MEMBRAN SEPARASI
is a VERY THIN film that allows some types of matter to pass through while leaving others behind

semi-permeable membrane

Membran = materials which have voids in them letting some molecules pass more conveniently than some other molecules
Driving force:

1. Pressure difference
   - RO
   - UF
   - MF
   - Pervaporation

2. Concentration difference
   - Dialysis
   - Membrane extraction

3. Voltage difference,
   - Electrodialysis

4. Temperature difference,
   - Membrane distillation
TYPES OF PROCESSES

Dissolved salts

Colloids

Suspended solids

Viruses

Bacteria

Org. macro. molecules

Parasites

Polio virus

Smallest micro-organism

Crypto-sporidium

Hair

Reverse Osmosis

Ultrafiltration

Sand filtration

Nanofiltration

Microfiltration

ZW1000: 0.02 um

ZW500: 0.04 um

Nur Istianah-KPP-Ekstraksi-2014
Fig. 6.11 Size separation capabilities of different membrane systems.
(From Anon. (1997).)
**REVERSE OSMOSIS/ hyperfiltration**

*Figure 1.2. Principle of reverse osmosis.*
**REVERSE OSMOSIS**

- only remove some suspended materials larger than 1 micron
- the process eliminates the dissolved solids, bacteria, viruses and other germs contained in the water
- only water molecules allowed to pass via very big pressure
- asymmetric type membranes (decrease the driving pressure of the flux)
- almost all membranes are made polymers, cellulosic acetate and matic polyamide types rated at 96%-99+% NaCl rejection
REVERSE OSMOSIS

• Applications in food industries:
  – the concentration of whey from cheese manufacture (the most use)
  – concentrate and purify fruit juices (Robe, 1983), enzymes, fermentation liquors and vegetable oils
  – concentrate wheat starch, citric acid, egg white, milk, coffee, syrups, natural extracts and flavours
  – to clarify wine and beer
  – to demineralise and purify water from boreholes or rivers or by desalination of sea water.
REVERSE OSMOSIS

• ‘dealcoholisation’ to produce low-alcohol beers, cider and wines,
• recovery of proteins or other solids from distillation residues, dilute juices,
• waste water from corn milling or other process washwaters.
REVERSE OSMOSIS

• future directions:
  – municipal and industrial waste treatment
  – process water for boilers
  – de-watering of feed streams
  – processing high temperature feed- streams
MICROFILTRATION

- largest pores
- a sterile filtration with pores 0.1-10.0 microns
- micro-organisms cannot pass through them
- operated at low pressure differences
- used to filter particles.
- may or may not be asymmetric
- lower pressures than RO
• wide array of applications:
  – parenterals and sterile water for pharmaceutical industry
  – food & beverages
  – chemical industry
  – microelectronics industry
  – fermentation
  – laboratory/analytical uses
Figure 1.3. Waterpurifier using microfiltration hollow fibers.
MICROFILTRATION

• applications in the near future:
  – biotechnology (concentration of biomass)
  – diatomaceous earth displacement
  – non-sewage waste treatment (removing intractable particles in oily fluids)
  – paints (separating solvents from pigments)
ULTRAFILTRATION

- to separate a solution; mixture of desirable and undesirable components
- has smaller pores than microfiltration membranes
- driving force $\rightarrow$ pressure differential (2-10 bars to 25-30 bars)
- used to separate species with pore sizes 10-1000 Å (103-0.1 microns)
- Can be obtained down to a molecular weight cutoff (MWCO) level of 1000 Daltons (Da) and up to as high as 1,000,000 Da.
- asymmetric; the pores are small
• wide range of applications:
  – oil emulsion waste treatment
  – treatment of whey in dairy industries
  – concentration of biological macromolecules
  – electrocoat paint recovery
  – concentration of textile sizing
  – concentration of heat sensitive proteins for food additives
  – many more...
wide range of applications in the near future:
- ultrafiltration of milk
- bioprocessing (separation and concentration of biologically active components)
- protein harvesting
- refining of oils
ULTRAFILTRATION

• Application in food processing:
  – concentrate milk prior to the manufacture of dairy products (the most use),
  – To concentrate whey to 20% solids or selectively to remove lactose and salts.
  – *In cheese manufacture*, ultrafiltration has advantages in producing a higher product yield and nutritional value, simpler standardisation of the solids content, lower rennet consumption and easier processing.
ULTRAFILTRATION

• Application in food processing:
  – concentration of sucrose and tomato paste
  – treatment of still effluents in the brewing and distilling industries
  – separation and concentration of enzymes, other proteins or pectin
  – removal of protein hazes from honey and syrups
  – treatment of process water to remove bacteria and contaminants (greater than 0.003 m in diameter) (Mackintosh, 1983)
  – pre-treatment for reverse osmosis membranes to prevent fouling by suspended organic materials and colloidal materials.
### Table 6.6  Loss of nutrients during membrane concentration of milk

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Reverse osmosis</th>
<th>Ultrafiltration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Fat</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>0</td>
<td>43</td>
</tr>
<tr>
<td>Energy</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>Thiamin</td>
<td>0</td>
<td>38</td>
</tr>
<tr>
<td>Riboflavin</td>
<td>0</td>
<td>39</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>8</td>
<td>41</td>
</tr>
<tr>
<td>Vitamin B&lt;sub&gt;6&lt;/sub&gt;</td>
<td>3</td>
<td>36</td>
</tr>
<tr>
<td>Vitamin B&lt;sub&gt;12&lt;/sub&gt;</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Vitamin C</td>
<td>-</td>
<td>87</td>
</tr>
<tr>
<td>Folic acid</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Pantothenic acid</td>
<td>0</td>
<td>32</td>
</tr>
<tr>
<td>Biotin</td>
<td>0</td>
<td>37</td>
</tr>
</tbody>
</table>

From Glover (1971).
NANOFILTRATION

- less pore sizes than ultrafiltration membranes
- the mass transfer mechanism is diffusion & separate small molecules from the solution (assymmetric)
- NF is capable of removing ions that contribute significantly to the osmotic pressure
- Can be operated at lower pressures than RO
- cellulosic acetate and aromatic polyamide type membranes (salt rejections; 95% for divalent salts to 40% for monovalent salts)
- can typically operate at higher recoveries; conserving total water usage due to a lower concentrate stream flow rate (advantage over reverse osmosis)
- not effective on small molecular weight organics (e.g. methanol)
• typical applications:
  – desalination of food, dairy and beverage products or byproducts
  – partial desalination of whey, UF permeate or retentate as required
  – desalination of dyes and optical brighteners
  – purification of spent clean-in-place (CIP) chemicals
  – color reduction or manipulation of food products
  – concentration of food, dairy and beverage products or byproducts
  – fermentation byproduct concentration
ION EXCHANGE

▪ Ion-exchange and electrodialysis: separation methods that remove electrically charged ions and molecules from liquids.

▪ Solutes such as metal ions, proteins, amino acids and sugars are transferred from a feed material and retained on a solid ion-exchange material by a process of electrostatic adsorption (i.e. attraction between the charge on the solute and an opposite charge on the ion-exchanger). They can then be separated by washing off the ion-exchanger.

▪ They are constructed using a porous matrix made from polyacrylamides, polystyrene, dextrans or silica.

▪ The applications in food processing include decolourisation of sugar syrups, protein recovery from whey or blood, water softening and dimineralisation and separation of valuable materials such as purified enzymes (Grandison, 1996)
a liquid feed mixture is separated by **partial vaporisation** through a non-porous, selectively permeable membrane. Partial vaporisation is achieved by reducing the pressure on the permeate side of the membrane (vacuum pervaporation) or less commonly, sweeping an inert gas over the permeate side (sweep gas pervaporation).

**Application:**
- Vacuum pervaporation at ambient temperatures using hydrophilic membranes is used to dealcoholise wines and beers,
- hydrophobic membranes are used to concentrate aroma compounds, such as alcohols, aldehydes and esters,
**Material of membrane**

**Hydrophilic polymers**

preferentially permit water permeation
(e.g. poly (vinyl alcohol) or cellulose acetate)

**Hydrophobic polymers**

preferentially permit permeation of organic materials.
e.g. Poly (dimethylsiloxane) or poly (trimethylsilylpropyne)
<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. (°C)</th>
<th>He</th>
<th>H₂</th>
<th>CH₄</th>
<th>CO₂</th>
<th>O₂</th>
<th>N₂</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone rubber</td>
<td>25</td>
<td>300</td>
<td>550</td>
<td>800</td>
<td>2700</td>
<td>500</td>
<td>250</td>
<td>(S2)</td>
</tr>
<tr>
<td>Natural rubber</td>
<td>25</td>
<td>31</td>
<td>49</td>
<td>30</td>
<td>131</td>
<td>24</td>
<td>8.1</td>
<td>(S2)</td>
</tr>
<tr>
<td>Polycarbonate (Lexane)</td>
<td>25–30</td>
<td>15</td>
<td>12</td>
<td></td>
<td>5.6, 10</td>
<td>1.4</td>
<td></td>
<td>(S2)</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>25</td>
<td>1.0</td>
<td></td>
<td>0.17</td>
<td>0.034</td>
<td>0.008</td>
<td></td>
<td>(S2)</td>
</tr>
<tr>
<td>Polyester (Permasep)</td>
<td></td>
<td>1.65</td>
<td>0.035</td>
<td>0.31</td>
<td></td>
<td>0.031</td>
<td></td>
<td>(H1)</td>
</tr>
<tr>
<td>Silicone—polycarbonate</td>
<td>25</td>
<td>210</td>
<td></td>
<td>970</td>
<td>160</td>
<td>70</td>
<td></td>
<td>(W2)</td>
</tr>
<tr>
<td>copolymer (57% silicone)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Teflon FEP</td>
<td>30</td>
<td>62</td>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
<td>(S1)</td>
</tr>
<tr>
<td>Ethyl cellulose</td>
<td>30</td>
<td>35.7</td>
<td>49.2</td>
<td>7.47</td>
<td>47.5</td>
<td>11.2</td>
<td>3.29</td>
<td>(W3)</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>30</td>
<td>40.8</td>
<td>56.0</td>
<td>2.72</td>
<td>23.3</td>
<td>7.47</td>
<td>2.55</td>
<td>(W3)</td>
</tr>
</tbody>
</table>
The important factors in determining the performance of a membrane

- Thickness
- Chemical composition
- Molecular structure
Membrane Configurations

Flat membranes

Three basic structures are commonly used for membranes: homogeneous, asymmetric, and composite.

Spiral wound membranes

Constructed from flat sheet membranes separated by spacer screens, and susceptible to fouling by particulates.

Hollow-fiber membranes

Very-small-diameter hollow fibers, the high-pressure feed enters the shell side at one end and leaves at the other end (closed).
Flate

Spiral

Hollow
Fig. 6.13 Membrane structures: (a) asymmetrical membrane cross-section; (b) symmetrical membrane cross-section; (c) hollow-fibre asymmetrical membrane cross-section; (d) flat sheet asymmetrical membrane cross-section. (Courtesy of Environmental Technology Best Practice Programme.)
<table>
<thead>
<tr>
<th>No</th>
<th>Teknik Proses</th>
<th>Tujuan Proses</th>
<th>Pustaka</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Ultrafiltrasi</td>
<td>Pemurnian isolat protein kedelai</td>
<td>Debra and Cheryan (1981)</td>
</tr>
<tr>
<td>3</td>
<td>Ultrafiltrasi</td>
<td>Penyederhanaan proses produksi sari buah apel</td>
<td>Thomas, et.al. (1986)</td>
</tr>
<tr>
<td>4</td>
<td>Ultrafiltrasi</td>
<td>Pemisahan komponen kasein</td>
<td>Woychik et.,al (1992)</td>
</tr>
<tr>
<td>5</td>
<td>Ultrafiltrasi</td>
<td>Penurunan kandungan bakteri pada kecap</td>
<td>Tien and Chiang (1992)</td>
</tr>
</tbody>
</table>
Advantages:

- Continuous separation
- Low energy requirement
- Meet various separation demands
- Reduce the loss of volatiles or changes to nutritional or eating quality of food
- Simple installation with lower labour and operating costs
Disadvantages:

- higher capital costs than evaporation
- maximum concentration to 30% total solids
- fouling of the membranes (deposition of polymers), which reduces the operating time between membrane cleaning.
Movement of molecules through reverse osmosis membranes is by diffusion and not by liquid flow. The molecules dissolve at one face of the membrane, are transported through it and then removed from the other face. The flow rate of liquid (the ‘transport rate’ or ‘flux’) is determined by the solubility and diffusivity of the molecules in the membrane material, and by the difference between the osmotic pressure of the liquid and the applied pressure.
Flux (in kg/h.m²)

Membrane thickness

Diffusivity

Osmotic pressure

applied pressure

Concentration and molar volume of solvent

\[ N_w = \frac{P_w}{L_m} (\Delta P - \Delta \pi) = K (\Delta P - \Delta \pi) \]

\[ P_w = \frac{D_w \bar{c}_w V_w}{RT} \]

\[ J = NA \]
The pressure difference across the membrane (the trans-membrane pressure) is found using:

\[ P = \frac{P_f + P_r}{2} - P_p \]

\[ (1) \]

\( P \) (Pa) : trans-membrane pressure,

\( P_f \) (Pa) : pressure of the feed (inlet),

\( P_r \) (Pa) : pressure of the retentate (outlet) (high molecular weight fraction) and

\( P_p \) (Pa) : pressure of the permeate (low molecular weight fraction)
Water flux increases with an increase in applied pressure, increased permeability of the membrane and lower solute concentration in the feed stream.

\[ J_w = kA (\Delta P - \Delta \pi) \] ................... (2)

- \( J_w (\text{kg/h}) \) = solvent (water) flux,
- \( K (\text{kg/m}^2\text{.h.Pa}) \) = mass transfer coefficient/permeability const.
- \( A (\text{m}^2) \) = area of the membrane,
- \( \Delta P (\text{Pa}) \) = applied pressure and
- \( \Delta \pi (\text{Pa}) \) = change in osmotic pressure.

Osmotic pressure is found for dilute solutions using:

\[ \pi = MRT \] ................... (3)

\( M = \text{molarity} \), \( T (\text{K}) \), \( R = 8.314 \text{ kPa.m}^3\text{mol}^{-1}\text{K}^{-1} \)
### Experimental Osmotic pressure

<table>
<thead>
<tr>
<th>Sodium Chloride Solutions</th>
<th>Sea Salt Solutions</th>
<th>Sucrose Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>g mol NaCl/kg H₂O</td>
<td>Density (kg/m³)</td>
<td>Osmotic Pressure (atm)</td>
</tr>
<tr>
<td>0</td>
<td>997.0</td>
<td>0</td>
</tr>
<tr>
<td>0.01</td>
<td>997.4</td>
<td>0.47</td>
</tr>
<tr>
<td>0.10</td>
<td>1001.1</td>
<td>4.56</td>
</tr>
<tr>
<td>0.50</td>
<td>1017.2</td>
<td>22.55</td>
</tr>
<tr>
<td>1.00</td>
<td>1036.2</td>
<td>45.80</td>
</tr>
</tbody>
</table>

* Value for standard seawater.
Larger solutes become concentrated at the membrane surface. The flux is therefore controlled by the applied pressure, and the solute concentrations in the bulk of the liquid and at the membrane surface:

\[ J_s = kA \ln \left( \frac{c_1}{c_2} \right) \]  

\( J_s \) = solute flux  
\( c_1 \) = concentration of solutes at the membrane  
\( c_2 \) = concentration of solutes in the liquid
Contoh soal

Hitunglah tekanan osmotic larutan yang mengandung 0.10 g mol NaCl/kg H2O pada suhu 25°C dengan densitas air 997.0 kg/m3.

_Penyelesaian:_

\[
\pi = MRT = \frac{n}{V_m} \cdot RT
\]

\[
V_m = \frac{m}{\rho}
\]

\[
\pi = \frac{2 \times 10^{-4} \times (8.314)(298.15)}{1/997} = 494.28 kPa
\]
Contoh soal

Jus buah yang mengandung 9% w/w partikel padat (solid) telah diberi perlakuan pre-concentration pada 35°C dengan reverse osmosis untuk kemudian dilakukan ‘concentration’ pada evaporator. Jika tekanan operasi RO adalah 4000 kPa dan koefisien transfer massa sebesar 6.3x10^{-3} kg.m^{-2}h^{-1}kPa^{-1}, hitung luasan area membran yang diperlukan untuk menghilangkan 5 ton permeate selama 8 jam. (asumsikan mayoritas partikel padat berbentuk sucrose dan konstanta gas universal (R= 8.314 kPa.m^{-3}mol^{-1}K^{-1})
Penyelesaian:

Molar concentration \((M) = \text{concentration (g/L)} : \text{molecular weight}\)

\[ M = \frac{90}{342} = 0.264 \text{ mol m}^{-3} \]

Tekanan osmotic (persamaan 3)

\[ \pi = 0.264 \times 8.314 \times (35+273) = 676 \text{ kPa} \]

Flux (kg/jam feed): \( J = \frac{5000 \text{ kg}}{8 \text{ jam}} = 625 \text{ kg/jam} \)

Persamaan 2:

\[ 6.25 = 6.3 \times 10^{-3} \times A \times (4000 - 676) \]

\[ A = 29.9 \text{ m}^2 = 30 \text{ m}^2 \]
Latihan soal

Hitunglah tekanan osmotic larutan berikut pada suhu 25°C dengan densitas air 997.0 kg/m³.
(a) Larutan 0.5 g mol NaCl/kg H₂O
(b) Larutan 1.0 g sucrose/kg H₂O
(c) Larutan 1.0 g MgCl₂/kg H₂O
Latihan soal

Sebuah membran *cellulose-acetate* dengan area 4x10^{-3} m² digunakan pada suhu 25°C untuk menentukan konstanta permeabilitas RO larutan garam yang mengandung 12 kg NaCl/m³ (ρ=1005.5 kg/m³) dan dihasilkan produk larutan dengan konsentrasi 0.486 kg NaCl/m³ (ρ=997.3 kg/m³). Flow rate produk adalah 3.84x10^{-8} m³/s dan tekanan operasi sebesar 56.0 atm. Hitunglah konstanta permeabilitas RO tersebut!

Densitas air pada 25°C adalah 997 kg/m³
THANKS FOR YOUR ATTENTION

The best person is one give something useful always