

1

Fundamentals of Fouling

Robert Field

1.1

Introduction

Before examining fouling, it is important to understand some of the ways in which membrane flux is reduced below that of the corresponding pure water flux (or more generally pure solvent flux). The reduction can be divided into two separate parts: First, concentration polarization is a natural consequence of the selectivity of a membrane. This leads to an accumulation of particles or solutes in a mass transfer boundary layer adjacent to the membrane surface. Dissolved molecules accumulating at the surface reduce the solvent activity and this reduces the solvent flow through the membrane. This can be represented as a reduction in the effective transmembrane pressure (TMP) driving force due to an osmotic pressure difference between the filtrate and the feed solution immediately adjacent to the membrane surface. This phenomenon is inevitable, but is reversible with an elimination of TMP and hence flux.

Second, there is fouling, that is to say a buildup of material (e.g., adsorbed macromolecules, gels, or deposited particles on or in the membrane surface). Fouling may take the following forms:

- **Adsorption:** This occurs when specific interactions between the membrane and the solute or particles exist. A monolayer of particles and solutes can form even in the absence of permeation flux, leading to an additional hydraulic resistance. If the degree of adsorption is concentration-dependent, then concentration polarization exacerbates the amount of adsorption.
- **Pore blockage:** When filtering, pore blockage can occur, leading to a reduction in flux due to the closure (or partial closure) of pores.
- **Deposition:** A deposit of particles can grow layer by layer at the membrane surface, leading to an important additional hydraulic resistance. This is often referred to as a cake resistance.
- **Gel formation:** For certain macromolecules, the level of concentration polarization may lead to gel formation in the immediate vicinity of the membrane surface, for example, a solution of concentrated proteins.

In simplistic terms, one can say that fouling is concerned with non-dissolved material that is either deposited on the membrane surface (or on layers that are already adhering to the membrane surface), or material deposited in the pore mouths or on walls, or indeed a mixture of both.

Initially, our attention is restricted to porous membranes and in order to understand the fundamentals of fouling an appreciation of transport to the membrane surface and the physical laws that govern transport through the membrane will be developed, and an appropriate model given. Fouling leads to an increase in resistance giving less flux for a given TMP difference or a higher TMP if flux is kept invariant, by, for example, using a metering pump to maintaining a fixed permeate flow rate. Understanding the other resistances is important and it is imperative to distinguish a reduction in driving force across the membrane (which is the effect of concentration polarization) from an increase in resistance because of fouling of the membrane. Therefore the concept of concentration polarization is introduced with care followed by a model for transport in the absence of fouling. This then allows one to place the terms that are caused by fouling in context.

1.2

Concentration Boundary Layer

Now consider that the minor component is rejected (e.g., salt in reverse osmosis, proteins in ultrafiltration, or oil droplets in microfiltration) (see Figure 1.1). Then the minor component will be of higher concentration in the boundary layer. This layer of

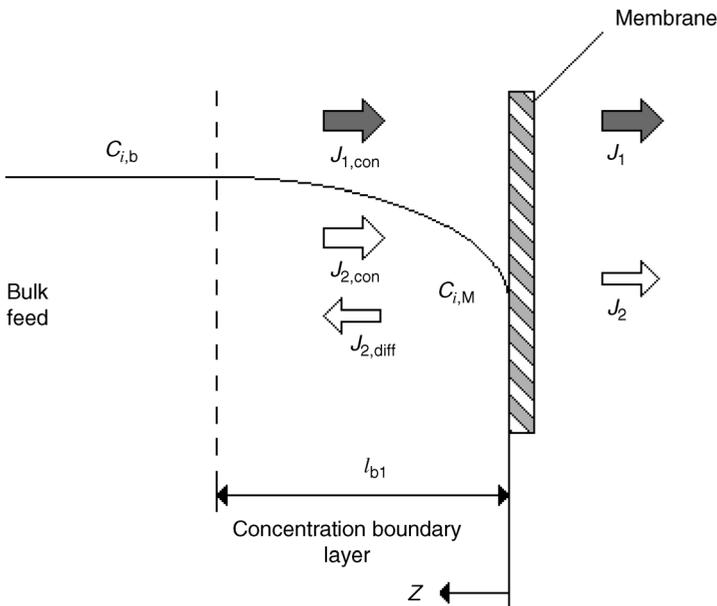


Figure 1.1 Concentration polarization.

a higher concentration is a mass transfer boundary layer, across which the concentration changes, while the overall process is called concentration polarization. It is a natural consequence of membrane selectivity. As a result of the higher concentration of the rejected component there is back-diffusion of it from this thin layer adjacent to the membrane and into the bulk. The extent of accumulation in this layer and its thinness can be estimated from the expressions developed below.

Under steady-state conditions the following relationships describe the relevant fluxes (in $\text{kmol}/(\text{m}^2 \text{ s})$). These are based on Figure 1.1.

Component 1:

$$j_{1,\text{con}} = j_1 \quad (1.1)$$

Component 2:

$$j_{2,\text{con}} = j_{2,\text{diff}} + j_2 \quad (1.2)$$

The following assumptions are made to obtain a mass balance on the feed side of the membrane:

- steady state,
- Fickian diffusion,
- no chemical reaction,
- the concentration gradient parallel to the membrane is negligible, and
- constant density and the diffusion coefficient is independent of solute concentration.

Hence, in general for general component i , together with introduction of volumetric flux, J :

$$J \cdot C_i = J \cdot C_{i,\text{P}} - D_{ji} \frac{dC_i}{dz} \quad (1.3)$$

Integration of Equation (1.3) taking the following boundary conditions into account,

$$z = 0 \quad C_i = C_{i,\text{M}}$$

$$z = l_{\text{bl}} \quad C_i = C_{i,\text{b}}$$

yields:

$$J = \left(\frac{D_{ji}}{l_{\text{bl}}} \right) \cdot \ln \left(\frac{C_{i,\text{M}} - C_{i,\text{P}}}{C_{i,\text{b}} - C_{i,\text{P}}} \right) \quad (1.4)$$

The subscripts M and P refer to the membrane surface and permeate respectively and l_{bl} is the thickness of the mass transfer boundary layer.

From the above equation it is seen that for every component i the concentration at the surface is exponentially related to flux:

$$C_{i,\text{M}} = (C_{i,\text{b}} - C_{i,\text{P}}) \cdot \exp \left(\frac{J \cdot l_{\text{bl}}}{D_{ji}} \right) \quad (1.5)$$

In Equations (1.4) and (1.5) the term (D_{ji}/l_b) can be described as a mass transfer coefficient $k_{i,b}$. The mass transfer boundary layer is also referred to as the concentration polarization layer as the average concentration within this layer is significantly higher, due to the exponential relationship (1.5) than in the bulk. As there is a distinct difference between the two regions, polarization is said to have occurred.

The curvature of the concentration profile depends upon flux and so the relationship between the mass transfer coefficient $k_{i,b}$ ($= D_{ji}/l_b$) and those that can be calculated from conventional chemical engineering correlations need to be treated with care [1]. It can be shown that $k_{i,b}$ approaches a conventional mass transfer coefficient as the flux through the membrane approaches zero ($J \rightarrow 0$). For systems with low fluxes, as in reverse osmosis (RO) or electrodialysis or ultrafiltration (UF) deliberately operated at low fluxes, the correlations linking Sherwood number (which includes the mass transfer coefficient), Reynolds number, and Schmidt number can be used. However, when there is moderate to severe concentration polarization, and this can be related to the value of a boundary layer Peclet number ($J/k_{i,b}$), caution should be exercised when using conventional correlations. In general, the mass transfer coefficient should be obtained from experiments using Equation (1.4). For a solute that is fully rejected the equation becomes:

$$J = k_{i,b} \cdot \ln\left(\frac{C_{i,M}}{C_{i,b}}\right) \quad (1.6)$$

Now as (and this may seem surprising) $C_{i,M}$ has been found to be approximately constant, a plot of flux versus $\ln(C_{i,b})$ is often found to give a straight line of negative slope and this is taken to be $k_{i,b}$.

In general, the boundary layer Peclet number is an important processes parameter on the feed side in liquid membranes processes, while in the case of gas phases the polarization effect is far less important due to the larger (about 10^5 higher) diffusion coefficient in gas phases compared to liquid phases. In passing, it was mentioned that the mass transfer boundary layer is thin; its thickness is given by $D_{ji}/k_{i,b}$. When D_{ji} is simply small, the boundary layer is thin, but for macromolecules, D_{ji} is very small and the boundary layer is very thin. The resulting highly localized high concentrations are relevant to fouling.

1.3

Modeling Ultrafiltration in the Absence of Fouling

The basic mechanism of both microfiltration (MF) and UF is the sieving mechanism, with rejection of molecules whose size is greater than that of the pores. Furthermore, since both processes use porous membranes, the pore flow model can, in principal, be applied if allowance is made for fouling and concentration polarization. However, and particularly in UF, the boundary layer on the feed side of the membrane is the focus.

Darcy's law, which states that flux is proportional to applied pressure difference, can generally be used to describe the flux through an unfouled membrane:

$$J = P \cdot (p_F - p_P) = P \cdot \Delta p \quad (1.7)$$

where J is the volumetric flux and Δp is the TMP.

The permeability constant, P , is a function of membrane structure, including pore size distribution and porosity of the membrane, as well as viscosity of the permeate. Commonly, two approaches are used to describe P . First, when the membrane can be compared to an arrangement of near-spherical particles (as is the case in ceramic membranes), the Carman–Kozeny equation can be applied:

$$J = \frac{\varepsilon^3}{K \cdot \eta \cdot S^2 \cdot (1-\varepsilon)^2} \cdot \frac{\Delta p}{l_{\text{pore}}} \quad (1.8)$$

where ε is voidage, η is dynamic viscosity of the permeate, K is a constant, l_{pore} is the thickness of the porous layer, and S is the specific area (surface area per unit volume). K and S depend upon the particulate nature of the structure.

A different method is required for the majority of membranes. When the structure of the membrane can be assumed to be uniform capillaries (which is the case for track etched membranes) the appropriate approach is to use the Hagen–Poiselle equation. The flux can then be described by:

$$J = \frac{\varepsilon \cdot d_{\text{pore}}^2}{32 \cdot \eta \cdot \tau} \cdot \frac{\Delta p}{l_{\text{pore}}} \quad (1.9)$$

where τ is the tortuosity of the capillaries and d_{pore} is the diameter of the capillaries. Again the flux is inversely proportional to the viscosity of the permeate.

The flux through most unfouled membranes cannot be described by the idealized equations above as these structure do not conform to either of these two idealized forms. Also if a solute is present there will be concentration polarization. Instead the following equation is used to describe the flux in the absence of any fouling:

$$J = \frac{\Delta p - \Delta \pi}{\eta R_m} \quad (1.10)$$

where R_m is the empirically measured membrane resistance and the term $\Delta \pi$ is zero if the feed is a pure solvent. The inclusion of the dynamic viscosity of the permeate, η , makes due allowance for temperature changes because temperature affects this physical property and little else.

In general, the driving force that exists between the bulk feed on one side and that on the permeate side (i.e., $p_F - p_P$) will be reduced by the osmotic pressure difference that occurs due to solute rejection. The term $\Delta p - \Delta \pi$ represents the driving force across the membrane itself. The inclusion of the dynamic viscosity of the permeate,

η , as a separate term (as opposed to its inclusion within R_m) is to be preferred. The separate term R_m is then a constant for a given structure.

An alternative to Equation (1.10) is the following wherein R_{cp} is the resistance of the concentration polarization layer

$$J = \frac{\Delta p}{\eta(R_m + R_{cp})} \quad (1.11)$$

It was shown by Wijmans *et al.* [2] that the two expressions are thermodynamically equivalent with the concentration boundary layer impeding the flow of the solvent and thus “consuming” part of the overall driving force. While the value of $\Delta\pi$ can be calculated through solution of a set of equations, the value of R_{cp} can only be inferred from experiments or from a calculated value of $\Delta\pi$.

If the solute is completely rejected Equation (1.4) will link flux and $C_{i,M}$ (provided bulk concentration, $C_{i,b}$ and mass transfer coefficient, $k_{i,b}$ are known) while Equation (1.10) links flux, Δp , and $\Delta\pi$ (provided the membrane resistance and permeate viscosity are known). The relationship between solute osmotic pressure and concentration can be expressed by equations such as:

$$\pi = aC + bC^2 + dC^3 \quad (1.12)$$

which enables one to relate $\Delta\pi$ to $C_{i,M}$. An excellent approximation is to make $\pi(\text{at } M) = \Delta\pi$. Sufficient information is now available to plot flux as a function of TMP with the values of $\Delta\pi$ and $C_{i,M}$ also being noted.

The above equations can be adopted for RO and MF to give idealized fluxes in the absence of fouling. However osmotic effects are often small in MF applications.

1.4

Modeling Membrane Filtration in the Presence of Fouling

Now that a sound basis has been provided, additional terms can be added to account for the hydraulic resistance that is due to material accumulation on the membrane surface and/or in the membrane pores. This is known as fouling. Whether it is on the membrane surface or in the pores will affect the relationship between flux and TMP and this is considered later. At this stage a threefold division of the overall fouling resistance is introduced. These resistances can be considered to be in series with the membrane resistance. Hence:

$$J = \frac{\Delta P - \Delta\pi}{\mu(R_m + R_{ads} + R_{rev} + R_{irrev})} \quad (1.13)$$

The first of the additional hydraulic resistances, R_{ads} , is for the resistance due to surface or pore adsorption that occurs independently of flux. This is measured by contacting the membrane with the feed in the absence of flux (for say a few hours) and then measuring a pure solvent flux at a known TMP. This enables a hydraulic resistance to be calculated and the difference between it and R_m gives R_{ads} . The experiment can be repeated for other contact times.

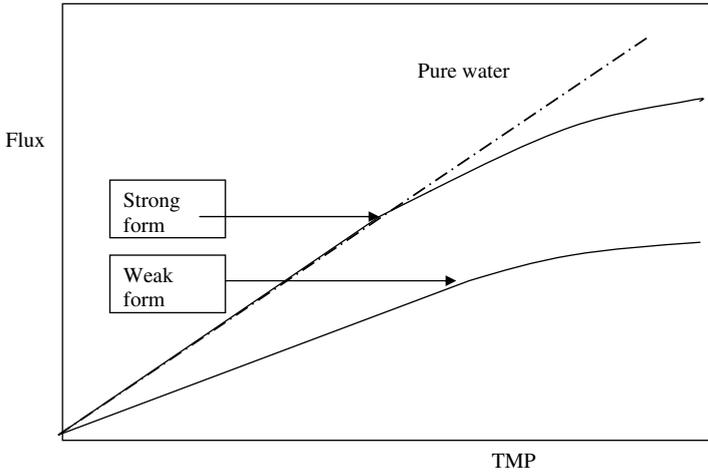


Figure 1.2 Forms of critical flux as originally defined by Field *et al.* [3]. TMP, transmembrane pressure.

The other terms reflect the fouling that occurs during operation. The increased resistance that occurs during operation can be divided into a reversible component, R_{rev} (i.e., one that occurs during operation but is not present after switching from the feedback to pure solvent), and an irreversible component, R_{irrev} that reflects the deposition of material that is only removable (at best) by a cleaning operation.

This classification allows one to distinguish additional resistances (such as adsorption) that are independent of the pressure and permeate flux from fouling phenomena driven by the solvent transfer through the membrane. Fouling of the latter type can be reversible (R_{rev}) or irreversible (R_{irrev}) when the pressure is decreased.

When considering these fouling mechanisms, the strong form of critical flux, J_{cs} , has been developed to discriminate no fouling conditions (where R_m is the only resistance in Equation (1.13) from fouling conditions where other resistances also apply. It has been defined [3] as the flux at which the flux–TMP curve starts to deviate from linearity (Figure 1.2). So with the assumption that osmotic pressure effects are negligible

$$\begin{aligned} \text{for } J < J_{cs} : J &= \frac{\Delta P}{\mu R_m} \\ \text{for } J > J_{cs} : J &= \frac{\Delta P}{\mu(R_m + (R_{rev} + R_{irrev}))} \end{aligned} \quad (1.14)$$

where at least one of R_{rev} or R_{irrev} is non-zero and where R_{ads} is considered as negligible.

For UF, the flux through the membrane can ideally be described in analogy to MF with allowance for osmotic effects due to concentration polarization. This yields a pair of equations:

$$J_{\text{ideal}} = (\Delta p - \Delta \pi) / \mu R_m$$

$$J_{\text{actual}} = \frac{\Delta p - \Delta \pi}{\mu(R_m + R_f)} \quad (1.15)$$

where the ideal may apply at sufficiently low fluxes. The simplest definition of critical flux is the flux at which fouling is first observed for a given feed concentration and given crossflow velocity. It should be a design consideration for all pressure-driven processes.

For an advanced discussion of how the concept of critical flux has developed, see Bacchin *et al.* [4].

If there is operation at constant TMP, then Equation (1.15) shows that increasing of R_f with time will lead to flux decline. Typically, there is an initial rapid decrease followed by a longer more gradual decline, followed in many cases by a steady state being reached. As discussed later, the flux of solutes and particles towards the membrane surface reduces as the volumetric flux decreases. Thus the accumulation will cease when there is a balance between “flux of solids in” and “removal away.” With accumulation finished, the volumetric flux through the membrane will be steady unless reduced by adverse changes in the accumulated material. In all cases, operation at a high initial flux is to be avoided as it leads to an excessive flux of foulants towards the membrane surface.

If instead of operation at constant TMP there is operation at constant flux, then fouling leads to increases in TMP. If the fouling rate is low, this mode of operation has much to commend it. With a constant flux, the rate of TMP increase is generally either linear or concave upwards. In Figure 1.3 the data from 15 min to 60 min can be represented by a straight line which is indicative of cake formation on top of the membrane; the slightly higher slope before that time reflects the fact that the initial layers of cells partially blocked the membrane and so had a greater effect per unit

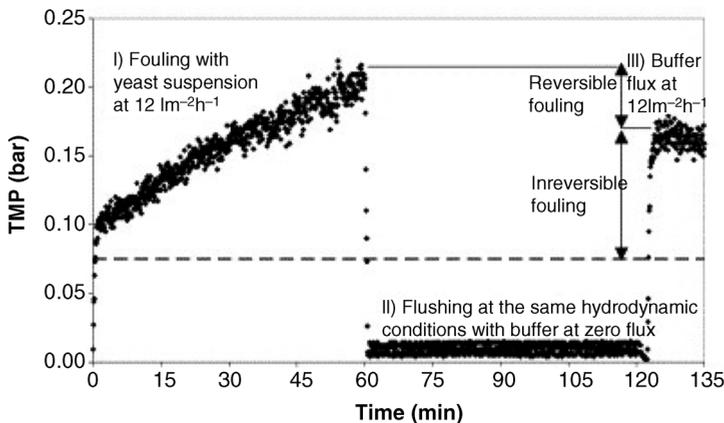


Figure 1.3 Example of operation at constant flux showing slightly higher fouling rate in the first 15 min compared with post 15 min. The level of irreversible fouling is shown to be greater than that of reversible fouling [5]. TMP, transmembrane pressure.

mass of yeast cells convected to the membrane surface. Figure 1.3 also illustrates the distinction between the reversible component of fouling, R_{rev} , that is, one that is readily removed after switching from the feed to buffer (the presence of salts in the buffer is irrelevant), and an irreversible component, R_{irrev} , that reflects the deposition of material that is only removable (at best) by a cleaning operation.

So far we have mentioned fouling as adversely affecting the hydraulics – decreasing flux (for fixed TMP) or increasing TMP (for a given flux) – but the changing of the effective pore size distribution will also cause operating problems if transmission of certain solutes is desired. This is the case in beer filtration, where retention of cells but passing of proteins is essential. In the analysis of membrane performance in this case it must be remembered that it is a separating device. For example, in desalination using RO, the driving force for salt passage may not be as adversely affected in a fouled membrane as that of the water flux. Thus the percentage of salt on the permeate side will increase. As one is aiming to reject 99.5% of the salt, small changes can be significant.

1.5

Fouling Overview: its Nature and Key Influences

Fouling has sometimes been seen as a reduction in the active area of the membrane which leads, therefore, to a reduction in flux below the theoretical capacity of the membrane for the given driving force. If the pores are partially blocked or restricted this is true, but a cake layer on the surface of a membrane is a resistance that is in series with the membrane resistance. A consideration of the various modes of fouling will be found in Section 1.6. At this point it is noted that trouble-causing substances can be divided into two categories: those that damage the membrane and those that foul the membrane. As a fouled membrane requires cleaning, damage to the membrane might, if care is not taken, occur in the cleaning phase. Fouling during filtration clearly has a negative influence on the economics of any membrane process and so it must be understood and counter-measures must be adopted to mitigate the effects. For MF and UF, the fouling can be very severe with the process flux often being less than 5% of the pure water flux.

Several parameters influence the fouling rate, such as:

- nature and concentration of solutes and solvents;
- membrane type;
- pore-size distribution;
- surface characteristics and material of membranes; and
- hydrodynamics of the membrane module.

Roughly four types of foulant have been distinguished: (i) organic precipitates (macromolecules, biological substances, etc.); (ii) colloids; (iii) inorganic precipitates (metal hydroxides, calcium salts, etc.) and (iv) particulates. A more comprehensive list is given in Table 1.1, the last entry of which relates to biofilms. For certain applications, the problem is not one of foulants in the feed but biofilms that form

Table 1.1 Examples of foulants and fouling modes in membrane processes.

Foulants	Fouling mode
Large suspended particles	Particles present in the original feed (or developed due to concentration polarization) can block module channels as well as forming a cake layer on the surface
Small colloidal particles	Colloidal particles can create a fouling layers (e.g., ferric hydroxide from brackish water can become a slimy brown fouling layer). In recovery of cells from fermentation broth, some colloids can be present
Macromolecules	Gel or cake formation on membrane. Macromolecular fouling within the structure of porous membranes
Small molecules	Some small organic molecules tend to have strong interactions with some polymeric membranes (e.g., anti-foaming agents, such as polypropylene glycols used during fermentation, adhere strongly to certain polymeric membranes)
Proteins	Interactions with surface or pores of membranes
Chemical reactions leading to scaling	Concentration increase and pH changes can lead to precipitation of salts and hydroxides
Biological	Growth of bacteria on the membrane surface and excretion of extracellular polymers

Modified after Scott [10].

from the constituents in the feed. This is particularly important in water applications. Biofouling is covered in detail in Chapter 2. The influence of all of these foulants is made adverse by the effect of concentration polarization; as noted earlier the surface concentration is expected to increase exponentially with flux (Equation 1.5). Thus lower fluxes will give less fouling, with the effect being non-linear. Furthermore, this equation indicates that improved mass transfer will also lead to lower surface concentrations, which is why hydrodynamics of the membrane module was listed as one of the five main influences. A higher crossflow velocity will improve mass transfer and reduce fouling.

To the mass balance Equation (1.3), one can add, when appropriate, an electrostatic term. Such terms are often important. Indeed the UF of electro-dip coat paints, which are mentioned in more detail in Section 1.9, depends upon a repulsive force between the paint particles and the membrane surface. Under these circumstances one can consider the critical flux as the flux at which the convective term is equal to the electrostatic one; beyond this flux, fouling will be severe. In general, the net flux of material towards the membrane can be viewed as being a combination of fluxes, some of which tend to move material away from the membrane surface while the convective flux, among other fluxes, moves material towards the surface. The overall material flux, N , is given by:

$$N = JC - D \frac{dC}{dz} + p(\zeta) + q(\tau) \quad (1.16)$$

where D is the Brownian diffusion coefficient, $p(\zeta)$ represents the term for migration

of the solutes/particles due to interactions between the membrane surface and the surfaces of the solutes/particles, and $q(\tau)$ represents the effect of the local hydrodynamics on the mass flux. The possible settlement of non-buoyant particles onto the membrane surface has not been included. Now, as discussed elsewhere [4], $p(\zeta)$ can be positive in the case of electrostatic attraction, which corresponds to adsorption of the solute onto the membrane, whereas a negative $p(\zeta)$ corresponds to repulsion. The consequences of this have been developed by several authors [6, 7]. The particle–membrane repulsion is efficient as long as the migration so induced exceeds the magnitude of the migration due to the convective flux. This is the case for UF plants treating electro-dip coat paints.

The term $q(\tau)$ represents the effect of the local hydrodynamics on the material flux. It depends, but not exclusively, on the shear forces. The term includes migrations (e.g., lateral migration) and diffusive effects which necessitate concentration gradients. The latter encompass turbulent diffusion and shear-induced diffusion. These effects have been discussed extensively in a review [8] and several papers (e.g., [9]). These effects increase with increasing particle size and are important for feeds with particulates.

It has been argued that the critical events in fouling could be thought of as being linked to a critical concentration at the surface rather than a critical flux. This has some merit with regard to scaling effects in RO. With RO, a certain flux and a given water chemistry can lead to surface concentrations that exceed the solubility product of certain salts and a tendency for scaling can then be expected. Although the trigger is a certain value of $C_{i,M}$ (Equation 1.5), the controllable variable is the flux, J , and so it is still more useful for the process engineer to think in terms of the critical flux concept.

The penultimate entry in Table 1.1 relates to scaling. In RO, the removal of a permeate that has hardly any salt leads to enrichment (in salts) of the retentate and consideration has to be given to whether the solubility limits of salts such as BaSO_4 and CaCO_3 are likely to be exceeded. As the pH to remove CaCO_3 during a cleaning cycle might well be outside of the range tolerated by the membrane, precipitation of CaCO_3 is definitely to be avoided. Scale inhibitors can be added to the feed and it is interesting that a recent paper [11] gave the cost of scale inhibition as 5.8% of the total cost, which was exactly the same percentage as for membrane replacement. Incidentally the three greater costs were capital recovery, expenditure on pumping, and labor costs. This shows not only the importance of antiscaling chemicals but also that membrane replacement costs in RO are no longer an important issue.

1.6 Modeling of Fouling

For porous membranes the active area of the membrane is the pores. Hence, most fouling mechanisms are related to them and the processes which lead to a reduction in the number of active pores. Based on this, generally four fouling mechanisms for porous membranes can be observed. As shown in Figure 1.4, these are:

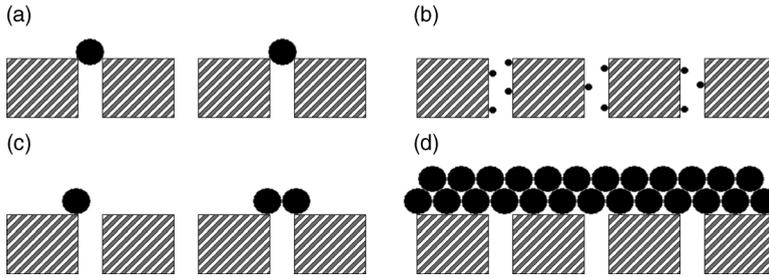


Figure 1.4 Fouling mechanisms of porous membranes. (a) Complete pore blocking; (b) internal pore blocking; (c) partial pore blocking; (d) cake filtration.

- 1) complete pore blocking,
- 2) internal pore blocking,
- 3) partial pore blocking, and
- 4) cake filtration.

In Table 1.2 the phenomenological background concerned with each mode, their effect on the mass transport and the relevant transport equations are given but with no allowance being made for crossflow. The origin of the index n will soon become apparent. The equations are a reworking of Hermia's [12] and are applicable to dead-end filtration and only the initial time periods of crossflow membrane operation. More will be said soon about allowing for crossflow.

Hermia's original unifying equation took the following form:

$$\frac{d^2 t}{dV^2} = k \left(\frac{dt}{dV} \right)^n \quad (1.17)$$

It may be thought strange that time of filtration is differentiated with respect to the volume of filtrate collected per unit area but this is the mathematical form that emerges if the focus is upon volume of filtrate collected. For those with a focus upon membrane operations, flux and flux decline are the normal foci and then Equation (1.17) takes the simple form:

$$\frac{dJ}{dt} = -kJ^{3-n} \quad (1.18)$$

In this form one aspect of the index n becomes immediately clear: the smaller the value of n , the greater the decrease in the magnitude of the rate of flux decline. As J decreases, the term J^{3-n} becomes smaller more rapidly the greater the value of the index.

Those mathematically inclined might like to note that for $n \neq 2$, the following equation can, in the absence of any crossflow effect, be used to describe the influence of fouling on the flux through the membrane [13]. Apart from $n = 2$, it summarizes the equations in Table 1.2.

Table 1.2 Fouling mechanisms, phenomenological background and transport equations.

Fouling mechanism	n	Phenomenological background	Effect mass transport	Transport equation in absence of cross-flow
Complete pore blocking (see Figure 1.4a)	2	Particles larger than the pore size completely block pores	Reduction of the active membrane area. Depends on feed velocity.	$J = J_0 \cdot K_b \cdot t$
Internal pore blocking (see Figure 1.4b)	1.5	Particles smaller than pore size enter the pores and get either adsorbed or deposited onto the pore walls. This restricts the flow of permeate	Increase in membrane resistance due to pore size reduction. Internal pore blocking is independent of feed velocity. Mitigation by cross-flow is absent	$J = J_0 \cdot \left(1 + \frac{1}{2} \cdot K_s \cdot (A \cdot J_0)^{0.5} \cdot t\right)^{-2}$
Particle pore blocking (see Figure 1.4c)	1	Particles reaching surface may seal a pore or bridge a pore or partially block it or adhere on inactive regions	Reduction of active membrane area. The effect is similar to pore blocking but not as severe	$J = J_0 \cdot (1 + K_f \cdot (A \cdot J_0) \cdot t)^{-1}$
Cake filtration (see Figure 1.4d)	0	Formation of a cake on the membrane surface by particles which neither enter the pores nor seal the pores	The overall resistance becomes the resistance of the cake plus the resistance of the membrane (which may already be fouled by other mechanisms)	$J = J_0 \cdot (1 + 2 \cdot K_c \cdot (A \cdot J_0)^2 \cdot t)^{-\frac{1}{2}}$

Modified after Giorno [14].

$$J = J_0(1 + K(2-n)(A \cdot J_0)^{(2-n)}t)^{(1/n-2)} \quad (1.19)$$

In the above equation the phenomenological coefficients n and K depend on the fouling mechanism. The form of the equation for specific values of n is given in Table 1.2. It must be noted that these include no allowance for crossflow, which can be expected to influence three of the four modes. The exception is internal pore blocking.

A more sophisticated approach was developed in the 1990s with allowance for crossflow [3]. Equation (1.18) is modified to allow for backflux. It then becomes:

$$\frac{dJ}{dt} = -k(J - J_{ss})J^{2-n} \quad (1.20)$$

where J_{ss} is the steady-state flux reached at long times.

In the presence of crossflow the flux at long times generally approaches a non-zero value. If a cake has been formed, then the value of J_{ss} will correspond to the critical flux for cake formation under the specific process conditions (concentration, crossflow velocity, etc.) for the system under consideration. The integrated forms of Equation (1.20) can be found in the appendix of [3] for values of n equal to 2, 1, and 0.

Internal pore blocking is a particularly serious mode of fouling because it is exempt from the mediating effects of crossflow and cleaning may be more difficult. Thus the correct choice of pore size is very important. One of the reasons for modeling fouling is to determine whether the flux decline is due to internal pore blocking, that is, whether $n = 1.5$ or not. Now if the fit for a particular model such as cake filtration for the time interval 15–75 min is excellent then one can take this as being the mode for that time interval and extrapolate back to cover the period 0–15 min. If there are differences between the data and the model for this period (and often there are) then another mode of fouling was dominant at earlier times. One can then concentrate upon an analysis of the early time data. By obtaining this information, an understanding of why one membrane is performing differently from another can be developed. Sometimes a larger pore size gives a higher initial flux (as expected) but an unexpected lower flux than a smaller pore-sized membrane. This is typical for the MF of cell broth, where $0.2 \mu\text{m}$ is often to be preferred to $0.5 \mu\text{m}$; in many biotechnological applications, the larger size often suffers from excessive internal pore blocking.

In addition to the concept of a critical flux, it is useful to consider whether or not there is a threshold flux below which fouling is low and above which fouling is high. Limiting membrane fluxes to a region where fouling is minimal may well give the economic operation regime. With just some moderate fouling, only simple periodic cleaning may be needed without the need for intensive chemical cleaning. This is particularly relevant to water treatment by UF, where some fouling is inevitable but observation suggests a breakpoint in the fouling rate. The concept of a threshold flux will be introduced and illustrated in Section 1.9.

Table 1.3 Approaches to prevent and reduce fouling.

Direct methods	Indirect methods
Turbulence promoters (e.g., modified membrane spacers)	Pretreatment by filtration
Pulsed or reverse flow	Treatment of the membrane surface
Rotating or vibrating membranes	Preparation of more hydrophilic membranes
Stirred cells with rotating blades close to the membrane	
Ultrasonic enhancement	Selection of appropriate operating mode
Periodic maintenance cleaning	Selection of optimum operating conditions
<ul style="list-style-type: none"> • Chemical cleaning • Hydraulic cleaning • Mechanical cleaning 	
Periodic backwash with permeate or gas	
Generation of a dynamic membrane layer	

1.7

Prevention and Reduction of Fouling

Having examined the modeling of flux decline, the approaches to prevention and reduction of fouling are now mentioned. Table 1.3 gives an overview of several approaches to reduce the influence of fouling. These have been divided into direct and indirect methods. Some of the direct methods, such as the use of turbulence, are clearly similar to the measures taken to reduce the intensity of a concentration boundary layer. The selection of appropriate operating models has been placed with indirect methods. This encompasses the choice of whether one is choosing crossflow or dead-end (direct) filtration with periodic backflush. For a highly fouling feed the former is essential, but for drinking water filtration the latter is now the norm because it can be made to work at greatly reduced energy costs compared with traditional crossflow membrane filtration.

It may seem strange to have included cleaning in a list of fouling *prevention* measures but regular intermittent cleaning (e.g., chemically enhanced backwash) can reduce the need for major cleaning-in-place (CIP) procedures. It is suggested that in many industries, cleaning procedures might be viewed as consisting of two types: those for regular maintenance and those for recovery. Clearly, well-adapted maintenance cleans prevent the need for excessive recovery cleans.

While introducing low-fouling RO for wastewater treatment, Uemura and Henmi [15] state that 80% of operating problems in RO in general are related to fouling. To avoid this three factors are mentioned as important. First, the correct choice of membrane element, second, appropriate pretreatment upstream of the RO plant, and third, suitable sterilization and cleaning procedures. The importance of the first stage was illustrated by showing data on the treatment of a local wastewater. Although Toray's new low fouling elements, TML-20, had a lower initial flux

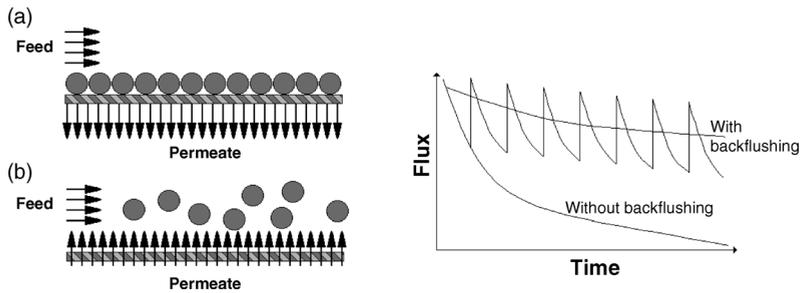


Figure 1.5 Backflushing. (a) Standard mode and (b) backflushing concept and anticipated outcome.

compared with their conventional RO elements, the difference was negligible after one day of operation and the TML-20 elements had superior normalized fluxes ($\text{m}^3/\text{d MPa}$ at 25°C) from day 2 onwards. At day 15 the difference was 30%. This illustrates that fouling prevention starts with correct choice of materials selection and operating procedures. Interestingly the data on the TML-20 elements suggest that one can operate these elements, at least for this wastewater, below a critical flux (weak form), given correct pretreatment, and so have very long periods between cleans.

Figure 1.5 illustrates the use of flushing to remove cake layers on the feed side and, therefore, reduce the influence of fouling. It is carried out by reversing the flow of the permeate through the membrane. This can dislodge some of the foulants, particularly particulates, and re-establishes the flux at a high level. In order to maintain a high overall flux, backflushing is carried out periodically and requires module types and membranes that can withstand the reverse flow. It is an essential operation in dead-end operated UF and MF systems. Backflushing with the inclusion of a low concentration of cleaning chemicals, such as ppm levels of chlorine, is called a chemically enhanced backwash. These backwashes can clean the membrane pores.

The efficiency of backflushing depends upon its frequency, duration, and intensity, and the type of fouling. The intensity might be defined in terms of the reverse flux or the pressure ratio ($\text{TMP}_{\text{back}}/\text{TMP}_{\text{forward}}$). A high-frequency backwash strategy was designed by Sanjeev and Davis [16] for washed yeast suspensions, and with the optimal system they achieved fluxes 20 times that of the long-term flux in the absence of backflushing. Unlike unwashed cells, their washed cells would have lacked extracellular polysaccharides (EPS). This would strongly have influenced the results. Interestingly, for their easy-to-remove deposit they showed that the dependency upon crossflow velocity was small. The deposit has been labeled as “easy-to-remove” because they found little dependency upon reverse flux and because EPS was absent. Thus, unlike the results shown in Figure 1.3, their system fouled mainly in a reversible manner.

It is well known that the use of baffles and pulsating flow can be helpful in improving heat transfer and both areas have been researched in UF and MF, but for tubular systems there has been little or no commercialization. Of greater interest are the use of two-phase flow and vibrations. Two-phase flow heat transfer coefficients are

much higher than those in single phase and the use of air-sparging has been well investigated for membrane systems, particularly for membrane bioreactors [17].

In the 1990s the New Logic vibratory shear-enhanced processing (VSEP) system emerged as an exciting alternative, especially for feeds with high solid levels. While the feed slurry is pumped slowly between parallel membrane leaf elements, a high shear is created by a vigorous vibration of these elements in a direction tangential to the membrane surfaces. The shear waves produced by the membrane's vibration induce solids and foulants to be lifted off the membrane surface and remixed with the bulk feed. The high-shear processing allows the membrane to operate closer to the clean water flux. The company state that the throughput is typically between 3 to 10 times the throughputs of conventional crossflow systems [18].

From this brief introduction to prevention and reduction of fouling one can see that a variety of approaches have been developed. While prevention is the aim, and this can sometimes be achieved on the laboratory scale with well-defined feeds, the reality is that the objective is one of reduction. For new applications, pilot plant tests to establish the extent of fouling rates and the efficacy of cleaning methods are essential. Further contextual remarks are made with respect to particular applications.

1.8 Reverse Osmosis and Fouling

One must not assume that the success reported by Uemura and Henmi [15] in wastewater treatment, referred to above, will be readily replicated worldwide because waters, including seawater, are highly variable. For example, in other areas of the world such as the Red Sea coast the high microbe load and inlet temperature present a major challenge in RO plants, and a chlorine-tolerant but relatively low-flux RO membrane made from cellulose triacetate might well be selected ahead of a chlorine-intolerant high-flux membrane. If chlorine-tolerant, high-flux RO membranes can be produced in the future then they will give a huge boost to desalination by RO; the plant design and control would be simplified as the chlorine-control units prior to the RO elements (that currently involve careful sodium bisulfate (NaHSO_3) addition) would no longer be required.

Just as the microbial challenge varies from location to location, so does the availability of low-grade heat and the cost of power. Thus process optimization for one site will be different from that of another. One constant is that membrane fouling remains the most common reason for performance problems. These are not just reduced flux but also reduced salt rejection, increased TMP, and increased longitudinal pressure drop in the direction of feed flow. As biofouling is considered in the next chapter, further comments are confined to scaling.

The major ions that lead to scaling are calcium, magnesium, barium, bicarbonate, and sulfate. These can lead to precipitation of the following salts as the retentate becomes increasingly concentrated: CaSO_4 , CaCO_3 , BaSO_4 , $\text{Mg}(\text{OH})_2$. Silica (SiO_2) can also be a major problem. With effective antiscalant dosing, the system can be

operated at significantly higher recoveries (i.e., more product water per unit of feedwater) than would otherwise be the case. This is why nearly 6% of operating costs can be spent on the dosing of antiscalant chemicals at the few ppm level. The dosing must be accompanied by good pH control. Then the frequency of maintenance cleaning will generally be less than monthly.

1.9

Fouling in Ultrafiltration and Microfiltration

Remarks are made with regard to two very well-established applications, namely oily-water treatment and the UF of electro-dip coat paints, and then two more recent applications, namely membrane bioreactors (MBRs) and drinking water filtration. One of the early successes of UF was the concentration of oil–water emulsions. Rautenbach and Albrecht [19] reported that in 1979 there were about 250 UF units in operation in Germany alone and that these had been operating for 3 years or more. At the same time, such units were also a major application success for Koch, among others in the United States. The feed is concentrated for ready disposal and the permeate contains almost no oil (<50 mg/l). Typically, units are either tubular, or capillary or plate-and-frame modules. With the right hydrodynamic conditions, decent steady-state fluxes are achieved, and fouling, although significant, is well controlled.

Another early success was the recovery of paint particles from the washing stage that follows the dip-coat painting/priming of car bodies or the painting of household appliances. The earlier process of precipitation and sludge removal was replaced by UF, which not only gave a permeate of high quality but also recovered valuable paint resins and pigments. The overall process was better controlled and paint losses greatly reduced. Also water consumption was reduced as the water permeate could be recycled. Around 30 years ago the paint process was anodic but now it is cathodic and the membrane manufacturers had to adapt their systems; otherwise the attractive forces would have led to severe fouling. Interestingly, some membrane manufacturers offer chemicals that impart a positive charge on the membrane surface in order to more effectively repel cathodic paint particles. This pretreatment retards fouling. As it is hard to give a permanent positive charge to membranes, the pretreatment is probably essential if one is to remove the foulants completely.

The early UF units were either tubular or capillary modules but some manufacturers now prefer spiral-wound membranes for this use. One would anticipate that the spiral-wound units would be prone to more fouling than tubular and capillary modules because they have small gaps with feed spacers that are known to give laminar-like conditions at the surface but turbulent-like pressure drops in the direction of flow [20]. However, such units offer much more surface area per unit volume, and with the development of advanced cleaning chemicals that solubilize deposits more effectively, they are incorporated into some of the systems of choice.

Thus advances in cleaning (and pretreatment) have opened up the options and led to new optimal solutions.

Two greatly expanding applications of UF are wastewater treatment and drinking water filtration. The former relates particularly to aerobic MBRs. With aeration in MBRs providing decent shear at membrane surfaces, the critical flux hypothesis suggests that it is worth exploring whether one can operate below it or close to it. Zenon and Kubota have exploited this idea, the former with their hollow fiber system, the latter with a flat-plate system. In both cases the membranes are submerged in the aeration tank and operated at constant flux with the driving force being provided by suction on the permeate side. The systems give a combination of biologic treatment with excellent filtration that excludes bacteria and viruses from the final product water, the permeate. The systems can be adapted to treat municipal, commercial, or industrial wastewaters and the permeate can be reused.

The ZeeWeed[®] MBR system from Zenon can be backflushed, which limits the need for chemical cleans. The literature suggests that the economic flux is a controlled flux in excess of the critical and thus the system is operated with gentle fouling.

The strategy for Kubota may be currently similar but some interesting data for a particular water from Ishida *et al.* [21] with the Kubota system reported that one could obtain $0.5 \text{ m}^3/\text{m}^2$ per day with a steady pressure of 30 kPa, which was subcritical operation. However as the storm overload condition necessitated operation at higher fluxes/TMPs there was some fouling under these conditions. With 70 kPa, they initially obtained $1.05 \text{ m}^3/\text{m}^2$ per day but this declined to $0.94 \text{ m}^3/\text{m}^2$ per day due to fouling. On returning from supercritical conditions to the original flux, the TMP was initially a third higher than previously but there was some removal of foulants and the flux settled at 35 kPa.

The advantages of simple modes of operation are obvious for unmanned systems and, in the UK at least, the Kubota system seems to be preferred at the small commercial scale and the Zenon at the larger commercial scale. Subcritical flux operation was originally reviewed by Howell [22] who discussed the complexities of mixtures in which different components have different critical fluxes. Sometimes cleaning is easier if one operates above the critical flux of a component that acts as a filter aid and is also easy to remove.

UF is also expanding into the drinking water market where the excellent filtration capability of UF guarantees that filtered surface waters are not only free of turbidity and suspended solids but also of bacteria. Unlike conventional systems that combine a number of processes and require a higher degree of monitoring, membrane systems can often run unattended with remote monitoring. For drinking water the modern tendency is to operate UF with controlled fluxes which exceed the critical and thus allow fouling. Fouling is then removed fairly frequently, and almost completely, by a backflush, which may well be chemically enhanced. Under such dynamic operating conditions, the intermittent operation can sustain a flux with only moderate increases in TMP. This flux provides a compromise between capital expenditure (which is reduced by using high flux) and operating costs (which are reduced by restricting the fouling rate). Pilot trials can be used to

establish the relationship between flux and fouling rate for a particular application and process design. Pilot plant data for four different water sources showed [23] that the fouling rate, as monitored by daily TMP increases, was approximately constant below a “threshold flux” and linear with additional flux above this value. This analysis provides a method for analyzing pilot data and developing guidelines for design and operation. The equations are a development of Equation (1.14). In the form below, they are for constant flux operation and the distinction is between “low” fouling and “high” fouling and not between “no” fouling and the beginning of fouling.

$$\begin{aligned} \text{Rate of permeability loss} &= a + b \cdot (J - J^*) \quad \text{for } J > J^* \\ \text{Rate of permeability loss} &= a \quad \text{for } J \leq J^* \end{aligned} \quad (1.21)$$

where a and b are constants and J^* is the threshold flux.

The critical flux concept, initially proposed for steady-state systems, is limited in describing the pseudo steady-state dead-end systems normally used in water applications of UF, because a low degree of fouling is inherent to dead-end, even at low flux. The economic flux for a plant is that flux at which there is an acceptable degree of fouling, but that the fouling is easily removed in a cleaning procedure of acceptable frequency. It seems from recent analysis of permeability decline versus flux that there is a threshold flux, above which there is an exponential increase in fouling rate [23]. For a given feed source, membrane system, and process design, the economic flux will be dependent on the threshold flux and CIP frequency. Depending upon the value b in Equation (1.21), one might design to be below the threshold flux, J^* , rather than at J^* in order to allow for plant upsets. The threshold flux approach is particularly applicable to the dead-end/direct flow systems, but could find wider application. In essence, one is seeking to find if there are key breakpoints in the rate of permeability versus flux curve.

1.10

Fouling in Pervaporation and Gas Separation

With the exception of RO, the fouling of dense membranes has often been neglected because the feeds are relatively very clean. In gas separation the membranes are protected from particulate matter by the inclusion of upstream filtration and fouling of the membranes should not be an issue at all. Minor components in the feedstream can adversely affect the membrane itself or the seals but this is a different issue.

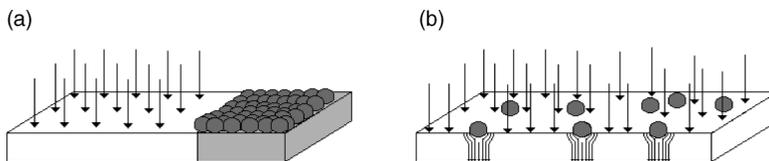


Figure 1.6 Fouling mechanisms of dense membranes. (a) Surface blocking; (b) particle blocking.

Likewise fouling should never be an issue with vapor permeation but the liquid feed of pervaporation can pose fouling problems. Recent observations [24] have shown that fouling can affect these dense membranes.

For dense membranes, two types of fouling can be identified (Figure 1.6): (a) surface blocking and (b) particle blocking.

In the case of surface blocking it is assumed that the blocked membrane area is not available for mass transport and, therefore, the active membrane area is reduced. One might also label this as surface blinding. The flux through the partly blocked membrane can be described as a function of the theoretical flux through the unblocked membrane by:

$$J = J_o \cdot \frac{(A_{\text{tot}} - A_{\text{blocked}}(t))}{A_{\text{tot}}} \quad (1.22)$$

In the case of particle blocking there are two contributory effects: (i) a reduced active membrane area due the particles and (ii) an increased diffusion path through the membrane as can be seen in Figure 1.6. The fouling of dense membranes will not be discussed further.

1.11

Concluding Remarks

Fouling, cleaning, and process design are inextricably linked and process solutions will continue to evolve. The value of the critical flux and threshold flux concepts is that they can be used to guide membrane plant design. A life cycle analysis of membrane plants has shown that the main environmental impact of membranes is from the energy required to power their operation. Membranes are becoming cheaper and so operating plants around the threshold flux is economic and practical as demonstrated by trends in the water industry. These designs also put less stress on the membrane and reduce the environmental impact of frequent chemical cleaning and membrane replacement. This chimes with current emphases within society.

List of Main Symbols

Symbol	Definition	Typical units
A	area	m^2
C	concentration	kg/m^3
D	diffusion coefficient	m^2/s
j	solute or component flux	$\text{kmol}/(\text{m}^2 \text{ s})$
J	volumetric flux	m/s
K	fouling constant or constant in Equation (1.8)	–

Symbol	Definition	Typical units
k	mass transfer coefficient or constant in Equation (1.17)	m/s
l	length, thickness	m
p	pressure	Pa
P	permeability	$l/m^2 h$ per bar
R	resistance	m^{-1}
t	time	s
z	z-coordinate, normal to membrane	m

Greek Symbols

Symbol	Definition	Unit
η	dynamic viscosity	Pa s
π	osmotic pressure	Pa
ρ	density	kg/m^3

Subscripts

Symbol	Definition
0	standard, reference
b	bulk or complete pore blocking
bl	boundary layer
B	boundary layer or complete pore blocking
C	cake filtration
con	convective
diff	diffusive
i	component i or particle pore blocking
j	component j
P	permeate
M	membrane

References

- Vasan, S.S. and Field, R.W. (2006) On maintaining consistency between the film model and the profile of the concentration polarisation layer. *J. Memb. Sci.*, **279**, 434–438.
- Wijmans, J.G., Nakao, S., Van Den Berg, J.W.A., Trolstra, F.R., and Smolders, C.A. (1985) Hydrodynamic resistance of concentration polarization boundary layers in ultrafiltration. *J. Memb. Sci.*, **22**, 117–135.
- Field, R.W., Wu, D., Howell, J.A., and Gupta, B.B. (1995) Critical flux concept for microfiltration fouling. *J. Memb. Sci.*, **100**, 259–272.
- Bacchin, P., Aimar, P., and Field, R.W. (2006) Critical and sustainable fluxes

- review. Theory, experiments and applications. *J. Memb. Sci.*, **281**, 42–69.
- 5 Hughes, D. and Field, R.W. (2006) Crossflow filtration of washed and unwashed yeast suspensions at constant shear under nominally sub-critical conditions. *J. Memb. Sci.*, **280**, 89–98.
 - 6 McDonogh, R.M., Fane, A.G., and Fell, C.J.D. (1989) Charge effects in the crossflow filtration of colloids and particulates. *J. Memb. Sci.*, **43**, 69–85.
 - 7 Bowen, W.R., Mongruel, A., and Williams, P.M. (1996) Prediction of the rate of cross-flow membrane ultrafiltration: a colloidal interaction approach. *Chem. Eng. Sci.*, **51**, 4321–4333.
 - 8 Belfort, G., Davis, R.H., and Zydney, A.L. (1994) The behavior of suspensions and macromolecular solutions in crossflow microfiltration. *J. Memb. Sci.*, **96**, 1–58.
 - 9 Li, H., Fane, A.G., Coster, H.G.L., and Vigneswaran, S. (2000) An assessment of depolarisation models of crossflow microfiltration by direct observation through the membrane. *J. Memb. Sci.*, **172**, 135–147.
 - 10 Scott, K. (1995) *Handbook of Industrial Membranes*, Elsevier, New York.
 - 11 Dudley, L.Y., del Vigo Pisano, F., and Fazel, M. (2000) Optimising membrane performance-practical experiences, in *Membrane Technology in Water and Wastewater Treatment* (ed. P. Hillis), Royal Society of Chemistry, London.
 - 12 Hermia, J. (1982) Constant pressure blocking filtration laws: Application to power-law non-newtonian fluids. *Trans. Ind. Chem. Eng.*, **60**, 183–187.
 - 13 Field, R.W. (1996) Mass transport and the design of membrane systems, Chapter 4, in *Industrial Membrane Separation Technology* (eds K. Scott and R. Hughes), Blackie, Edinburgh.
 - 14 Giorno, L., Donato, L., Todisco, S., and Drioli, E. (1998) Study of fouling phenomena in apple juice clarification by enzyme membrane reactor. *Separ. Sci. Technol.*, **33**, 739–756.
 - 15 Uemura, T. and Henmi, M. (2008) Thin-film composite membranes for reverse osmosis, in *Advanced Membrane Technology and Applications* (eds N. Li, A.G. Fane, W.S. Ho, and T. Matsuura), John Wiley & Sons, Inc., New York.
 - 16 Sanjeev, G.R. and Davies, R.H. (2004) Crossflow microfiltration with high frequency reverse filtration. *AIChE J.*, **41**, 501–508.
 - 17 Cui, Z.F., Chang, S., and Fane, A.G. (2003) The use of gas bubbling to enhance membrane processes. *J. Memb. Sci.*, **221**, 1–35.
 - 18 New Logic Research Inc. (2009) Technology. <http://www.vsep.com/technology/index.html> (accessed April 2, 2009).
 - 19 Rautenbach, R. and Albrecht, R. (1989) *Membrane Processes*, John Wiley & Sons Ltd, Chichester.
 - 20 Dacosta, A.R., Fane, A.G., and Wiley, D.E. (1994) Spacer characterization and pressure-drop modeling in spacer-filled channels for ultrafiltration. *J. Memb. Sci.*, **87**, 79–98.
 - 21 Ishida, H., Yamada, Y., Tsuboi, M., and Matsumura, S. (1993) Kubota submerged membrane activated sludge process – its application into activated sludge process with high concentration of MLSS. Paper presented at ICON'93, Heidelberg, Germany.
 - 22 Howell, J.A. (1995) Subcritical flux operation of microfiltration. *J. Memb. Sci.*, **107**, 165–171.
 - 23 Pearce, G.K. and Field, R.W. (2007) Development of the sustainable flux concept to provide guidelines for fouling control in UF/MF system design. Paper presented at the Proceedings of the AWWA Membrane Technology Conference, Florida, pp. 1–9.
 - 24 Lipnizki, F., Hausmanns, S., and Field, R. (2004) Influence of impermeable components on the permeation of aqueous 1-propanol mixtures in hydrophobic pervaporation. *J. Memb. Sci.*, **228**, 129–138.

