Membrane Filtration

(from *MWH's Water Treatment Principles and Design* by Crittenden et al.)

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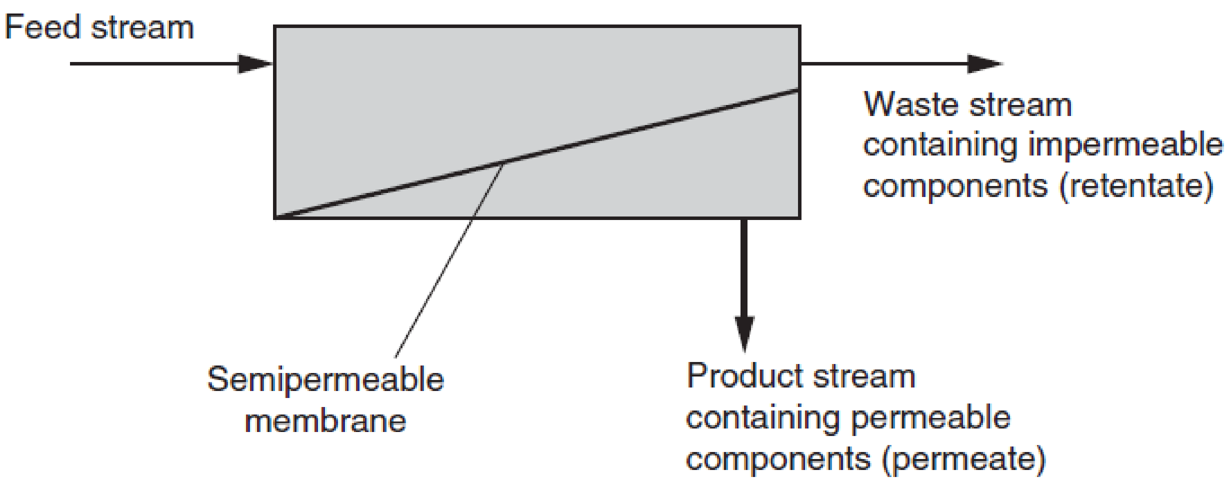
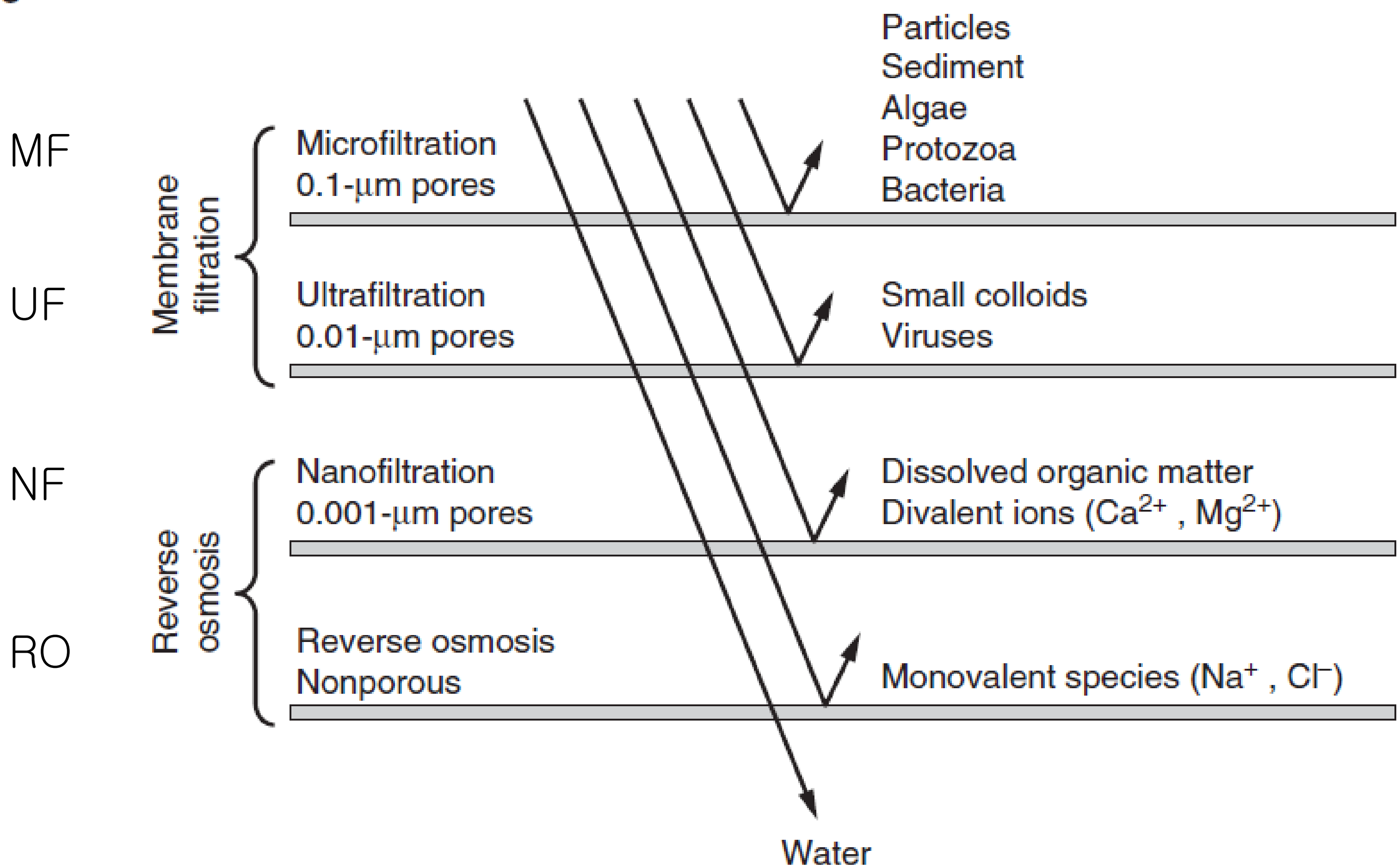
Membrane Filtration



Schematic of separation process through semipermeable membrane.

Classification of Membrane Processes

Membrane Filtration



Hierarchy of pressure-driven membrane processes.

Reverse Osmosis

- *Osmosis* is the preferential diffusion of water through a semipermeable membrane in response to a concentration gradient.
- Reverse osmosis is for removal of truly dissolved solutes (ions such as sodium, chloride, calcium, or magnesium, and dissolved NOM).
- Used for desalination, micropollutant removal, and softening

Differences between Membrane Processes

Table
Comparison between membrane filtration and reverse osmosis

Process Characteristic	Membrane Filtration	Reverse Osmosis
Objectives	Particle removal, microorganism removal	Seawater desalination, brackish water desalination, softening, NOM removal for DBP control, specific contaminant removal
Target contaminants	Particles	Dissolved solutes
Membranes types	Microfiltration, ultrafiltration	Nanofiltration, reverse osmosis
Typical source water	Fresh surface water (TDS $<$ 1000 mg/L)	Ocean or seawater, brackish groundwater (TDS $=$ 1000–20,000 mg/L), colored groundwater (TOC $>$ 10 mg/L)
Membrane structure	Homogeneous or asymmetric	Asymmetric or thin-film composite
Most common membrane configuration	Hollow fiber	Spiral wound
Dominant exclusion mechanism	Straining	Differences in solubility or diffusivity
Removal efficiency of targeted impurities	Frequently 99.9999% or greater	Typically 50–99%, depending on objectives
Most common flow pattern	Dead end	Tangential Cross-flow

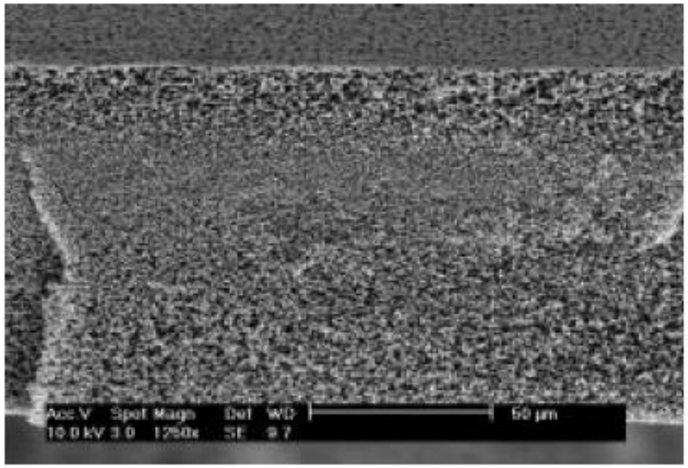
Table
Comparison between membrane filtration and reverse osmosis

Process Characteristic	Membrane Filtration	Reverse Osmosis
Operation includes backwash cycle	Yes	No
Influenced by osmotic pressure	No	Yes
Influenced by concentration polarization	No	Yes
Noteworthy regulatory issues	Challenge testing and integrity monitoring	Concentrate disposal
Typical transmembrane pressure	0.2–1 bar (3–15 psi)	5–85 bar (73–1200 psi)
Typical permeate flux	30–170 $L/m^2 \cdot h$ (18–100 $gal/ft^2 \cdot d$)	1–50 $L/m^2 \cdot h$ (LMH) (0.6–30 $gal/ft^2 \cdot d$)
Typical recovery	$>$95%	50% (for seawater) to 90% (for colored groundwater)
Competing processes	Granular filtration	Carbon adsorption, ion exchange, precipitative softening, distillation

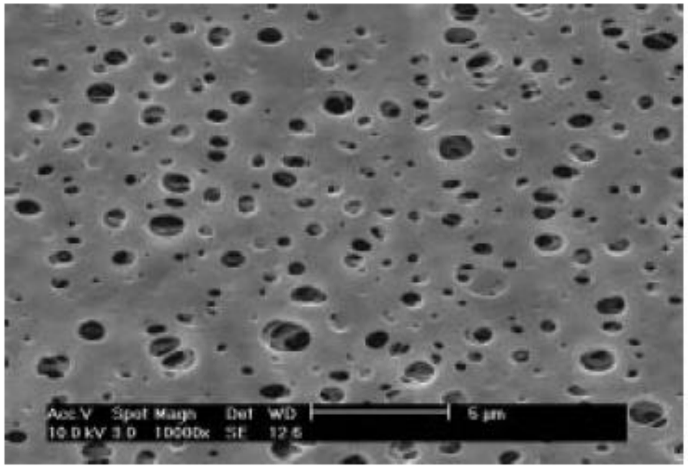
Table
Non-pressure-driven membrane processes

Membrane Process	Driving Force
Dialysis	Concentration gradient
Electrodialysis	Electrical potential
Electrodialysis reversal	Electrical potential
Pervaporation	Pressure gradient
Forward osmosis	Osmosis
Membrane distillation	Vapor pressure
Thermoosmosis	Temperature gradient

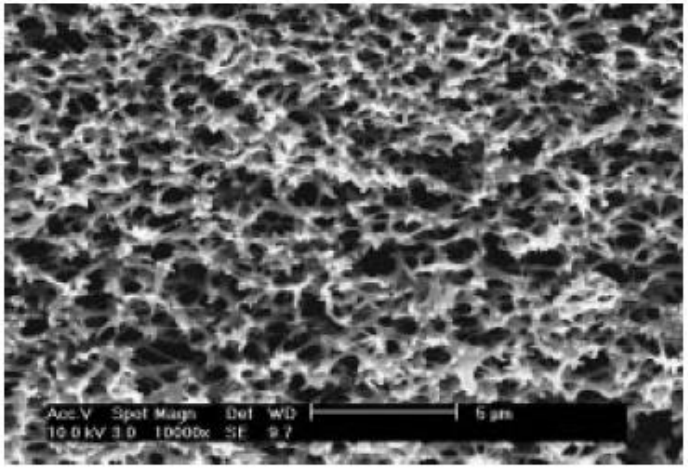
Principal Features of Membrane Processes



(a)

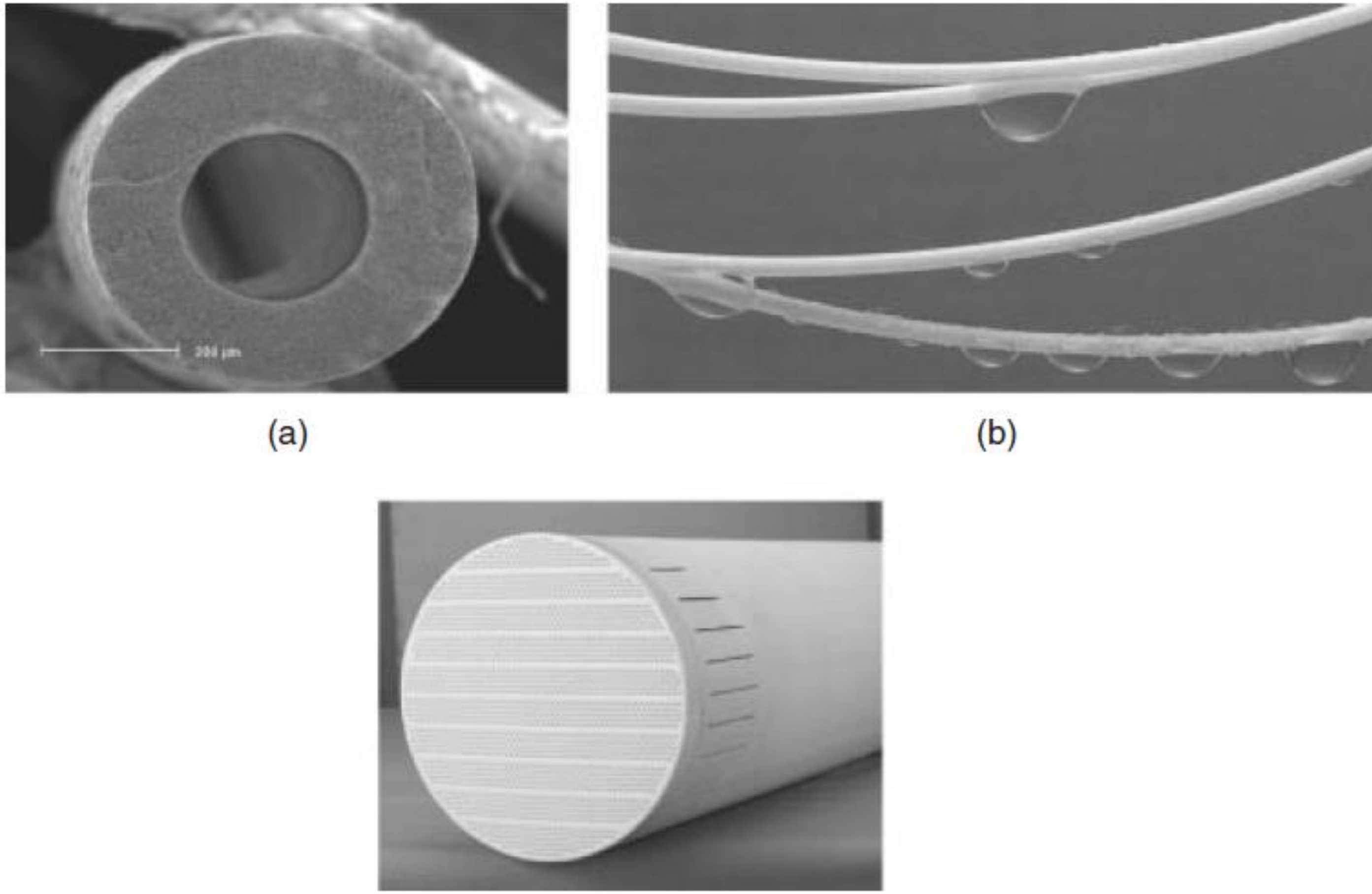


(b)



(c)

Figure
Scanning electron microscope images of a 0.2-µm polyethersulfone microfiltration membrane: (a) cross section of the entire membrane, (b) high magnification of the membrane surface, and (c) high magnification of the membrane internal structure.



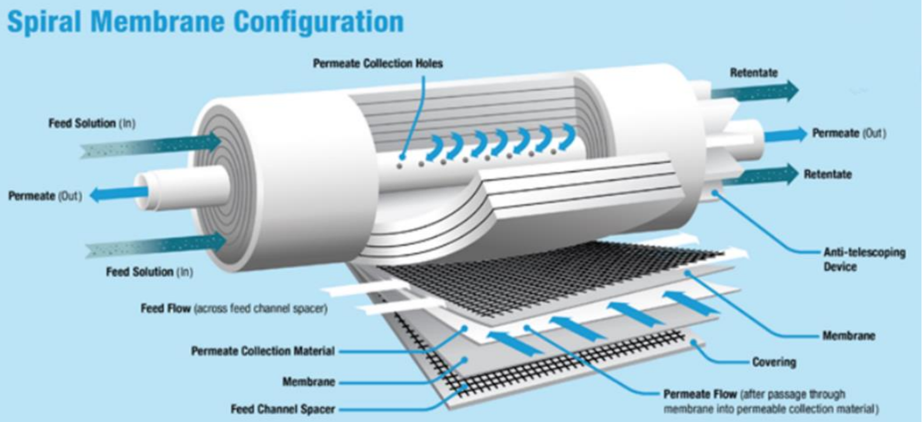
(a) (b) (c)

Figure
(a) Scanning electron microscope image of end view of a hollow-fiber membrane (courtesy of US Filter Memcor Products), (b) water permeating hollow-fiber membranes (courtesy of Suez Environnement), and (c) end view of a ceramic tubular membrane (courtesy of NKG).

Table

Membrane configurations

Configuration	Description
Hollow fiber	Membranes are cast as hollow tubes and filtration occurs as water passes through the wall of the fibers (see Fig. 12-4b). The module packing density (specific surface area) is 750–1700 m^2/m^3.
Tubular	Membranes are constructed as a monolithic structure with one or more channels through the structure (see Fig. 12-4c). Ceramic membranes are typically tubular membranes. These membranes can be operated at a high cross-flow velocity, which is ideal for applications where the particle concentration is high. The module packing density is up to 400–800 m^2/m^3.
Flat sheet	Membranes are cast as a sheet and used as a single layer or as a stack of sheets. Common in laboratory separations but not as common at an industrial scale. Packing density depends on spacing of t
Spiral wound	Flat-sheet membranes, s permeate and retentate tube so that the permea toward the central collec membranes but not in w clogging of flow paths w with backwashing effecti details on the construction of spiral-wound elements. The packing density is 700–1000 m^2/m^3.



Configuration	Description
Hollow fine fiber	Membranes cast as hollow tubes with an outside diameter of 0.085 mm (about the thickness of human hair). Hollow fine fibers are used only as RO membranes; see Chap. 17 for additional details. The packing density is 5600–7400 m^2/m^3.
Track etched	Flat-sheet membranes that are cast as a dense sheet of polymer material and exposed to a radioactive beam, which damages the material along "tracks," or straight pathways through the material. The material is then immersed in an etching bath that dissolves the material along the pathways, widening the tracks to form pores of uniform cylindrical dimensions. The result is a flat-sheet membrane with a narrow, controllable, and extremely uniform pore size distribution, which is advantageous in laboratory separations. Track-etched membranes are not currently used in industrial-scale applications.

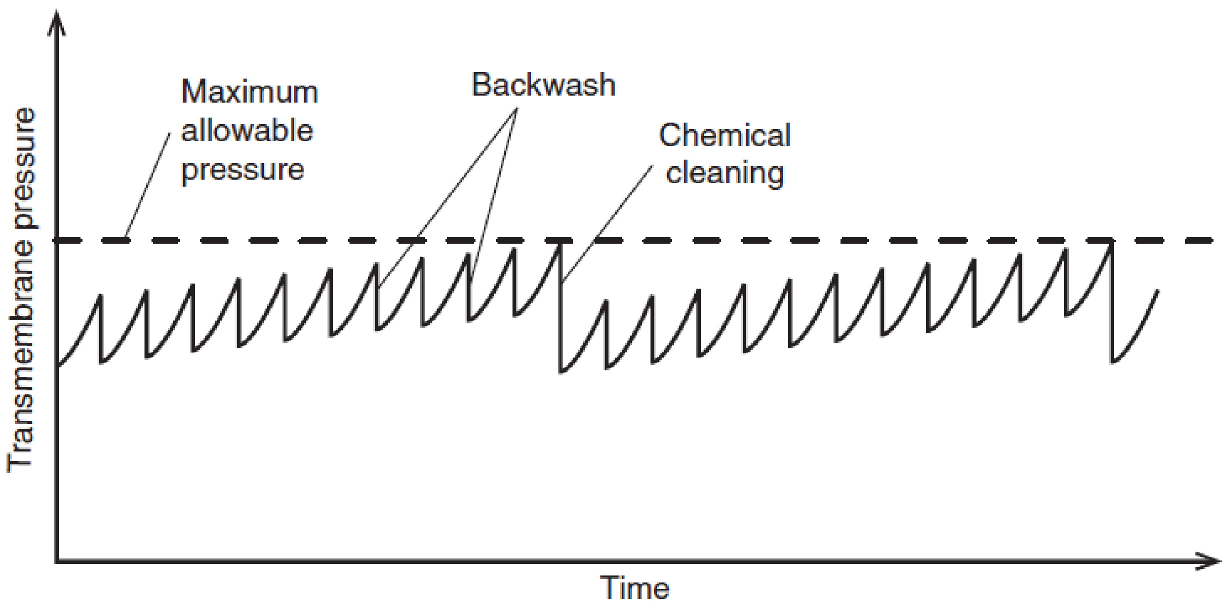
Table

Operating characteristics of membrane and rapid granular filters

Criteria	Membrane Filtration	Rapid Granular Filtration
Filtration rate (permeate flux)	0.03–0.17 m/h[a] (0.01–0.07 gpm/ft^2)	5–15 m/h[a] (2–6 gpm/ft^2)
Operating pressure	0.2–1 bar (7–34 ft)	0.18–0.3 bar (6–10 ft)
Filtration cycle duration	30–90 min	1–4 d
Backwash cycle duration	1–3 min	10–15 min
Ripening period	None	15–120 min
Recovery	>95 %	>95 %
Filtration mechanism	Straining	Depth filtration

Adsorption

[a]Conventional units for membrane permeate flux are $L/m^2 \cdot h$ and $gal/ft^2 \cdot d$. The conversions to the units shown in this table are $1\ L/m^2 \cdot h = 10^{-3}$ m/h and $1440\ gal/ft^2 \cdot d = 1\ gpm/ft^2$.



Figure

Transmembrane pressure development during membrane filtration.

Module Configuration

√ PRESSURE-VESSEL CONFIGURATION (가압식)

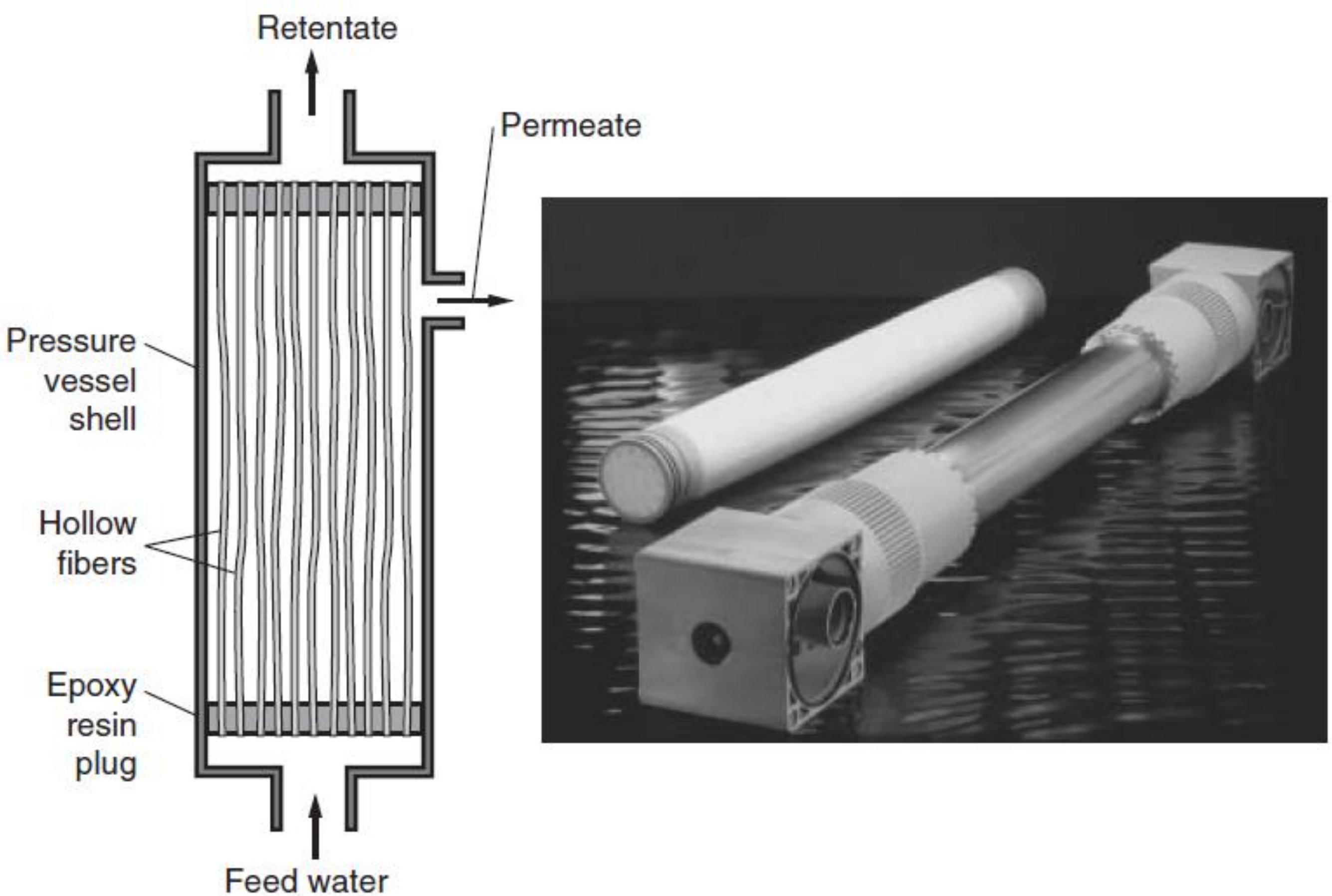


Figure
Pressure-vessel configuration for membrane filtration: (a) schematic of a single cross-flow membrane module and (b) photograph (courtesy of US Filter Memcor Products).

Figure
Full-scale membrane filtration facility using the pressure-vessel configuration.

√ SUBMERGED CONFIGURATION (침지식)

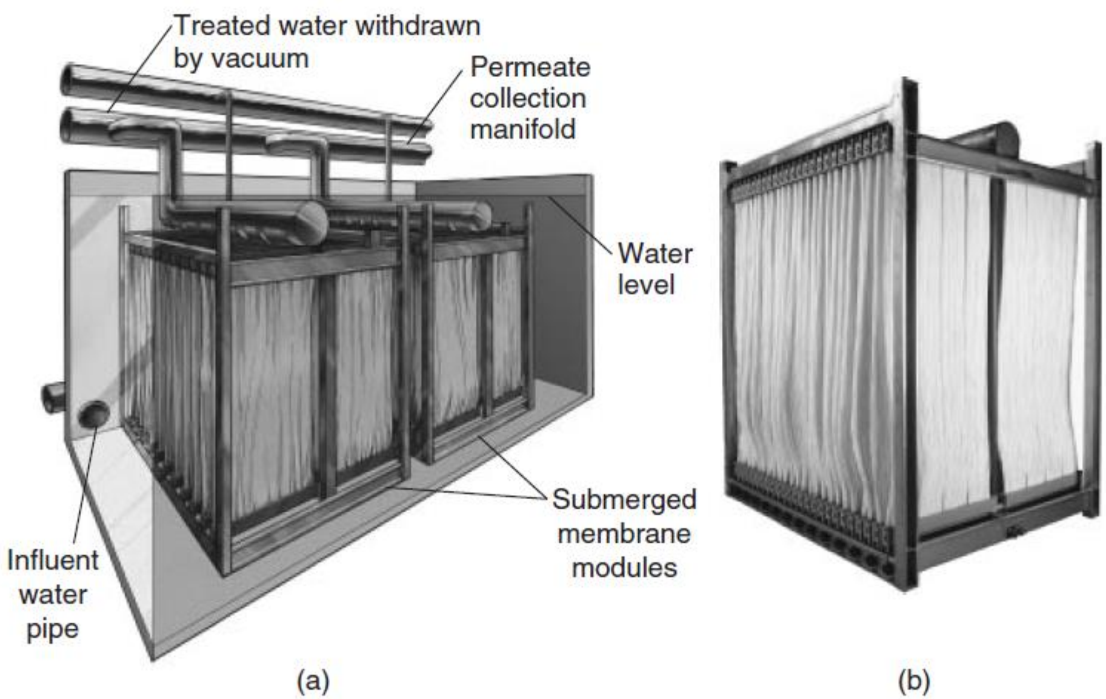


Figure
Submerged configurations for membrane filtration: (a) schematic of a submerged membrane module and (b) photograph of a single module.

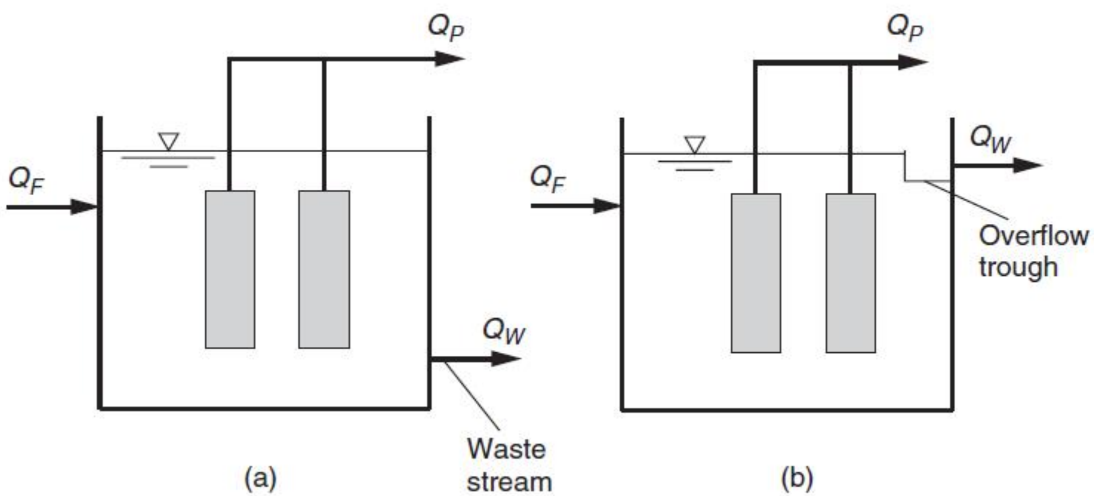
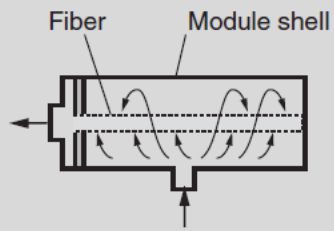
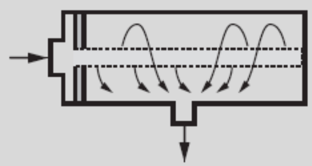
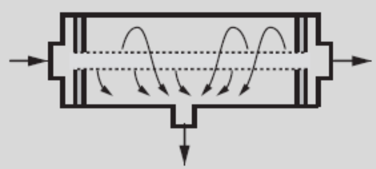


Figure
Feed-and-bleed and semibatch modes of operation. In feed-and-bleed, Q_P and Q_W are both continuous, the sum of the two flows equals Q_F. In semibatch, Q_P is continuous and equal to Q_F, Q_W only flows when solids are being wasted.

Flow Direction through Hollow Fibers

Table
Comparison of hollow-fiber membrane configurations

Configuration	Advantages	Disadvantages
Outside in 	❑ Can treat more water at same flux because outside of fiber has more surface area ❑ Less sensitive to presence of large solids in the feed water	❑ Cannot be operated in cross-flow mode
Inside out (dead-end mode) 	❑ Less expensive to operate than inside out in cross-flow mode	❑ Large solids in feed water can clog lumen ❑ Can treat less water at same flux because inside of fiber has less surface area
Inside out (cross-flow mode) 	❑ Can be operated at higher flux with high-turbidity feed water because cross-flow velocity flushes away solids and reduces impact of particles forming cake at membrane surface Reduced fouling	❑ Large solids in feed water can clog lumen ❑ Can treat less water at same flux because inside of fiber has less surface area ❑ Pumping costs associated with recirculating feed water through lumen can be expensive

Cross-Flow and Dead-End Flow Regimes

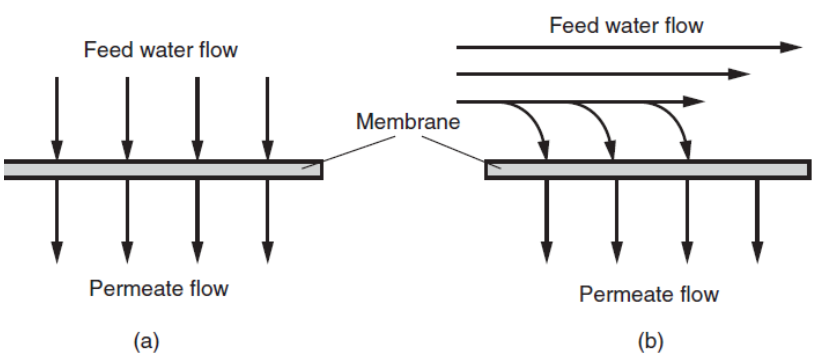


Figure __ _-
Flow regimes in membranes:
(a) dead-end filtration and
(b) cross-flow filtration.

Example **Comparison of outside-in and inside-out filtration**

A Dow Filmtec SFX-2860 membrane module contains 5760 fibers. The fibers are 1.87 m long with an outside diameter of 1.3 mm and inside diameter of 0.7 mm. Calculate the water production from one module if the flux is 75 $L/m^2 \cdot h$ and the flow direction is (1) outside in and (2) inside out. Compare the two answers.

Solution

1. Compute the product water flow for outside-in flow.
   a. Determine the outside surface area per fiber:

$$a\,(\text{per fiber}) = \pi\, dL = \pi(1.3\ \text{mm})(1.87\ \text{m})(10^{-3}\ \text{m/mm})$$
$$= 7.64 \times 10^{-3}\ \text{m}^2/\text{fiber}$$

   b. Compute the product water flow:

$$Q = Ja = (75\ \text{L/m}^2 \cdot \text{h})(7.64 \times 10^{-3}\ \text{m}^2/\text{fiber})(5760\ \text{fibers})$$
$$= 3300\ \text{L/h}$$

2. Compute the product water flow for inside-out flow.
   a. Determine the inside surface area per fiber:

$$a\,(\text{per fiber}) = \pi\, dL = \pi\,(0.7\ \text{mm})\,(1.87\ \text{m})\,(10^{-3}\ \text{m/mm})$$
$$= 4.11 \times 10^{-3}\ \text{m}^2/\text{fiber}$$

   b. Compute the product water flow:

$$Q = Ja = (75\ \text{L/m}^2 \cdot \text{h})(4.11 \times 10^{-3}\ \text{m}^2/\text{fiber})(5760\ \text{fibers})$$
$$= 1780\ \text{L/h}$$

3. Compare the outside-in and inside-out flow configurations:

$$\text{Ratio} = (3300/1780) \times 100\% = 186\%$$

Comparison to Rapid Granular Filtration

√ Destabilization is not necessary

-The void spaces in a membrane filter are much smaller; particles are literally strained from the water so destabilization is not necessary.

-No requirement of coagulation, flocculation, and sedimentation facilities for effective particle removal.

-Reduce the facilities for chemical storage and handling and residual-handling and allow membrane plants to be more compact and automated.

-Furthermore, the more compact installation can result in considerable cost savings in densely populated areas or other areas where land costs are high.

√ Performance is not dependent on the feed water quality

-The most significant advantage, however, is that the filtered water turbidity from membrane filters is independent of the concentration of particulate matter in the feed.

Compact & Stable !!

Properties of Membrane Materials

Material Properties

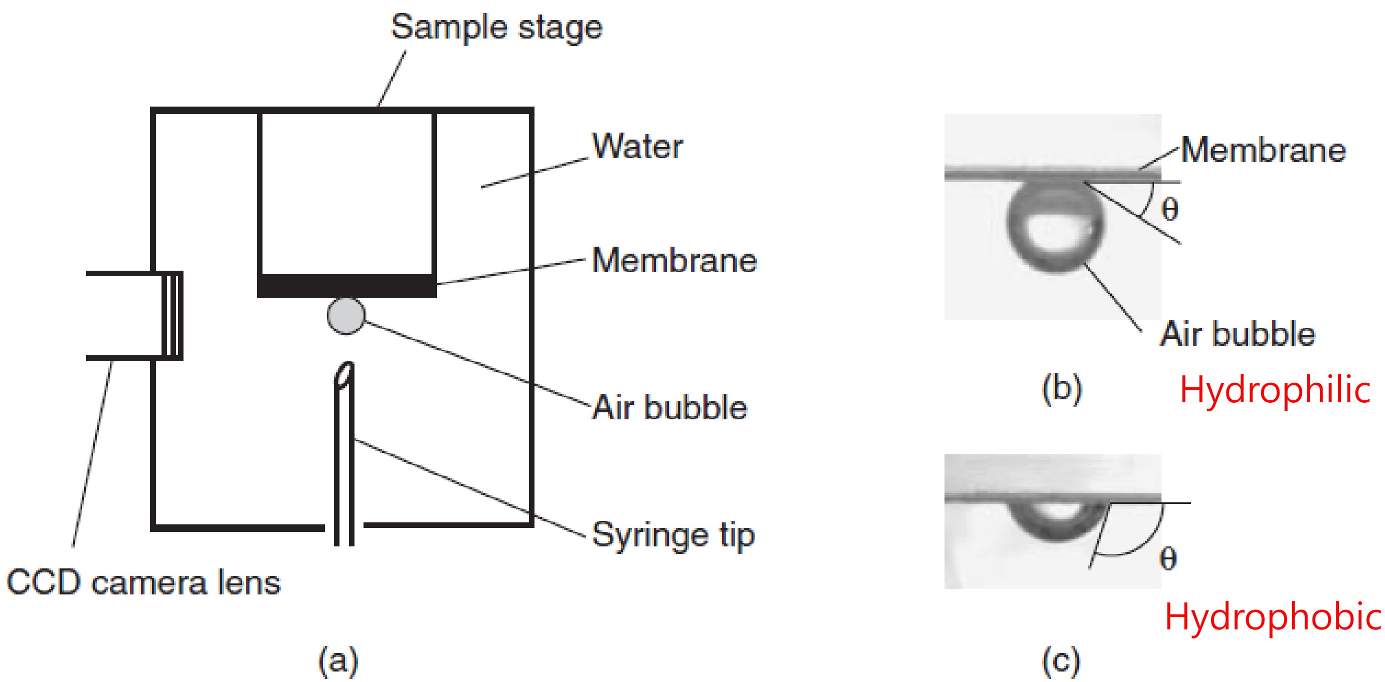
Table
Important properties of membrane materials[a]

Property	Method of Determination	Impact on Membrane Performance
Retention rating (pore size or molecular weight cut-off)	Bubble point, challenge tests	Controls the size of material retained by the membrane, making it one of the most significant parameters in membrane filtration. Also affects head loss.
Hydrophobicity	Contact angle	Reflects the interfacial tension between water and the membrane material. Hydrophobic materials “dislike” water; thus, constituents from the water accumulate at the liquid–solid interface to minimize the interfacial tension between the water and membrane. In general, hydrophobic materials will be more susceptible to fouling than hydrophilic materials.
Surface or pore charge	Streaming potential	Reflects the electrostatic charge at the membrane surface. Repulsive forces between negatively charged species in solution and negatively charged membrane surfaces can reduce fouling by minimizing contact between the membrane and fouling species. In UF, electrostatic repulsion can reduce the passage of like-charged solutes. Membranes fabricated of uncharged polymers typically acquire some negative charge while in operation.
Surface roughness	Atomic force microscopy	Affects membrane fouling; some studies have shown rough materials will foul more than smooth materials.

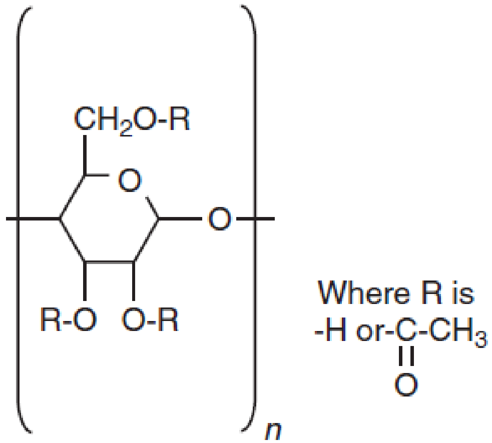
Property	Method of Determination	Impact on Membrane Performance
Porosity (surface and bulk)	Thickness/weight measurements	Affects the head loss through the membrane; higher porosity results in lower head loss.
Thickness	Thickness gauge, electron microscopy	Affects the head loss through the membrane; thinner membranes have lower head loss.
Surface chemistry	ATR/FTIR, SIMS, XPS	Affects fouling and cleaning by influencing chemical interactions between the membrane surfaces and constituents in the feed water.
Chemical and thermal stability	Exposure to chemicals and temperature extremes	Affects the longevity of the membrane; greater chemical and temperature tolerance allows more aggressive cleaning regimes with less degradation of the material.
Biological stability	Exposure to organisms	Affects the longevity of the membrane; low biological stability can result in the colonization and physical degradation of the membrane material by microorganisms.
Chlorine/oxidant tolerance	Exposure to chlorine/ oxidants	Affects the ability to disinfect the membrane equipment. Routine disinfection prevents microbial growth on the permeate side of membrane surfaces and prevents biological degradation of membrane materials (increasing the longevity of the membrane).
Mechanical durability	Mechanical tests	Affects the ability of the material to withstand surges due to operation of valves and pumps.
Internal physical structure, tortuosity	Electron microscopy	Affects the hydrodynamics of flow and particle capture. There are no standard procedures for quantifying the tortuosity or internal structure of membranes.
Cost	Material cost	Affects the cost of the membrane system.

[a]Abbreviations: ATR/FTIR = attenuated total reflectance/Fourier transform infrared spectrometry, SIMS = secondary ion mass spectrometry, XPS = X-ray photoelectron spectrometry.

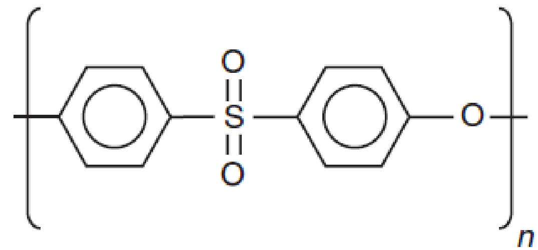
Figure
Captive bubble contact angle measurements for determination of hydrophobicity: (a) contact angle measurement apparatus, (b) hydrophilic surface (low contact angle), and (c) hydrophobic surface (high contact angle).



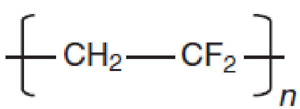
Material Chemistry



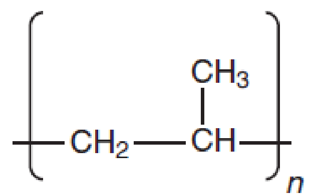
Cellulose acetate (CA)



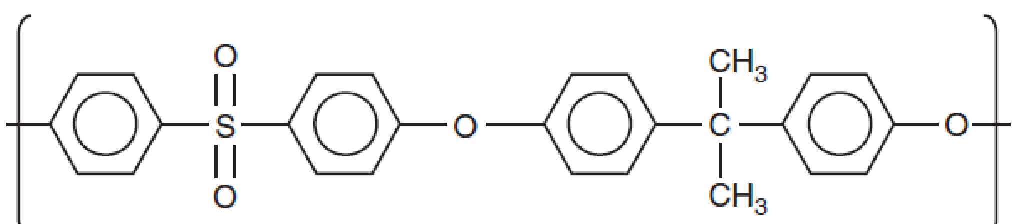
Polyethersulfone (PES)



Polyvinylidene fluoride (PVDF)



Polypropylene (PP)



Polysulfone (PS)

Figure
Chemical structure of common polymeric MF and UF membrane materials.

Table

Characteristics of common membrane materials

Membrane Material	Characteristics
Cellulose acetate (CA)	CA is the most hydrophilic of common industrial-grade membrane materials, which helps to minimize fouling and maintain high flux values. The material is easy to manufacture, inexpensive, and available in a wide range of pore sizes. Has been losing favor for membrane filters because of higher susceptibility to biological degradation, lack of tolerance to continuous exposure or high concentrations of free chlorine, gradual decline in the flux over its lifetime due to compaction, and lack of tolerance to aggressive cleaning chemicals or temperatures above 30°C.
Polysulfone (PS)/ polyethersulfone (PES)	PS and PES are moderately hydrophobic and have excellent chemical tolerance and biological resistance. They can withstand free chlorine contact to 200 mg/L for short periods of time for cleaning, pH values between 1 and 13, and temperatures to 75°C. Aggressive cleaning and disinfecting is possible.
Polyvinylidene fluoride (PVDF)	PVDF is moderately hydrophobic and has excellent durability, chemical tolerance, and biological resistance. It can withstand continuous free chlorine contact to any concentration, pH values between 2 and 10, and temperatures to 75°C. Aggressive cleaning and disinfecting is possible.

Membrane Material	Characteristics
Polypropylene (PP)	PP is the most hydrophobic of common industrial-grade membrane materials. Only MF membranes are available in PP; the material is too hydrophobic to allow water to pass through the small pore spaces in UF membranes. It is durable, chemically and biologically resistant, and tolerant of moderately high temperatures and pH values between 1 and 13, which allows aggressive cleaning. It has been losing favor for membrane filters because it is not tolerant to chlorine, which hinders the ability to control biological growth.
Ceramic	Ceramic membranes are configured as rigid monolithic elements. The material is hydrophilic, rough, and can withstand high operating pressure and temperature. They have excellent chemical and pH tolerance. Aggressive cleaning and disinfecting is possible.

Membrane Structure

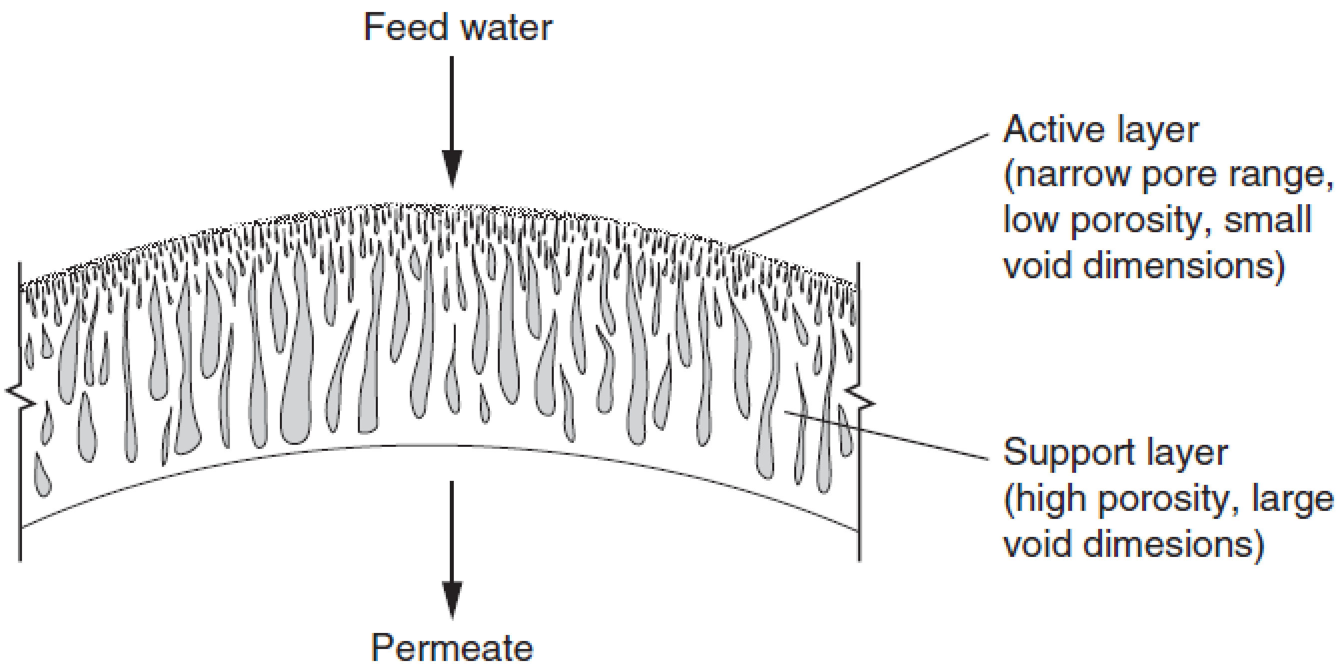


Figure
Structure of an asymmetric UF membrane.

Particle Capture in Membrane Filtration

Retention Rating

-For MF, pore size is typically used for retention rating.
-For UF, pore size or MWCO is used for retention rating
-The standard procedure for determining the MWCO value of a UF membrane involves filtration of dextran solutions with varying average molecular weights

$$d_H = 0.11\ (\mathrm{MW})^{0.46}$$

where d_H = hydrodynamic diameter of dextran molecule, nm
MW = molecular weight, g/mol

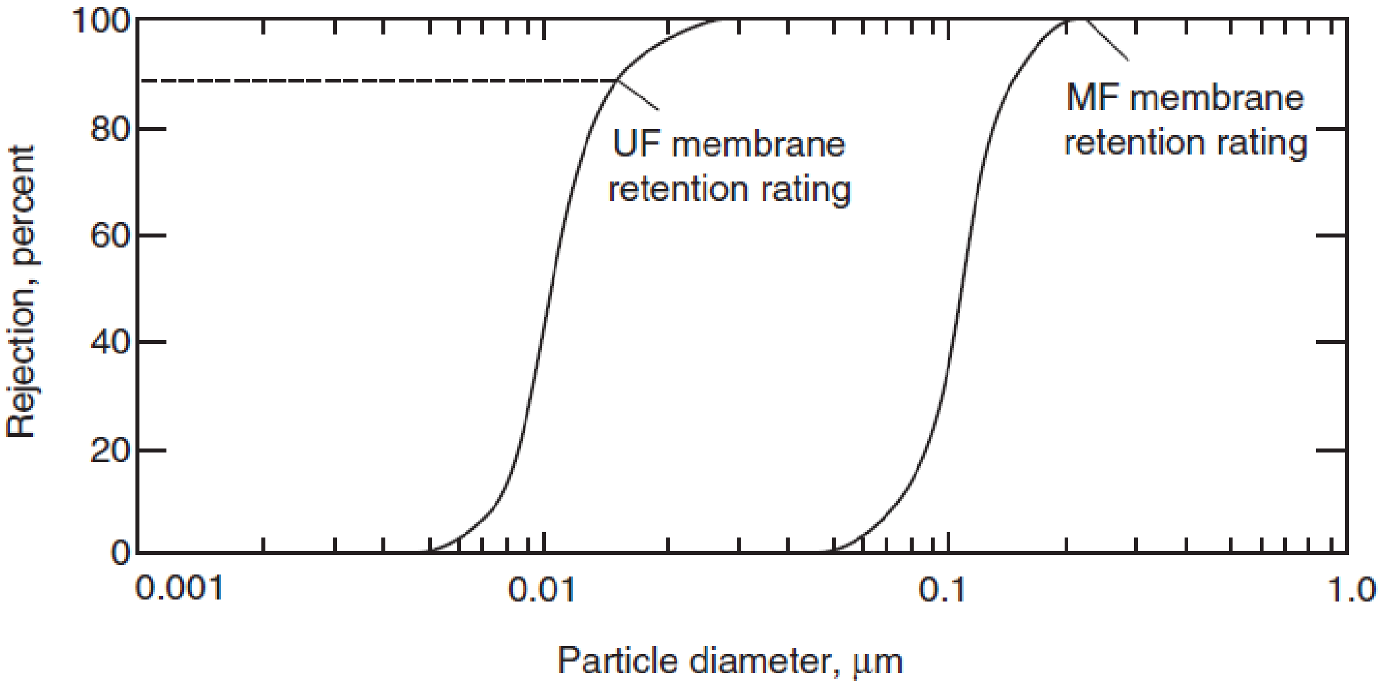


Figure
Determination of retention ratings for MF and UF membranes.

Rejection and Log Removal

$$R = 1 - \frac{C_p}{C_f}$$

where R = rejection, dimensionless

C_p = permeate concentration, mol/L or mg/L

C_f = feed water concentration, mol/L or mg/L

$$\text{LRV} = \log(C_f) - \log(C_p) = \log\left(\frac{C_f}{C_p}\right)$$

log removal value (LRV)

Example Calculation of rejection and log removal value

During testing of a prototype membrane filter, bacteriophage concentrations of $10^7\ \text{mL}^{-1}$ and $13\ \text{mL}^{-1}$ were measured in the influent and effluent, respectively. Calculate the rejection and log removal value.

Solution

1. Calculate rejection using Eq. 12-3:

$$R = 1 - \frac{C_p}{C_f} = 1 - \frac{13\ \text{mL}^{-1}}{10^7\ \text{mL}^{-1}} = 0.9999987$$

2. Calculate log removal value using Eq. 12-4:

$$\text{LRV} = \log\left(\frac{C_f}{C_p}\right) = \log\left(\frac{10^7\ \text{mL}^{-1}}{13\ \text{mL}^{-1}}\right) = 5.89$$

Filtration Mechanisms

STRAINING **ADSORPTION** **CAKE FORMATION**

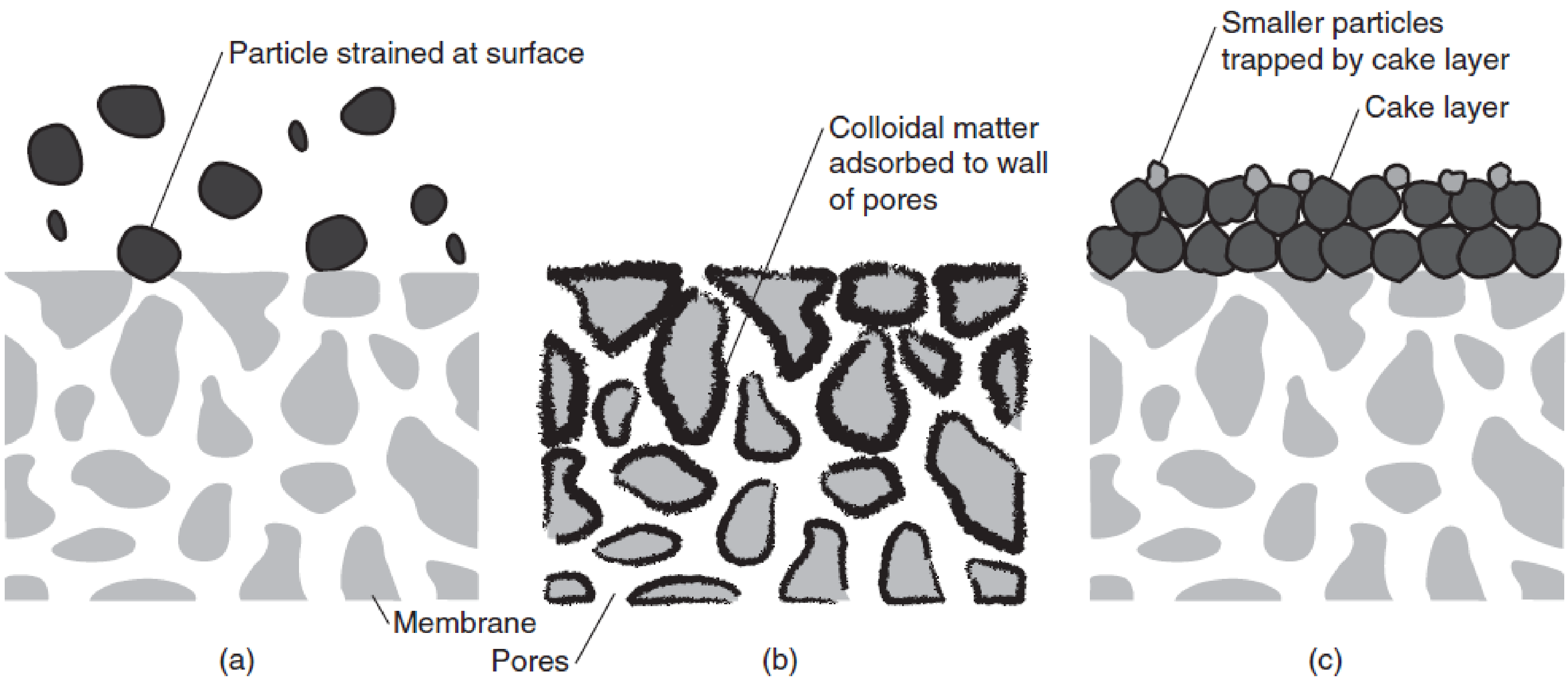


Figure
Mechanisms for rejection in membrane filtration. (a) Straining occurs when particles are physically retained because they are larger than the pores. (b) Adsorption occurs when material small enough to enter pores adsorbs to the walls of the pores. (c) Cake filtration occurs when particles that are small enough to pass through the membrane are retained by a cake of larger material that collects at the membrane surface.

Removal of Microorganisms

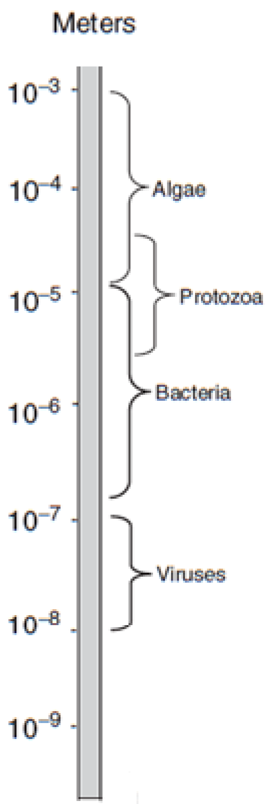
√ REMOVAL OF PROTOZOA AND HELMINTHS

-At least 10 times larger than the retention ratings of MF and UF membranes.

-Rejection of greater than 7 log (limited by the initial population) has been observed for both MF and UF membranes

√ REMOVAL OF BACTERIA

-In many studies, bacteria are removed to below the detection limit by MF and UF



√ REMOVAL OF VIRUSES

-The efficiency depends on the virus species and the membrane.

-For MF, straining, adsorption and cake filtration all contribute to rejection, and virus rejection can vary from LRV < 1 to LRV > 4.

-For UF, complete rejection (LRV > 7.2) of MS2 bacteriophage, a model virus with a diameter of about 25 nm, with a 100,000-Da UF membrane but LRV < 1 with a 500,000-Da UF membrane.

100,000-Da $\Rightarrow$ d_H = 21 nm

500,000-Da $\Rightarrow$ d_H = 46 nm

Hydraulics of Flow Through Membrane

Darcy's law:

$$v = k_P \frac{h_L}{L}$$

where v = superficial fluid velocity, m/s
k_P = hydraulic permeability coefficient, m/s
h_L = head loss across porous media, m
L = thickness of porous media, m

Similarly for membrane filtration

$$J = \frac{Q}{a} = \frac{\Delta P}{\mu \kappa_m}$$

where J = volumetric water flux through membrane, $L/m^2 \cdot h$ or m/s
Q = flow rate, L/h
a = membrane area, m^2
ΔP = differential pressure across membrane, bar
μ = dynamic viscosity of water, $kg/m \cdot s$
κ_m = membrane resistance coefficient, m^{-1}

Example Calculation of membrane resistance coefficient

An MF membrane is tested in a laboratory by filtering clean, deionized water and the flux is found to be 850 $L/m^2 \cdot h$ at 20°C and 0.9 bar. Calculate the membrane resistance coefficient.

Solution

Rearrange Eq. 12-6 to solve for the membrane resistance coefficient. The dynamic viscosity of water at 20°C, from Table C-1 in App. C, is 1.00×10^{-3} kg/m · s. Also recall that 1 bar = 100 kPa = 10^5 N/m^2 = 10^5 kg/s^2 · m.

$$\kappa_m = \frac{\Delta P}{\mu J} = \frac{(0.9 \times 10^5 \text{ kg/s}^2 \cdot \text{m})(3600 \text{ s/h})(10^3 \text{ L/m}^3)}{(1.00 \times 10^{-3} \text{ kg/m} \cdot \text{s})(850 \text{ L/m}^2 \cdot \text{h})}$$

$$= 3.81 \times 10^{11} \text{ m}^{-1}$$

Temperature and Pressure Dependence

$$J_s = J_m \left(\frac{\mu_m}{\mu_s}\right)$$

where J_m = flux at measured temperature, $L/m^2 \cdot h$
J_s = flux at standard temperature (typically 20°C), $L/m^2 \cdot h$
μ_m = dynamic viscosity of water at measured temperature, $kg/m \cdot s$
μ_s = dynamic viscosity of water at standard temperature, $kg/m \cdot s$

Increasing T → Decreasing μ → Increasing J

$$J_s = J_m (1.03)^{T_s - T_m}$$

where T_m = measured temperature, °C
T_s = standard temperature, °C

$$J_{sp} = \frac{J_s}{\Delta P}$$

where J_{sp} = specific flux at standard temperature, $L/m^2 \cdot h \cdot bar$

Example Calculation of specific flux

A membrane plant has a measured flux in March of 80 $L/m^2 \cdot h$ at 0.67 bar and 7°C. Four months later, in July, the measured flux is 85 $L/m^2 \cdot h$ at 0.52 bar and 19°C. Has a change in specific flux occurred? What is the change in percent? Has fouling occurred?

Solution

1. Calculate the specific flux in March.
   a. Calculate the flux in March at a standard temperature of 20°C using Eq. 12-8:

$$J_s = J_m(1.03)^{T_s - T_m} = (80\ \text{L/m}^2 \cdot \text{h})(1.03)^{20°\text{C} - 7°\text{C}}$$
$$= 117\ \text{L/m}^2 \cdot \text{h}$$

   b. Calculate the specific flux in March using Eq. 12-9:

$$J_{sp} = \frac{J_s}{\Delta P} = \frac{117\ \text{L/m}^2 \cdot \text{h}}{0.67\ \text{bar}} = 175\ \text{L/m}^2 \cdot \text{h} \cdot \text{bar}$$

2. Calculate the specific flux in July.
   a. Calculate the flux in July at a standard temperature of 20°C using Eq. 12-8:

$$J_s = J_m(1.03)^{T_s - T_m} = (85\ \text{L/m}^2 \cdot \text{h})(1.03)^{20°\text{C} - 19°\text{C}}$$
$$= 87.6\ \text{L/m}^2 \cdot \text{h}$$

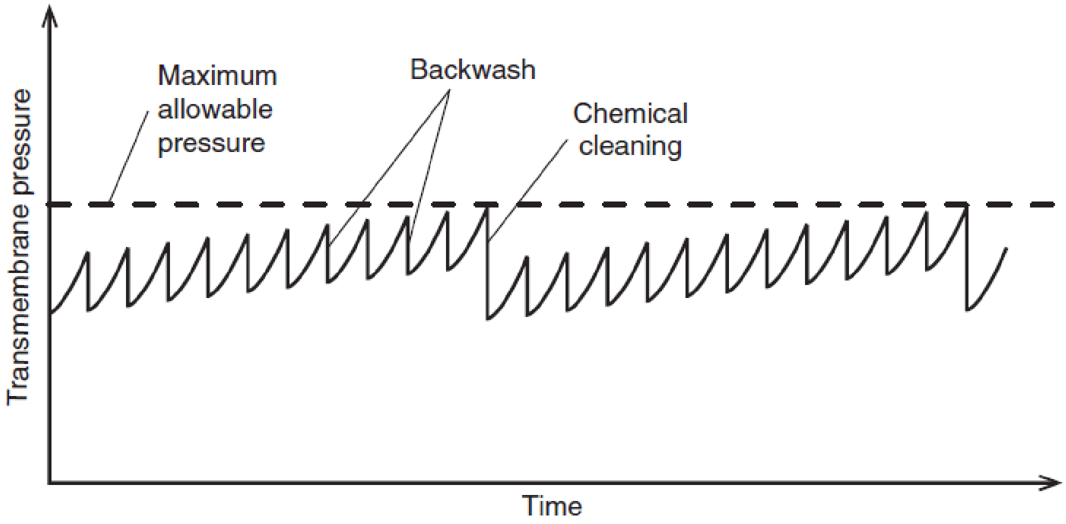
   b. Calculate the specific flux in July using Eq. 12-9:

$$J_{sp} = \frac{J_s}{\Delta P} = \frac{87.6\ \text{L/m}^2 \cdot \text{h}}{0.52\ \text{bar}} = 168\ \text{L/m}^2 \cdot \text{h} \cdot \text{bar}$$

3. Calculate the percent loss of performance due to fouling:

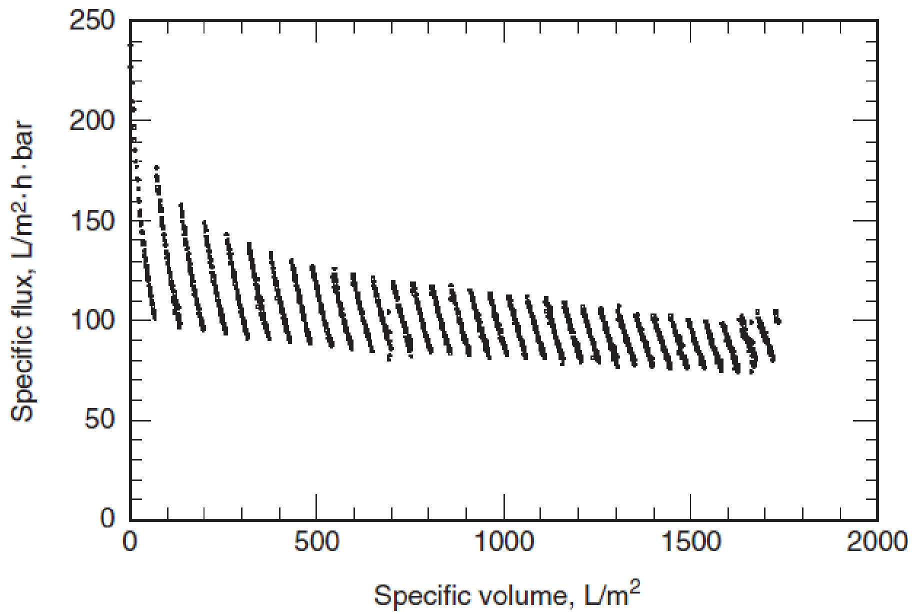
$$\frac{175\ \text{L/m}^2 \cdot \text{h} \cdot \text{bar} - 168\ \text{L/m}^2 \cdot \text{h} \cdot \text{bar}}{175\ \text{L/m}^2 \cdot \text{h} \cdot \text{bar}} \times 100$$
$$= 4\%\ \text{loss of flux due to fouling}$$

Membrane Fouling



Operation at a constant flux

Figure
Transmembrane pressure development during membrane filtration.



Operation at a constant pressure

Figure
Fouling of a membrane filter during filtration of natural water.

Mechanisms of Fouling

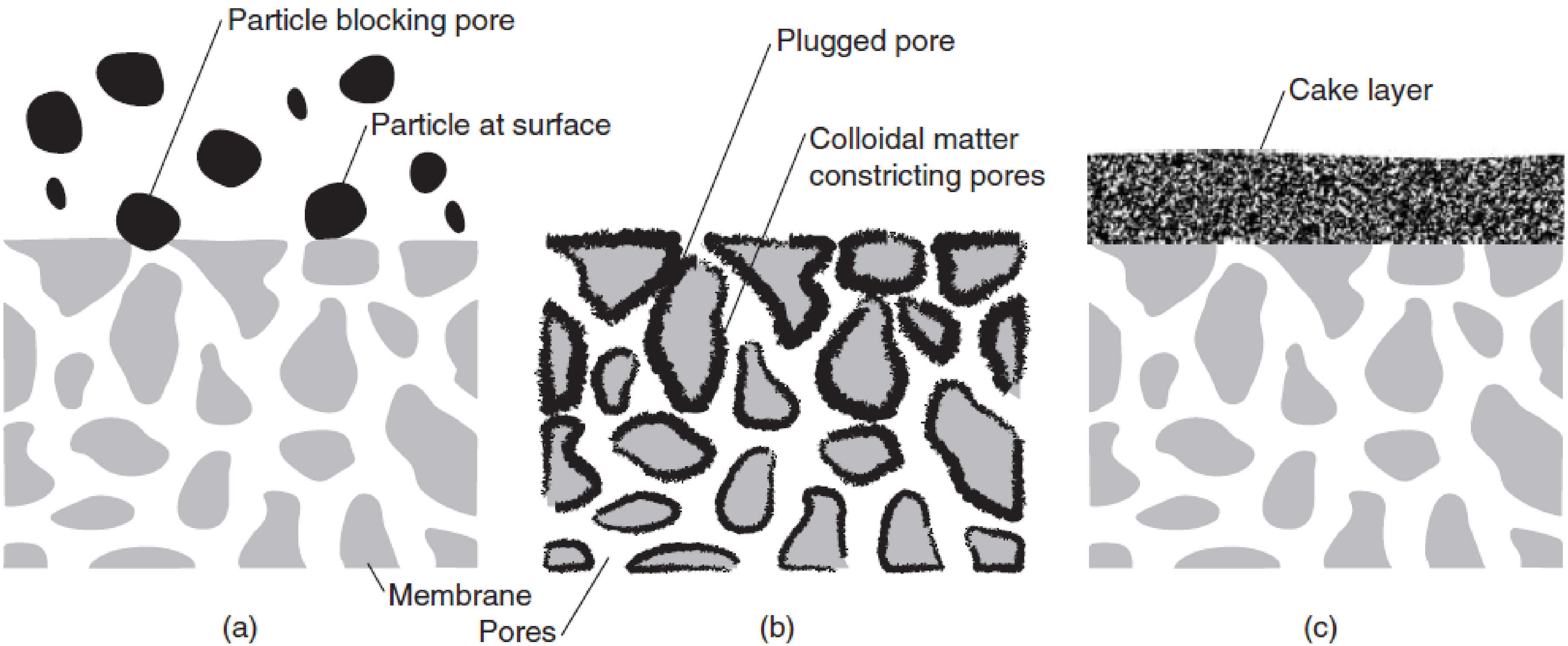


Figure
Mechanisms for fouling in membrane filtration: (a) Pore blocking, (b) pore constriction, and (c) cake layer formation.

Reversibility of Fouling

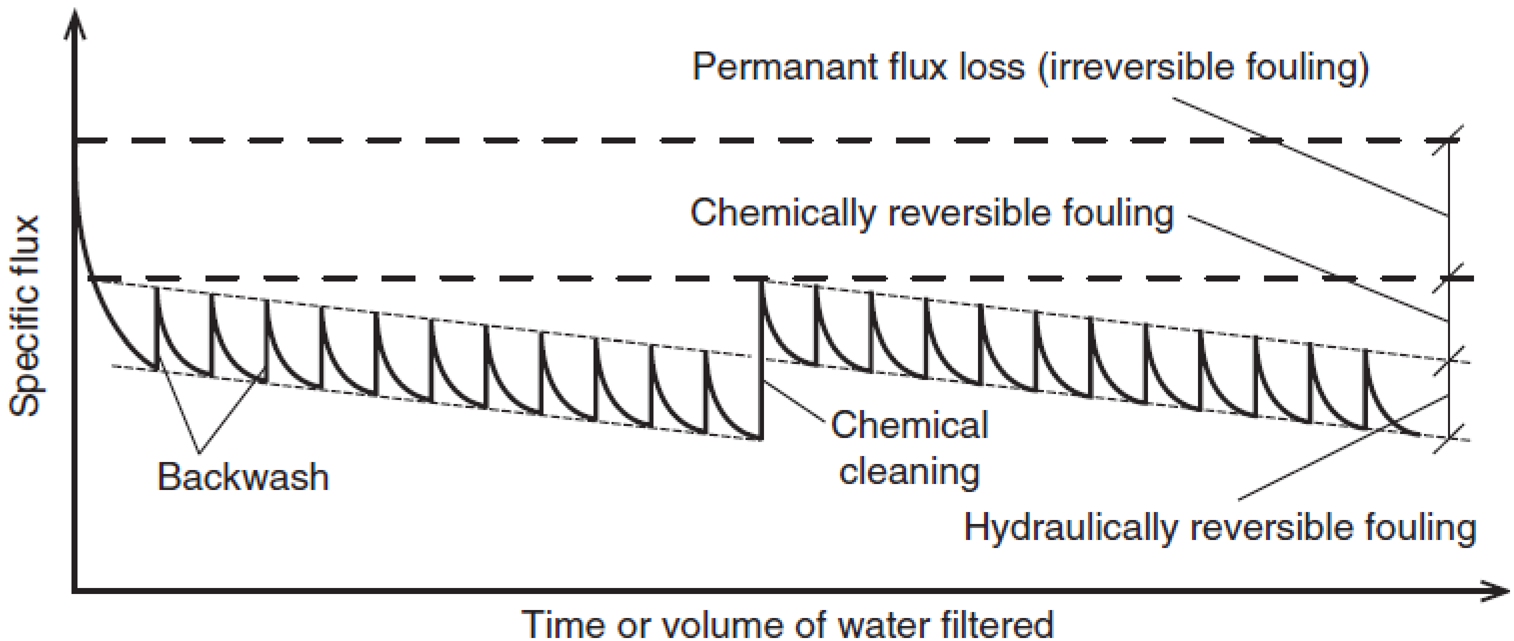


Figure Variation in specific flux during filtration of natural waters. The loss of specific flux from the initial clean membrane permeability, which cannot be recovered by backwashing or cleaning, is called irreversible fouling; that which can be recovered is called reversible fouling.

Resistance-in-Series Model

$$J = \frac{\Delta P}{\mu\,(\kappa_m + \kappa_{ir} + \kappa_{hr} + \kappa_{cr})} = \frac{\Delta P}{\mu\left(\kappa_m + \kappa_c + \kappa_p\right)}$$

where
κ_m = membrane resistance coefficient, m^{-1}
κ_{ir} = irreversible fouling resistance coefficient, m^{-1}
κ_{hr} = hydraulically reversible fouling resistance coefficient, m^{-1}
κ_{cr} = chemically reversible fouling resistance coefficient, m^{-1}
κ_c = cake layer resistance coefficient, m^{-1}
κ_p = pore constriction resistance coefficient, m^{-1}

- The resistance-in-series equation can be defined in different ways.
- E.g., The resistance-in-series equation can be applied to any number of individual resistances, which may be due to irreversible and reversible components, specific fouling materials (organic fouling resistance, biological fouling resistance, etc.), fouling mechanisms (cake fouling resistance, pore constriction fouling resistance, etc.).

Example Calculation of resistance coefficients

The MF membrane in Example 12-3 is used under full-scale conditions in a water treatment facility, producing a flux of 84 $L/m^2 \cdot h$ at 1.1 bar just before cleaning and 106 $L/m^2 \cdot h$ at 0.52 bar immediately after cleaning, both at a standard temperature of 20°C. Calculate values for the membrane resistance coefficient, irreversible fouling resistance coefficient, and chemically reversible fouling resistance coefficient.

Example Calculation of membrane resistance coefficient

An MF membrane is tested in a laboratory by filtering clean, deionized water and the flux is found to be 850 $L/m^2 \cdot h$ at 20°C and 0.9 bar. Calculate the membrane resistance coefficient.

Solution

Rearrange Eq. 12-6 to solve for the membrane resistance coefficient. The dynamic viscosity of water at 20°C, from Table C-1 in App. C, is 1.00×10^{-3} kg/m · s. Also recall that 1 bar = 100 kPa = 10^5 N/m^2 = 10^5 kg/s^2 · m.

$$\kappa_m = \frac{\Delta P}{\mu J} = \frac{(0.9 \times 10^5 \text{ kg/s}^2 \cdot \text{m})(3600 \text{ s/h})(10^3 \text{ L/m}^3)}{(1.00 \times 10^{-3} \text{ kg/m} \cdot \text{s})(850 \text{ L/m}^2 \cdot \text{h})}$$

$$= 3.81 \times 10^{11} \text{ m}^{-1}$$

c. Rearrange Eq. 1 to solve for κ_{ir}:

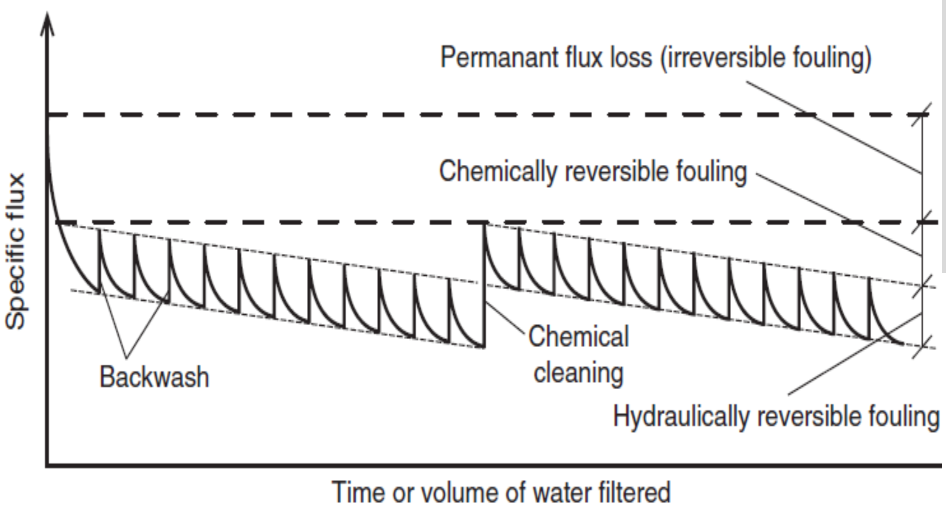
$$\kappa_{ir} = \frac{\Delta P}{\mu J} - \kappa_m = \frac{(0.52 \times 10^5\ \text{kg/s}^2 \cdot \text{m})(3600\ \text{s/h})(1 \times 10^3\ \text{L/m}^3)}{(1.00 \times 10^{-3}\ \text{kg/m} \cdot \text{s})(106\ \text{L/m}^2 \cdot \text{h})}$$
$$- 3.81 \times 10^{11}\ \text{m}^{-1}$$
$$= 1.39 \times 10^{12}\ \text{m}^{-1}$$

3. Determine the chemically reversible fouling resistance coefficient.
   a. Prior to cleaning, three components of resistance are present:

$$J = \frac{\Delta P}{\mu\,(\kappa_m + \kappa_{ir} + \kappa_{cr})}$$

   b. Rearrange the above equation to solve for κ_{cr}:

$$\kappa_{cr} = \frac{\Delta P}{\mu J} - \kappa_m - \kappa_{ir}$$
$$= \frac{(1.1 \times 10^5\ \text{kg/s}^2 \cdot \text{m})\,(3600\ \text{s/h})\,(1 \times 10^3\ \text{L/m}^3)}{(1.00 \times 10^{-3}\ \text{kg/m} \cdot \text{s})\,(84\ \text{L/m}^2 \cdot \text{h})}$$
$$- 3.81 \times 10^{11}\ \text{m}^{-1} - 1.39 \times 10^{12}\ \text{m}^{-1}$$
$$= 2.94 \times 10^{12}\ \text{m}^{-1}$$



Fouling by Particles

$$\kappa_C = \frac{36\kappa_K (1-\varepsilon)^2 \delta_C}{\varepsilon^3 d_P^2}$$

where κ_C = cake layer resistance coefficient, m^{-1}
κ_K = Kozeny coefficient, unitless (typically 5)
ε = cake porosity, dimensionless
δ_C = thickness of cake layer, m
d_P = diameter of retained particles, m

$$\delta_C(t) = \frac{CV}{\rho_P a (1-\varepsilon)}$$

where $\delta_C(t)$ = thickness of cake layer at time t, m
C = concentration of particles, mg/L
V = volume of feed water filtered, m^3
ρ_P = density of particles, kg/m^3
a = membrane area, m^2

$$\kappa_C = \alpha_C \frac{CV}{a}$$

where α_C = specific cake resistance, m/g

Biofouling

-Biofouling is the loss of system performance due to the formation of a biofilm

-Biofilm formation: Adhesion of microorganisms on the membrane surface, excretion of extracellular material to form organic films

-Biofouling is particularly important for wastewater applications, e.g., MBR.

-Disinfectants are often used to control the biofouling (a related issue: chlorine-resistant membranes).

Natural Organic Matter Fouling

-The most problematic and least controllable membrane fouling is due to the adsorption of natural organic matter (NOM) to the membrane surface.

-Surface cake formation and pore constriction have both been proposed as mechanisms for fouling

Table

Factors contributing to membrane fouling by dissolved organic matter (DOM)

Factor	Observed Effects
Hydrophobicity	Hydrophobic membranes adsorb more DOM and therefore foul more rapidly than hydrophilic membranes (Matthiasson, 1983; Laîné et al., 1989; Cheryan, 1998). Hydrophobic fractions of DOM and hydrophobic sources of DOM are expected to cause greater fouling, which has been observed in some research (Crozes et al., 1993; Yuan and Zydney, 1999; Schäfer et al., 2000). However, researchers have also reported that hydrophilic fractions of DOM may be implicated in greater fouling (Amy and Cho, 1999; Carroll et al., 2000; Lin et al., 2000).
Electrostatic charge	Most DOM is negatively charged, and many MF and UF membranes acquire a slight negative charge during operation. Conditions that increase electrostatic repulsion might reduce fouling. The magnitude of the negative charge on membrane (Causserand et al., 1994; Nyström et al., 1994; Combe et al., 1999) and the negative charge on DOC both tend to increase at higher pH. As expected, low-pH conditions increase the adsorption of DOM to membranes (Jucker and Clark, 1994; Combe et al., 1999) and the fouling due to DOM adsorption (Kulovaara et al., 1999).
Size/molecular weight	Size may be an essential factor in determining which components of DOM cause fouling. Several studies suggest that high-MW and colloidal materials cause greater fouling (Lin et al., 1999, 2000; Yuan and Zydney, 1999, 2000; Habarou et al., 2001; Howe and Clark, 2002). Fouling by this colloidal fraction is consistent with the ability of larger material to constrict pores more efficiently than dissolved materials.

Factor	Observed Effects
Colloidal stability	Since colloids must be smaller than the pore size to enter the membrane matrix, an additional mechanism must explain their attachment to the pore walls. A model developed by Huang et al. (2008a) and supported by experimental results indicated that colloids with low particle–membrane stability and high particle–particle stability caused the greatest fouling.
Ionic strength	High ionic strength reduces electrostatic repulsion (and particle stability) by compressing the double layer, and irreversible fouling has been shown to increase at high ionic strength (e.g., seawater) (Kulovaara et al., 1999).
Calcium concentration	Calcium ions may act as a positively charged bridge between DOM and membrane surfaces. Calcium has been shown to neutralize the negative charge on DOM and increase the adsorption of NOM on membranes (Jucker and Clark, 1994) and contribute to greater flux decline (Schäfer et al., 2000).

Blocking Filtration Laws for Membrane Fouling

-Models that simulate fouling mechanisms under specific laboratory operating condition

-The filtration blocking laws apply only to constant-pressure, dead-end filtration.

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

where t = time, s
V = volume, L
k = blocking law filtration coefficient, units vary depending on n
n = blocking law filtration exponent, unitless

$$V = \int J_t a \, dt$$

$$\Rightarrow \quad dV/dt = J_t a$$

$$\Rightarrow \quad dt/dV = 1/J_t a$$

$$\Rightarrow \quad d^2t/dV^2 = d(1/J_t a)/dt \cdot (dt/dV)$$

$$= -a(dJ_t/dt) \cdot (J_t a)^{-2} \cdot (dt/dV)$$

$$= -a(dJ_t/dt) \cdot (dt/dV)^3$$

Table
Blocking filtration laws

Flux Equation	Equation Number	Filtration Coefficient, k	Filtration Exponent, n
Complete Blocking Filtration Law (Pore Sealing)			
$J_t = J_0 \exp\left(-1.5\frac{CJ_0 t}{\rho_P d_P}\right)$	(12-16)	$\frac{1.5CJ_0}{\rho_P d_P}$	2
❑ Models blockage of the entrance to pores by particles retained at the membrane surface. ❑ Each retained particle blocks an area of the membrane surface equal to the particle's cross-sectional area. ❑ Flux declines in proportion to the membrane area that has been covered. ❑ No superposition of particles occurs. Each particle lands on the membrane surface and not on other particles, so flux reaches zero when a monolayer of particles has been retained.			
Standard Blocking Filtration Law (Internal Pore Constriction)			
$J_t = \frac{J_0}{\left(1+\frac{CJ_0 t}{L\rho_P}\right)^2}$	(12-17)	$\frac{2C}{L\rho_P}\left(\frac{J_0}{a}\right)^{0.5}$	1.5
❑ Models the reduction of the void volume within the membrane. ❑ Assumes the membrane is composed of cylindrical pores of constant and uniform diameter. ❑ Particles deposit uniformly on the pore walls; pore volume decreases proportionally to the volume of particles deposited. ❑ L = membrane thickness, m			

Table *(Continued)*

Flux Equation	Equation Number	Filtration Coefficient, k	Filtration Exponent, n
Intermediate Blocking Filtration Law (Pore Sealing with Superposition)			
$J_t = \dfrac{J_0}{\left(1 + 1.5\dfrac{CJ_0 t}{\rho_P d_P}\right)}$	(12-18)	$\dfrac{1.5C}{\rho_P d_P a}$	1
❑ Models blockage of the entrance to pores by particles retained at the membrane surface. ❑ Extension of the complete blocking filtration law. ❑ Relaxes the "monolayer" assumption in the complete blocking filtration law by allowing particles to land on previously retained particles or on the membrane surface by evaluating the probability that a particle will block a pore.			
Cake Filtration Law			
$J_t = \dfrac{J_0}{\left(1 + 2\dfrac{\alpha_C C J_0 t}{\kappa_M}\right)^{0.5}}$	(12-19)	$\dfrac{\alpha_C C}{\kappa_M J_0 a^2}$	0
❑ Models the formation of a cake on the surface of a membrane using the resistance-in-series model. ❑ The retained particles have no impact on the membrane itself, i.e., no pore blocking or pore constriction.			

Membrane Fouling Index

-It is useful to have empirical models that can compare fouling under different conditions, such as with different source waters, different membrane products, or at different scales.

-A fouling index can be derived using the resistance-in-series model with two resistance terms: one for clean membrane resistance and another for fouling resistance:

$$J = \frac{\Delta P}{\mu \left(\kappa_m + \kappa_f\right)}$$

where κ_f = resistance due to all forms of fouling, m^{-1}

$$\kappa_f = k V_{sp}$$

where k = rate of increase in resistance, m^{-2}

V_{sp} = specific throughput, volume of water filtered per membrane area, m^3/m^2

$$J_{\text{sp}} = \frac{J_s}{\Delta P} = \frac{1}{\mu\left(\kappa_m + kV_{\text{sp}}\right)}$$

For a new membrane, $V_{\text{sp}} = 0$ so $\kappa_f = 0$, so

$$J_{\text{sp0}} = \frac{1}{\mu\kappa_m}$$

$$(< 1) \quad J'_{\text{sp}} = \frac{J_{\text{sp}}}{J_{\text{sp0}}} = \frac{1/\left[\mu\left(\kappa_m + kV_{\text{sp}}\right)\right]}{1/(\mu\kappa_m)} = \frac{\kappa_m}{\kappa_m + kV_{\text{sp}}}$$

$$(> 1) \quad \frac{1}{J'_{\text{sp}}} = 1 + (\text{MFI})\, V_{\text{sp}}$$

where $\text{MFI} = k/\kappa_m$ = membrane fouling index, m^{-1}

Example Calculation of the membrane fouling index

A laboratory membrane experiment using a backwashable single-fiber membrane module was carried out to collect the data in Fig. 12-16. The membrane had a total area of 23.0 cm^2 and the initial permeability of the new membrane was 225.0 L/m$^2 \cdot$h$\cdot$bar. The test was run at a constant pressure of 1.023 bar and temperature of 22°C. The membrane was backwashed every 30 min. Time and volume filtered were recorded at 2-min intervals and the data from filter run 6 is shown in the first two columns of Table 1 below. The flux at the beginning of each of the first 10 filter runs is also shown in Table 2 below. Calculate the fouling index during filter run 6 and the hydraulically irreversible fouling index (fouling that corresponds to the flux that could not be recovered by backwashing).

J_{sp0}

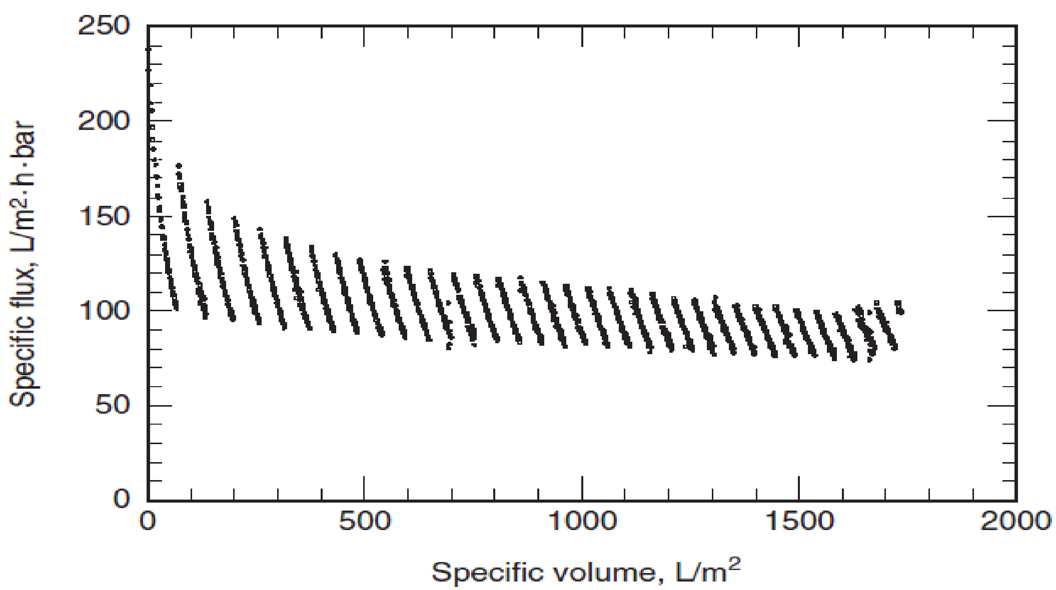


Figure
Fouling of a membrane filter during filtration of natural water.

Solution

1. Divide the volume filtered by the membrane area to determine the specific throughput. Results are in column (3) in Table 1. For the second row,

$$V_{sp} = \frac{(743.92 \text{ mL})(10^4 \text{ cm}^2/\text{m}^2)}{(23.0 \text{ cm}^2)(10^3 \text{ mL/L})} = 323.4 \text{ L/m}^2$$

2. Calculate the volume filtered in each time increment by subtracting the previous volume. Results are in column (4) in Table 1. For the second row,

$$\Delta V = 743.92 \text{ mL} - 732.63 \text{ mL} = 11.29 \text{ mL}$$

3. Divide the volume filtered in each increment by membrane area and time to determine flux. Then correct for temperature and pressure using Eqs. 12-8 and 12-9 to determine specific flux. Results are in column (5) in Table 1. For the second row,

$$J_m = \frac{(11.29 \text{ mL})(10^4 \text{ cm}^2/\text{m}^2)(60 \text{ min/h})}{(23.0 \text{ cm}^2)(2 \text{ min})(10^3 \text{ mL/L})} = 147.3 \text{ L/m}^2 \cdot \text{h}$$

$$J_{sp} = \frac{J_m (1.03)^{T_s - T_m}}{\Delta P} = \frac{147.3 \text{ L/m}^2 \cdot \text{h}\,(1.03)^{20-22}}{1.023 \text{ bar}}$$

$$= 135.7 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$$

4. Divide the specific flux (J_{sp}) by the initial specific flux (J_{sp0}). Results are in column (6) in Table 1. For the second row,

$$J'_{sp} = \frac{135.7}{225.0} = 0.60$$

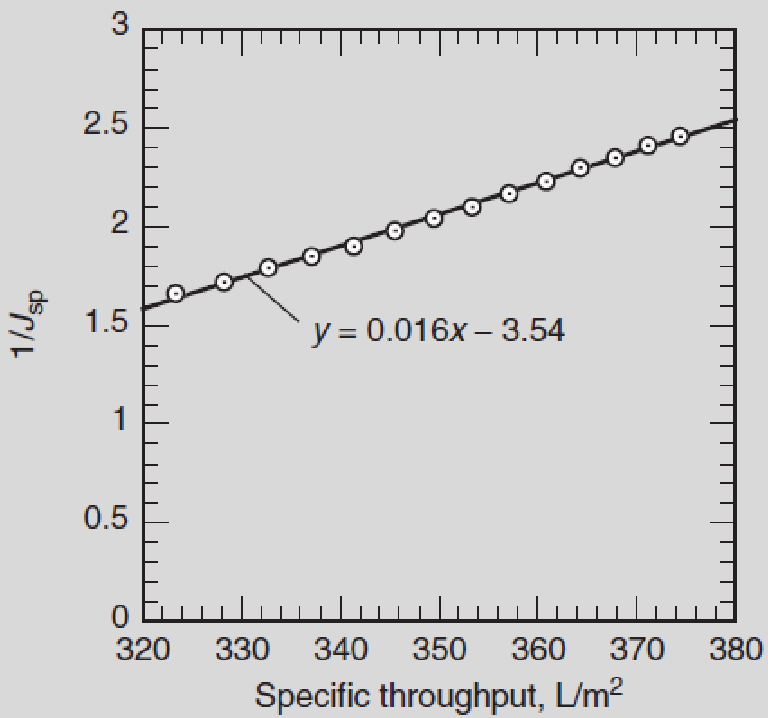
5. Invert the normalized flux from column 6. Results are in column (7) in Table 1.

Example 12-6 Table 1

Raw data

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Filtration Time, min	Volume Filtered, mL	Specific throughput, L/m^2	Delta volume, mL	Specific flux, $L/m^2 \cdot h$	Normalized specific flux, J'_{sp}	Inverse normalized specific flux, $1/J'_{sp}$
0	732.63	—	—	—	—	—
2	743.92	323.4	11.29	135.7	0.60	1.66
4	754.79	328.2	10.87	130.6	0.58	1.72
6	765.26	332.7	10.47	125.8	0.56	1.79
8	775.40	337.1	10.14	121.9	0.54	1.85
10	785.17	341.4	9.77	118.4	0.53	1.90
12	794.63	345.5	9.46	113.7	0.51	1.98
14	803.79	349.5	9.16	110.1	0.49	2.04
16	812.70	353.3	8.91	107.1	0.48	2.10
18	821.34	357.1	8.64	103.8	0.46	2.17
20	829.73	360.8	8.39	100.8	0.45	2.23
22	837.88	364.3	8.15	97.9	0.44	2.30
24	845.85	367.8	7.97	95.8	0.43	2.35
26	853.62	371.1	7.77	93.4	0.42	2.41
28	861.22	374.4	7.60	91.3	0.41	2.46

6. Plot the inverse of the normalized specific flux ($1/J'_{sp}$) as a function of the specific throughput (V_{sp}), as shown in the following figure:



$$\frac{1}{J'_{sp}} = 1 + (\text{MFI})\, V_{sp}$$

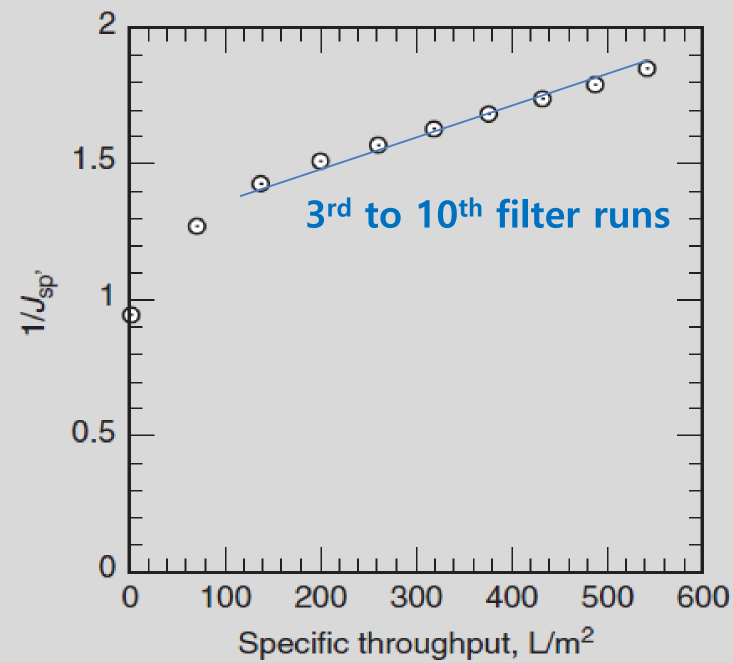
The slope of the line is the membrane fouling index for filter run 6, $\text{MFI}_6 = 0.016\ \text{m}^2/\text{L} = 16\ \text{m}^{-1}$. Note that the intercept of the graph is not 1.0 as is suggested by Eq. 12-25. This result is because backwashes remove foulants and reset membrane performance to a higher flux, whereas the specific volume progresses continuously. For an initial filter run (i.e., before any backwashes or cleanings), the intercept is very close to 1.0.

7. Determine the hydraulically irreversible membrane fouling index (MFI_{hi}). The MFI_{hi} represents the flux that cannot be recovered by backwashing and can be evaluated by considering the net reduction in flux at the beginning of each filter run (immediately after backwashing). Data from the first 10 filter runs of the experiment shown in Fig. 12-16 is shown in Table 2 below. Column (1) is the filter run number, Column (2) is the specific throughput at the beginning of each filter run, and Column (3) is the average specific flux over the first 30 of each filter run.

Example 12-6 Table 2

(1) Filter Run	(2) Specific throughput, L/m^2	(3) Specific flux, $L/m^2 \cdot h$	(4) Normalized specific flux, J'_{sp}	(5) Inverse normalized specific flux, $1/J'_{sp}$
1	2.2	238.0	1.06	0.95
2	71.3	176.9	0.79	1.27
3	137.6	157.7	0.70	1.43
4	200.0	149.0	0.66	1.51
5	260.5	143.3	0.64	1.57
6	319.0	138.0	0.61	1.63
7	376.4	133.6	0.59	1.68
8	432.6	129.3	0.57	1.74
9	487.9	125.5	0.56	1.79
10	542.4	121.6	0.54	1.85

8. A graph of the inverse of the normalized flux ($1/J'_{sp}$) as a function of the specific throughput is shown in the following figure:



The graph indicates more rapid fouling during the first two filter runs (i.e., the first two runs are not linear with the rest of the data), and a linear regression through all of the data would not reflect the longer-term fouling index. The long-term hydraulically irreversible membrane fouling index can be calculated as a straight line between runs 3 and 10:

$$\mathrm{MFI_{hi}} = \frac{(1/J'_{sp})_{10} - (1/J'_{sp})_3}{(V_{sp})_{10} - (V_{sp})_3} = \frac{1.850 - 1.427}{542.4\ \mathrm{L/m^2} - 137.6\ \mathrm{L/m^2}}$$

$$= 0.00104\ \mathrm{m^2/L}$$

$$\mathrm{MFI_{hi}} = (0.00104\ \mathrm{m^2/L})(10^3\ \mathrm{L/m^3}) = 1.04\ \mathrm{m^{-1}}$$