Effluent Treatment Processes for Energy Industry (10626584)

Lecture 20:
Membrane Filtration

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Membrane filtration processes

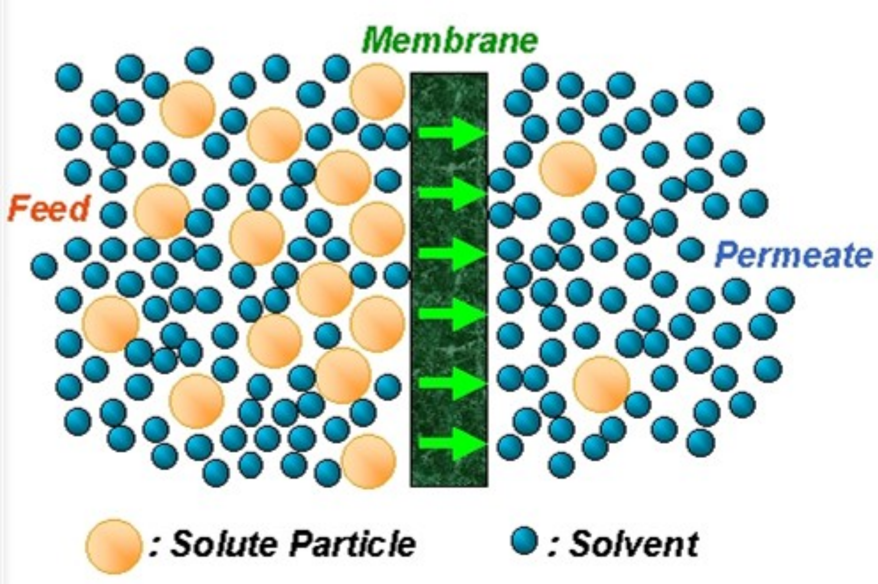
Objectives

By the end of this lecture, students will be able to define:

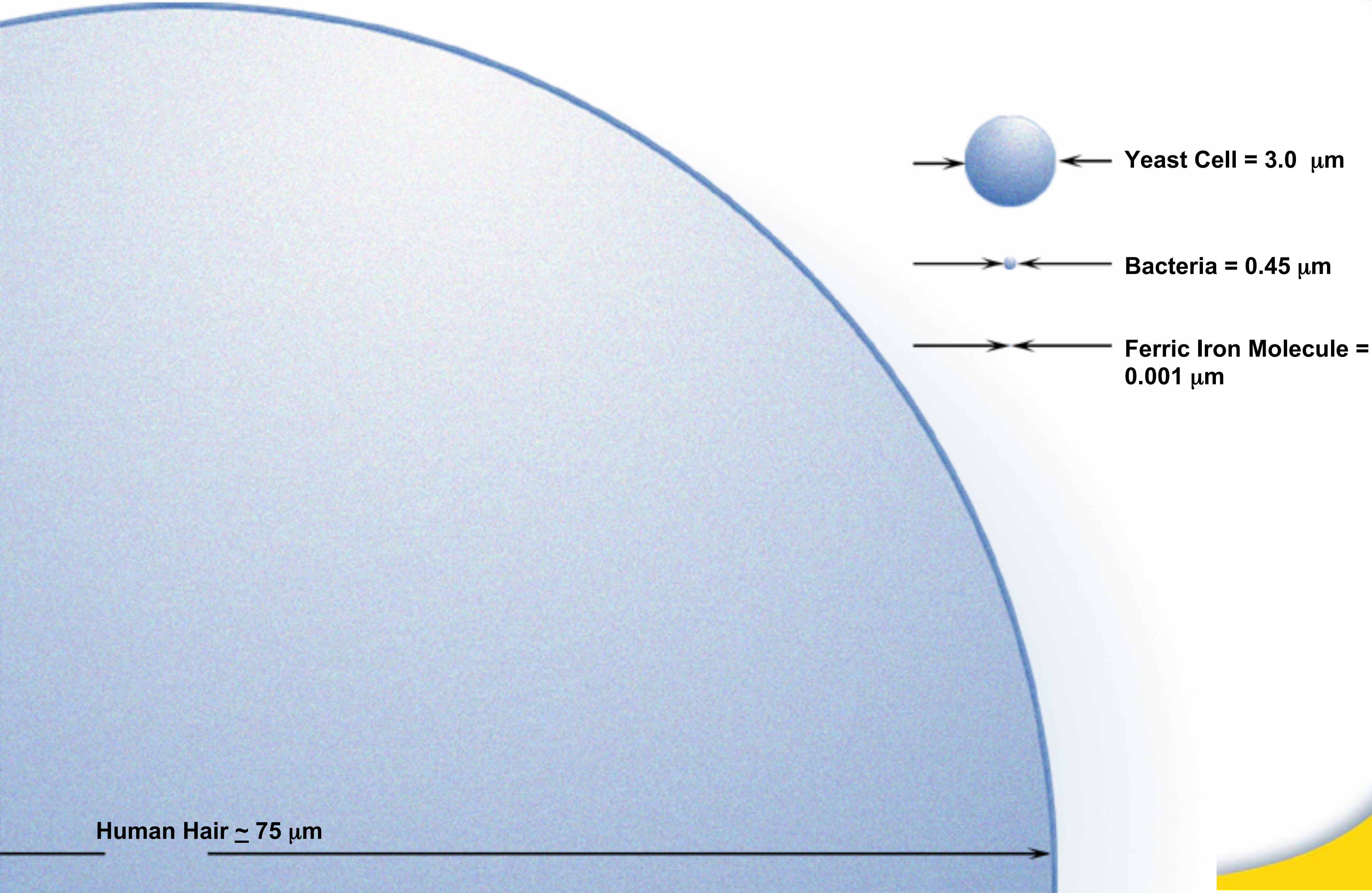
- Membrane process terminology
- Membrane classifications
- Membrane configurations
- Membrane operation
- Membrane fouling and fouling index
- Application of membrane technology
- Electrodialysis

Membrane filtration processes

- Filtration: removal of particulate or colloidal matter from a liquid
- Membrane filtration: the range of the particle sizes is extended to include dissolved constituents (typically 0.0001 to 1.0 μm)
- The role of membrane is to serve as a selective barrier that will allow the passage of certain constituent found in the liquid



Particle Size

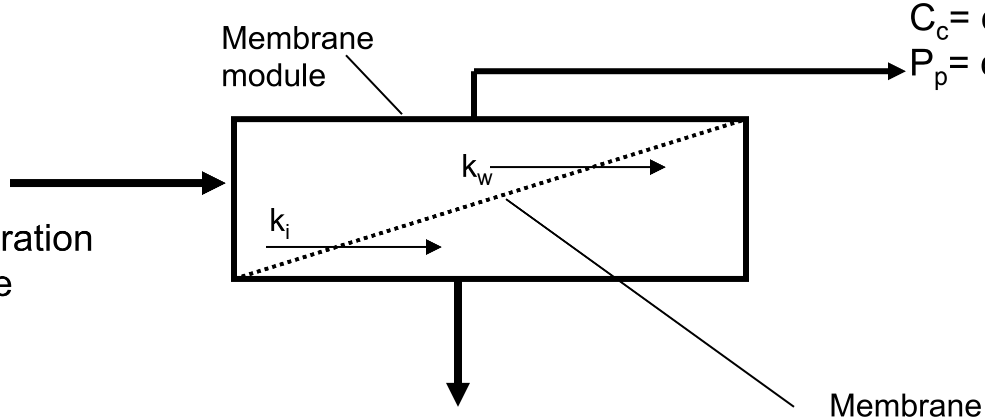


Membrane filtration processes

Membrane Terminology:

Concentrate (c)
Q_c=concentrate flowrate
C_c= concentrate concentration
P_p= concentrate pressure

Feedwater (f)
Q_f=feedwater flowrate
C_f= feedwater concentration
P_f= feedwater pressure



Permeate (p)
Q_p=permeate flowrate
C_p= permeate concentration
P_p= permeate pressure

Note: k_w, k_i are water and solute mass transfer coefficient

- Feed water: also known as feed stream
- Permeate: also known as the product stream or permeating stream
- Concentrate: also known as the retentate, reject, retained phase, or waste stream
- Flux: the rate at which the permeate flows through the membrane, typically expresses as ($kg/m^2.d$)

Membrane terminology

Term	Description
Array or train	Multiple interconnected stages in series
Brine	Concentrate stream containing total dissolved solids greater than 36,000 mg/L.
Concentrate, retentate, retained phase, reject, residual stream	The portion of the feed stream that does not pass through the membrane that contains higher TDS than the feed stream
Feed stream, feedwater	Input stream to the membrane array
Flux	Mass or volume rate of transfer through the membrane surface
Fouling	Deposition of existing solid material in the element on the feed stream of the membrane. Fouling can be either reversible or irreversible
Lumen	The interior of a hollow fiber membrane
Mass transfer coefficient (MTC)	Mass or volume unit transfer through membrane based on driving force
Membrane element	A single membrane unit containing a bound group of spiral-wound or hollow fine-fiber membranes to provide a nominal surface area
Module	A complete unit comprised of the membranes, the pressure support structure for the membranes, the feed inlet and outlet permeate and retentate ports, and an overall support structure
Molecular weight cutoff (MWCO)	The molecular weight of the smallest material rejected by the membrane, usually expressed in Daltons (D)
Permeate, product, permeating stream	The portion of the feed stream that passes through the membrane that contains lower TDS than the feed stream
Reject ion	Percent solute concentration reduction of permeate stream relative to feed stream
Pressure vessel	A single tube that contains several membrane elements in series
Scaling	Precipitation of solids in the element due to solute concentration on the feed stream of the membrane
Size exclusion	Removal of particles by sieving
Solvent	Liquid containing dissolved constituents (TDS), usually water
Solute	Dissolved constituents (TDS) in raw, feed, permeate, and concentrate streams
Stage or bank	Pressure vessels arranged in parallel
Submerged membrane vessel or reactor	Membrane elements are submerged (or immersed) in an open reactor
System arrays	Number of arrays needed to produce the required plant flow
Train or array	Multiple interconnected stages in series

[a]Adapted in part from AWWA (1996), Cheryan (1998), and Taylor and Wiesner (1999).

Membrane filtration processes

Membrane processes

- Microfiltration (MF)
- Ultrafiltration (UF)
- Nanofiltration (NF)
- Reverse osmosis (RO)
- Dialysis
- Electrodialysis (ED)

Membrane filtration processes

Membrane process	Membrane driving force	Typical separation mechanism	Operating structure (pore size)	Typical operating range, μm	Permeate description	Typical constituents removed
Microfiltration	Hydrostatic pressure difference or vacuum in open vessels	Sieve	Macropores (>50 nm)	0.08–2.0	Water + dissolved solutes	TSS, turbidity, protozoan oocysts and cysts, some bacteria and viruses
Ultrafiltration	Hydrostatic pressure difference	Sieve	Mesopores (2–50 nm)	0.005–0.2	Water + small molecules	Macromolecules, colloids, most bacteria, some viruses, proteins
Nanofiltration	Hydrostatic pressure difference	Sieve + solution/ diffusion + exclusion	Micropores (<2 nm)	0.001–0.01	Water + very small molecules, ionic solutes	Small molecules, some hardness, viruses
Reverse osmosis	Hydrostatic pressure difference	Solution/ diffusion + exclusion	Dense (<2 nm)	0.0001–0.001	Water, very small molecules, ionic solutes	Very small molecules, color, hardness, sulfates, nitrate, sodium, other ions
Dialysis	Concentration difference	Diffusion	Mesopores (2–50 nm)	—	Water + small molecules	Macromolecules, colloids, most bacteria, some viruses, proteins
Electrodialysis	Electromotive force	Ion exchange with selective membranes	Micropores (<2 nm)	—	Water + ionic solutes	Ionized salt ions

Membrane process classification

- The type of material from which the membrane is made
- The nature of the driving force
- The separation mechanism
- The normalized size of the separation achieved

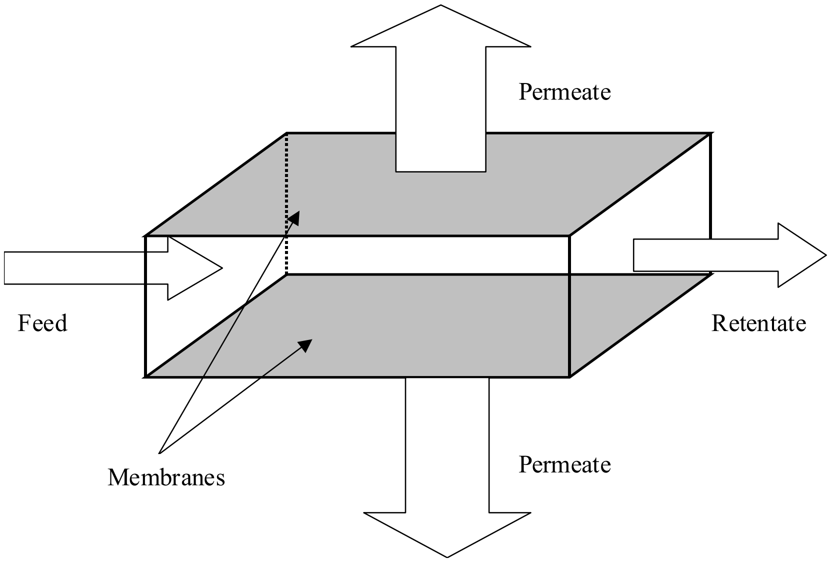
Membrane filtration processes

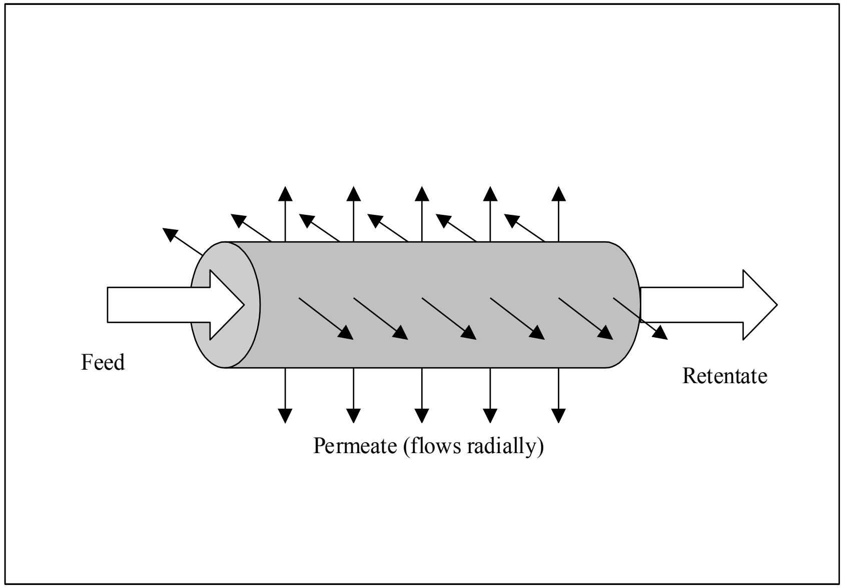
Membrane Materials

- Membranes used for wastewater treatment typically consist of a thin skin having a thickness of about 0.20 to 0.25 μm supported by a more porous structure of about 100 μm in thickness

There are three basic forms:

- Flat sheet
- Tubular membrane
- Hollow fibre membrane





- The choice of membrane and system configuration is based on minimizing membrane clogging and deterioration, typically based on pilot-plant studies

Membrane filtration processes

Membrane Materials

Polymeric (organic):
Cellulose
Cellulose acetate
Polysulfone (PS)
Polyethersulfone (PES)
Polyamides (PA)
Polyvinylidedefluoride (PVDF)
Polyacrylonitrile (PAN)

Inorganic:
γ-alumina
α-alumina
Borosilicate glass
Pyrolyzed carbon
Zirconia/stainless steel
Zirconia carbon

Membrane filtration processes

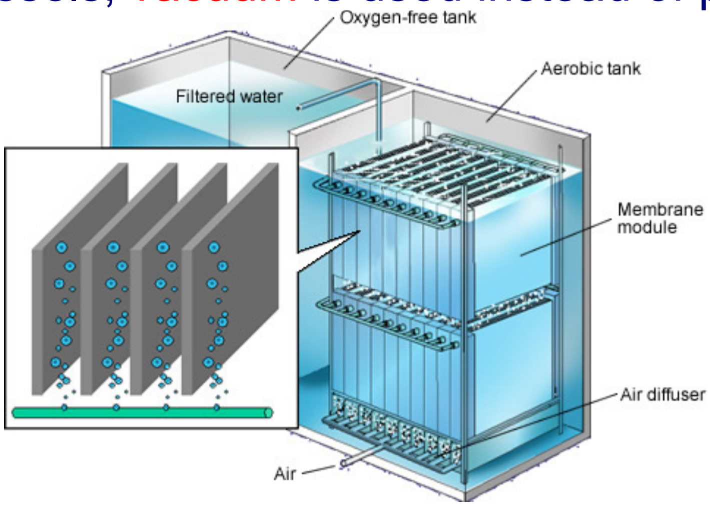
Membrane properties:

- Mechanical strength, e.g., tensile strength, bursting pressure
- Chemical resistance, e.g., pH range, compatibility with solvents
- Permeability to different species, e.g., pure water, solutes
- Average porosity and pore size distribution

Membrane filtration processes

Driving Force:

- The distinguishing characteristic of the first four membrane processes (i.e., MF, UF, NF, and RO) is the application of the hydraulic pressure to bring about the desired separation.
- MF submerged in open vessels, vacuum is used instead of pressure

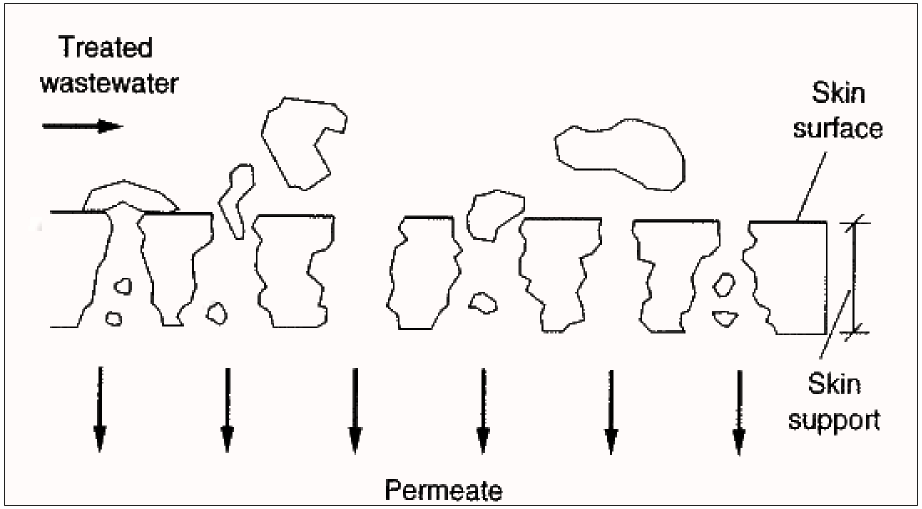


- Dialysis involves the transport of constituents through a semipermeable membrane on the basis of concentration differences.
- Electrolysis involves the use of an electromotive force and ion-selective membranes to accomplish the separation of charged ionic species

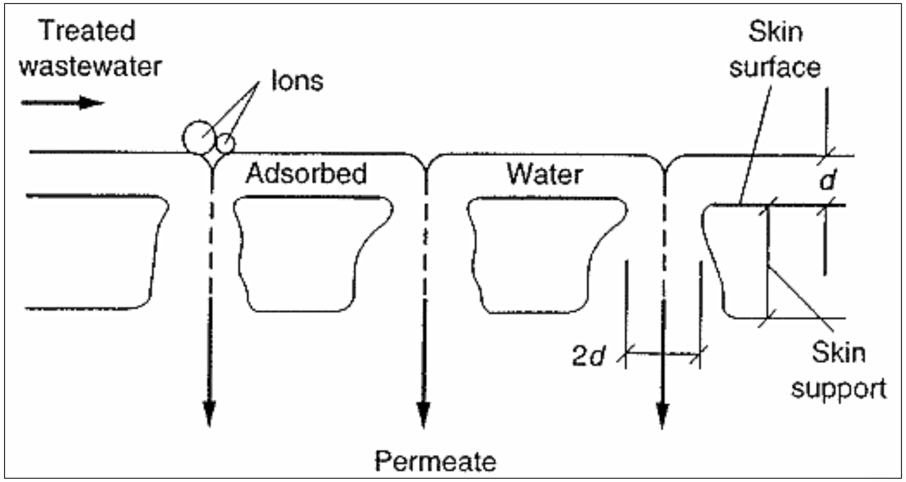
Membrane filtration processes

Removal Mechanisms

- The separation of particles in MF and UF is accomplished primarily by straining (sieving)
- NF and RO, small particles are rejected by the water layer adsorbed on the surface of the membrane (*dense* membrane)
- Staining is also important in NF membranes, especially at the larger pore size openings.



Straining (sieving) mechanism

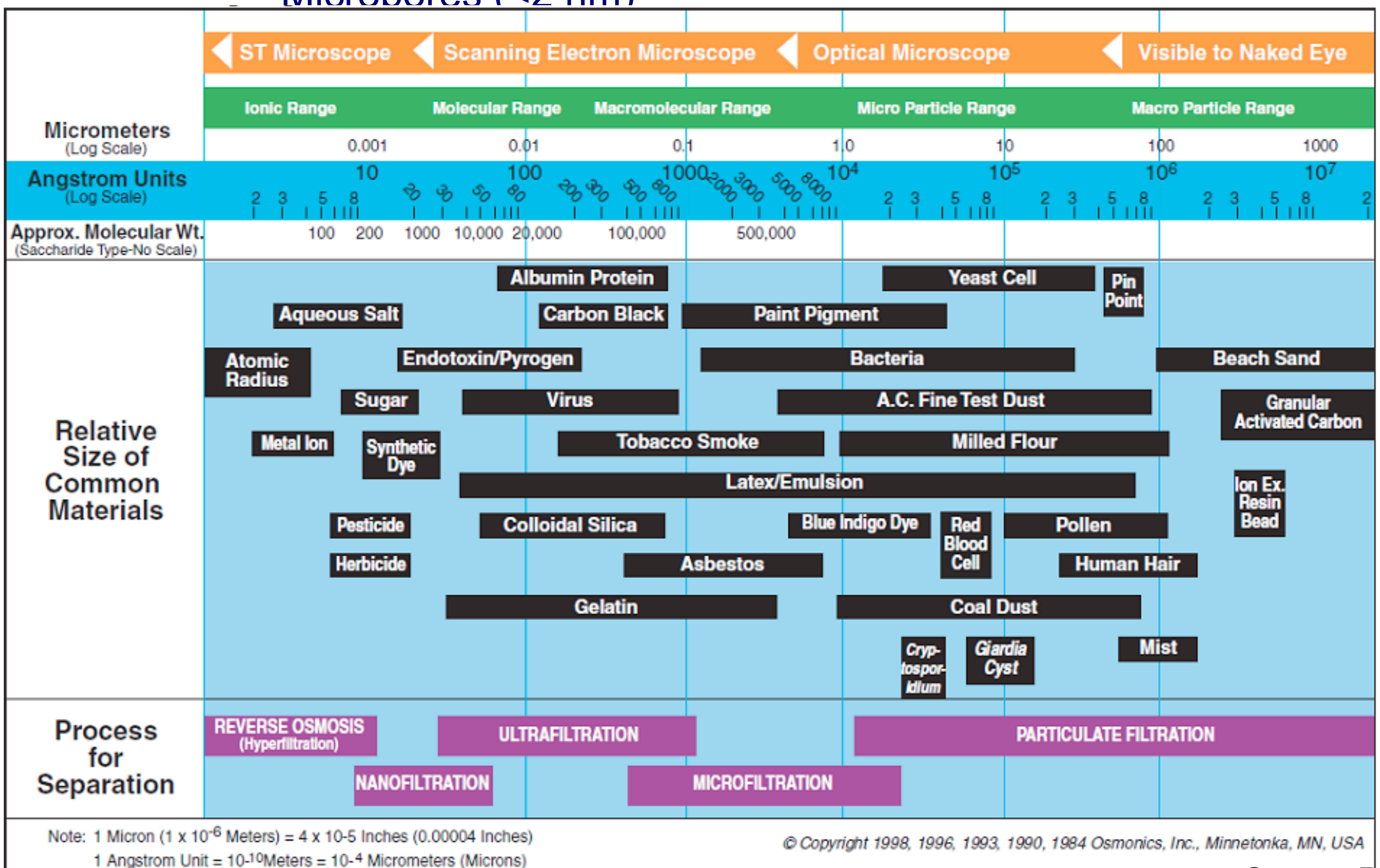


Dense membrane

Membrane filtration processes

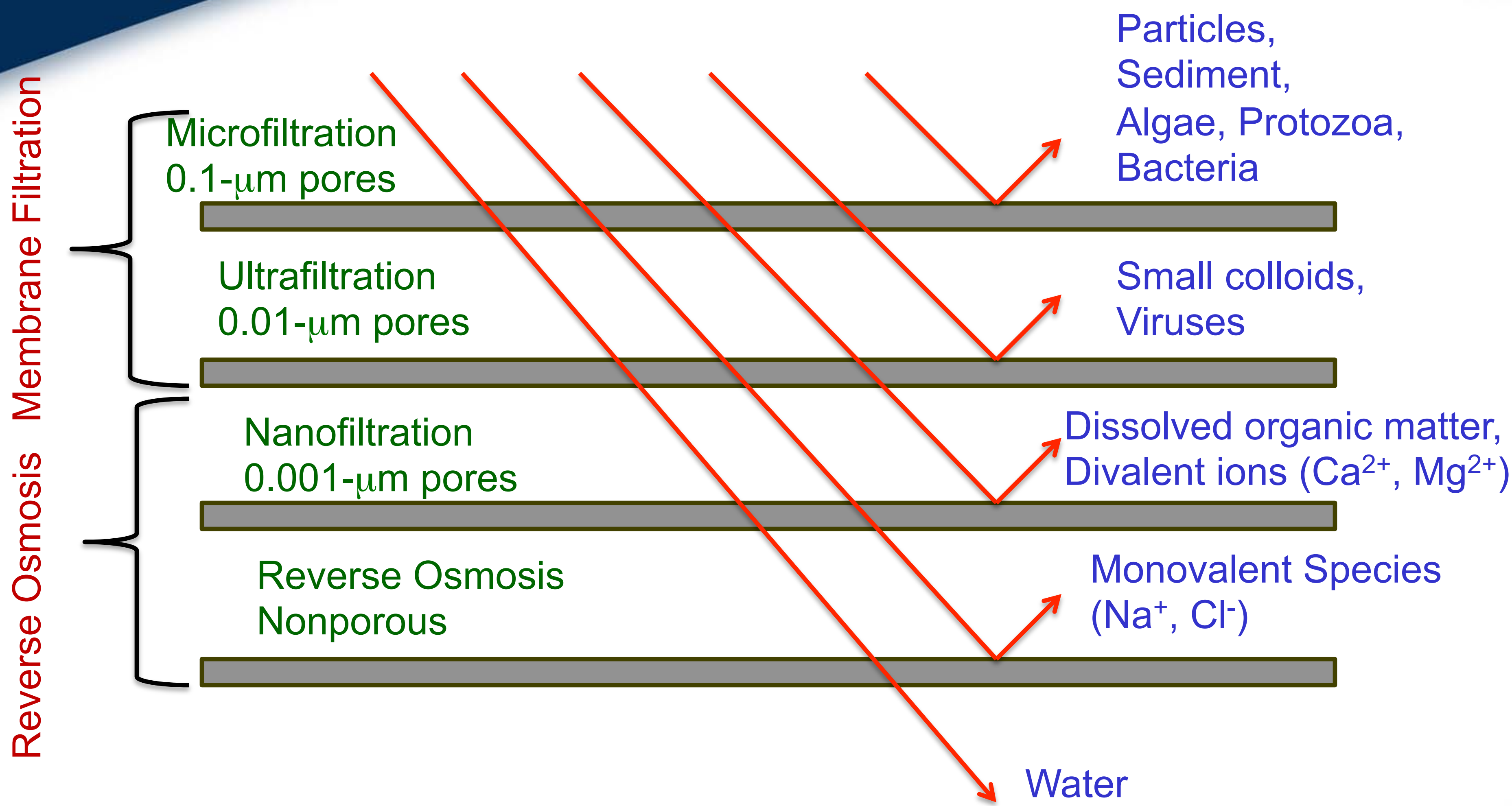
Size of separation:

- The pore sizes in membranes are identified as:
  - Macropores (>50 nm)
  - Mesopores (2 to 50 nm)
  - Micropores (<2 nm)



Source: RADCLIFF (2004)

Hierarchy of pressure-driven membrane processes

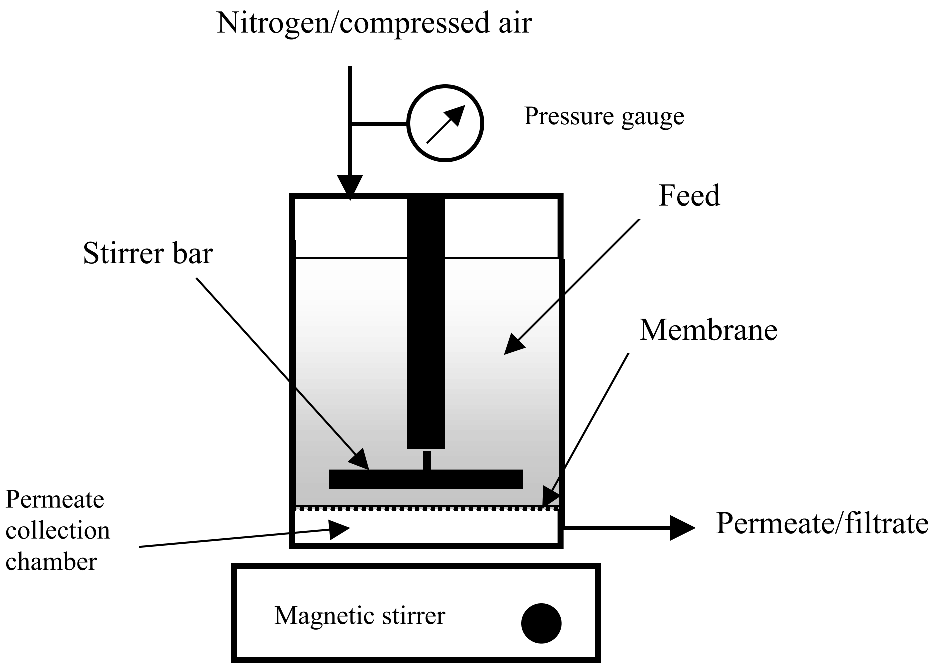


Membrane filtration processes

Membrane Configurations

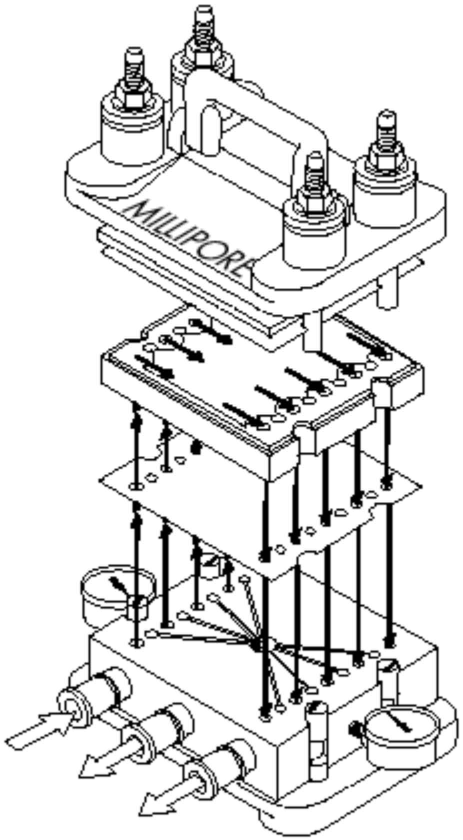
- In membrane field, the term *module* is used to describe:
  - a complete unit comprised of the membrane
  - the pressure support structure for the membranes
  - the feed inlet and outlet permeate and retentate ports
  - overall support structure
- The principal types of membrane modules used for wastewater treatment are:
  - Stirred cell module
  - Flat sheet tangential flow (TF) module
  - Spiral wound membrane module
  - Tubular membrane module
  - Hollow fibre membrane module

Stirred cell



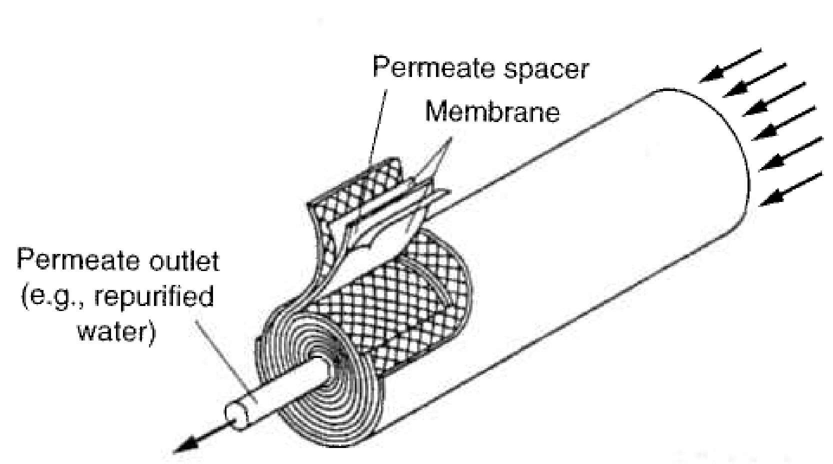
- Useful for small scale and research applications
- Used for UF and MF
- Provides uniform conditions near the membrane surface

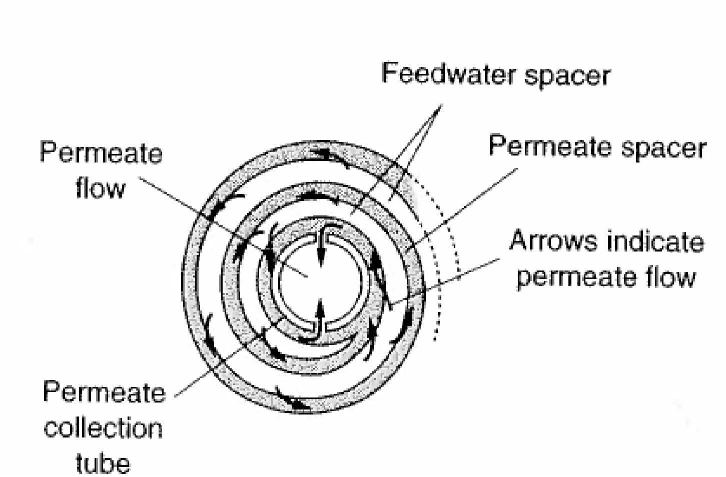
Flat sheet tangential flow



- Design is similar to plate and frame filter press
- Easily disassembled for cleaning and replacement of defective membranes
- Can be used to filter suspended solids and viscous fluids
- Relatively low packing density
- Used for UF, MF and NF
- Design calculations based on empirical correlations

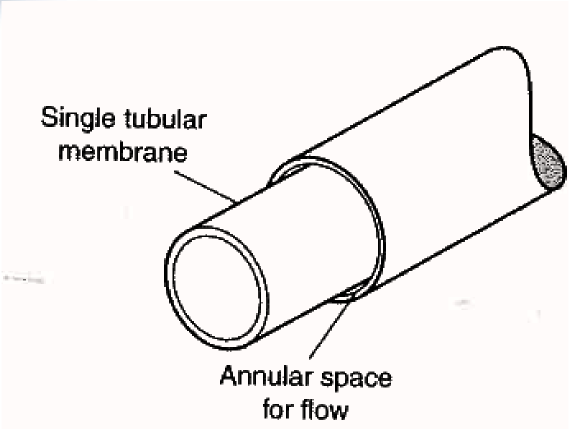
Spiral wound membrane module

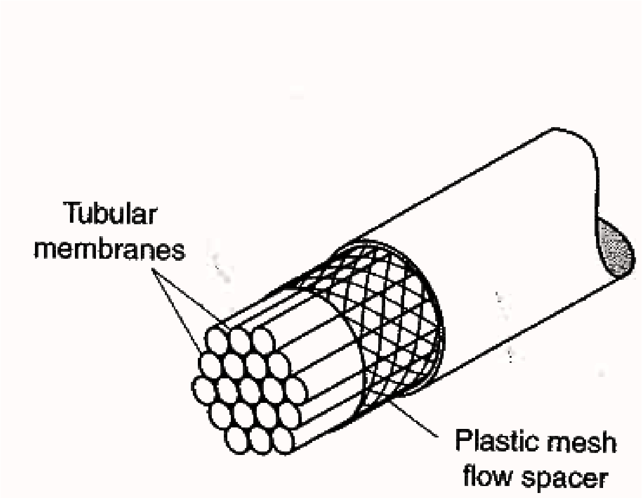




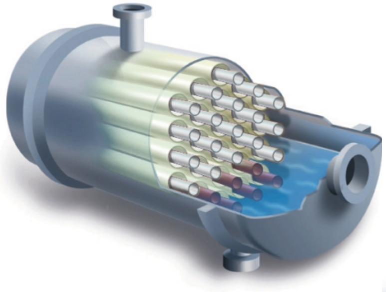
- The spiral wound membrane envelope
- Feed flowing around the envelope
- Permeate collected inside envelope
- Design calculations are empirical
- High membrane packing density
- Low cost
- Unable to handle suspended solids
- Difficulty to clean
- Used for NF and UF

Tubular membrane module

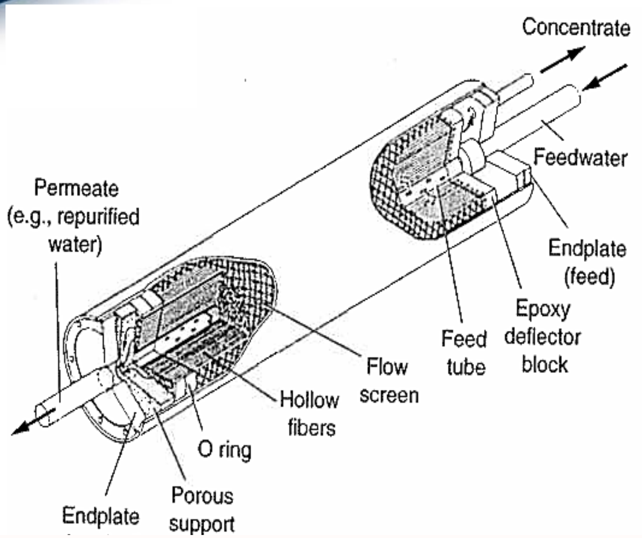


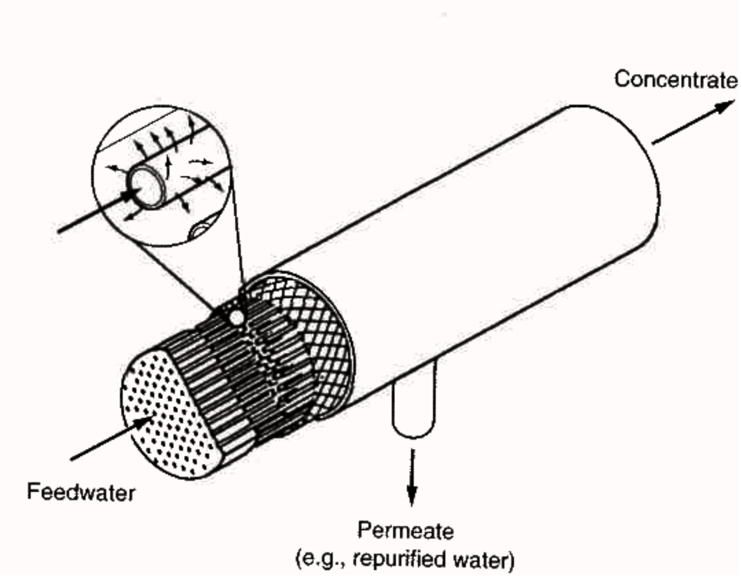


- Several tubular membranes arranged as in a shell and tube type heat exchanger
- Feed stream enters the tube lumen
- Permeate passes through tube wall: collected on shell side
- Retentate collected at other end of tubes
- Low fouling, easy cleaning, easy handling of suspended solids and viscous fluids and high transmembrane pressures
- High capital cost, low packing density, high pumping costs, and limited achievable concentrations
- Used for all types of pressure driven separations



Hollow fibre membrane module





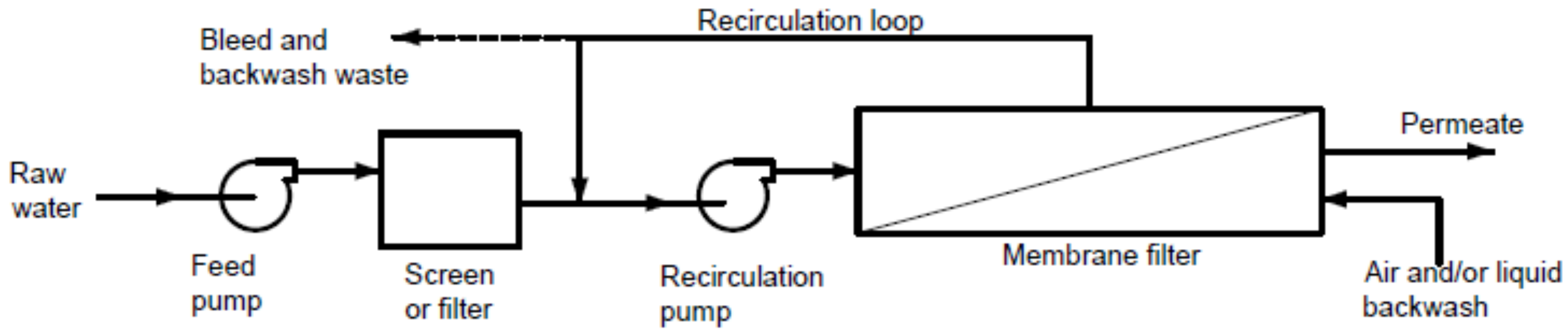
- Similar in design to the tubular membrane, i.e., shell and tube configuration.
- Advantages: Low pumping power, very high packing density, and ability to achieve high concentrations in the retentate
- Disadvantages: Fragility of the fibres, inability to handle suspended solids Used for UF, MF and dialysis

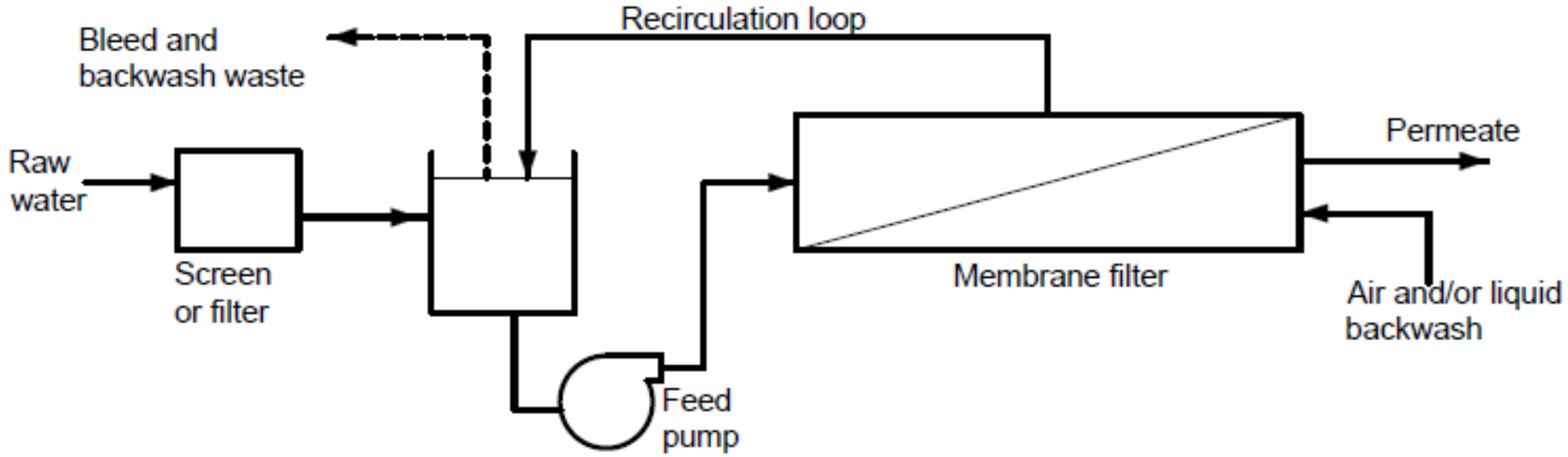
Membrane Operation

- A pump: is used to pressurized the feed solution and to circulate it through the module
- A valve: is used to maintain the pressure of retentate
- The permeate is withdrawn at the atmospheric pressure

Microfiltration and Ultrafiltration

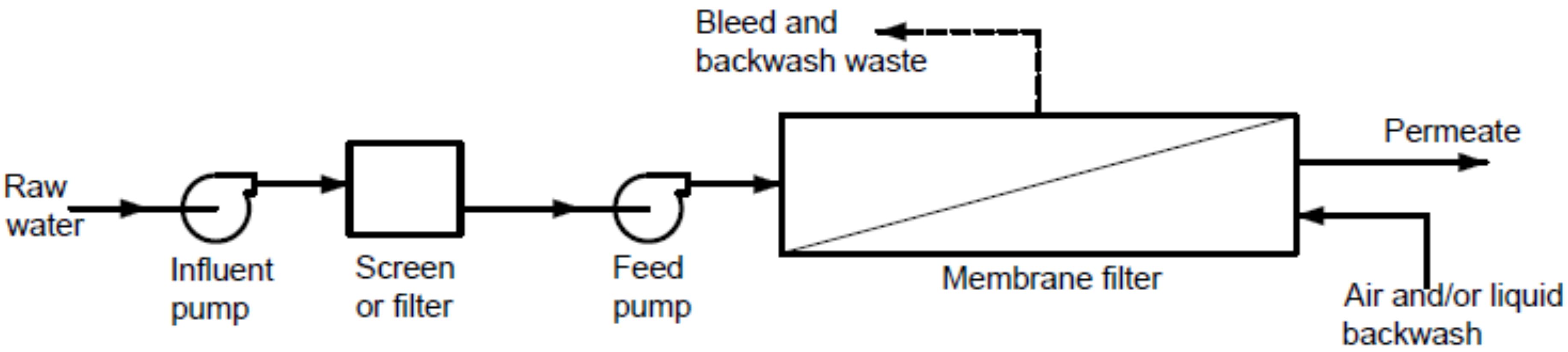
- Cross flow:





Microfiltration and Ultrafiltration

- Dead-end:



- Cross flow:

$$P_{tm} = \left[\frac{P_f + P_c}{2}\right] - P_p$$

P_{tm}: transmembrane pressure gradient, kPa
P_f: Inlet pressure of feed stream, kPa
P_c: Pressure of concentrate stream, kPa
P_p: Pressure of permeate stream, kPa

Overall pressure drop across the filter module

$$P = P_f - P_p$$

- Direct-feed mode of operation:

$$P_{tm} = P_f - P_p$$

- Permeate flow:

$$Q_p = F_w A$$

Q_p: Permeate stream flowrate, kg/s
F_w: Transmembrane water flux rate, $kg/m^2.s$
A: Membrane area, m^2

Microfiltration and Ultrafiltration

- Characteristics of the membrane and operation parameters:

Recovery rate:

$$r,\% = \frac{Q_p}{Q_f} \times 100$$

Q_p: *Permeate stream flowrate, kg/s*
Q_f: *Feed stream flow rate, kg/s*

Rejection rate:

$$R,\% = \frac{C_f - C_p}{C_f} \times 100 = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

Mass balance:

$$Q_f = Q_p + Q_c$$

$$Q_f C_f = Q_p C_p + Q_c C_c$$

R_{LOG}

- In membrane filtration, the concentration of some components (such as microorganisms) in the permeate can be several order of magnitude lower than in the feed.

- Many significant figures must be retained to quantify rejection if rejection rate equation (R,%) is used.

- In this case, log rejection is used as per the following equation:

$$R_{LOG} = -log(1 - R) = log\left(\frac{C_F}{C_P}\right)$$

Example

- During testing a prototype membrane filter, bacteriophage concentrations of 10^7/mL and 13/mL were measured in the influent and effluent, respectively. Calculate the rejection *R* and log rejection R_{LOG}.

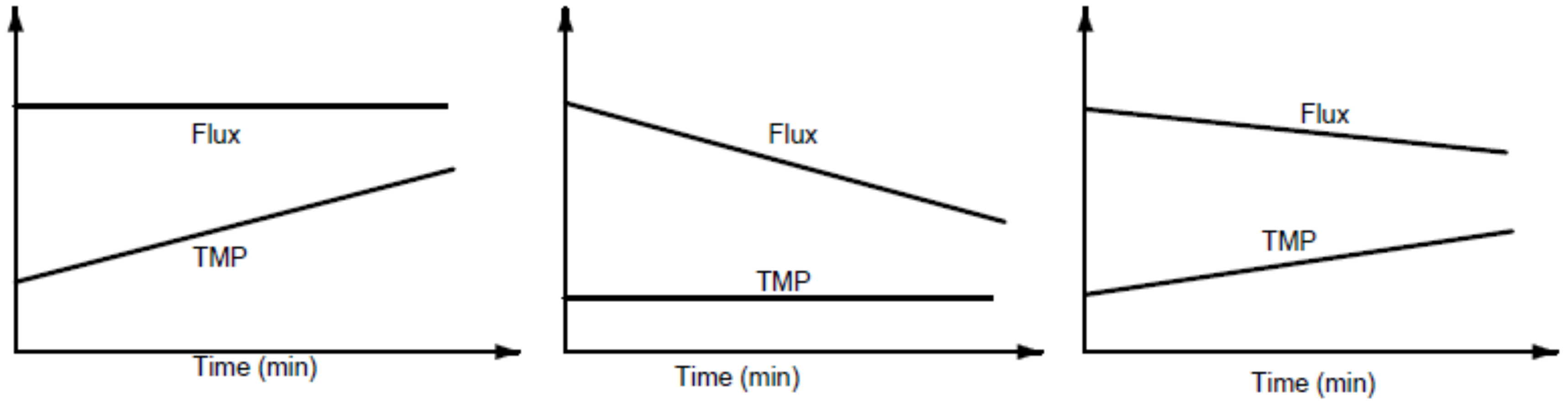
$$R = 1 - \frac{C_P}{C_F} = 1 - \frac{13}{10^{17}} = 0.9999987$$

$$R_{LOG} = log\left(\frac{C_F}{C_P}\right) = log\left(\frac{10^7}{13}\right) = 5.89$$

Microfiltration and Ultrafiltration

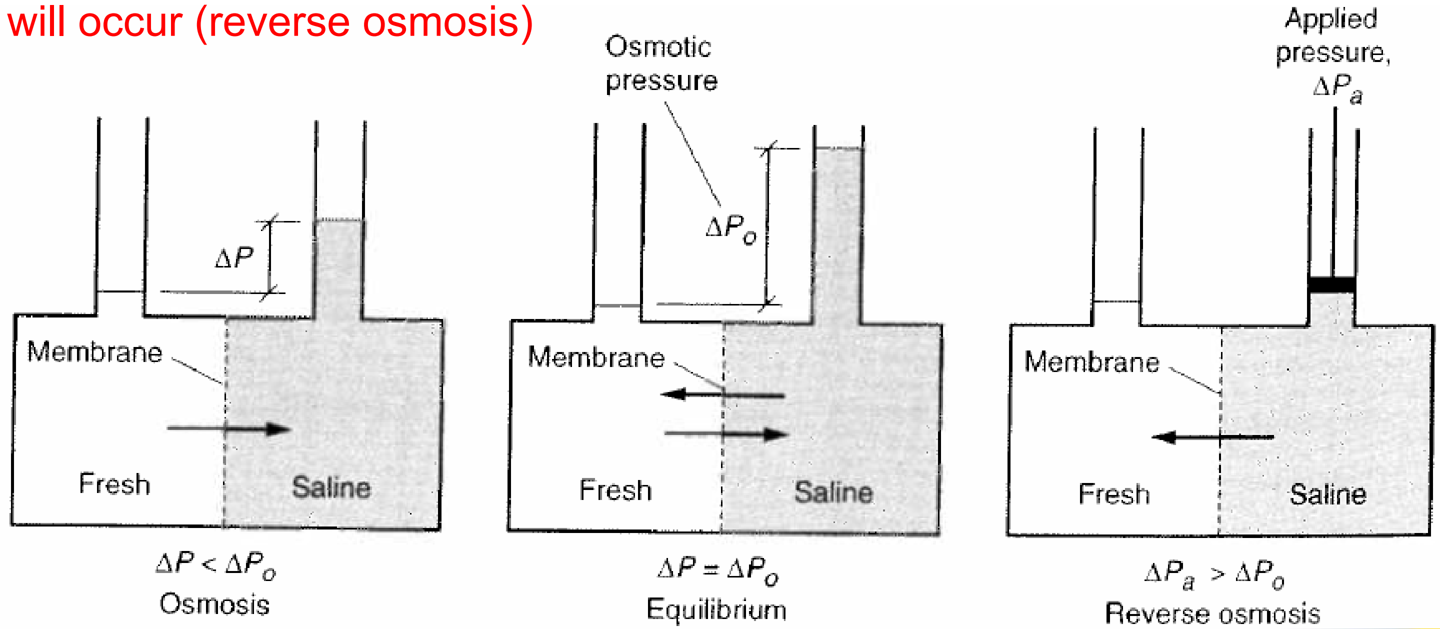
- **Operating modes**

1. Constant flux in which the flux rate is fixed and TMP is allowed to vary, increase, with time
2. Constant TMP in which the TMP is fixed and the flux rate is allowed to vary, decrease, with time
3. Both the flux rate and the TMP are allowed to vary with time. It is the most effective mode of operation



Reverse Osmosis

- Two solutions having different solute concentrations are separated by a semipermeable membrane, a difference in chemical potential will exist across the membrane
- Water will diffuse through the membrane from the lower-concentration (higher-potential) side to the higher-concentration (lower–potential) side
- Flow continues until the pressure difference balances the chemical potential difference, osmotic pressure
- If a pressure gradient opposite in direction and greater than the osmotic pressure is imposed across the membrane, flow from higher concentration to lower concentration will occur (reverse osmosis)



Reverse Osmosis

- Used to remove small solutes such as ions and salts from solvents
- Solvent is forced through RO membrane towards the lower solute concentration, i.e., opposite to osmosis
- Normal transmembrane pressure range is 200 to 300 psi
- Extreme cases require transmembrane pressure up to 600 psi
- Recently developed membranes allow as low as 125 psi in some applications

Reverse Osmosis: modeling

- Models have been developed to determine the surface area of membrane and the number of arrays required.

$$F_w = k_w(\Delta P_a - \Delta \Pi) = \frac{Q_p}{A}$$

$$\Delta P_a = \left[\frac{P_f + P_c}{2}\right] - P_p$$

$$\Delta \Pi = \left[\frac{\Pi_f + \Pi_c}{2}\right] - \Pi_p$$

F_w: Water flux rate, kg/m^2.s, m/s
k_w: water mass transfer coefficient involving temperature, membrane characteristics, and solute characteristics, s/m, m/s.bar
ΔP_a: Average imposed pressure gradient, kg/m.s^2, bar

$\Delta \Pi$: Osmotic pressure gradient, kg/m.s^2, bar

Q_p: Permeate stream flow, kg/s, m^3/s
A: Membrane area, m^2

Reverse Osmosis: modeling

- **Solute flux:**

$$F_i = k_i \Delta C_i = \frac{Q_p C_p}{A}$$

F_i: Flux of solute species i, kg/m^2.s
k_i: Solute mass transfer coefficient, m/s
ΔC_i: Solute concentration gradient , kg/m^3

$$\Delta C_i = \left[\frac{C_f + C_c}{2}\right] - C_p$$

C_i: Solute concentration in feed stream, kg/m^3
C_c: Solute concentration in concentrate stream, kg/m^3
C_p: Solute concentration in permeate stream, kg/m^3

Membrane Fouling

- Fouling: is used to describe the potential deposition and accumulation of constituents in the feed stream on the membrane
- It is an important consideration in the design and operation
- It affects pretreatment needs, cleaning requirements, operation conditions, cost, and performance
- It can occur in 3 general forms:

a. A buildup of the constituents in the feedwater on the membrane surface

b. The formation of chemical precipitate due to the chemistry of feedwater

c. Damage to the membrane due to the presence of chemical substances that can react with the membrane

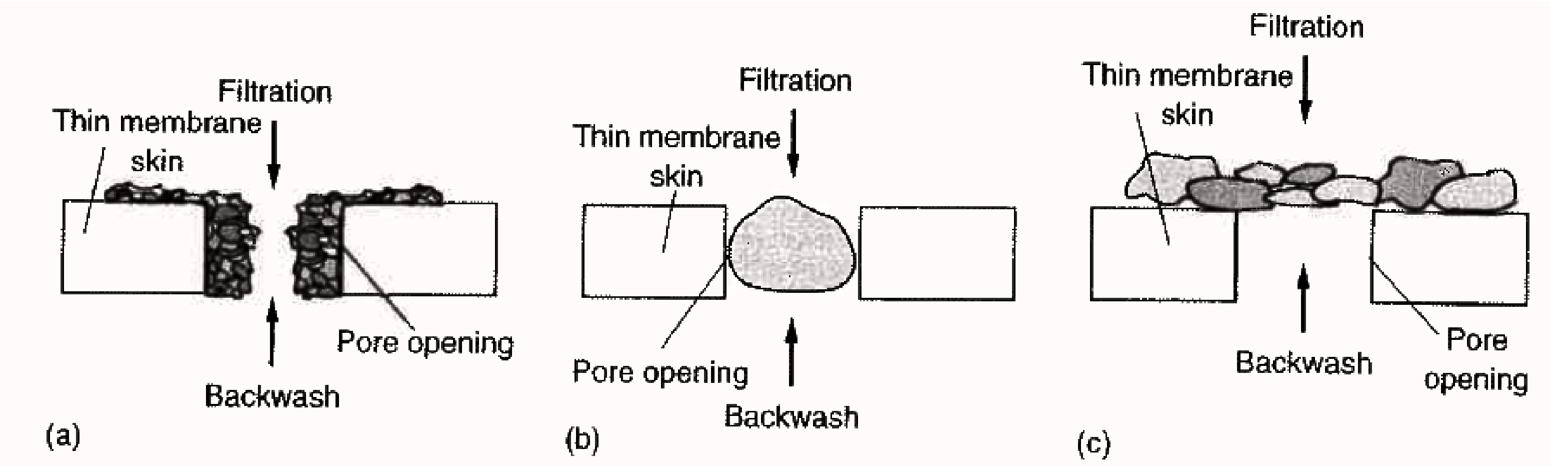
Membrane Fouling

Type of membrane fouling	Responsible constituents	Remarks
Fouling (cake formation sometimes identified as biofilm formation)	Metal oxides Organic and inorganic colloids Bacteria Microorganisms Concentration polarization	Damage to membranes can be limited by controlling these substances (for example, by the use of microfiltration before reverse osmosis)
Scaling (precipitation)	Calcium sulfate Calcium carbonate Calcium fluoride Barium sulfate Metal oxide formation Silica	Scaling can be reduced by limiting salt content, by adding acid to limit the formation of calcium carbonate, and by other chemical treatments (e.g., the addition of antiscalants)
Damage to membrane	Acids Bases pH extremes Free chlorine Bacteria Free oxygen	Damage to membranes can be limited by controlling these substances. Extent of damage depends on the nature of the membrane

Membrane Fouling: Buildup of solids

Three mechanisms:

- Pore narrowing
- Pore plugging
- Gel/cake formation caused by concentration polyrization (known as CP layer). CP layer, formed when the majority of the solid matter in the feed is larger than the pore sizes or molecular weight cutoff of the membrane.



Control of membrane fouling

Three approaches:

- Pretreatment of the feedwater
- Membrane backflushing
- Chemical cleaning of the membranes

Fouling index

- To assess the treatability of a given wastewater with NF and RO membranes
- Are determined experimentally from simple membrane tests
- The sample must be passed through a 0.45 μm- Millipore filter with a 47-mm internal diameter at 210 kPa gage
- The time to complete data collection for these tests varies from 15 min to 2 h, depending on the fouling nature of water

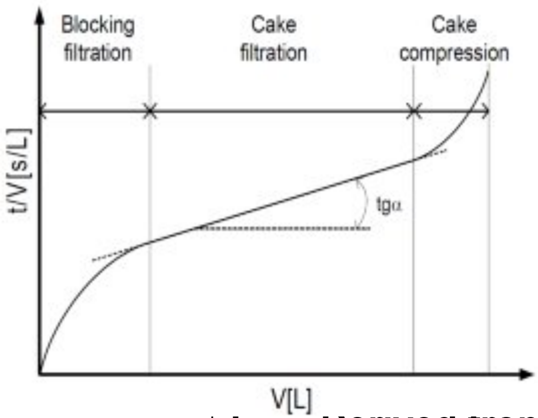
The Silt Density Index, SDI:

$$\boxed{SDI = \frac{100[1-(t_i/t_f)]}{t}}$$

Where t_i = time to collect initial sample of 500 mL

t_f = time to collect final sample of 500 mL

t = total time for running the test



Fouling index

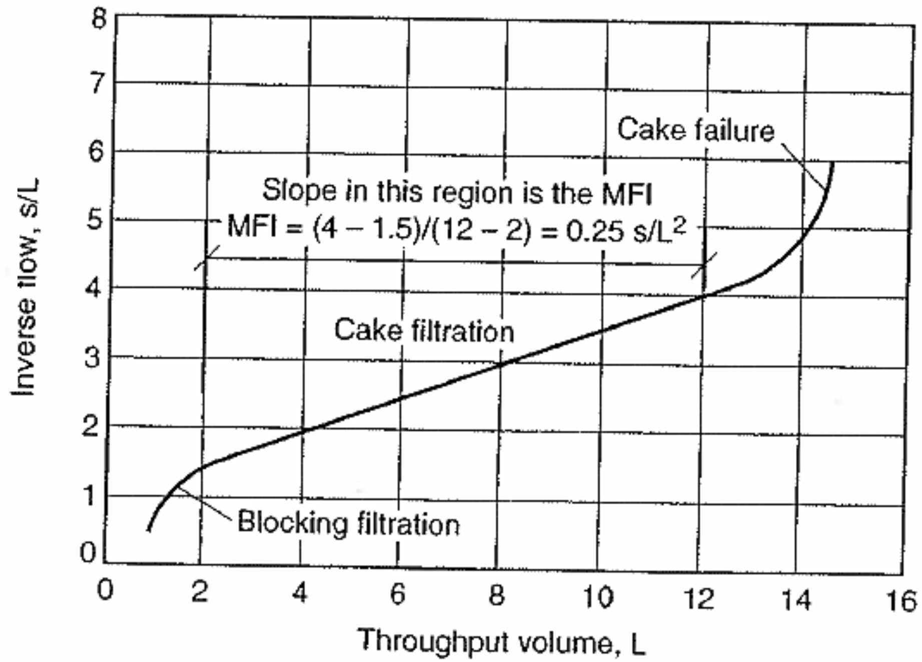
ouling Index, MFI:

l using the same equipment and procedure used for SDI, but the overed every 30 s over 15-min filtration period.

- Derived from a consideration of cake filtration

$$\frac{1}{Q} = a + MFI \times V$$

where Q = average flow, L/s
a = constant
MFI = modified fouling index, s/L^2
V = volume, L



Approximate values for fouling indexes:

Membrane process	Fouling index: SDI	Fouling index: MFI, s/L^2
Nanofiltration	0–2	0–10
Reverse osmosis hollow fiber	0–2	0–2
Reverse osmosis spiral wound	0–3	0–2

[a] Adapted in part from Taylor and Wiesner (1999) and AWWA (1996).

Membrane Application

Microfiltration Membranes

- Are the most numerous on the market, and are the least expensive
- Commonly made of polypropylene, nylon, etc
- It can be used in a variety of ways in wastewater treatment and water reuse systems:
  - In advanced treatment application: as a replacement for depth filtration to reduce turbidity, remove residual suspended solids, and reduce bacteria
  - As a pretreatment step for reverse osmosis
- Separation is purely size based
- Microfiltration is commonly used for clarification, sterilization and slurry concentration

Membrane Application

Ultrafiltration Membranes

- Are used for many of the same application as described for MF
- The primary mechanism is size exclusion
- Used to remove dissolved compounds with high molecular weight, such as colloids, proteins, and carbohydrates
- Do not remove sugar or salts
- Used typically in industrial applications for the production of high-purity process rinse water

Membrane Application

Nanofiltration Membranes

- Also known as “loose” RO or “tight” UF
- Commonly made of polyamide or polyvinyl acetate
- Overlap with ultrafiltration
- Can reject particle as small as 0.001 μm
- Is used for the removal of selected dissolved constituents from wastewater such as multivalent metalic ions responsible for hardiness
- It can be used for the removal of bacteria and viruses

Membrane Application

Reverse Osmosis Membranes

- Worldwide, is used primarily for desalination
- In wastewater treatment, RO is used for the removal of dissolved constituents from wastewater remaining after advanced treatment with depth filtration or microfiltration
- RO membranes exclude ions, but require high pressures to produce the deionized water
- The performance of RO is a site-specific, especially with respect to fouling
- Extreme cases require transmembrane pressure up to 600 psi
- Recently developed membranes allow as low as 125 psi in some applications

Membrane Application

Typical characteristics of membrane technologies used in wastewater-treatment applications[a]

Membrane technology	Typical operating range, μm	Operating pressure		Rate of flux		Membrane details	
		lb/in^2	kPa	gal/ft$^2\cdot$d	L/m$^2\cdot$d	Type	Configuration
Microfiltration	0.08–2.0	1–15	7–100	10–40	405–1600	Polypropylene, acrylonitrile, nylon, and polytetrafluoroethylene	Spiral wound, hollow fiber, plate and frame
Ultrafiltration	0.005–0.2	10–100	70–700	10–20	405–815	Cellulose acetate, aromatic polyamides	Spiral wound, hollow fiber, plate and frame
Nanofiltration	0.001–0.01	75–150	500–1000	5–20	200–815	Cellulose acetate, aromatic polyamides	Spiral wound, hollow fiber
Reverse osmosis	0.0001–0.001	125–1000	850–7000	8–12	320–490	Cellulose acetate, aromatic polyamides	Spiral wound, hollow fiber, thin-film composite

[a] Adapted from Crites and Tchobanoglous (1998).

Note: kPa × 0.1450 = lb/in^2

L/m$^2\cdot$d × 0.024542 = gal/ft$^2\cdot$d

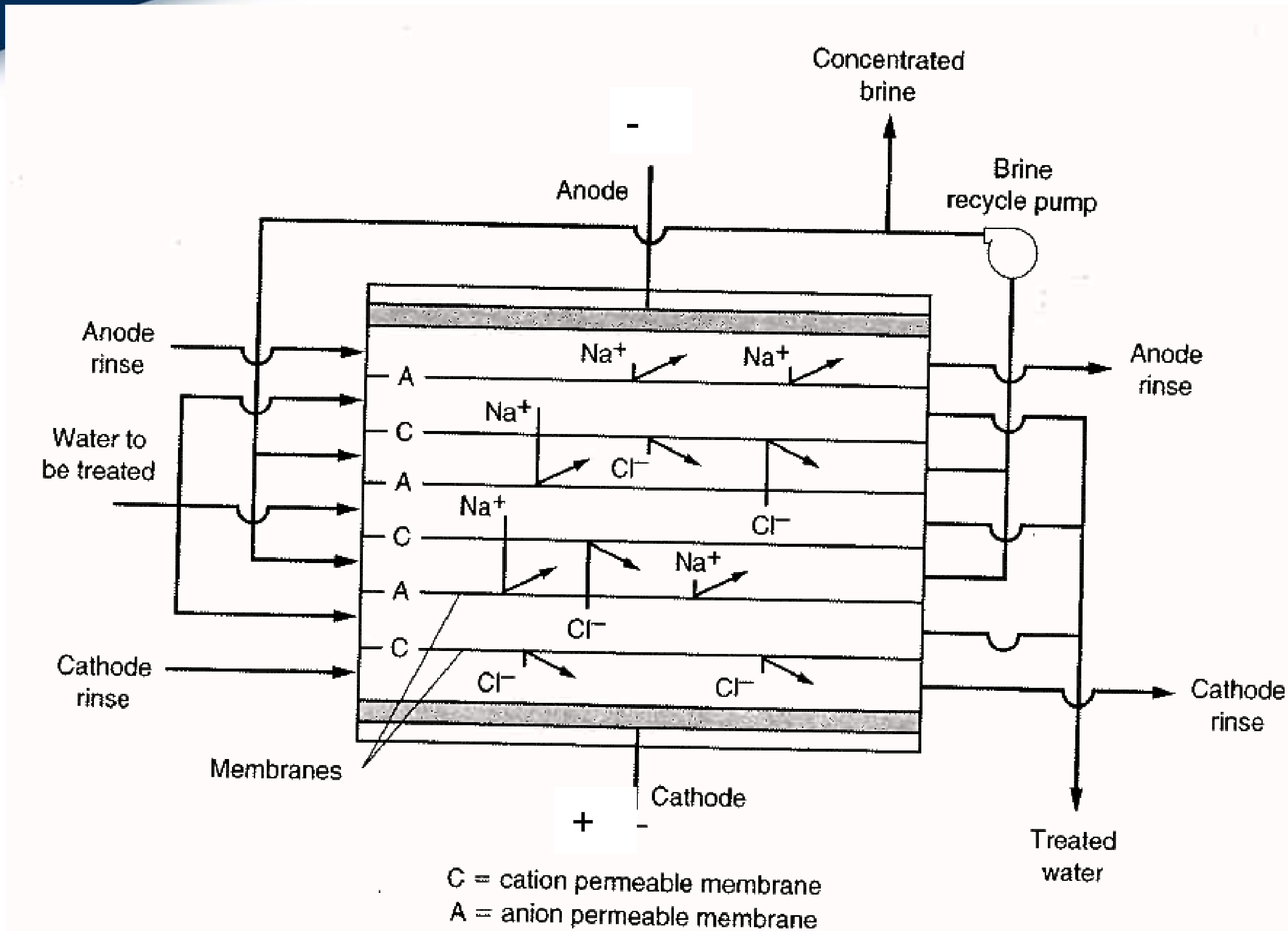
Electrodialysis

- Ionic component of a solution is separated through the use of semipermeable ion-selective membranes

- The mode of transport is diffusion

- Theory of electrodialysis: Application of an electrical potential between two electrodes causes an electric current to pass through the solution, which in turn, causes a migration of cations towards the negative electrode and a migration of anions toward the positive electrode

Electrodialysis



Electrodialysis

- The current required for ED can be estimated using Faraday's laws of electrolysis

$$\boxed{Gram\ eq / unit\ time = QN\eta}$$

where Q = flowrate, L/s
N = normality of solution, eq/L
η = electrolyte removal as a fraction

- For a stack of membranes:

$$\boxed{I = \frac{FQN\eta}{nE_c}}$$

where I = current, amp
F = Faraday's constant
= 96,485 amp·s/gram equivalent = 96,485 A·s/eq
n = number of cells in the stack
E_c = current efficiency expressed as a fraction

- The power required can be estimated using Ohm's law:

$$\boxed{P = E \times I = R(I)^2}$$

where P = power, W
E = voltage, V
= $R \times I$
R = resistance, Ω
I = current, A

Electrodialysis

The following factors affect the dissolved solid removal:

- Wastewater temperature
- Current density
- Type and amount of ions
- Permselectivity of the membrane
- Fouling and scaling potential of wastewater
- Wastewater flow rate
- Number and configuration of stages