmembrane pressure (TMP) required to maintain fixed fluxes through a microfiltration membrane with two types of silica particle suspensions. They found that as the flux was increased in steps the TMP was at first a constant value for each flux until, once a certain flux was exceeded, the TMP rose with time continuously and over the 30 minutes of the experiment almost linearly. On plotting the TMP against the flux it was found that the relationship was linear up until the point where the TMP started to increase. For one of the types of silica the linear portion of the graph coincided with the PWP line. The pure water pressure (PWP) is the pressure required to maintain a given flux with pure water. For the other particle the linear portion was steeper than the PWP showing that some initial fouling had occurred. In the first case the critical flux was termed a *strong form of the critical flux* for the second case it was termed a *weak form of the critical flux.*

Hysteresis effects

If one operates a membrane system under controlled flux for some tens of minutes and then increases the flux stepwise in a forward and then reverse direction, whilst observing the transmembrane pressure, a hysteresis curve can be obtained.[20] The greater the area of the hysteresis the greater the irreversible fouling. If no immediately irreversible fouling is observed the forward and reverse curves follow the same track and it could be said that the critical flux has not been exceeded. It might be that this could be thought of as a dynamic critical flux. Even though these plots may be curved,

if repeated cycles lead to the same curve then there is no permanent fouling. Such systems have been observed and show that cakes deposited at high flux can be removed at lower fluxes. Permanent fouling is observed when the curve finishes at a higher TMP than it started.

Macromolecules

Macromolecules may be charged; the charge may be dependent on pH; they may possess hydrophobic properties in all or parts of the molecule and they will thus interact with a membrane which can have these same range of properties. It is often observed that if a molecule is rejected by the membrane there is a maximum flux which can be achieved as transmembrane pressure is increased. This flux is termed the limiting flux and is controlled by a combination of the entropic or osmotic pressure, the solution viscosity in the boundary layer and shear.

Electrostatic repulsion

The charge on a colloidal particle or macromolecule can change with pH as can the charge on the membrane. If the membrane and the particle have the same sign charge there will be a repulsion given by the Boltzmann equation. This force - not taken into account by Sethi and Wiesner[4] was shown to be most important in the moderate size region by Bacchin et al.[6]. Further developments by Bowen and Jenner [21] have shown that the flux calculated by the fundamental equations can predict the flux of a silica particle without the use of adjustable parameters.

Adsorption

The adsorption of macromolecules onto the membrane can occur because of a strong attractive interaction between the membrane and the solute. Huisman et al.[22] showed that the fouling of a membrane by protein was initially influenced by the protein-membrane interactions and later by the protein-protein interactions.

Charge effects are muted at moderate ionic strengths as the Debye length is shortened. Under these circumstances the potential barrier to particle coagulation will disappear and there will be a coagulation between the particles and also coagulation between particles with the membrane.[23]

Hydrophobic effects

A hydrophobic membrane will strongly interact with hydrophobic particles leading to a strongly adsorbed layer. If a surfactant is added to the membrane it will become at least temporarily hydrophilic and this will reduce the interactions between the membrane and

particles. This was observed by Kuiper[18] using yeast and his microsieves.

Membrane bioreactor applications

A membrane bioreactor was constructed from acrylic sheet and a double-sided flat-sheet Kubota membrane of A4 size (kindly supplied by Kubota UK) placed in it. Air bubbled past the membranes at controlled rates. Permeate flow rate was via a computer controlled pump. Activated sludge was obtained from a local waste treatment plant and inoculated into the MBR. Simulated sewage was fed to the MBR.

Results

In Figure 1 we see a steady fouling at the lowest aeration rate, no fouling at the aeration rates of 10 or 14 $l.min^{-1}$ and further fouling (although at a reduced rate) when aeration is returned to the level of 6 $l.min^{-1}$.

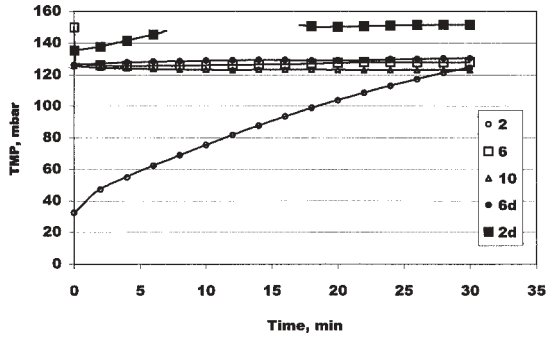

Figure 1. TMP at flux of 20 $l.m^{-2}h^{-1}$ for various air flow rates.

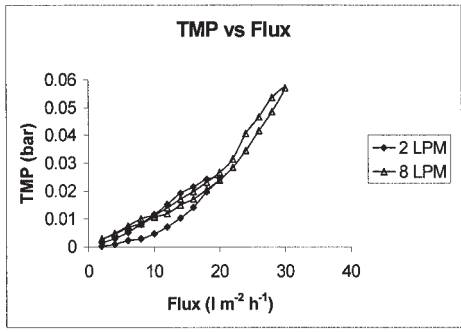

Figure 2. TMP during Flux Cycling at aeration rates of 2 and 4 $L.min^{-1}$. MLSS 1.5 $g.L^{-1}$.

Figure 2 shows the effect of cycling the fluxes at different air flow rates of 2 and 8 $L.min^{-1}$. Increasing the flux initially at the lower rate increases TMP linearly with a low slope but as flux increases beyond the critical flux the slope is progressively increased, and when the flux is reduced a hysteresis is observed. Hysteresis is less marked at the higher aeration rate. Whilst there has been some reduction in the total fouling this is not complete and there is still residual fouling. This leads to a change in the initial TMP/flux slope which is obtained.

The final set of experiments used intermittent permeation. At a flux of 10 $L.m^{-2}h^{-1}$ (not shown) the fouling observed is stabilised and is removed by stopping permeation even at low air flow rates. At a flux of 30 $L.m^{-2}h^{-1}$ fouling is severe and a high TMP is recorded as seen in Figure 3. Careful observation shows that the lowest two air flow rates cannot cope even with the break in permeation. The TMP is increased from cycle to cycle suggesting long term unsustainability. In every case there is significant reduction of the fouling by the break in permeation. At the highest air flow the fouling does not increase severely. This suggests the mechanism described by Kuiper17 applies, in which a particle once attached to the membrane is held there by the TMP. Air driven cross-flow can release it once the TMP has been released. This leads to an opportunity. Normally a wastewater treatment plant is required to handle high flow rates over a limited period, such as during rain, but mainly lower flows at other times then a changing aeration rate may allow overloading of the plant during a limited period, with a recovery period once the excess flow is no longer required.

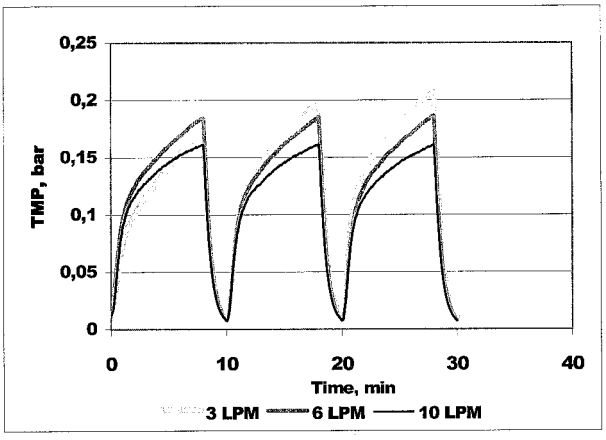

Figure 3. TMP vs time with permeation at 30 $l.m^{-2}h^{-1}$ for 8 minutes and off for 2 minutes. MLSS 1.5 $g.L^{-1}$.

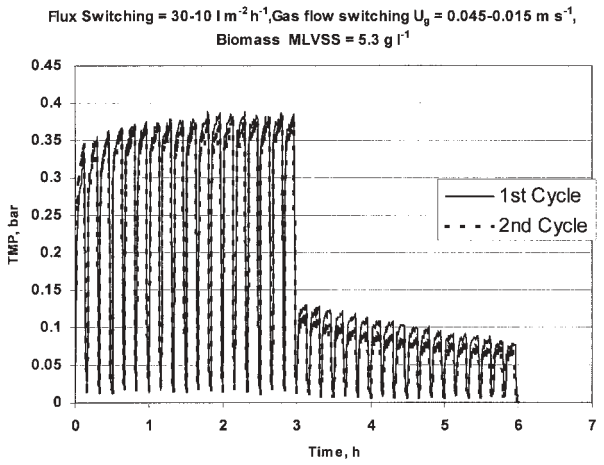

Figure 4. Continuous cycling of permeation and no permeation at two different air flow/permeation rate settings. Permeation is stopped for 2 minutes each 10 minutes, each condition is held for 3 hours.

Figure 4 shows a case where a high flux is used for 3 hours with a high air flow. Both are reduced after 3 hours by one-third and then both cycles are repeated. The second cycle is superimposed on the first to show that in fact the TMP was slightly lower the second time round. TMP built up steadily during the high flow rate and decreased steadily during the lower flow rates.

Macromolecular applications

Materials

Solutions of myoglobin[23] (Sigma) and of β-lactoglobulin and immunoglobulin[24] (Sigma) were filtered under controlled flux conditions in a flat sheet membrane system described elsewhere[19]. The membrane used for the myoglobin filtration was a C30G (30K MWCO regenerated cellulose) from Hoechst. The mixture was filtered through a PES 100 (100K MWCO, polyethersulphone membrane) from Intersep.

TMP was measured continuously with pressure transducers (Druck) and flux was controlled at selected values and held for 30-90 minutes. The protein mixture was monitored by having fluorescent tracers coupled to the proteins and detecting with a dual channel fluourescence detector.[24]

Results

Using a myoglobin protein solution at its iso-electric point a fouling rate was observed under a controlled flux that increased with flux and also protein concentration. Figure 5 shows the results of flux cycling for a 400 ppm myoglobin solution.[24] With a flux cycle there was a cleaning observed that could be related to the drop in flux. From the lack of an offset in the TMP when the cycle was complete it is surmised that all deposit had been removed, but in spite of that some hysteresis was observed. We must then regard fouling as being slowly reversible in this system rather than instantly reversible. The time taken over these cycles was 140 minutes. The time required to remove the contribution of the fouled layer may therefore be significant and raises the question of whether there has been a structuring of the protein on the surface. This has occurred even though no limiting flux has been reached in the experiments. There is no sharp rise in TMP with flux, as is seen when a limiting flux is reached due to osmotic or entropic pressure limitations. All of the experiments are conducted in what is classically termed the pressure-dependent region where flux can be increased by increasing TMP. These ideas conform to the theoretical calculations of Harmant and Aimar[23] who showed how a structured deposit will normally form on a surface if there is no electrical repulsion to keep the colloidal particles separated. This will happen at an isoelectric point and also in higher ionic strength solutions. Different self-cleaning rates are observed if the flux is reduced to much smaller values in a single reverse step as Figure 6 shows.

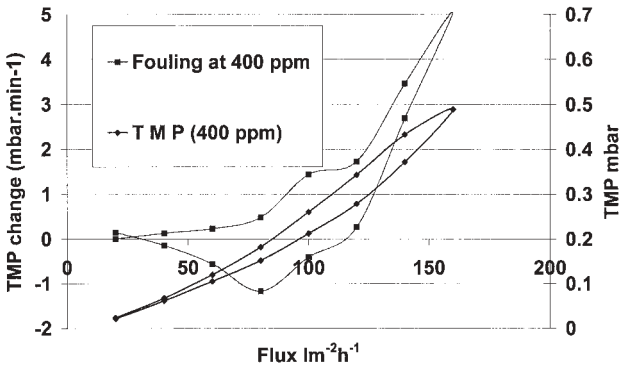

Figure 5. Rate of fouling and self cleaning as TMP change per min and TMP as function of flux.

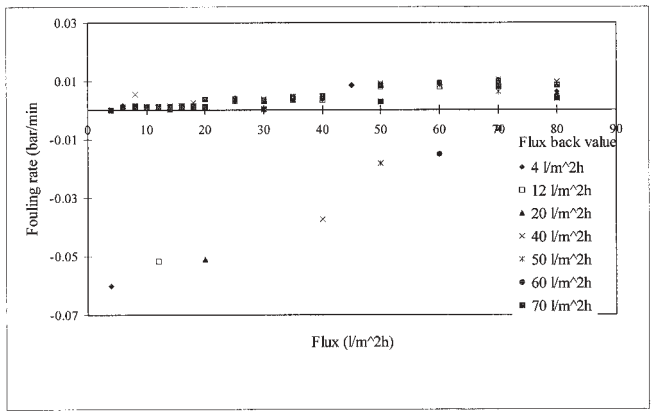

Figure 6: TMP rates of change as a function of flux with the reverse flux taken in a single step. Myoglobin ultrafiltration at different concentrations.

Fractionation of macromolecules

If one uses carefully controlled fluxes for macromolecular fractionation it is possible to show that it can be more effective than under a constant pressure - even when after the initial fouling has occurred the constant pressure seems to provide much the same fluxes although at an increased TMP. The data in Figure 7 shows the transmission of both gamma globulin and β-lactoglobulin as flux is changed in steps.[25] It can be seen that the transmission increases as flux is increased for both proteins. The separation factor reaches an optimum value just as the critical flux is reached and fouling starts as indicated by the increased resistance (Rm+Rf), defined as the ratio of TMP to flux.

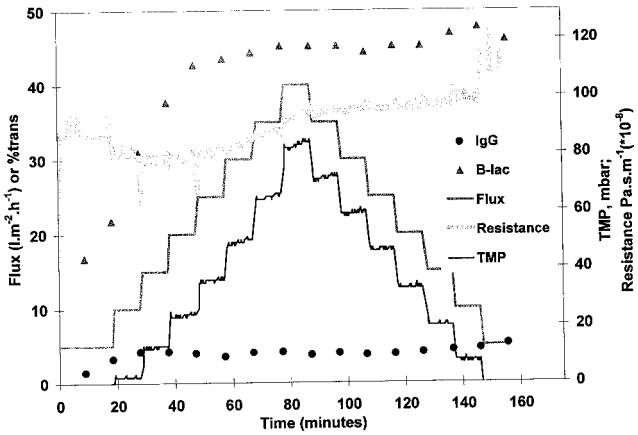

Figure 7. Controlled flux fractionation of IgG and β-lactoglobulin protein mixture. [24]

When the pressure is controlled rather than the flux the effect is as seen in Figure 8. Here the transmission of both proteins is rising with pressure but the flux is decreasing. The resistance steadily increases and eventually fouling is so severe that transmission for both proteins is reduced. The separation factor is always much poorer than for the experiments conducted at controlled flux.

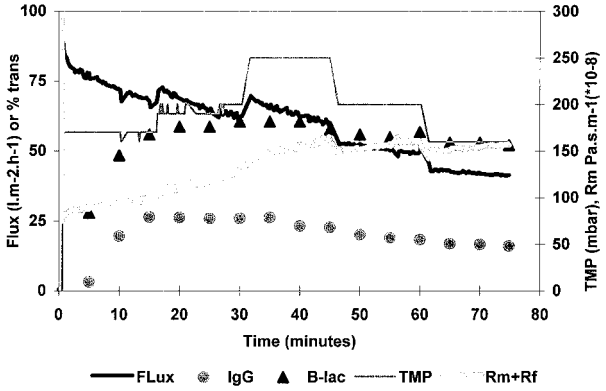

Figure 8. Controlled pressure fractionation of IgG and β- lactoglobulin. [24]

It is interesting to note that when pressure is reduced there is an immediate sharp drop in resistance which continues to rise thereafter. With the controlled flux experiments resistances ceased to rise when flux was reduced to the lowest fluxes.

Polysaccharide fractionation

Figure 9 shows the result of ultrafiltering a sugar beet protein extract using membranes of 10, 30 and 100 kD nominal MWCOs from Millipore.[26] It is clearly seen that the higher molecular weight material exhibits a decreasing rejection coefficient as flux increases. On the other hand the lowest molecular weight shown has a rejection which increases with flux.

This behaviour is seen more clearly in Figure 10 where the material of molecular weight ca 3000 daltons, which appears as a single peak in an HPLC analysis, exhibits a rising rejection with flux for a set of three different MWCO membranes.

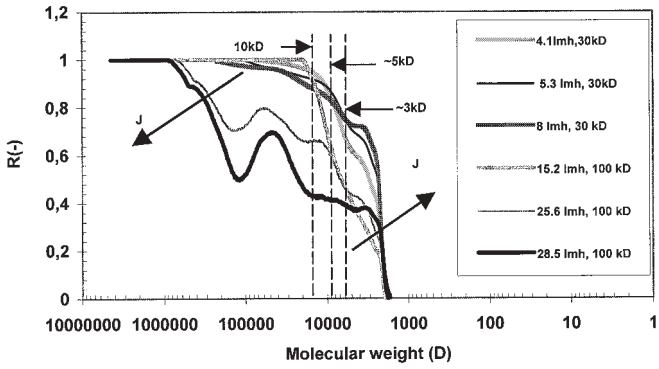

Figure 9. Rejection of polysaccharides as a function of Molecular weight. [26] TMP 70 kPa.

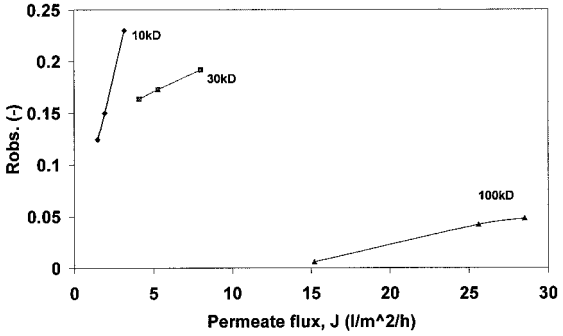

Figure 10. Rejection of polysaccharide as a function of flux. [26] TMP 70 kPa.

Conclusions

Critical flux concepts have practical importance for larger particles above 2 microns in diameter, under most operating conditions where shear is applied tangentially to the membrane surface. The concepts may be used in several ways to allow more efficient membrane operation using controlled flux to minimise excessive fouling. Operating near to the critical flux under controlled flux conditions, with intermittent regular pressure release or flux cessation, allows sustained operation with only an infrequent need for chemical cleaning.

For smaller colloids, less than 1 micron in size, the importance of charge is realised under low ionic strength. In more concentrated solutions the critical flux effect may not be seen and the hydrophobic forces may dominate, or Van der Waals forces may cause the formation of structured entities on the membrane surface. These can be gel-like but may form under conditions well away from the limiting flux, which had previously been thought to be a trigger point for gel formation. Under controlled flux it appears that fractionation may be more straightforward with better separation factors.

Acknowledgements

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