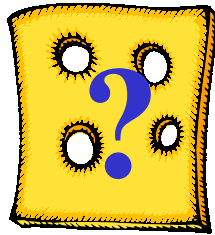
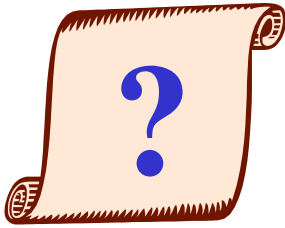


Membrane Separations

# What is a membrane?

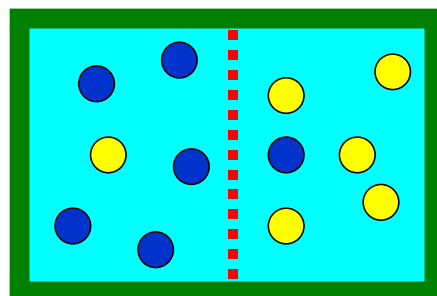
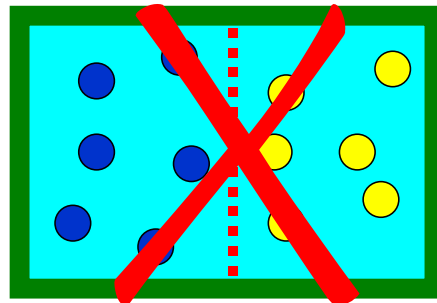
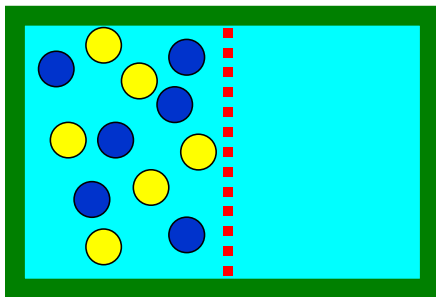


A membrane is...

...a physical barrier (no necessarily solid) that gives, or at least helps, the separation of the components in a mixture.

Membrane Separations

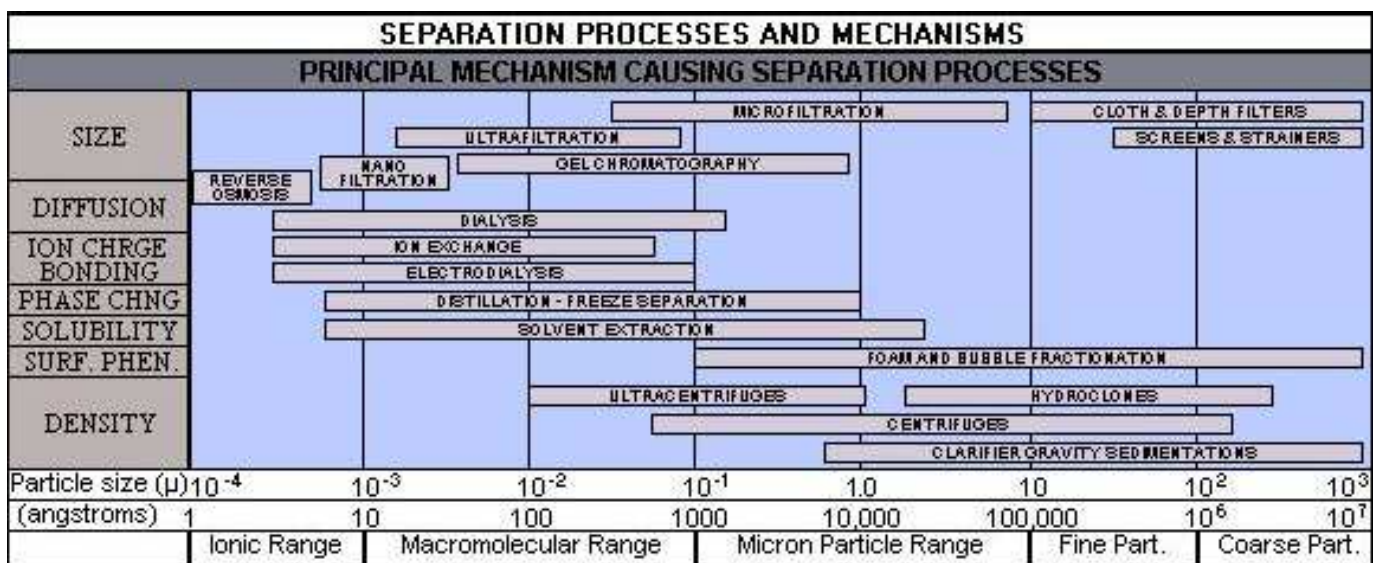
# The sorting demon...



## Membrane Separations

- Membrane processes are not based in thermodynamic equilibrium but based in the different transport rate of each species through the membrane.
- The membrane market is still growing. In the 1986-96 decade, the sales related to membrane products and systems doubled.
- In 1998, these sales were over 5000 million €

## Membrane Separations



## Membrane Separations

### Advantages

- **Energy savings.** The energy consumption is very low as there is no phase change.
- **Low temperature operation.** Almost all processes proceed at room temperature, thus they can deal with compounds that are not resistant at high temperatures.
- **Recovery.** Both the concentrate and the permeate could be recovered to use.
- **Water reuse.** When applied to recover water, they avoid the transport of large water volumes and permit the reduction of the Chemical Oxygen Demand (COD) loading in sewage plants.

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## Membrane Separations

### Advantages

- **Compact operation.** Which permits to save space .
- **Easy scale-up.** Because usually they are designed in modules, which can be easily connected.
- **Automatic operation.** The most of the membrane plants are managed by expert systems.
- **Tailored systems.** In many cases, the membranes and systems can be specifically designed according the problem.

## Membrane Separations

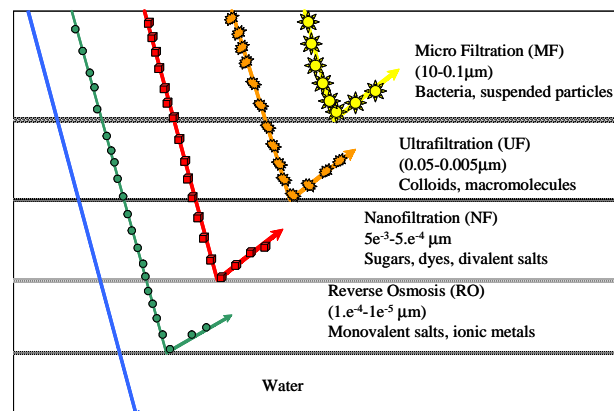
### Disadvantages

- **High cost.** Membranes (and associated systems) are costly, but for low selective separations.
- **Lack of selectivity.** In many cases, the separation factors are still insufficient.
- **Low fluxes.** The permeate flowrate available are still too low for some applications.
- **Sensitive to chemical attack.** Many materials can be damaged by acids, oxidants or organic solvents.
- **Lack of mechanical resistance.** Many materials do not withstand abrasion, vibrations, high temperatures or pressures.

## Membrane Separations

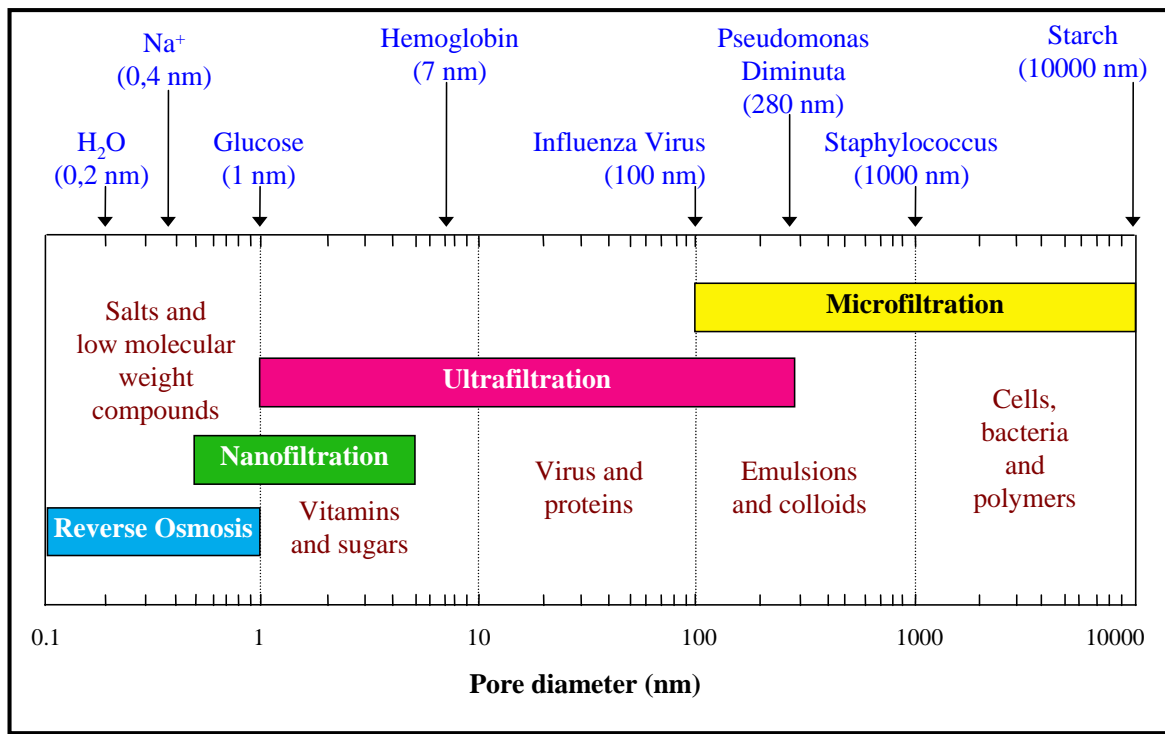
- The membrane operations more widely used are those based in applying a pressure difference between both sides of the membrane.

- Microfiltration (MF).
- Ultrafiltration (UF).
- Nanofiltration (NF).
- Reverse osmosis (RO).



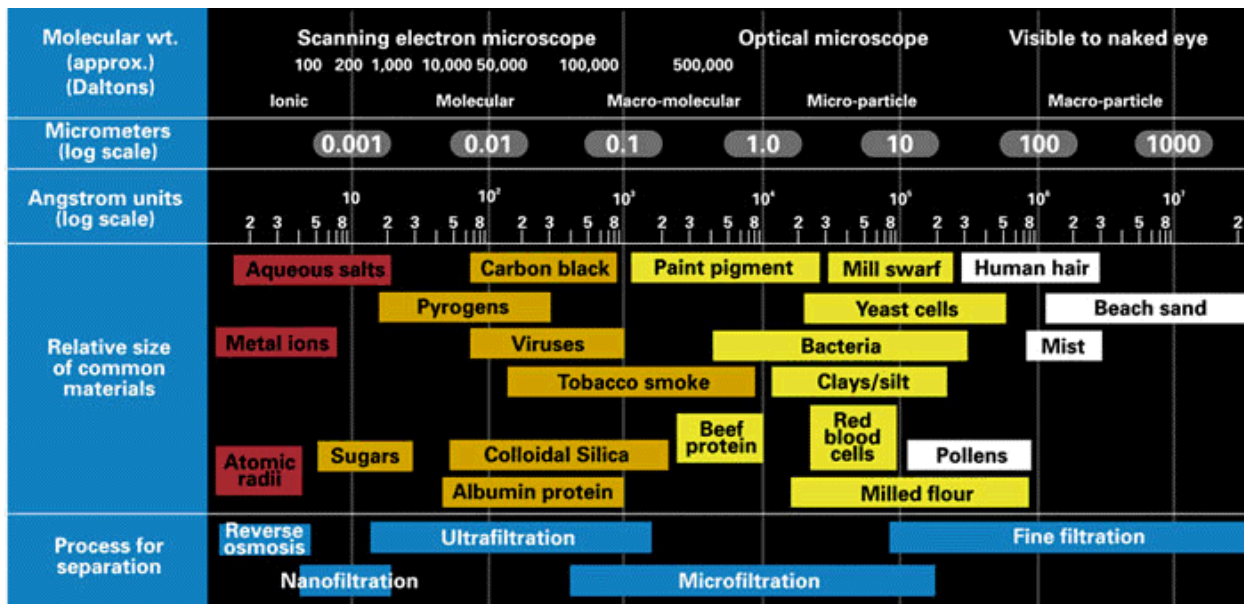
- Although similar in appearance, the mechanisms involved in the separation can be very very different.

## Membrane Separations



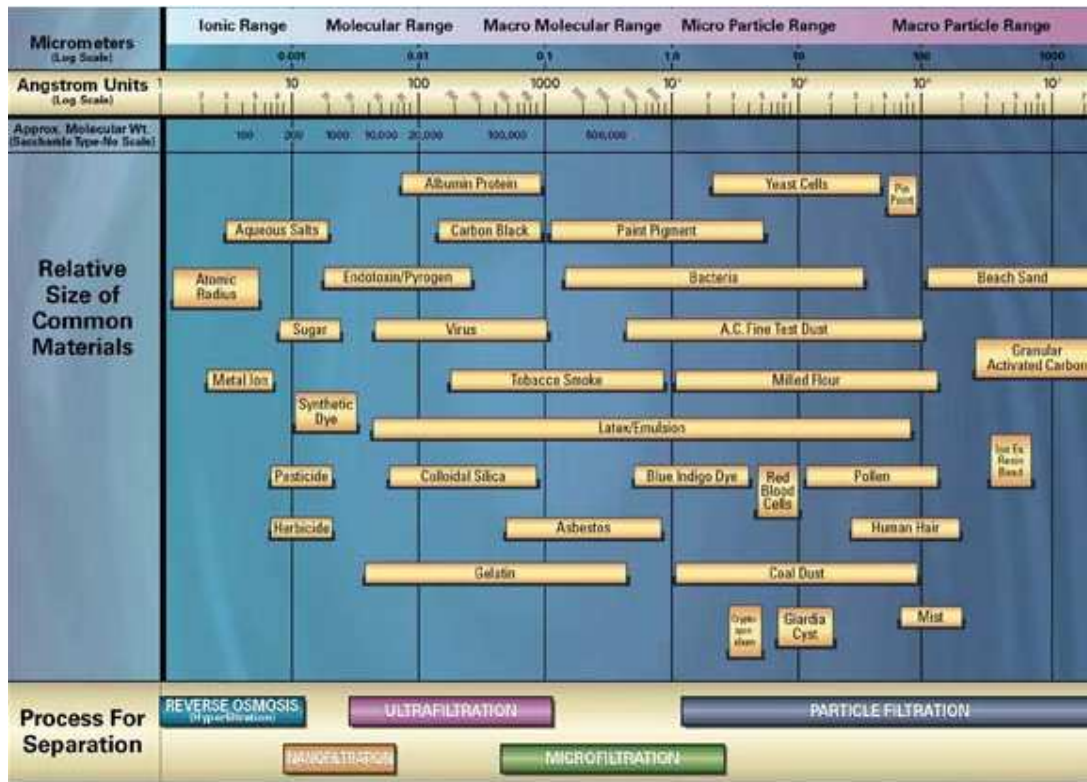
Name of the membrane process in function of the particle size.

## Membrane Separations



More examples.

## Membrane Separations



... and still more.

## Membrane Separations

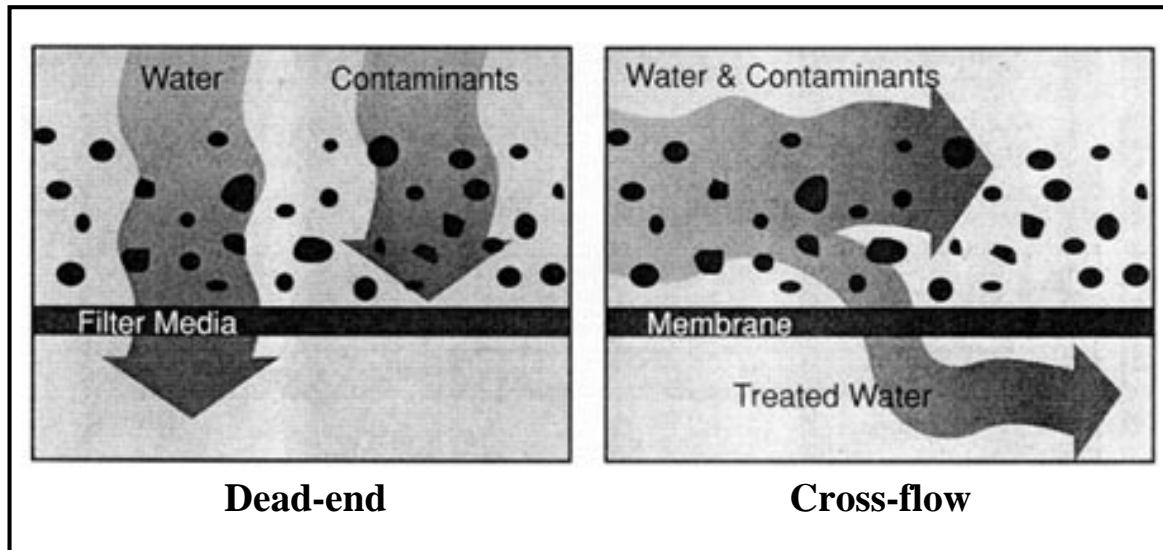
- There are other separation operations where a membrane is the responsible of the la selective separation of the compounds:

- Dialysis.
- Electro dialysis (ED).
- Pervaporation.
- Gas permeation (GP).
- Liquid membranes.

- In others, the membrane is not directly responsible for the separation but it actively participates:

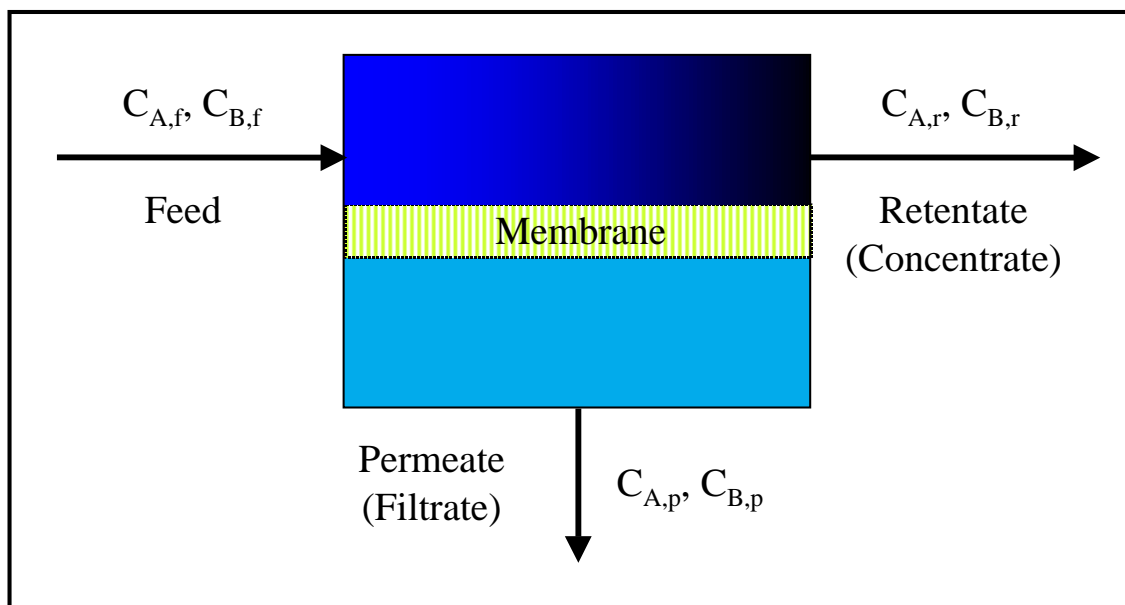
- Membrane extraction.
- Membrane distillation.
- Osmotic distillation.

## Membrane Separations



**Types of filtration operation.**

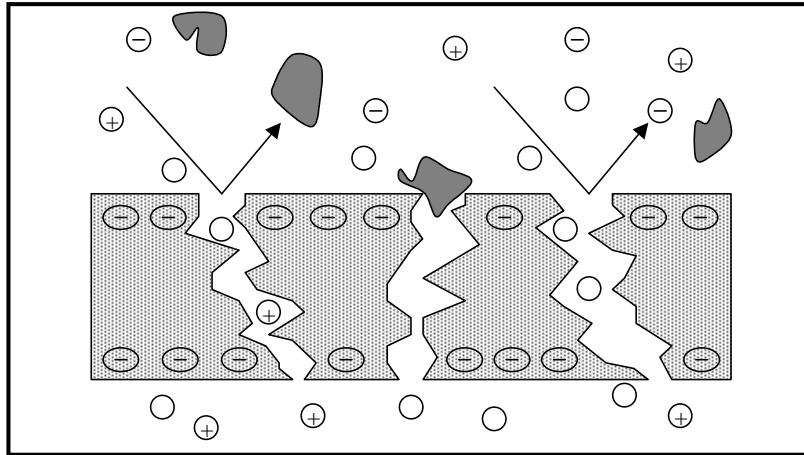
## Membrane Separations



**Simple scheme of a membrane module.**

## Membrane Separations

- Synthetic membranes are solid barriers that allow preferentially to pass specific compounds due to some driving force.



**(Very) Simple scheme for some mechanisms of selective separation on a porous membrane.**

## Membrane Separations

- The separation ability of a synthetic material depends on its physical, chemical properties.

- Pore size and structure
- Design
- Chemical characteristics
- Electrical charge

## Membrane Separations

- The membranes can be roughly divided in two main groups: porous and non porous.
- Porous membranes give separation due to...
  - size
  - shape
  - charge...of the species.
- Non porous membranes give separation due to...
  - selective adsorption
  - diffusion...of the species.

## Membrane Separations

### Main parameters.

- Rejection, R, if there is just one component (RO)

$$R(\%) = 100 \cdot \left( \frac{C_{A,f} - C_{A,p}}{C_{A,f}} \right) = 100 \cdot \left( 1 - \frac{C_{A,p}}{C_{A,f}} \right)$$

- Separation factor

$$\alpha_{A,B} = \frac{C_{A,p}/C_{B,p}}{C_{A,f}/C_{B,f}} = \frac{\beta_A}{\beta_B}$$

- Enrichment factor

$$\beta_A = \frac{C_{A,p}}{C_{A,f}}$$

for two or more component

## Membrane Separations

### Main parameters.

- In RO, often we use the Recovery (Y)

$$Y(\%) = \frac{Q_p}{Q_f} \cdot 100$$

$Q_p$ : Permeate flowrate ( $\text{m}^3/\text{s}$ )

$Q_f$ : Feed flowrate ( $\text{m}^3/\text{s}$ )

## Membrane Separations

### Main parameters.

- Passive transport in membranes. The permeate flux is proportional to a given driving force (some difference in a property).

$$\text{Flux (J)} = \text{Constant (A)} \cdot \text{Driving Force (X)}$$

Driving forces:

- Pressure (total or partial)
- Concentration
- Electric Potential

## Membrane Separations

### Main parameters.

Membrane processes and driving force.

<b>Process</b>	<b>Feed phase</b>	<b>Permeate phase</b>	<b>Driving Force</b>
Microfiltration	L	L	$\Delta P$
Ultrafiltration	L	L	$\Delta P$
Nanofiltration	L	L	$\Delta P$
Reverse Osmosis	L	L	$\Delta P$
Dialysis	L	L	$\Delta c$
Electrodialysis	L	L	$\Delta E$
Pervaporation	L	G	$\Delta P$
Gas Permeation	G	G	$\Delta P$

## Membrane Separations

### Main parameters.

- Permeate flux.

In MF and UF, porous membrane model is assumed, where the stream freely flows through the pores. Then, the transport law follows the Hagen-Poiseuille equation.

$$J_w = \frac{Q_w}{A_m} = \frac{\varepsilon \cdot r^2}{8 \cdot \mu \cdot \tau} \cdot \frac{\Delta P}{d}$$

$J_w$ : Solvent flux ( $\text{m}^3/\text{s} \cdot \text{m}^2$ )

$Q_w$ : Solvent flowrate ( $\text{m}^3/\text{s}$ )

$A_m$ : Membrane area ( $\text{m}^2$ )

$d$ : Membrane thickness (m)

$\mu$ : Viscosity ( $\text{Pa} \cdot \text{s}$ )

$\Delta P$ : Hydraulic pressure difference (Pa)

$r$ : Pore radius (m)

$\varepsilon$ : Porosity

$\tau$ : Tortuosity

## Membrane Separations

### Main parameters.

- The above model is good for cylindrical pores. However, if the membrane is rather formed by aggregated particles, then the Kozeny-Carman relation is preferred.

$$J_w = \frac{Q_w}{A_m} = \frac{\epsilon^3}{K \cdot \mu \cdot S^2 \cdot (1-\epsilon)^2} \cdot \frac{\Delta P}{d}$$

$J_w$ : Solvent flux ( $\text{m}^3/\text{s} \cdot \text{m}^2$ )

$Q_w$ : Solvent flowrate ( $\text{m}^3/\text{s}$ )

$S$ : Particle surface area ( $\text{m}^2/\text{m}^3$ )

$K$ : Kozeny-Carman constant

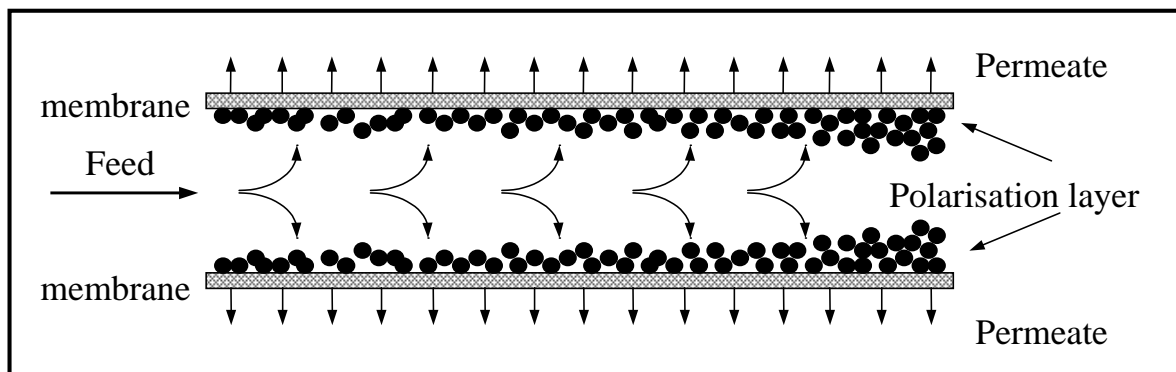
$d$ : Membrane thickness (m)

$A_m$ : Membrane area ( $\text{m}^2$ )

$\mu$ : Viscosity ( $\text{Pa} \cdot \text{s}$ )

## Membrane Separations

- In the operations governed by the pressure, a phenomenon called concentration polarisation appears, which must be carefully controlled. This is due to the solute accumulation neighbouring the membrane surface.

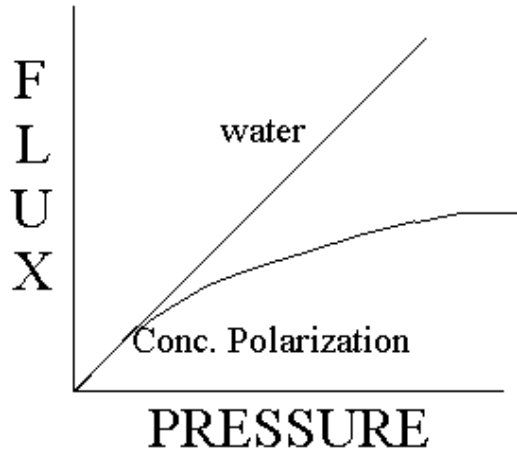


**Formation of the polarisation layer.**

Membrane Separations

- Concentration polarisation.

**Flux vs. Pressure**

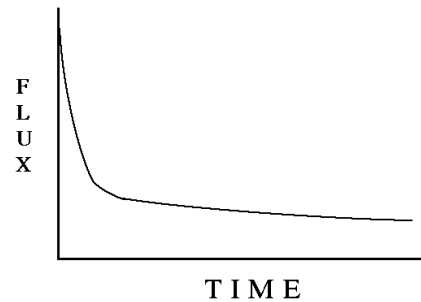


(It is not fouling!!!)

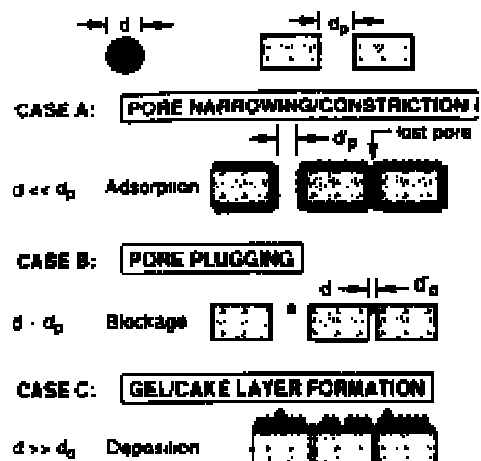
Membrane Separations

- Fouling: Irreversible reduction of the flux throughout the time.

- Pore size reduction by irreversible adsorption of compounds.
- Pore plugging.
- Formation of a gel layer over the membrane surface (cake).



**FOULING SCHEMATICS**



## Membrane Separations

### - Fouling: Cake.

- The presence of a cake is included in the transport mechanism by the addition of a new resistance due to the cake layer.

$$\text{Flux: } J_v = \frac{\Delta P}{(R_m + R_c)} \quad \text{Resistance (} R_c \text{): } R_c = l_c \cdot r_c$$

$r_c$ : specific resistance of the cake     $l_c$ : cake thickness

## Membrane Separations

### - Fouling: Cake.

Kozany – Carman relationship:

$$r_c = 180 \frac{(1 - \epsilon)^2}{[(d_s)^2 \epsilon^3]}$$

$\epsilon$ : cake layer porosity  
 $d_s$ : solute particle diameter

$$l_c = \frac{m_s}{[\rho_s (1 - \epsilon) A]}$$

$m_s$ : cake mass  
 $\rho_s$  – solute density  
 $A$  – membrane area

If the rejection is 100% in dead-end filtration,

$$l_c = \frac{c_b V}{c_c A}$$

$c_b$ : bulk concentration  
 $c_c$ : cake concentration  
 $V$ : filtrate volume

Then the flux is

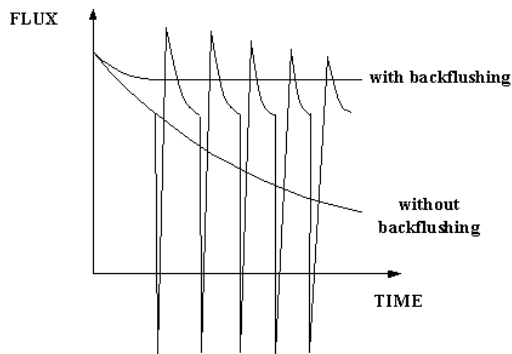
$$J = \frac{1}{A} \frac{dV}{dt} = \frac{\Delta P}{\left( R_m + \frac{r_c c_b V}{c_c A} \right)}$$

$$\frac{1}{J} = \frac{1}{J_w} + \left( \frac{r_c \cdot c_b}{\Delta P \cdot c_c} \right) \frac{V}{A}$$

$J_w$ : water flux

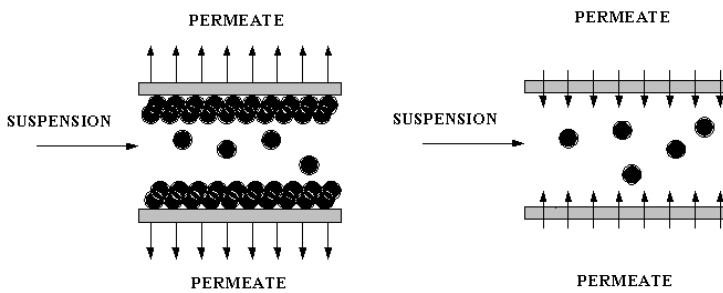
# Membrane Separations

- Fouling: back pressure.



Alternate pressuring and depressuring and by changing the flow direction at a given frequency.

Flux versus time behaviour in a given microfiltration process with and without back-flushing



After a given period of time, the feed pressure is released and the direction of the permeate reversed from the permeate side to the feed side in order to remove the fouling layer within the membrane or at the membrane surface.