Membrane Separation Processes

Whilst effective product separation is crucial to economic operation in the process industries, certain types of materials are inherently difficult and expensive to separate. Important examples include:

(a) Finely dispersed solids, especially those which are compressible, and a density close to that of the liquid phase, have high viscosity, or are gelatinous.

(b) Low molecular weight, non-volatile organics or pharmaceuticals and dissolved salts.

(c) Biological materials which are very sensitive to their physical and chemical environment.

The processing of these categories of materials has become increasingly important in recent years, especially with the growth of the newer biotechnological industries and with the increasingly sophisticated nature of processing in the food industries. A membrane may be defined as "an interphase separating two phases and selectively controlling the transport of materials between those phases". A membrane is an interphase rather than an interface because it occupies a finite, though normally small, element of space.

CLASSIFICATION OF MEMBRANE PROCESSES

Industrial membrane processes may be classified according to the size range of materials which they are to separate and the driving force used in separation.

Table 1. Classification of membrane separation processes for liquid systems

Name of process	Driving force	Separation size range	Examples of materials separated
Microfiltration	Pressure gradient	10–0.1 μm	Small particles, large colloids, microbial cells
Ultrafiltration	Pressure gradient	<0.1 μm–5 nm	Emulsions, colloids, macromolecules, proteins
Nanofiltration	Pressure gradient	~1 nm	Dissolved salts, organics
Reverse osmosis (hyperfiltration)	Pressure gradient	<1 nm	Dissolved salts, small organics
Electrodialysis	Electric field gradient	<5 nm	Dissolved salts
Dialysis	Concentration gradient	<5 nm	Treatment of renal failure

The nature of synthetic membranes

Membranes used for the pressure-driven separation processes, microfiltration, ultrafiltration and reverse osmosis, as well as those used for dialysis, are most commonly made of polymeric materials. Initially most such membranes were cellulosic in nature. These are now being replaced by polyamide, polysulphone, polycarbonate and a number of other advanced polymers. These synthetic polymers

have improved chemical stability and better resistance to microbial degradation. Membranes have most commonly been produced by a form of phase inversion known as immersion precipitation. This process has four main steps:

(a) The polymer is dissolved in a solvent to 10-30 per cent by mass,

(b) The resulting solution is cast on a suitable support as a film of thickness, approximately 100 pm,

(c) The film is quenched by immersion in a non-solvent bath, typicall water or an aqueous solution,

(d) the resulting membrane is annealed by heating. The third step gives a polymer-rich phase forming the membrane, and a polymer-depleted phase forming the pores.

- A parameter often quoted in manufacturer's literature is the nominal molecular weight cut-off (MWCO) of a membrane. This is based on studies of how solute molecules are rejected by membranes.{The nominal molecular weight cut-off is normally defined as the molecular weight of a solute for which R = 0.95. Values of MWCO typically lie in the range 2000-100,000 kg/kmol with values of the order of 10,000 being most common}.A solute will pass through a membrane if it is sufficiently small to pass through a pore, if it does not significantly interact with the membrane and if it does not interact with other, larger solutes. It is possible to define a solute rejection coefficient ***R*** by:

$$R = 1 - (C_p / C_f) \qquad (1)$$

where C_f **is** the concentration of solute in the feed stream and C_p is the concentration of permeate

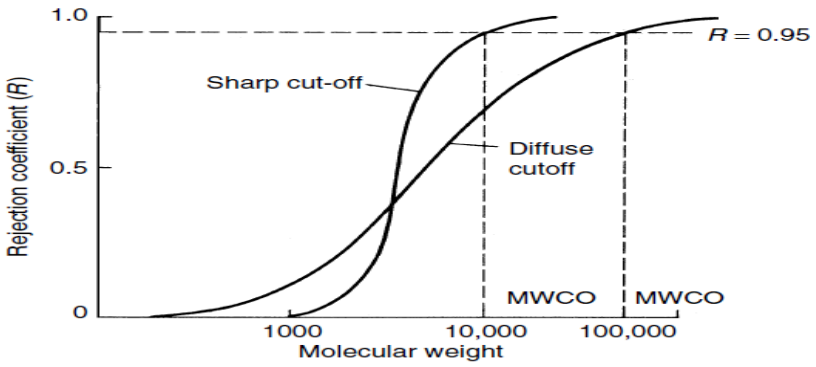


Figure (1). Dependence of rejection coefficient on molecular weight for ultrafiltration membranes

Ultrafiltration and *reverse osmosis* membranes have an asymmetric structure comprising a 1–2 μm thick top layer of finest pore size supported by a ~100 μm thick more openly porous matrix, as shown in Figure (2).

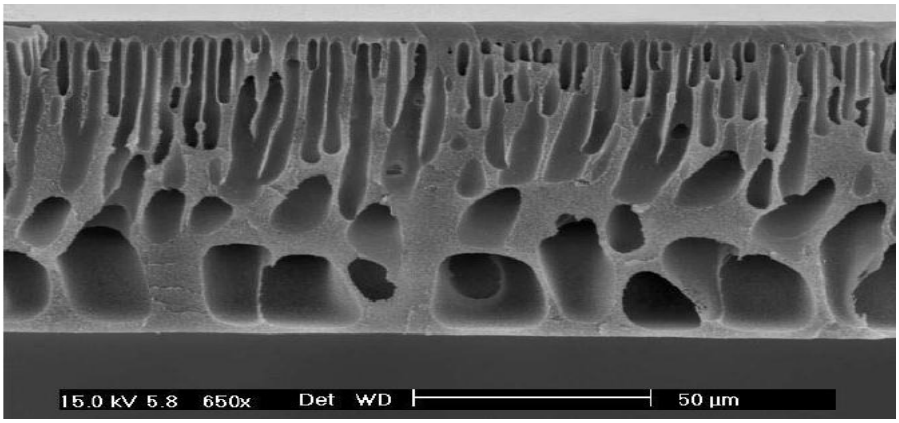


Figure (2). Electron micrograph of a section of an asymmetric ultrafiltration membrane showing finely porous "***skin***" layer on more openly porous supporting matrix

GENERAL MEMBRANE EQUATION

The general membrane equation is an attempt to state the factors which may be important in determining the membrane permeation rate for pressure driven processes. This takes the form:

$$J = \frac{|\Delta P| - |\Delta \Pi|}{(R_m + R_c)\mu} \qquad \ldots\ldots\ (2)$$

Where $\boldsymbol{J}$ is the membrane flux*, expressed as volumetric rate per unit area, $\boldsymbol{|\Delta P|}$ is the pressure difference applied across the membrane, the transmembrane pressure, $\boldsymbol{\Delta\pi}$ is the difference in osmotic pressure across the membrane, $\boldsymbol{R_m}$ is the resistance of the membrane, and R_c is the resistance of layers deposited on the membrane, the filter cake and gel foulants. If the membrane is only exposed to pure solvent, say water, then equation (2) reduces to $\boldsymbol{J = |\Delta P| / R_m\ \mu}$. For microfiltration and ultrafiltration membranes where solvent flow is most often essentially laminar through an arrangement of tortuous channels, this is analogous to the Carman–Kozeny equation.

CROSS -FLOW MICROFILTRATION

The concept of ***cross-flow*** microfiltration, described by BERTERA, STEVEN and METCALFE*(4)*, is shown in Figure (3) which represents a cross-section through a rectangular or tubular membrane module. The particle-containing fluid to be filtered is pumped at a velocity in the range 1–8 m/s parallel to the face of the membrane and with a pressure difference of 0.1–0.5 MN/m^2 (MPa) across the membrane. The liquid permeates through the membrane and the feed emerges in a more concentrated form at the exit of the module.

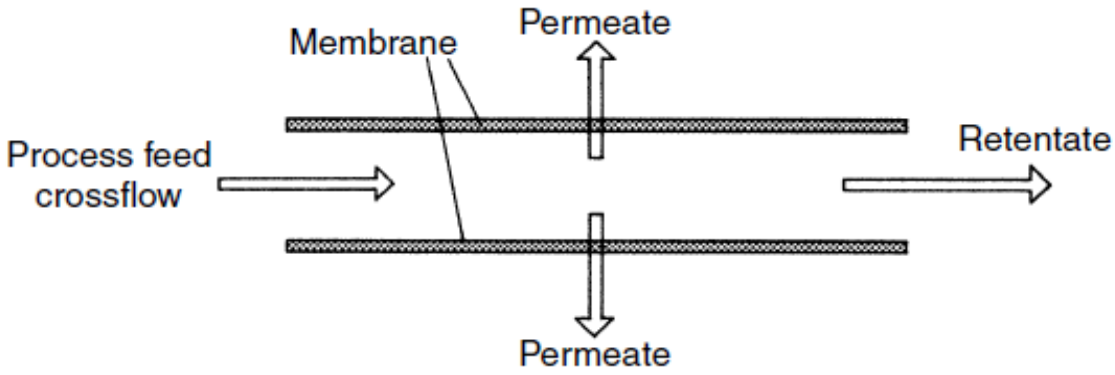


Figure (3). The concept of cross-flow filtration

All of the membrane processes listed in Table 8.1 are operated with such a cross-flow of the process feed. The advantages of cross-flow filtration over conventional filtration are:

(a) A higher overall liquid removal rate is achieved by prevention of the formation of an extensive filter cake.

(b) The process feed remains in the form of a mobile slurry suitable for further processing.

(c) The solids content of the product slurry may be varied over a wide range.

(d) It may be possible to fractionate particles of different sizes.

A flow diagram of a simple cross-flow system is shown in Figure 4. This is the system likely to be used for batch processing or development rigs and is, in essence, a basic pump recirculation loop. The process feed is concentrated by pumping it from the tank and across the membrane in the module at an appropriate velocity. The partially concentrated *retentate* is recycled into the tank for further processing while the *permeate* is stored or discarded as required. In cross-flow filtration applications, product washing is frequently necessary and is achieved by a process known as *diafiltration* in which wash water is added to the tank at a rate equal to the permeation rate. In practice, the membrane permeation rate falls with time due to membrane fouling; that is blocking of the membrane surface and pores by the particulate materials, as shown in Figure 5. The rate of fouling depends on the nature of the materials being processed, the nature of the membrane, the cross-flow velocity and the applied pressure. For example, increasing the cross-flow velocity results in a decreased rate of fouling. Backflushing

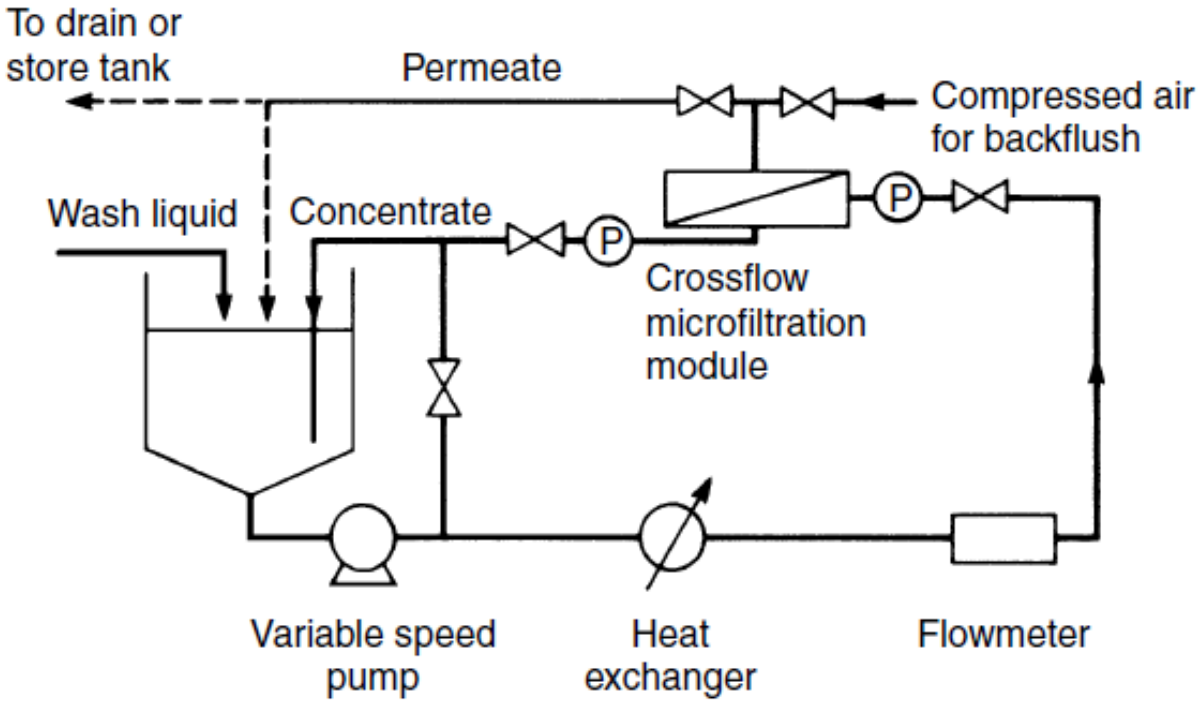


Figure (4). Flow diagram for a simple cross-flow system.

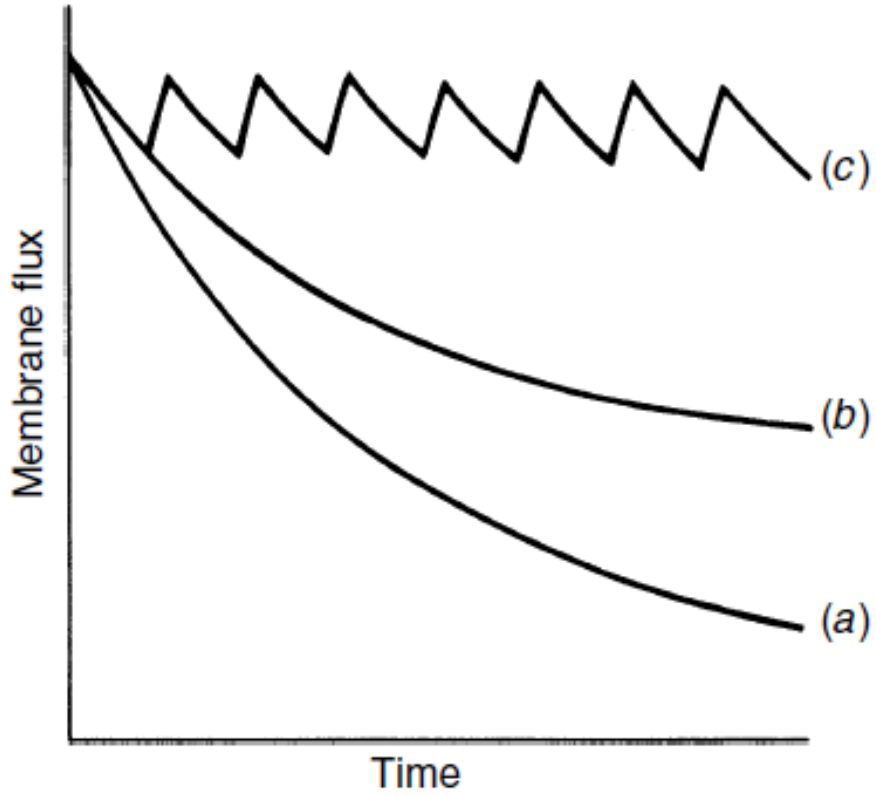


Figure (5). The time-dependence of membrane permeation rate during cross-flow filtration: (*a*) Low cross-flow velocity, (*b*) Increased cross-flow velocity, (*c*) Backflushing at the bottom of each "saw-tooth"

Ideally, cross-flow microfiltration would be the pressure-driven removal of the process liquid through a porous medium without the deposition of particulate material. The flux decrease occurring during cross-flow microfiltration shows that this is not the case. If the decrease is due to particle deposition resulting from incomplete removal by the cross-flow liquid, then a description analogous to that of generalised cake filtration theory,. Equation.2 may then be written as:

$$\boldsymbol{J = \frac{|\Delta P|}{(R_m + R_C)\mu}} \qquad (3)$$

Where R_c now represents the resistance of the cake, which if all filtered particles remain in the cake, may be written as:

$$\boldsymbol{R_C = \frac{rVC_b}{A_m} = \frac{rV_s}{A_m}} \qquad (4)$$

Where **r** is the specific resistance of the deposit, V the total volume filtered, Vs the volume of *particles* deposited, C_b the bulk concentration of particles in the feed (particle volume/feed volume) and A_m the membrane area. The specific resistance may theoretically be related to the particle properties for spherical particles

$$\boldsymbol{r = 180\left(\frac{1-e}{e^3}\right)\left(\frac{1}{d_s^2}\right)} \qquad (5)$$

where e is the void volume of the cake and d_s the mean particle diameter. Combining equations (3) and (4) gives:

$$J = \frac{1}{A_m}\frac{dV}{dt} = \frac{|\Delta P|}{(R_m + \mathbf{r}VC_b/A_m)\mu} \qquad (6)$$

Solution of equation (6) for V at constant pressure gives:

$$\frac{t}{V} = \frac{R_m\mu}{|\Delta P|A_m} + \frac{C_b\mathbf{r}\mu V}{2|\Delta P|A_m^2} \qquad (7)$$

Ultrafiltration is one of the most widely used of the pressure-driven membrane separation processes. The solutes retained or rejected by ultrafiltration membranes are those with molecular weights of 10^3 or greater, depending mostly on the MWCO of the membrane chosen. The process liquid, dissolved salts and low molecular weight organic molecules (500–1000 kg/kmol) generally pass through the membrane. The pressure difference applied across the membrane is usually in the range 0.1–0.7 MN/m^2 and membrane permeation rates are typically 0.01–0.2 m^3/m^2 h. In industry, ultrafiltration is always operated in the cross-flow mode. The separation of process liquid and solute that takes place at the membrane during ultrafiltration gives rise to an increase in solute concentration close to the membrane surface, as shown in Figure (6). This is termed concentration polarisation and takes place within the boundary film generated by the applied cross-flow. With a greater concentration at the membrane, there will be a tendency for solute to diffuse back into the bulk feed according to Fick's Law,. At steady state, the rate of back-diffusion will be equal to the rate of

removal of solute at the membrane, minus the rate of solute leakage through the membrane:

$$J(C - C_P) = -D\frac{dC}{dy} \qquad (8)$$

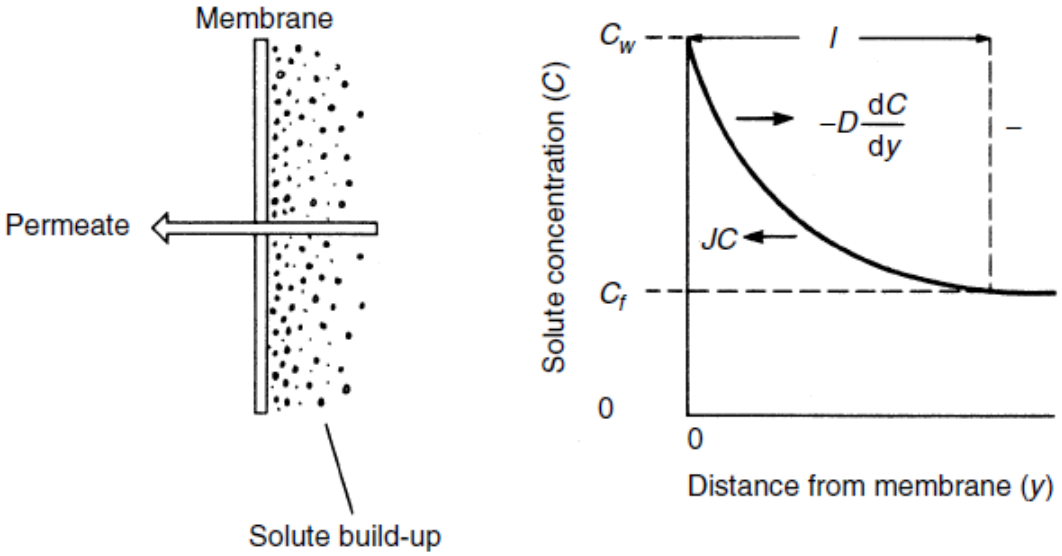


Figure (6). Concentration polarisation at a membrane surface

Here solute concentrations C and C_p in the permeate are expressed as mass fractions, D is the diffusion coefficient of the solute and y is the distance from the membrane. Rearranging and integrating from $C = C_f$ when $y = l$ the thickness of the film, to $C = Cw$, the concentration of solute at the membrane wall, when $y = 0$, gives:

$$-\int_{C_w}^{C_f}\frac{dC}{C-C_P} = \frac{J}{D}\int_0^l dy \qquad (9)$$

Or

$$\frac{C_w - C_P}{C_f - C_P} = exp\left(\frac{\pi}{D}\right) \qquad (10)$$

If it is further assumed that the membrane completely rejects the solute, that is, $R = 1$ and $C_P = 0$, then:

$$\frac{C_w}{C_f} = exp\left(\frac{\pi}{D}\right) \qquad (11)$$

Where the ratio C_w/C_f is known as the polarisation modulus. It may be noted that it has been assumed that l is independent of J and that D is constant over the whole range of C at the interface. The film thickness is usually incorporated in an overall mass transfer coefficient h_D , where $h_D = D/l$, giving:

$$J = h_D ln\left(\frac{C_w}{C_f}\right) \qquad (12)$$

The mass transfer coefficient is usually obtained from correlations for flow in nonporous ducts. One case is that of laminar flow in channels of circular cross-section where the parabolic velocity profile is assumed to be developed at the channel entrance

$$Sh = 1.62\left(Re\,Sc\frac{d_m}{L}\right)^{1/3} \qquad (13)$$

where *Sh* is the Sherwood number $(h_D\, d_m /D)$, d_m is the hydraulic diameter, *L* is the channel length, *Re* is the Reynolds number $(ud_m\rho/\mu)$, *Sc* the *Schmidt* number $(\mu/\rho D)$, with *u* being the cross-flow velocity, ρ the fluid density and μ the fluid viscosity. This gives:

$$h_D = 1.62\left(\frac{uD^2}{d_m L}\right)^{1/3} \qquad (14)$$

or for tubular systems:

$$h_D = 0.81\left(\frac{\gamma}{L}D^2\right)^{1/3} \qquad (15)$$

where $\dot{\gamma}$, the shear rate at the membrane surface equals $8u/dm$. For the case of turbulent flow correlation used:

$$Sh = 0.023Re^{0.8}Sc^{0.33} \qquad (16)$$

which for tubular systems gives:

$$h_D = 0.023\frac{u^{0.8}D^{0.67}}{d_m^{0.2}}\left(\frac{\rho}{\mu}\right)^{0.47} \qquad (17)$$

and for thin rectangular flow channels, with channel height *b*:

$$h_D = 0.02\frac{u^{0.8}D^{0.67}}{b^{0.2}}\left(\frac{\rho}{\mu}\right)^{0.47} \qquad (18)$$

For both laminar and turbulent flow it is clear that the mass transfer coefficient and hence the membrane permeation rate may be increased, where these equations are valid, by increasing the cross-flow velocity or decreasing the channel height. The effects are greatest for turbulent flow. For laminar flow the mass transfer coefficient is decreased if the channel length is increased. This is due to the boundary layer increasing along the membrane module. The mass transfer coefficient is, therefore, averaged along the membrane length.

This boundary-layer theory applies to mass-transfer controlled systems where the membrane permeation rate is independent of pressure, for there is no pressure term in the model. In such cases it has been proposed that, as the concentration at the membrane increases, the solute eventually precipitates on the membrane surface. This layer of precipitated solute is known as the *gel-layer*, and the theory has thus become known as the *gel-polarisation* model proposed by MICHAELS*(10)*. Under such conditions C_w in equation (12) becomes replaced by a constant C_G the concentration of solute in the gel-layer, and:

$$J = h_D ln\left(\frac{C_G}{C_f}\right) \qquad (19)$$

Example 1:

Obtain expressions for the optimum concentration for minimum process time in the diafiltration of a solution of protein content *S* in an initial volume V_0.

(a) If the gel-polarisation model applies.

(b) If the osmotic pressure model applies.
It may be assumed that the extent of diafiltration is given by:

$$V_d = \frac{Volume\ of\ liquid\ permeated}{Initial\ feed\ volume} = \frac{V_P}{V_O}$$

Solution:

(a) *Assuming the gel–polarisation model applies*

The membrane permeation rate, $J = h_D ln\left(\frac{C_G}{C_f}\right)$

Where C_G and C_f are the gel and the bulk concentrations respectively.

In this case: $\boldsymbol{C_f = \frac{S}{V_O}}$ and the volume V_d liquid permeated, $\boldsymbol{V_P = \frac{V_d S}{C_f}}$

The process time per unit area, $\boldsymbol{t = \frac{V_P}{J} = V_d\, S/(C_f\, h_D \ln(C_G/C_f))}$

Assuming C_f and h_D are constant, then:

$$dt/dC_f = -V_d S/[h_D C_f^2 \ln(C_G/C_f)] + V_d S/\{h_D C_f^2[\ln(C_G/C_f)]^2\}$$

If, at the optimum concentration C_f^* and $d_t/dC_f = 0$, then :

$\boldsymbol{1 = ln(C_G/C_f^*)}$

and: $\boldsymbol{C_f^* = C_G/e}$

Desalination

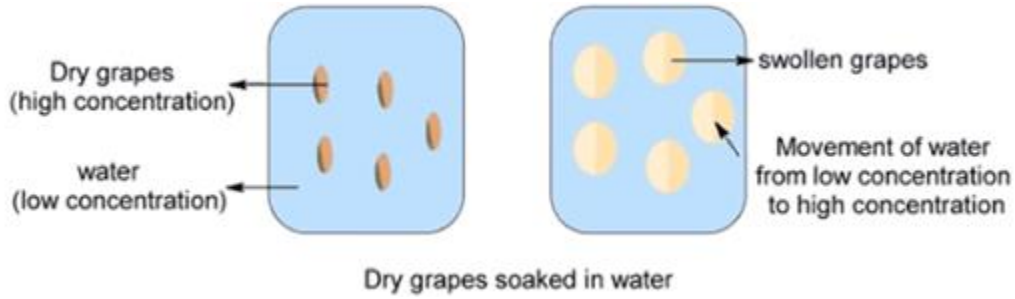
Removal of salts from water is known as desalination.

Methods of desalination

- ❖ Thermal desalination (Thermal)
- ❖ Reverse osmosis (Pressure)
- ❖ Electrodialysis (Electrical)

Osmosis

When two compartments containing solutions of different concentrations are separated by a semipermeable membrane , the *solvent moves from lower concentration to higher concentration side figure (7).*



Reverse Osmosis

When two compartments containing solutions of different concentrations are separated by a semipermeable membrane and **hydrostatic pressure greater than osmotic pressure** is applied on the concentrated side **the solvent moves from higher concentration to lower concentration side.**

(When brackish water (saline water) and pure water are separated by semipermeable – membrane, **water moves from saline to pure water compartment**).

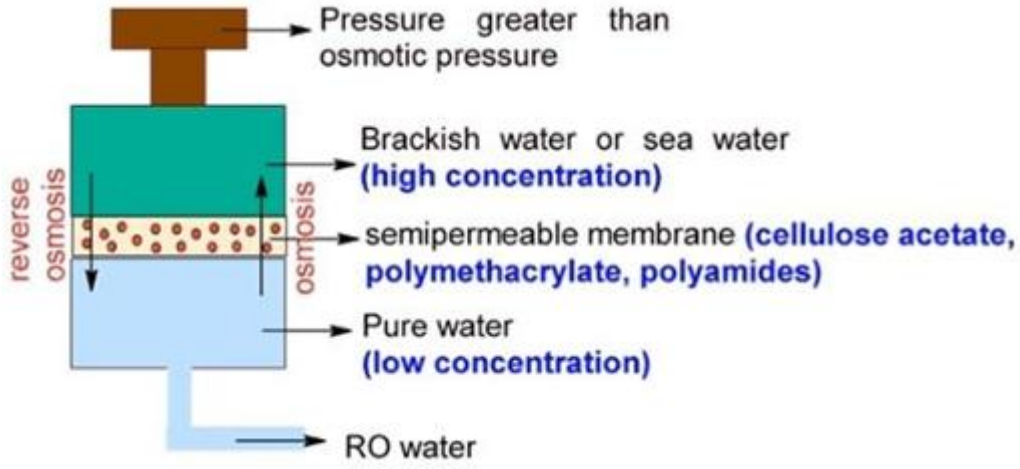


Figure (8): Example of Reverse Osmosis

Advantages

- The process is ***simple, cheap and reliable***.
- It not only removes the ionic salts but also the ***non- ionic, colloidal matter and high molecular weight organic matter.***
- Although the installation cost is high , the ***maintenance cost is low.***
- The ***membrane*** can be ***replaced in 3-4 minutes*** and hence can get uninterrupted water supply.

Limitations / Disadvantages

- The ***membrane cost is high***.
- Membrane should ***withstand pressure*** of 20-100 atm.

MEMBRANE MODULES AND PLANT CONFIGURATION

Membrane equipment for industrial scale operation of microfiltration, ultrafiltration and reverse osmosis is supplied in the form of modules. The area of membrane contained in these basic modules is in the range 1–20 m2. The modules may be connected together in series or in parallel to form a plant of the required performance. The four most common types of membrane modules are tubular, flat sheet, spiral wound and hollow fibre, as shown in Figures 8–12.

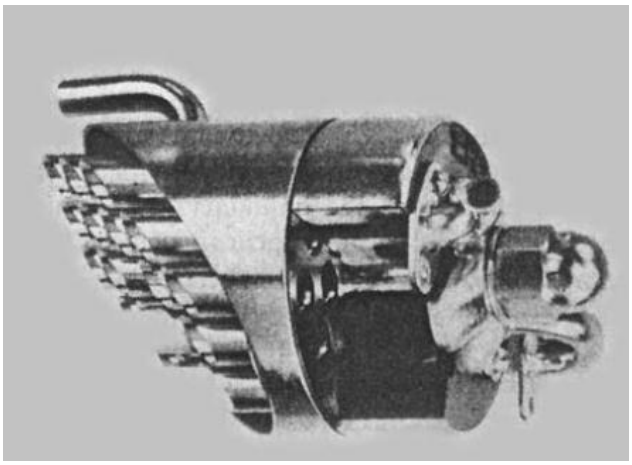


Figure (8). Tubular module

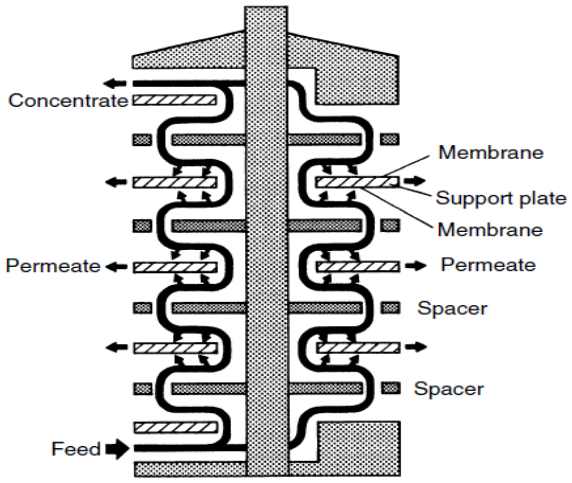


Figure (9). Schematic diagram of flat-sheet module

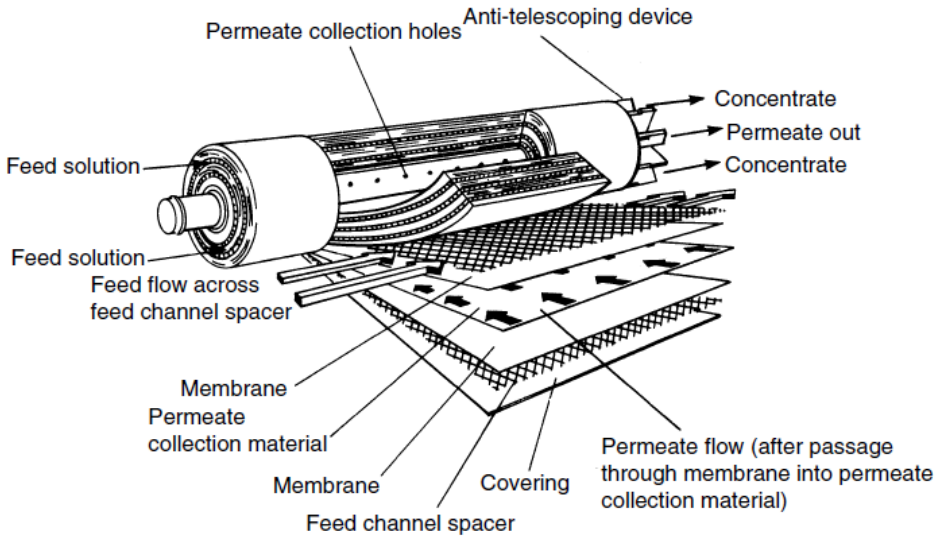
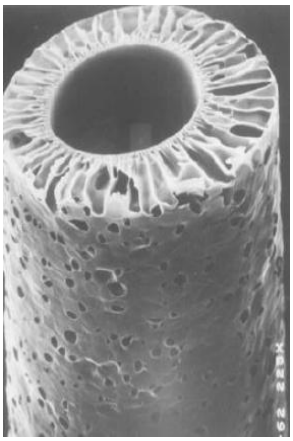


Figure (10). Schematic diagram of spiral-wound module

(a)



(b)

Figure (11). (*a*) Hollow-fibre module and, (*b*), a single fibre

Example (2):

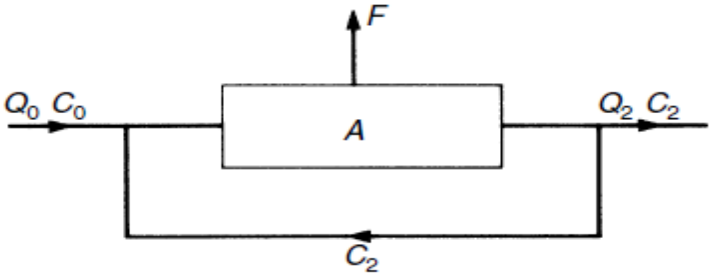
An ultrafiltration plant is required to treat 50 m^3/day of a protein-containing waste stream. The waste contains 0.5 kg/m^3 of protein which has to be concentrated to 20 kg/m^3 so as to allow recycling to the main process stream. The tubular membranes to be used are available as 30 m^2 modules. Pilot plant studies show that the flux J through these membranes is given by:

$$J = 0.02ln\left(\frac{30}{C_f}\right) \quad \frac{m}{h}.$$

where C_f is the concentration of protein in kg/m^3. Due to fouling, the flux never exceeds 0.04 m/h. Estimate the minimum number of membrane modules required for the operation of this process (a) as a single *feed and bleed* stage, and (b) as two *feed and bleed* stages in series. Operation for 20 h/day may be assumed.

Solution

(a) with a single *feed and bleed* stage, the arrangement is shown in Figure



Q_0 is the volumetric flowrate of feed
Q_2 the volumetric flowrate of concentrate
C_0 the solute concentration in the feed
C_2 the solute concentration in the concentrate
F the volumetric flowrate of membrane permeate
A the required membrane area
It is also assumed that there is no loss of solute through the membrane.
The concentration (C_l) at which the flux becomes fouling-limited is:

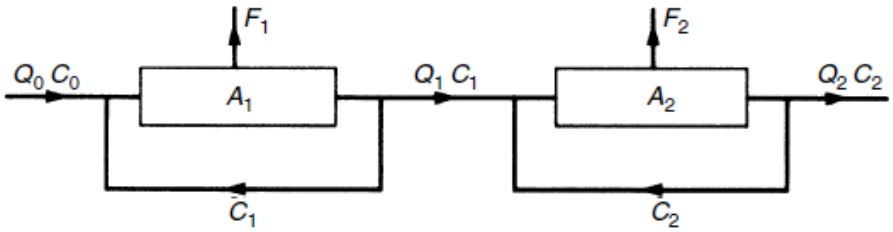
$$0.04 = 0.02ln\left(\frac{30}{C_f}\right)$$

C_l = 4 kg/m^3

Conservation of solute gives:
$Q_0C_0 = Q_2C_2$ (i)
A fluid balance gives:
$Q_0 = F + Q_2$ (ii)
Combining these equations and substituting known values:

$$2.438 = A\ 0.02ln\left(\frac{30}{20}\right)$$

and: A = 302 m^2
Thus, 10 modules will almost meet the specification for the single-stage process.
(b) with two *feed and bleed* stages in series, the arrangement is shown in Figure:



Conservation of solute gives:

$Q_0C_0 = Q_1C_1 = Q_2C_2$ (iii)

A fluid balance on stage 1 gives:

$Q_0 = Q_1 + F_1$ (iv)

A fluid balance on stage 2 gives:

$Q_1 = Q_2 + F_2$ (v)

Substituting given values in equations (iv) and (v) gives:

$$2.5 = \frac{1.25}{C_1} + 0.02A_1 ln\left(\frac{30}{C_l}\right) \quad \text{(vi)}$$

$$\frac{1.25}{C_1} = 0.0625 + 0.00811A_1 \quad \text{(vii)}$$

use trial and error to estimate the value of C_1
that gives the optimum values of $A1$ and $A2$. Thus:
If C_1 = 5 kg/m^3, then, A_1 = 63 m^2 and A_2 = 23 m^2.
That is, an arrangement of 3 modules −1 module is required.

If C_1 = 4 kg/m^3, then A_1 = 55 m2 and $A2$ = 31 m^2.
That is, an arrangement of 2 modules −1 module is almost sufficient.

If C_1 = 4.5 kg/m^3, then A_1 = 59 m^2 and A_2 = 27 m^2.
That is, an arrangement of 2 modules −1 module which meets the requirement.
This arrangement requires the minimum number of modules.

Example (3):

In the ultrafiltration of a protein solution of concentration 0.01 kg/m^3, analysis of data on gel growth rate and wall concentration C_w yields the second order relationship:

$$\frac{dl}{dt} = K_r C_w^2$$

where l is gel thickness, and K_r is a constant, 9.2 × 10^{-6} m^7/kg^{2}s.The water flux through the membrane may be described by:

$$J = \frac{|\Delta P|}{\mu_w R_m}$$

where |ΔP| is pressure difference, Rm is membrane resistance and μ_w is the viscosity of water.This equation may be modified for protein solutions to give:

$$J = \frac{|\Delta P|}{\mu_p\left(R_m + \frac{l}{P_g}\right)}$$

where P_g is gel permeability, and μ_p is the viscosity of the permeate
The gel permeability may be estimated from the Carman–Kozeny equation:

$$P_g = \left(\frac{d^2}{180}\right)\left(\frac{e^3}{(1-e)^2}\right)$$

where *d* is particle diameter and *e* is the porosity of the gel. Calculate the gel thickness after 30 minutes of operation.

Data:

Flux mm/s	$\lvert\Delta P\rvert$ (kN/m^2)
0.02	20
0.04	40
0.06	60

Viscosity of water	=	1.3 mNs/m^2
Viscosity of permeate	=	1.5 mNs/m^2
Diameter of protein molecule	=	20 nm
Operating pressure	=	10 kN/m^2
Porosity of gel	=	0.5
Mass transfer coefficient to gel, h_D	=	1.26×10^{-5} m/s

Solution:

The gel growth rate as a function of the wall concentration, C_w, is given by:

$$dl/dt = K_r C_w^2$$

Where l is the gel thickness, K_r is a constant = 9.2×10^{-6} m^7/kg s and C_w, the wall concentration given by:

$$C_w = C_f exp(u/h_D)$$

The permeate flux is given by:

$$J_{soln} = |\Delta P|/[\mu_P(R_m + l/P_g)]$$

where $|\Delta P|$ is the pressure difference, μ_p the viscosity of the permeate, R_m the membrane resistance and P_g, the gel permeability, which may be estimated from the Carman–Kozeny equation:

$$P_g = \left(\frac{d^2}{180}\right)\left(\frac{e^3}{(1-e)^2}\right)$$

where *d* is the particle diameter and *e* the porosity of the gel.

For water:

$$J_w = \frac{|\Delta P|}{\mu_w R_m}$$

and hence: $R_m = |\Delta P|/J\mu_w = (2.0 \times 10^3)/(1.3 \times 10^{-3} \times 0.02 \times 10^{-3})$

$= 7.60 \times 10^{11}$ 1/m

Also: $P_g = \left(\frac{d^2}{180}\right)\left(\frac{e^3}{(1-e)^2}\right) = \left[\frac{(20\times10^{-9})^2}{180}\right]\left[\frac{(0.5)^3}{(1-0.5)^2}\right] = 1.11 \times 10^{-18} m^2$

Thus: $dl/dt = K_r C_f^2 \exp\{2\Delta P/[h_D \mu_P(R_m + l/P_g)]$

and: $\int_0^l dt = \int_0^l dl/\{K_r C_f^2 \exp\{2\Delta P/[h_D \mu_P(R_m + l/P_g)]\}$