Basics of Membrane Technology

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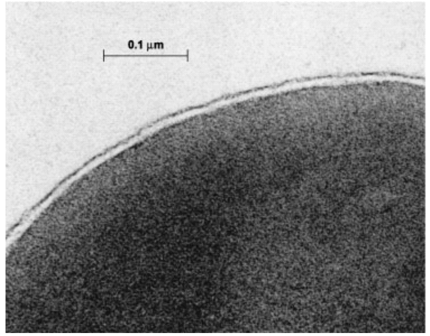
Outline

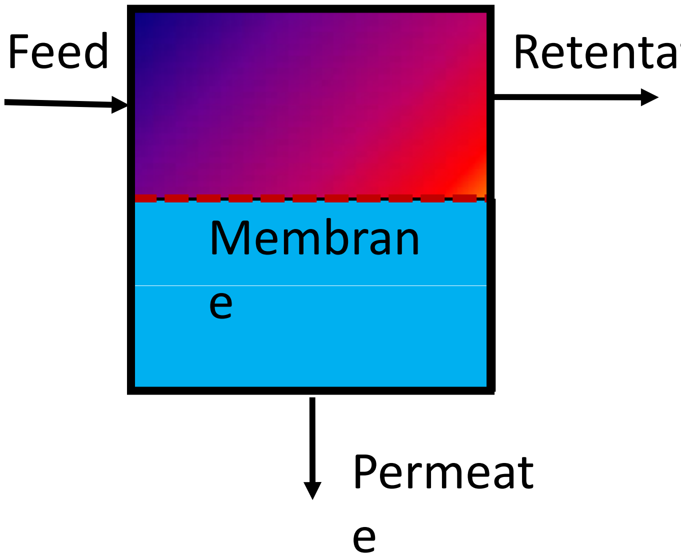
- Membranes: Overview and definitions
- Types of membranes and separation mechanisms
- Membrane materials
- Concentration polarization and fouling
- Membranes in water purification
- Summary and Outlook

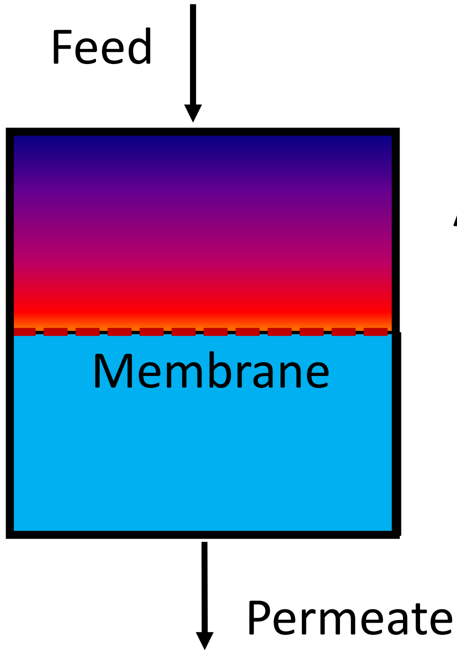
Membrane

- A permselective or semipermeable membrane: selective passage of certain species



A cross-flow element





A dead-end element

Membrane Processes

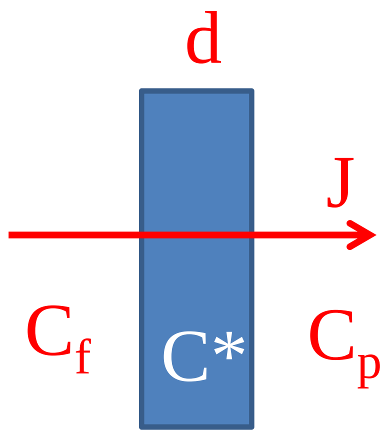
- A membrane process is a kinetics-controlled separation of a fluid mixture using a semipermeable membrane

- The process is rarely spontaneous and usually requires some input of energy. The energy may be supplied in different ways:

  – Mechanical potential gradient
  – Electric potential gradient
  – Chemical potential gradients (concentration or osmotic pressure or vapor pressure)
  – Heat (T gradient)

Standard Characteristics (permeation rate)

$J = [DK/d] \times \Delta C$



- <u>Flux</u> (J) = [Amount or Volume]/Area/Time
  [mol/m^2/s, m/s, LMH]

- <u>Solute Permeability</u> (ω) = Flux/Concentration
  [m/s, μm/s]

- <u>Intrinsic Solute Permeability</u> (P) = Permeability x Thickness
  [m^2/s]

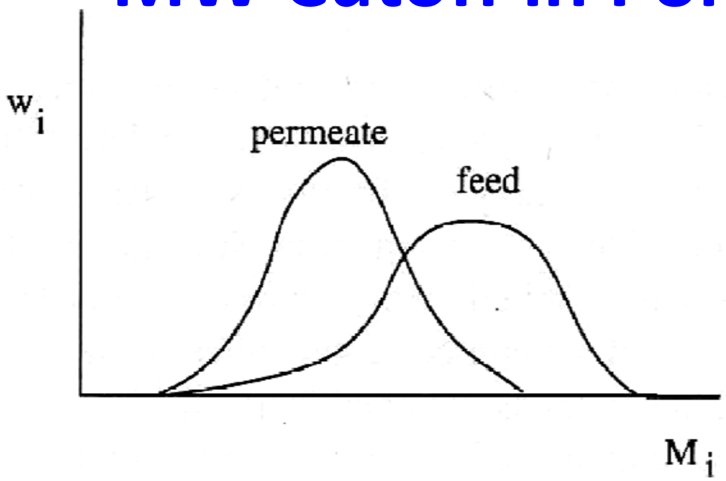
- <u>Hydraulic permeability</u> (L_p) = Flux/Pressure
  [m/s/Pa, LMH/bar]

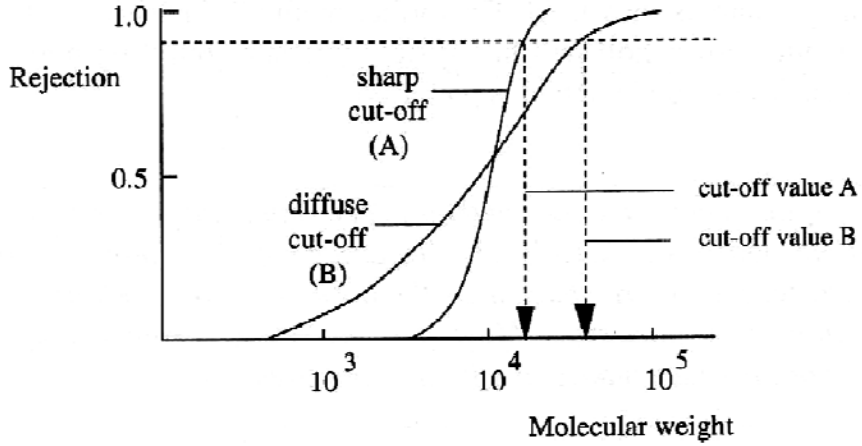
Standard Characteristics (selectivity and pore size)

$C_{feed} \rightarrow C_{perm}$

- Passage $P = C_p/C_f$
- Rejection $R = 1 - P = 1 - C_p/C_f$
- Selectivity coefficient $(\alpha_{1/2}) = P_1 / P_2 = [C_p/C_f]_1 / [C_p/C_f]_1$
- Pore size (average, maximal, nominal, cutoff)
- Molecular weight cutoff

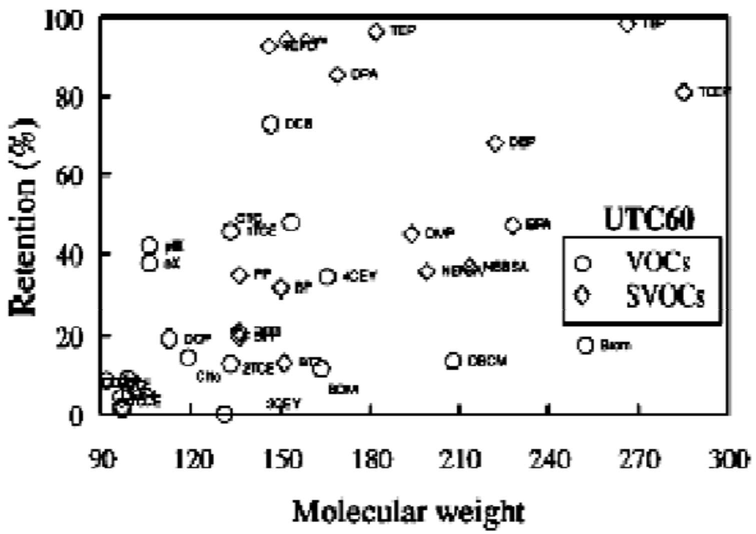
MW Cutoff in Porous and Dense Membranes

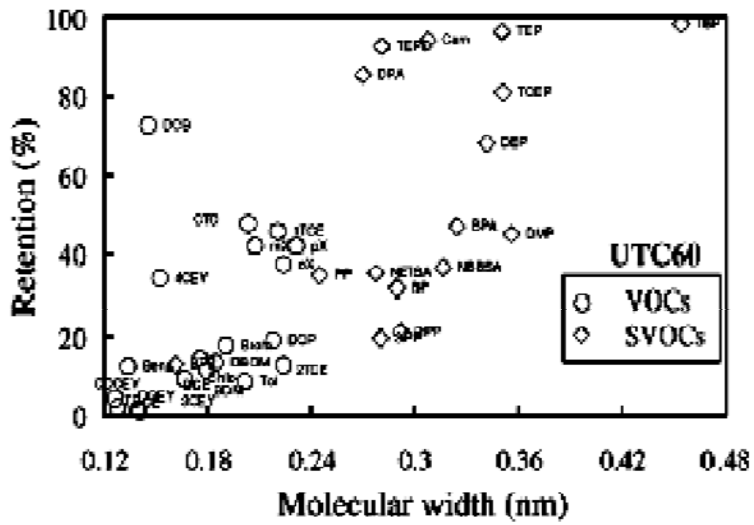




Typical MW distribution

Rejection curves in UF

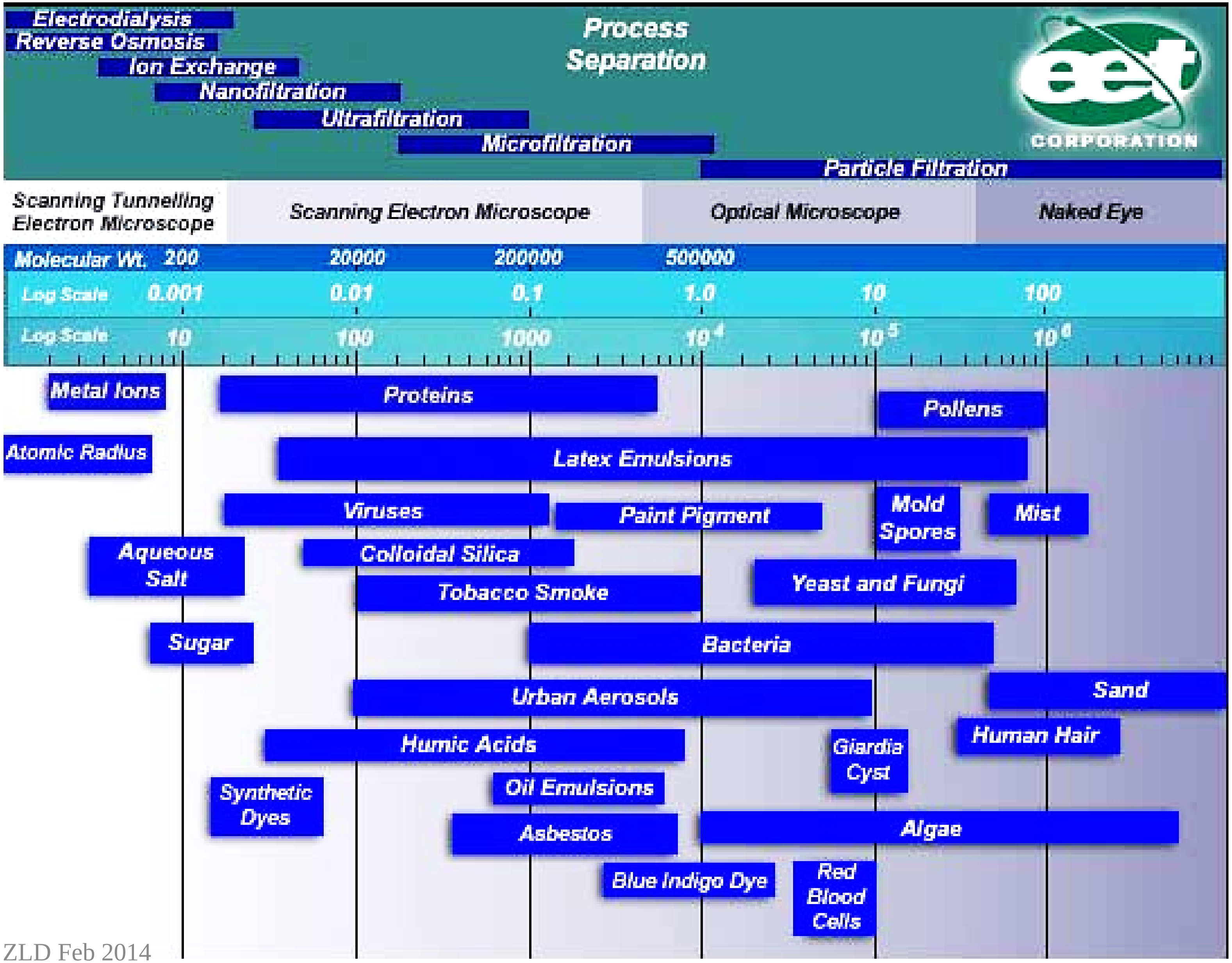




Agenson et al., JMS, 2003

Rejection vs. MW in RO/NF

Pressure-driven processes



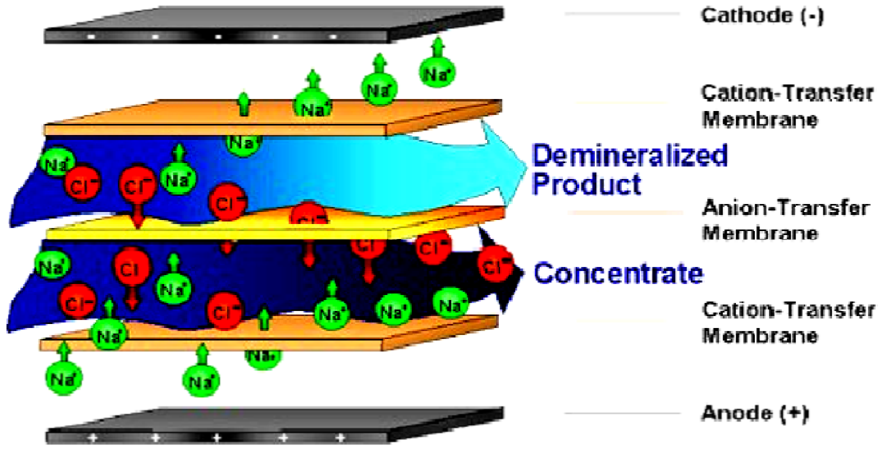
Pressure-driven processes

Process	Characteristic pore size, nm	Mechanism	Pressure, bar Flux, LMH	Applications
Microfiltration (MF)	50-10,000	Size	< 2 50-500	Microscopic particles, turbidity, cells and cell debris, precipitates, emulsions, disinfection, clarification, MBRs
Ultrafiltration (UF)	1-100	Size, Sometimes charge too	1-10 10-200	Colloids, micelles, polymers, viruses*, disinfection, MBRs
Nanofiltration (NF)	< 2	Size, charge, affinity	5-25 5-100	Oligomers, color/dyes, diafiltration, humic acids, hardness, catalysts (SRNF)
Reverse Osmosis (RO)	< 1	Size, charge, affinity	10-80 5-100	desalination, UPW, pyrogens, small organic pollutants

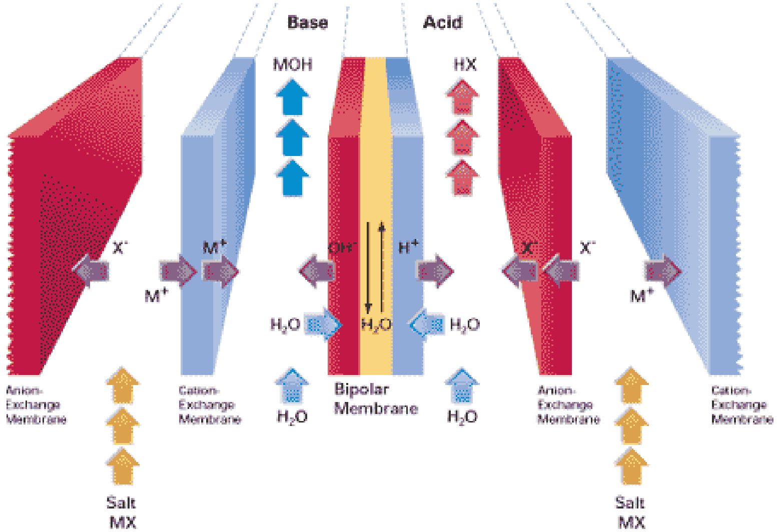
Electro-driven processes
(cation-anion or ion-molecule separations)

- Membrane electrolysis
- Electrodialysis
- Fuel cells
- Electrophoretically-enhanced processes
- Micro- and nanofluidics …

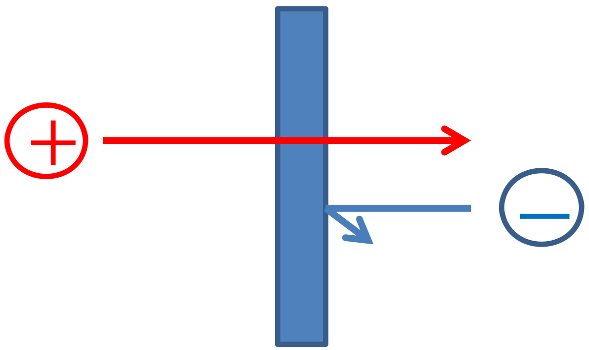
Electro-driven processes

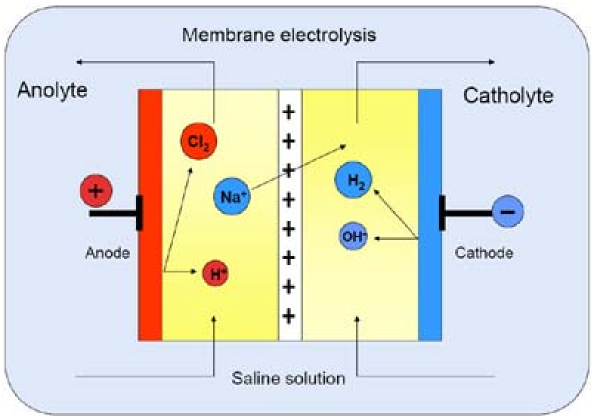


Electrodialysis/EDR

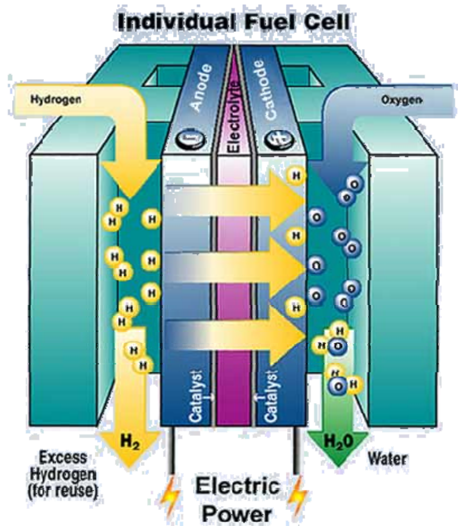


ED with bipolar membranes





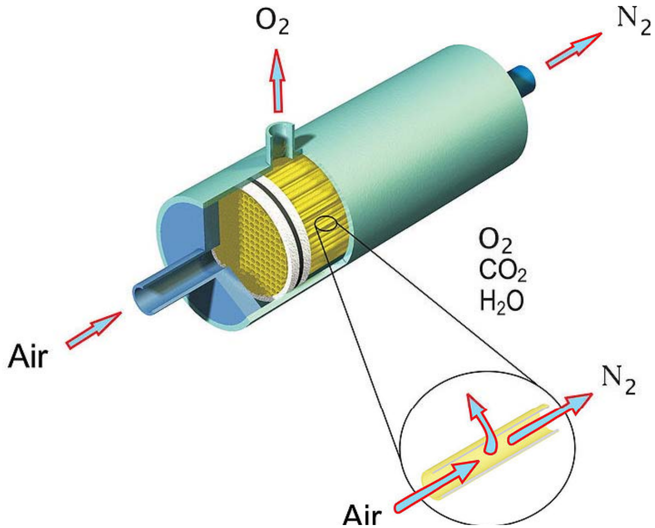
Membrane Electrolysis



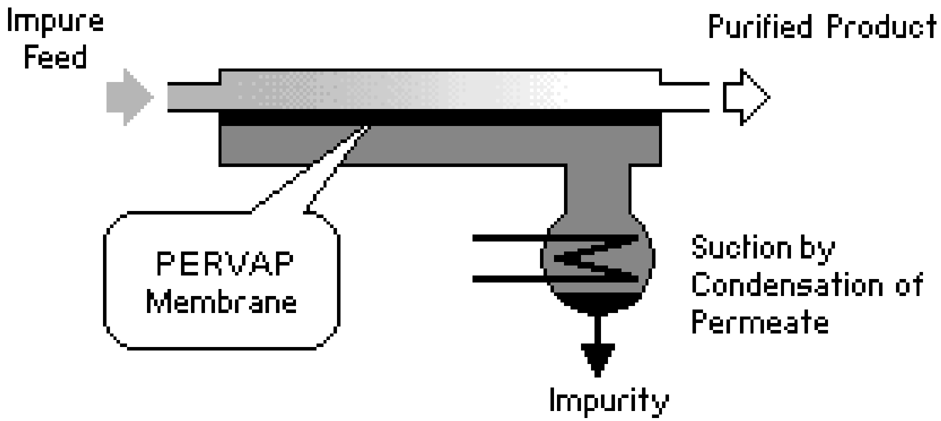
Fuel Cells

Other Processes (C- and T-driven)

- Gas separation
(pressure + concentration gradients)

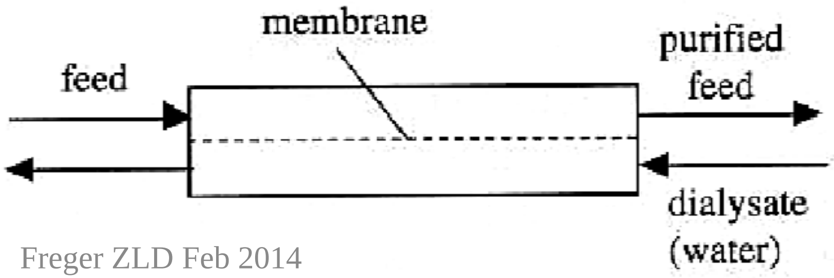


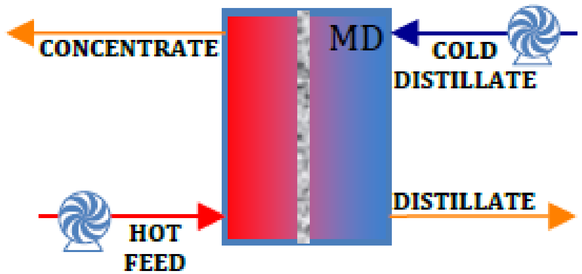
- Pervaporation and vapor permeation
(gas sweep or vacuum)



- Dialysis (concentration gradients + pressure)

- Membrane distillation
(T gradient + vacuum)





Transport Through Membranes

- Transport of solvent (water)

$$J_V = L_p(\Delta P - \sigma\Delta\pi)$$

L_p – hydraulic permeability, LMH/bar or m/s/Pa

A. Katchalsky-Katzir

- Transport of solutes (diffusion + convection)

$$J_s = \omega_s \Delta C + J_V C(1 - \sigma)$$

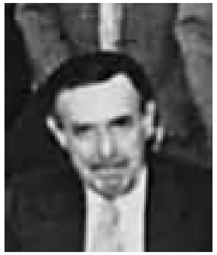
O. Kedem

$\omega_s = \frac{DK}{d}$ – solute permeability, m/s

D – diffusivity, K – partitioning , d – thickness

σ - reflection coefficient (extent of convection)

- Porous membranes: convection (size exclusion)
- Dense membranes: solution-diffusion (solubility in the membrane is important).
  E.g., high salt rejection in RO is mainly due to poor solublity of salt in the polyamide selective layer



K. Spiegler

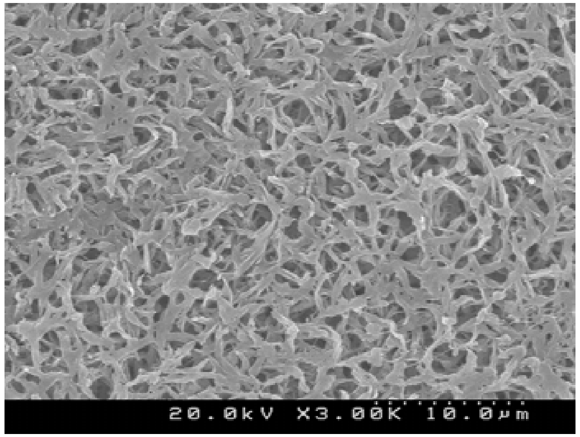
Materials for Membranes

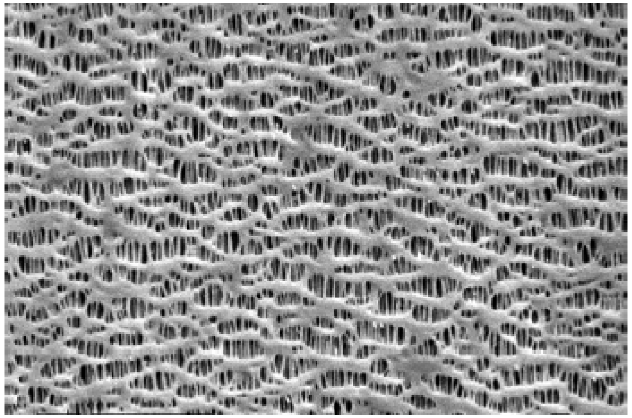
- Natural polymers and their derivatives (cellulose, CA, CN, chitosan)
- Synthetic polymers
  - Hydrophobic (PTFE, PVDF, polypropylene, polysulfone, PET)
  - Hydrophilic (Nylon, PAN)
- Inorganic materials
  - Oxides (alumina, titania)
  - Alumosilicates, zeolytes , titanosilicates
  - Carbon
  - Metals
- Advances materials
  - Mixed matrix membranes (MMM)
  - Carbon nanomaterials
  - Biomimetic materials

Membrane Manufacturing and Types

$J \propto r_p^{2}/d$

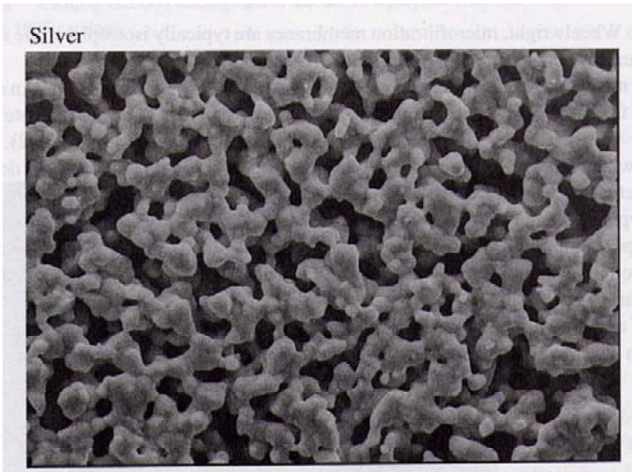
- Symmetric dense (electro-driven)
  - Solution casting
  - Melt extrusion
- Symmetric porous (filtration)
  - Phase inversion (non-solvent precipitation)
  - Stretching
  - Sintering
  - Track-etching
- Asymmetric (porous and dense)
  - Phase inversion (non-solvent precipitation)
- Composites (porous support + dense top layer)
  - Interfacial polymerization (IP)
  - Solution coating

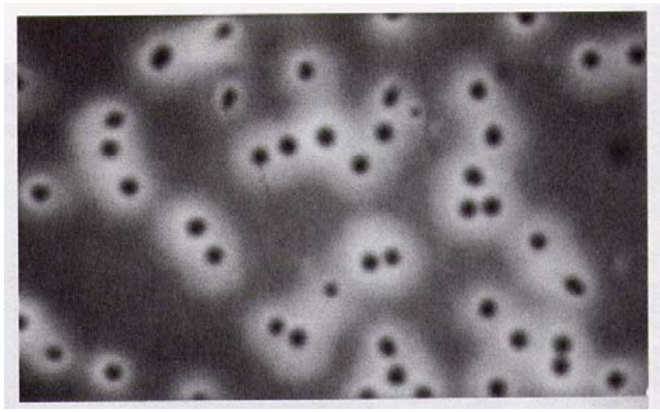




Phase inverstion (CA, PSf)

Stretched (PDMF, PTFE, PP)

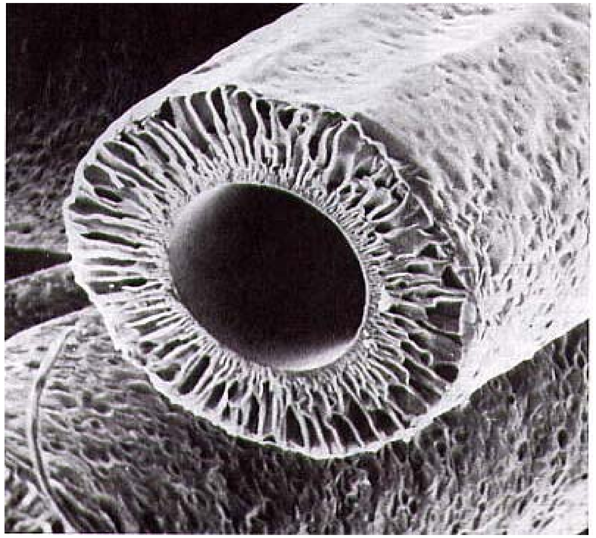




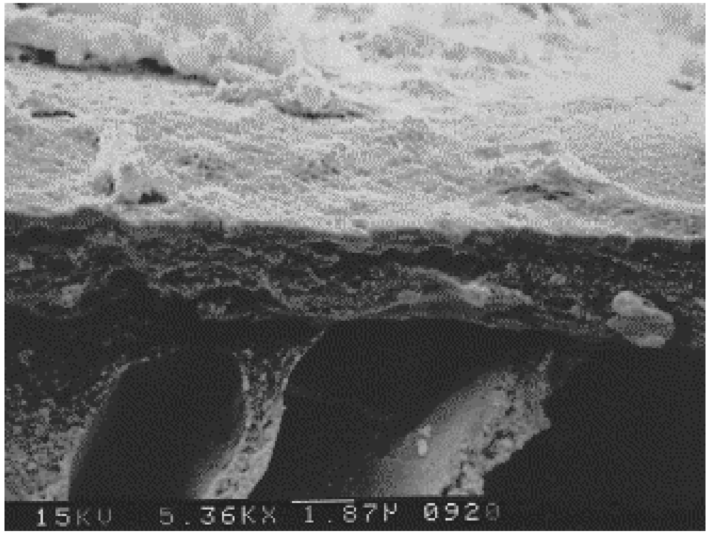
Sintered metal (Ag)

Track-etched (polycarbonate)

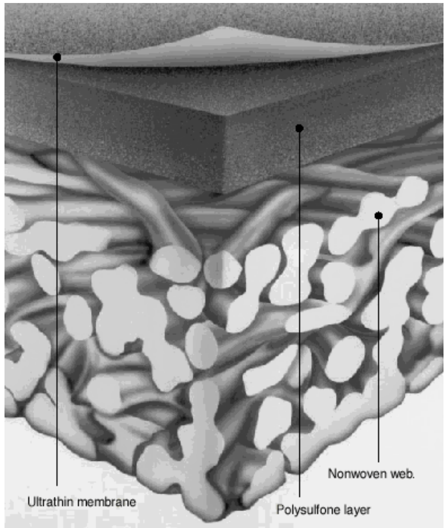
Asymmetric Membranes and Supports



asymmetric hollow fiber (inside-out)

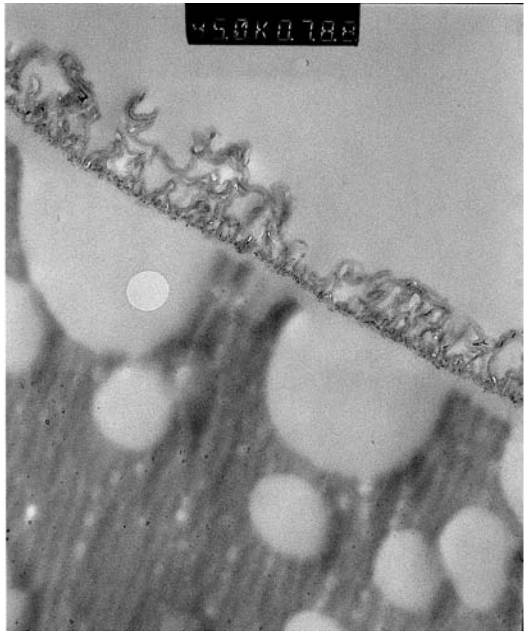


Top cross-section of a composite membrane

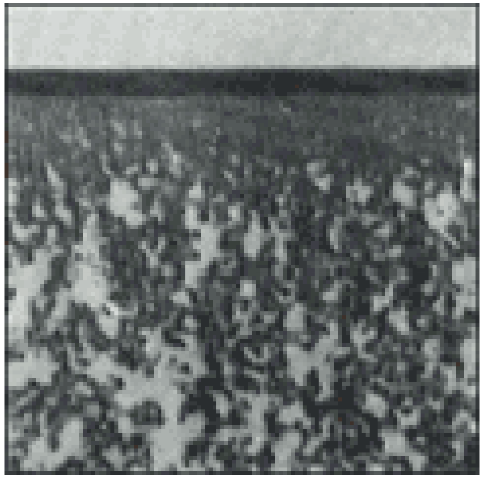


a composite membrane

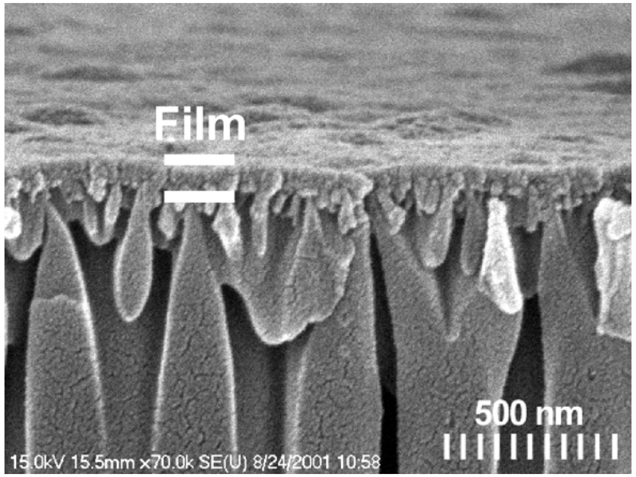
Composite Membranes



RO membrane with a top layer prepared by IP



NF membrane with a top layer prepared by coating

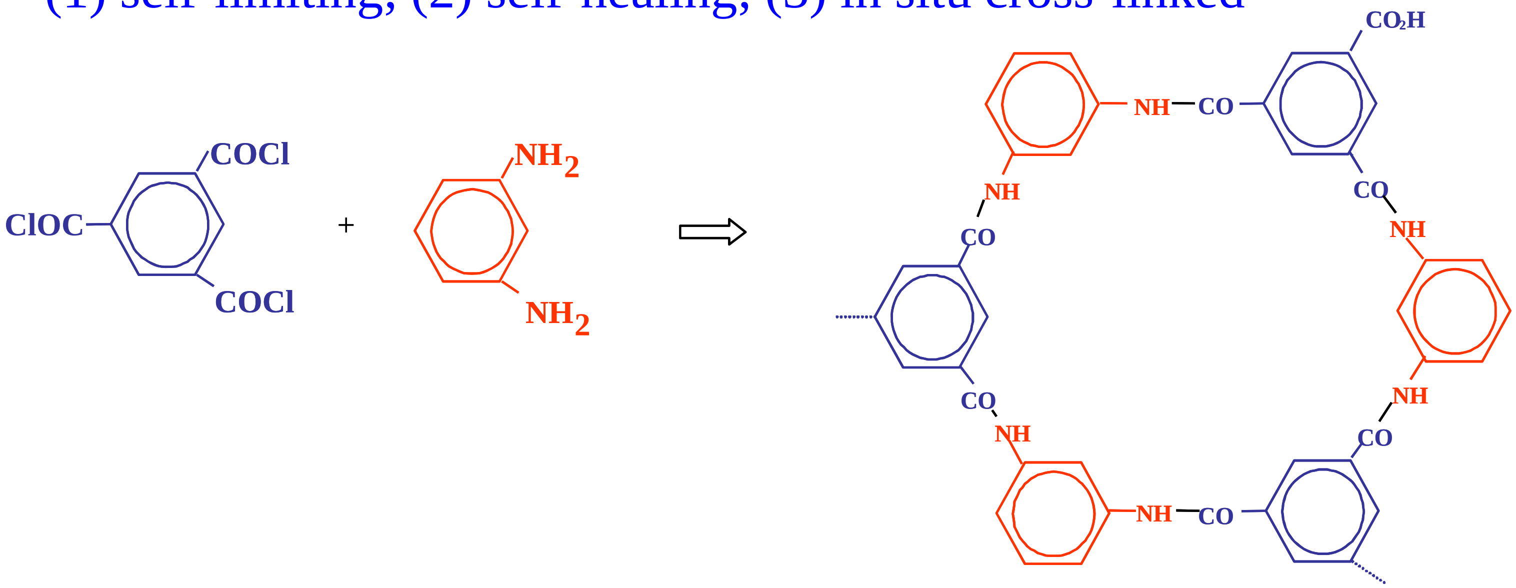


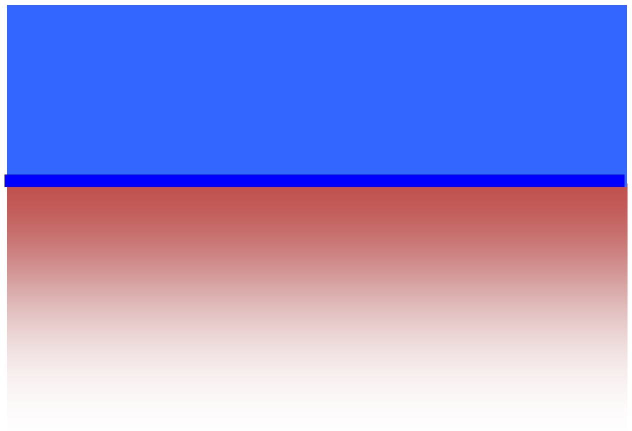
Stat-of-the-art gas separation membrane

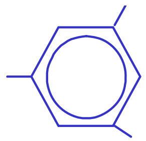
Sullivan & Bruening, *Chem. Mater.*, 2003

Interfacial Polymerization

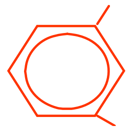
(1) self-limiting; (2) self-healing; (3) in situ cross-linked





Organic solution of 

Ultra-thin skin forms at the interface

Aqueous solution of 

Membrane Modules

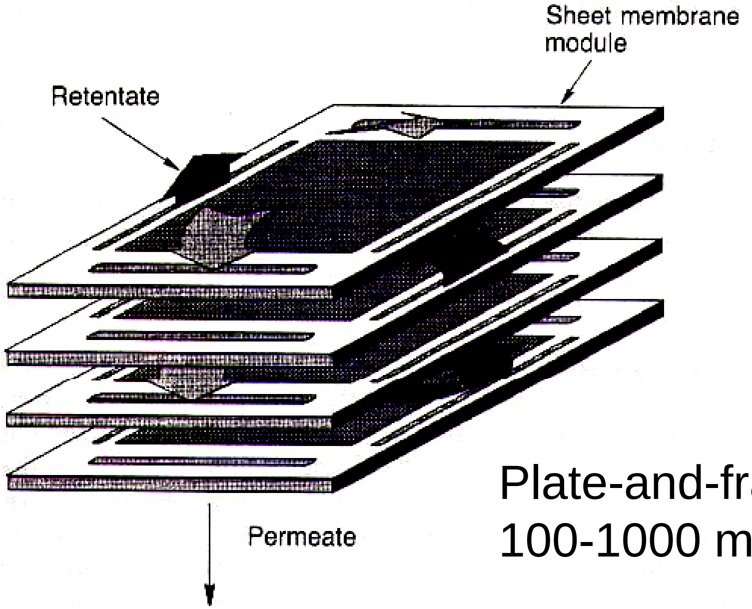
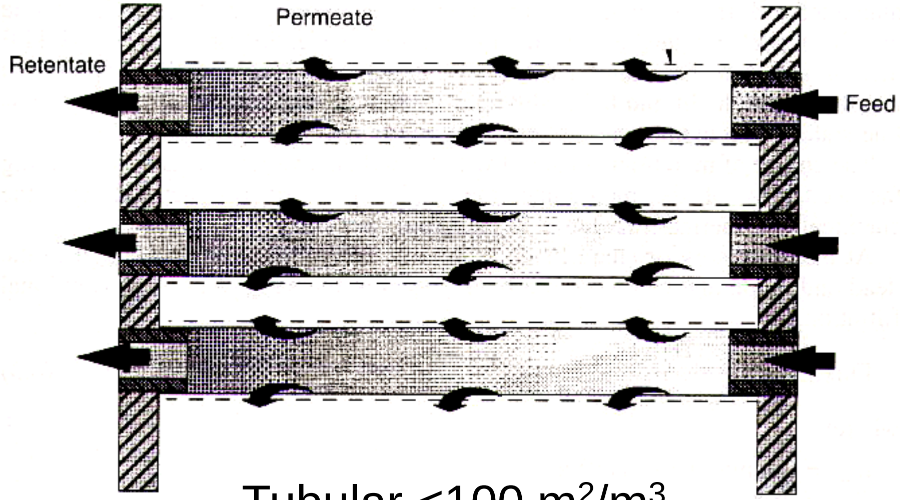
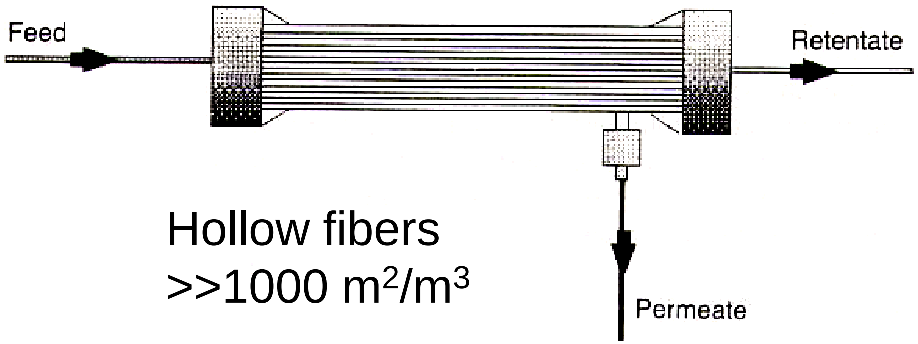


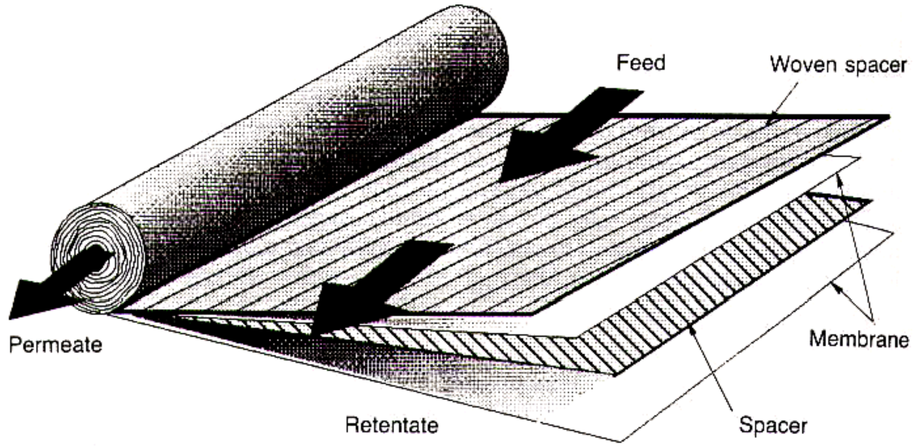
Plate-and-frame
100-1000 m^2/m^3



Tubular <100 m^2/m^3

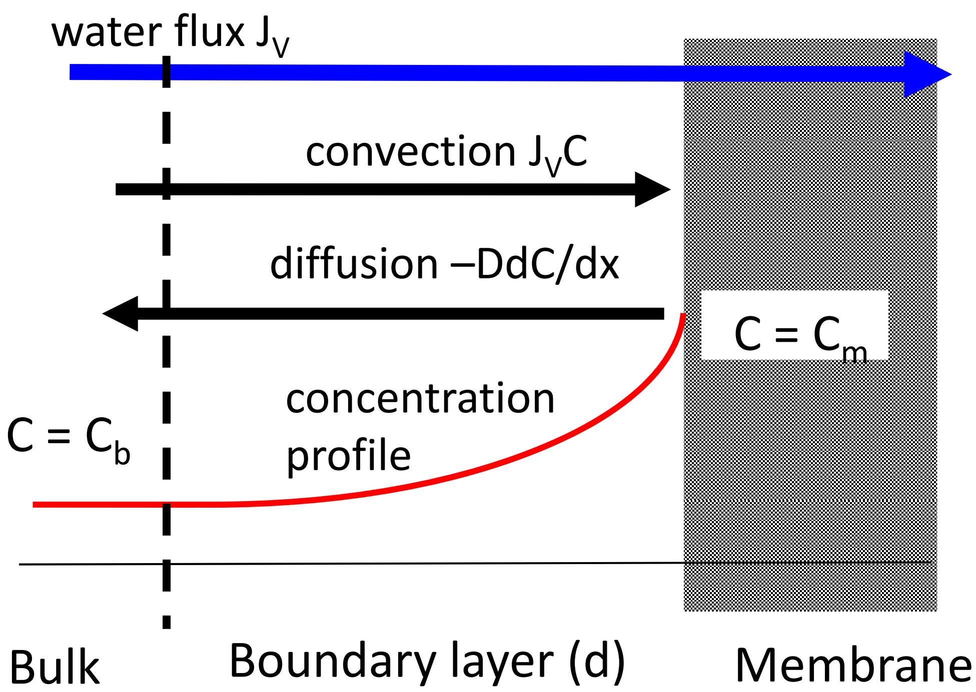


Hollow fibers
>>1000 m^2/m^3



Spiral-wound ~1000 m^2/m^3

Concentration Polarization



$$\frac{C_m - C_p}{C_b - C_p} = e^{\frac{J_v}{k}} \approx \frac{C_m}{C_b}; \quad \ln\frac{1 - R_{obs}}{R_{obs}} = \ln\frac{1 - R_{id}}{R_{id}} + \frac{J_V}{k}$$

Membrane Fouling

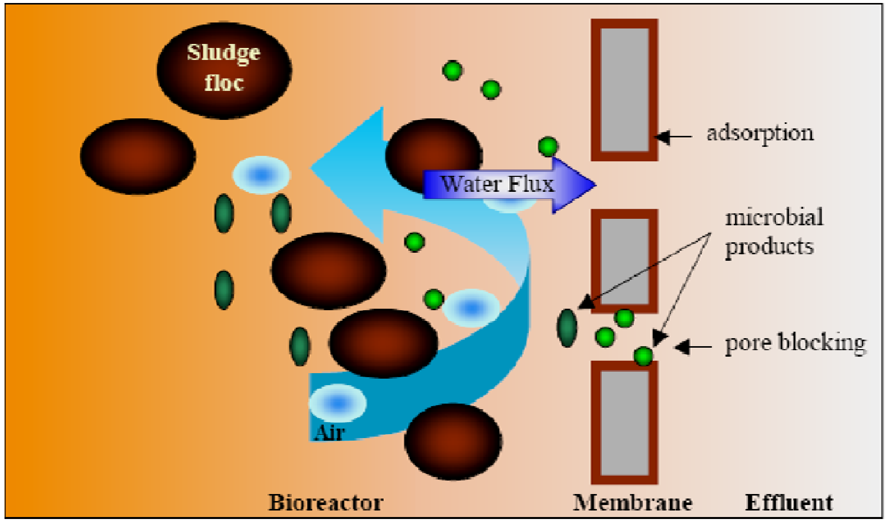
- Fouling is caused by various deposits on the membrane surface, external and internal. Fouling results in irreversible drop in performance due to increased hydraulic resistance and fouling-enhanced polarization.

- Mechanisms of fouling, especially in porous membranes, are very diverse. Fouling may be colloidal, inorganic (scaling by sparingly soluble salts, silica) and organic (e.g., by NOM or DOM). In many cases all types of fouling occur simultaneously, producing a synergistic effect. The main approaches to deal with fouling are technological (imposing flux limits, pretreatment, antiscalants, cleaning), but development of low-fouling membranes is gaining popularity.

- Hydrophobic membranes are in general more stable but also more prone to fouling than hydrophilic ones. This motivates attempts to modify membrane surface, which may improve anti-fouling properties without impairing other, beneficial characteristics.

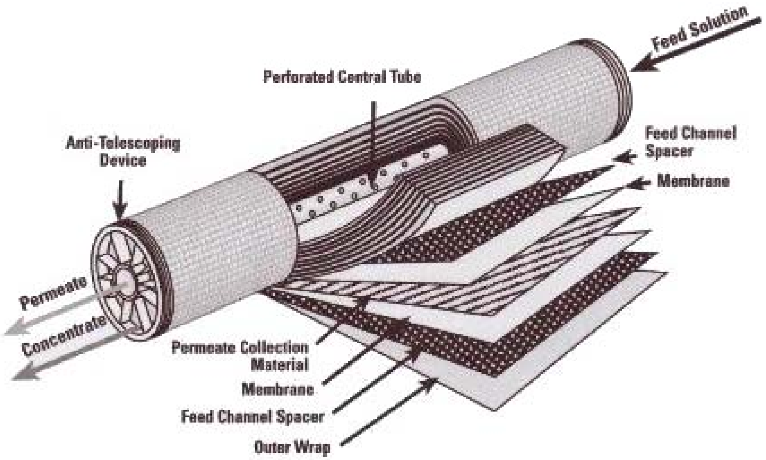
Fouling in membrane processes

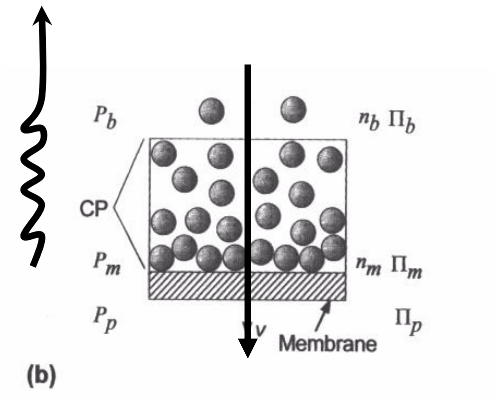
Microfiltration, ultrafiltration



- Adsorption of foulants to the membrane surface and pore blockage
- Increase in hydraulic resistance
- Increase in CP

Reverse osmosis, nanofiltration





•*** *Hoek and Elimelech ES&T 2003; Herzberg and Elimelech JMS, 2007***

Membrane Biofouing

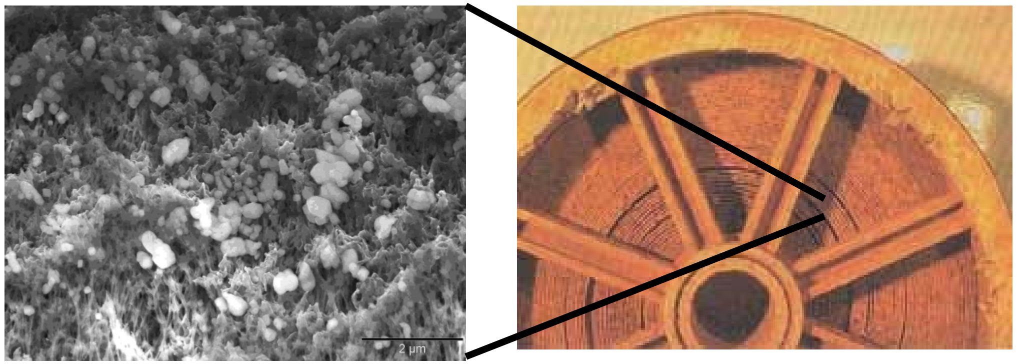
- Biofouling is different from other types of fouling in that the deposit (biofilm) is not brought with the feedstream, but develops in place, by consuming nutrients found in the feed.

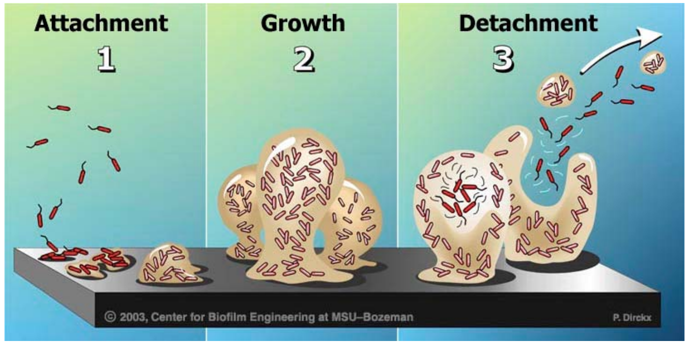
- Biofilms are complex bacterial consortia consisting of microorganisms embedded in a sticky EPS matrix that protects them.

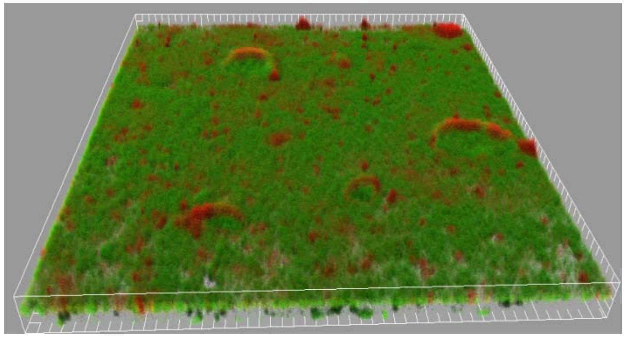
- Biofilms are ubiquitous and hard to prevent and control. Often they may be tolerated, but they are prone to sudden outbreaks without early warning. Excessive biofouling enhances other types of fouling and causes severe loss of performance and irreversible damage.

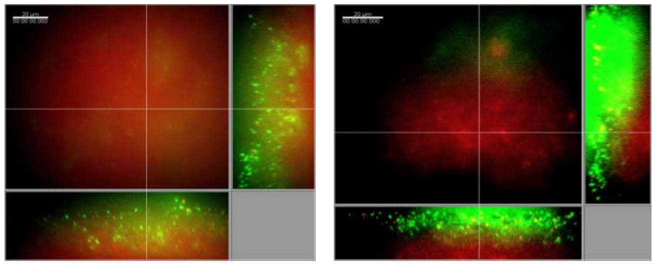
- Biofouling control and warning is the main technological challenge in desalination and some other important fields (biomedical devices, marine applications, dentistry etc.). Much effort is being dedicated to development of biofouling-resistant modified surfaces and technological tools (nutrient control, early warning etc.)

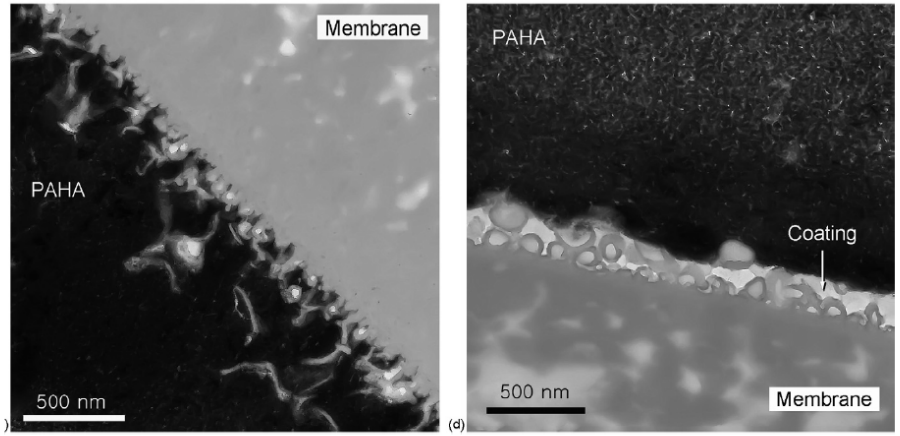
Microbial Biofilms and Membrane Biofouling

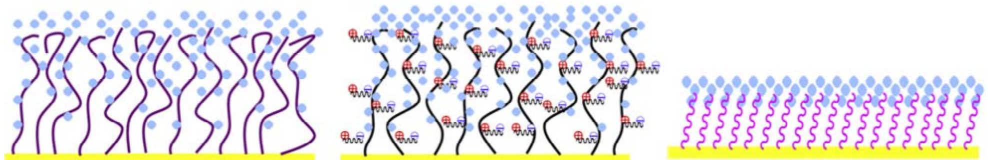




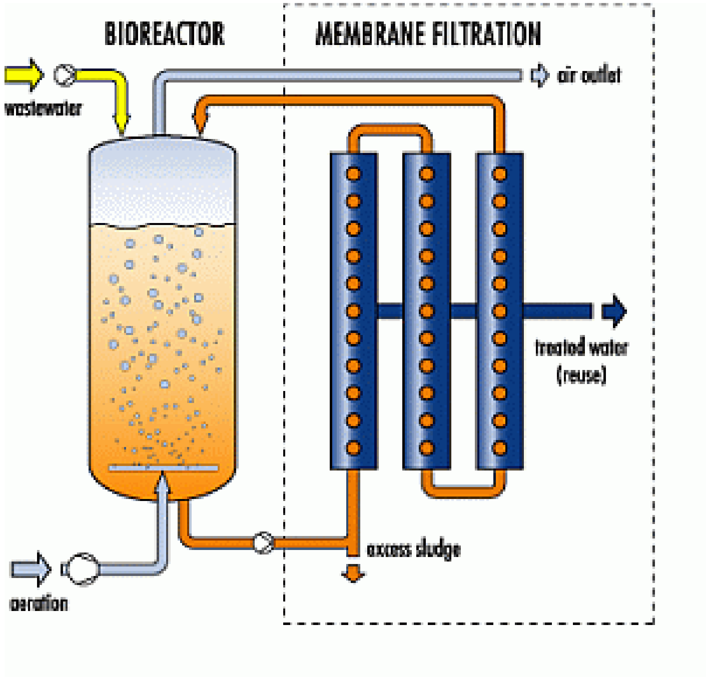








Membranes in Water Purification



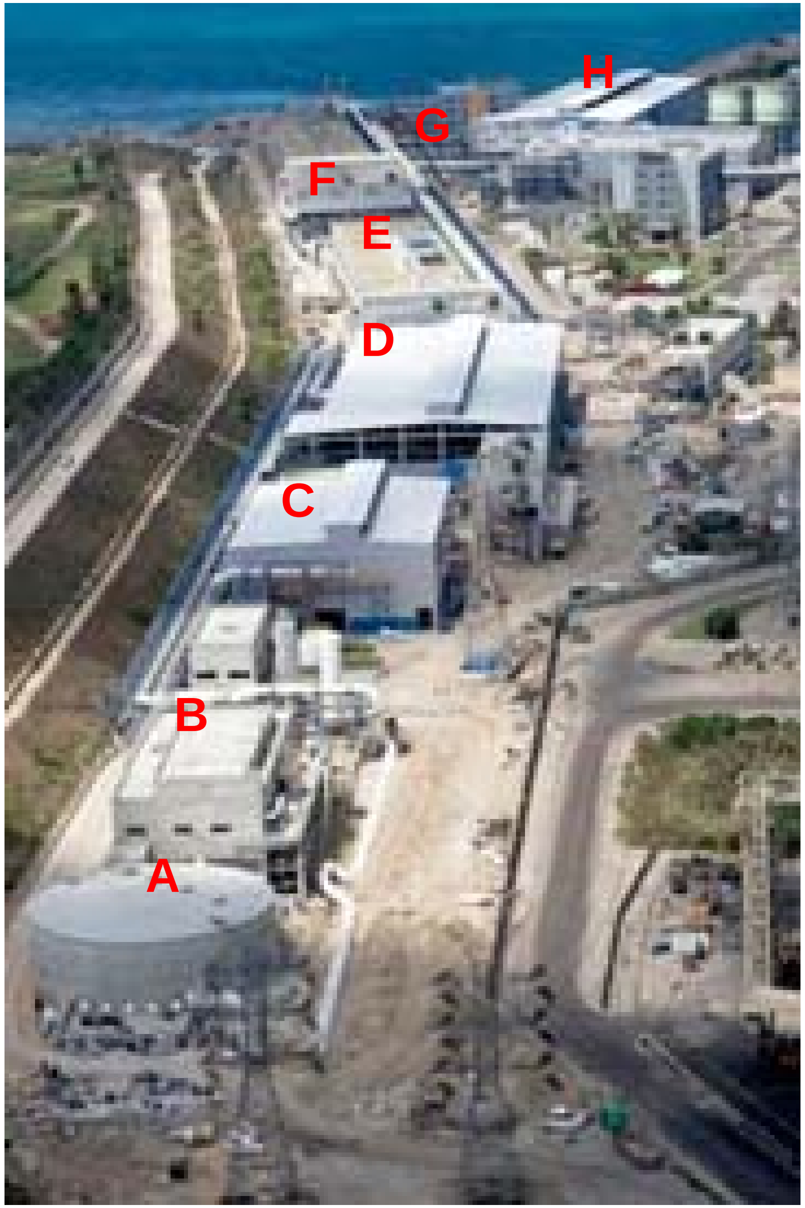
MBR concept
(UF, MF or NF)

GE's ZeeWeed®
Submerged UF-MBR

Home water purification system (MF, LPRO)

Membrane Desalination (SWRO, BWRO, LPRO, NF)

Hadera – 2010
Desalination plant
100-129 million M3/y



A: Product water tank
B: Post-treatment building
C: East SWRO, stage 2-4
D: East SWRO, stage 1
E: East gravity filter
F: West gravity filter
G: Admin, lab, control room
H. West SWRO, stage 2-4
I: West SWRO, stage 1

Summary and Outlook

- Membranes utilize differences in transport rates to separate solutes and solvents (mainly water) or gases using various physical mechanisms
- Membranes has become an important part of the separation toolbox and are available today for a wide variety of processes and in a variety of types and configurations
- Polarization, fouling and biofouling are the main problems in membrane technology and always need to be carefully addressed
- Subject to cost limitations, membranes and hybrid processes including membranes offer today the efficient solutions in water treatment and desalination and, as the technology improves and the society is more ready to pay, their use is expected to increase and expand on the future.

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