Separation and purification techniques

I. Membrane processes
II. Chromatographic separation

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I. Membrane separation processes

1. Classification of membrane processes
Filtration set-up (dead-end, cross-flow), criterions of membrane processes classification (mechanism, driving force, membrane types, properties of separated particles), basic terminology – permeate, retentate, filtrate, up-stream, down-stream process.

2. Membranes
Separation properties (permeability, porosity, pore size, selectivity, cut-off)
Membrane classification – structure, (porous, non-porous, symmetric, asymmetric, composite, homogenous, heterogeneous, mosaic, sandwich), material (organic, inorganic), shape (planar, tubular, hollow fibre), function and production, bio-membranes, liquid membranes.

3. Membrane modules
Character of the flow along the membrane
Construction, types, set-up. Lab scale, industrial scale, special modules (rotating, vibrating, membrane reactors)
4. Filtration process kinetics
Filtration theory, driving forces, character of separated particles and molecules (charge, size, shape, affinity, isoelectric point) Transport mechanisms, filtration equation, concentration polarization.

5. Permeate flux, membrane fouling and cleaning
Description of fouling
Factors affecting the membrane fouling (membrane properties, solution properties, character of the process), permeate flux enhancement (back-flush, turbulent flow, pulsing flow, constant pressure), Cleaning and sanitation.

6. Individual membrane processes
Diffusion, diffusion theory, diffusivity, solvation
Dialysis, osmosis, reverse osmosis, microfiltration, ultrafiltration, nanofiltration, pervaporation, das permeation, membrane distillation.
I. Membrane Separation Processes (MSP)

1. Classifications of MSP

Filtration principle = separation of at least two fluid components (gas or liquid) due to the different size.

MEMBRANE:
- selective barrier
- barrier between two phases
- a phase that forms barrier hinders mass transport but enables limited and controlled passage of certain components
- liquid, solid, gas character (or combination of all)
Membrane separates feed into:

- **Retentate (concentrate)**
  = enriched with substances retained by the membrane

- **Permeate (filtrate)**
  = a stream passing through the membrane, devoid of substances retained by the membrane
Basic mechanisms of substance separation on the membrane:

- Different particle size (sieving effect)
- Different charge of mixture components
- Different diffusivity
- Different solubility of components in the membrane

Aspects of membrane process's classification:

- Driving force
- Type of the membrane
- Properties of separated particles
Driving force of membrane processes

- Pressure
- Concentration
- Chemical potential
- Electric potential

Properties of separated particles:

- Size
- Shape
- Charge
# Membrane process's characteristics:

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<th>Retentate</th>
<th>Permeate</th>
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<td>Partial pressure</td>
<td>Non-volatile molecules, water</td>
<td>Volatile small molecules, water</td>
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A general set-up of the filtration process

Filtration apparatus

“Up-stream“ processes
“Down-stream“ processes
2. Membranes

Separation properties of the membrane are given by: permeability, selectivity and cut-off

A) Permeability
Permeation = a transport of atoms, molecules and ions in a permeable media due to the gradient (of concentration, temperature, pressure, electric potential)

Porosity
A flow through ideal semipermeable membrane can be expressed as:

\[ J = A \cdot (P_T - \pi_F) \]

\( J \) = permeate flow, expresses a velocity of component passage through the membrane
\( A \) = permeation coefficient (reciprocal resistance)
\( P_T \) = trans-membrane pressure
\( \pi_F \) = osmotic pressure of solvent
B) Selectivity

![Graph showing frequency of pore sizes]
C) Cut-off

Deffinition: 90 % of molecules with a molecular weight corresponding to cutt-off do not pass through the membrane.
Membrane classification:

- Membrane origin (natural, synthetic)
- Membrane structure (porous, non-porous, surface morphology)
- Membrane application (gas – gas, gas – liquid, liquid – liquid separations)
- A mechanism of separation (adsorption, diffusion, ion exchange, osmotic pressure, inert membrane)
Membrane structure:

1. Microporous membrane

- isotropic
- anisotropic
2. Asymmetric membrane (with active layer)

A thin active layer is deposed on a support
3. **Composite (sandwich) membrane**

Several layers – every layer produced by different technique
Membrane’s material

1. Organic

- cellulose acetate (low costs, low price, wide range of pore sizes, hydrophilic character – reduced fouling)
- polyamide (low resistance to Cl₂, biofouling)
- polysulphone (high temperature, pH and chemical Cl₂ resistance)
- other polymers: nylon, PVDF, PTFE, PP, polycarbonate

2. Inorganic (= mineral, ceramic)

also metallic (stainless steel)
support layer: ceramic, Al₂O₃, TiO₂
separation layer: TiO₂, zirconium, carbon-titanium, carbon-zirconium
**Ceramic membranes:**

**positives:**

+ inert toward most of chemical solutions (exceptions: HF, H₃PO₄ – Al membranes)
+ high temperature resistance (350 °C) – steam sterilization
+ wide pH range (1 – 13)
+ high pressure resistance (1 MPa)
+ high lifetime
+ back-flushing possible

**drawbacks:**

- high pore size (UF, MF, opened NF membranes)
- high pump discharge needed (2 – 6 m/s tangential velocity)
- high producing costs – high prices (high investment costs)
Membrane’s shapes

- Plate
- Tubular (channel inside > 4 mm)
- Capillary (low diameter)
- Hollow fibres (inner diameter 0.2 – 3 mm)
- Spiral-wound
- Pleated sheet cartridges (dead-end filtration)
Tubular membrane

Pleated-sheet membrane
Spiral wound membrane

Feed spacer

Feed flow

Membrane

Permeate flow

Permeate spacer

Membrane envelope

Residue flow

Perforated permeate collection pipe

www.mtrinc.com
Hollow fibres

Asymmetric structure

Microporous structure
Biomembranes

Enzyme immobilization on the membrane’s surface
- adsorption, chemical bonds

Liquid membranes

a) ELM = Emulsion Liquid Membrane – immiscible liquids
b) ILM = Immobilized Liquid Membrane
3. Membrane modules

- Rotary membranes: tubular and disk
- Vibrating membranes: disk

Rotary tubular module

Rotary disk module

Filtration area enlargement

Tubular membranes

- Integration into cartridges
- Connections of several modules (in parallel, in series, retentate recycling, gradual filtration)

Connections of several modules
Connections of several modules
Filtration area enlargement
Plate modules
Membrane reactors

Membrane used:
Hollow fibre, flat, rotating cylinder,

Advantages:
- Easier cleaning
- One-step operation (chemical reaction and separation in one stage)

Placement:
Inside the bioreactor or in outside recycling pipe
4. Filtration kinetics

Expressed as a volumetric permeate flow through 1 m$^2$ of the membrane under given conditions (temperature and pressure)

$$l \cdot h^{-1} \cdot m^{-2}$$

Affected by the permeability and pore density (porosity)

Low permeability can be compensate by higher membrane area

$$mass\_\text{flow} = area \cdot \frac{driving\_\text{force}}{resistance}$$
Filtration theory:

Pressure-driven processes:

driving force = pressure gradient

Pressure drop: \( P_T = P_F - P_P \)

Osmotic pressure within membrane: \( \Delta \pi = \pi_F - \pi_P \)

Real driving force: \( = P_T - \Delta \pi \)

Driving force of the process: \( = P_T \)
Concentration polarization:

Higher concentration of components in boundary layer close to the membrane comparing to bulk

- Forming of concentration profile – under extreme conditions – gel or precipitate formation, secondary membrane
- Increased membrane resistance
Concentration polarization:

\[ \langle V \rangle = \frac{1}{L} \int_0^L v(x) \, dx \]
Pressure-driven membrane processes

Driving force = pressure gradient

Real driving force: reduced by pressure drop in polarization layer, secondary membrane or gel layer

- Convective flow $J_s$
  \[ J_s = J \cdot c_1 \]

- Diffusion velocity (neglected concentration gradient $c$)
  \[ J_s = D \cdot \frac{dc}{dx} \]

- Filtration equation:
  \[ -G \cdot c_2 + D \cdot \frac{dc}{dx} + G' \cdot c_1 = 0 \]

Permeate flow  Diffusion  Convection
5. **Discharge, fouling, membrane cleaning**

Discharge = permeate flow \((l.h^{-1}.m^{-2})\)

Permeate flow rate drop within the filtration – problem!

The drop is caused by:
- concentration polarization
- silting of membrane pores called **fouling effect**
Factors influencing fouling effect

a) Membrane properties
- Pore size (permeability)
- Active layer thickness
- An affinity of dissolved components for the membrane

b) Character of filtered medium
- Viscosity
- Ionic strength
- pH
- Density
- Concentration
- Reactivity of molecules with the membrane
- Shape and size of separated molecules
- Sample pre-treatment – precipitation, addition of ballast material, pre-filtration (to improve the size ratio between molecules and pores)
Membrane purification

c) Conditions of process operation

- Pressure (increasing during filtration, consider irreversible fouling! – limit pressure)
- Temperature
- Hydrodynamics (character of a flow along membrane) – maintain turbulent flow:
  - Pulsation, ultrasound, air bubbling
  - Back-flushing (asymmetric and composite membranes – a risk of active layer detaching)

Membrane purification

- Back-flushing
- CIP (Cleaning in place) chemicals, detergents, high temperature
- Steam sterilization (ceramic)
- Chemically: ozone, Cl₂ – corrosive action, NaClO, HNO₃, NaOH – ceramic membrane
- Mechanically (after removal, sheet membranes)
- Enzymatically
Pure water flux $J_{v}$

Importance:
- To estimate an efficiency of membrane cleaning
- A ratio of pure water flux before filtration and after membrane cleaning should be less than 20%

Definition:
Permeate flow during filtration of pure water at 20 °C and given pressure calculated on 1 m$^2$ of membrane area:

$$J_v = \frac{J_P \cdot k_t}{S}$$

$J_v$ pure water flux (l.h$^{-1}$.m$^{-2}$)
$J_P$ permeate flow
$k_t$ temperature coefficient (20 °C)
$S$ membrane area (m$^2$)
Filtration efficiency

- Permeate and retentate properties
- Analytical methods
- Concentration of feed

Concentration factor / ratio
- VCR (VCF) volumetric
- MCR (MCF) mass

Definition:

\[ VCR = \frac{V_F}{V_R} \]

- \( V_F \) feed volume
- \( V_R \) retentate volume
Separation efficiency – Rejection, retention

Properties of permeate and rententate

Analytical methods

**Rejection factor R**
Expresses a relationship between concentration above and under the membrane

\[ R = 1 - \frac{c_{downstream}}{c_{upstream}} \]

\( c_{downstream}, c_{upstream} \) concentration of component \( (i) \) under, respectively above, the membrane

**Apparent rejection** – if \( c_{upstream} \) equals to the concentration in the bulk

**Intrinsic rejection** – if \( c_{upstream} \) equals to the concentration at the membrane surface

**Retention factor r**
Refers to feed and permeate

\[ r = 1 - \frac{C_iP}{C_iR} \]
A choice of separation process

Permeate flux ★ Separation efficiency

Determine demanded properties of the product
Define required purity
- 90 % industrial enzymes, organic acids,
- 99 % sugar solutions
- 99.9 %
- 99.99 % vaccines
Physical and chemical properties (stability !)

Define initial properties of mixture
Composition, chemical and physical properties, raw material properties, etc.

Choose the process
Different properties of products and contaminants
Use different physico-chemical properties of both
Remove the highest concentration of pollutants at the beginning
The most efficient process should be among first
The most expansive and demanding process should be among latest
6. Membrane techniques

Terminology:

**Diffusion**

= a movement of molecules in liquid phase in concentration gradient (from higher concentrated areas to the lower concentrated ones)

**1st Fick law:**

Describes a flow of liquid through the membranes ($J$), which is reciprocal to the concentration gradient ($dC$) along the membrane ($dx$), where $D =$ diffusion coefficient (diffusivity):

$$J = - \frac{D \cdot dC}{dx}$$
**Dialysis**

A transport of small molecules (dissolved in liquid) across the membrane (from hypertonic to hypotonic media); kidneys

driving force: concentration gradient

**Osmosis**

A transport of solvent across the membrane, which retains dissolved molecules (from hypotonic to hypertonic media)

driving force: chemical potential gradient

www.visionengineer.com/env/reverse_osmosis.shtml
Reverse osmosis (RO)

- A process reversal to osmosis.

- Driving force: pressure gradient through the membrane, needs to be higher than osmotic pressure ⇒ high working pressure (3 – 10 MPa).

  $p_{\text{effective}} > p_{\text{osmotic}}$

- Separation of particles of $10^{-4} \ \mu m = $ only solvent molecules permeate through the membrane

www.visionengineer.com/env/reverse_osmosis.shtml
Pressure-driven membrane processes (MF, UF, NF a RO)

- Conventional filtration - separation of particles bigger than 10 \( \mu \text{m} \).
- **BUT**: comparing to the conventional filtration, where only hydrostatic pressure is needed as a driving force (or maximum pressure of 0.1– 0.5 MPa) - membrane filtration (UF, NF and RO, especially requires higher pressure gradients).
- The smaller pore size, the higher pressure gradient is needed.
Separation aspects of membrane processes

- **Reverse Osmosis (RO)**: 30-60
- **Nano Filtration (NF)**: 20-40
- **Ultra Filtration (UF)**: 1-10
- **Micro Filtration (MF)**: <1

- **Bacteria, fat**
- **Proteins**
- **Lactose**
- **Minerals (salts)**
- **Water**

- **Pressure Bar**
- **Membrane pore size μm**

- **Feed**
- **Permeate (filtrate)**
- **Retentate (concentrate)**
**Microfiltration (MF)**

- Separates particles within the range of $10 - 10^{-1}$ μm (i.e. bacteria, yeasts, suspended solids, high molecular substances; M$>10^6$)
- Particles bigger than $5 - 10$ μm are better to separate by conventional filtration (dead-end filtration).
- Pressure difference needed: 0.02 do 0.5 MPa
- **Refining technique**, suspended solids are separated from dissolved substances.

**Ultrafiltration (UF)**

- Separates particles within the range of $10^{-2} - 10^{-3}$ μm (i.e. bacteria, viruses, colloids, macromolecular substances, MWCO 5000 – 500 000)
- Pressure difference needed: 0.1 do 1 MPa
- A technique for mutual concentration and fractionating of molecules or fine colloid suspensions
- **A sieving effect** is a separation mechanism of both processes (MF and UF).
Nanofiltration (NF)

Relatively new medium pressure membrane process for separation of compounds within a size of $10^{-3} - 10^{-4} \mu m$.

Separation mechanism:

1. sieving effect (large molecules, e.g. sucrose)
2. electrostatic forces between membrane and particles present in solution (ion separation).

Most of commercially produced NF membranes are negatively charged.

NF membranes separate dissociated compounds from non dissociated (e.g. organic acids pass the membrane more easy at low pH, but are retained at high pH in a form of their salts, MWCO < 500).

Membrane cut-off expressed as molecular weight or in Daltons

Operation pressure 2 - 4 MPa
NF phenomena

- The separation mechanism of NF is not totally explained
- Single salt rejection: the higher is the salt concentration the lower is the salt rejection: NF membranes negatively charged – polarization layer is formed (and the effective charge of the membrane is hidden and co-ions can easily pass through the membrane)
- Ion hydration (solvation) affects the separation: e.g. NaNO$_3$ retention is lower than the one of NaCl because of higher hydration of NaNO$_3$ molecule in water solution.
- High viscosity caused by salt or organic molecules prevents from the back diffusion in the concentration polarization layer and ions cumulate in permeate.
- Donnan effect – observed at cheese whey NF (at high VCR) – membrane showed a negative rejection of Cl$^-$ which preferably gathered in permeate: Proteins and other oraganic compounds are concentrated above the membrane (at pH 6.2 occurs gel formation and negatively charged layer). This enhance the cation transport through the membrane. Due to the electroneutrality principle, some anions must pass the membrain as well to keep the electro-neutrality – only the smallest one can pass (even against the concentration gradient; (Cuartas-Uribe, 2006).
Cut-off of pressure-driven membrane processes
Pervaporation (PV)

Mixture separation due to the evaporative process through the porous membrane - a selective barrier between two phases:

- Liquid feed – wet side of the membrane – swelling (atmospheric pressure)
- Gas permeate – dry side of the membrane – almost dry (low pressure of vapours)

**Principle** – phase change
1. sorption
2. diffusion
3. desorption and evaporation

**Driving force:** \( \Delta \mu_i \) expressed as \( \Delta p_i \)

http://chemelab.ucsd.edu/pervap/
Pervaporation (PV)

Driving force: chemical potential difference (expressed as a partial pressure), the pressure behind the membrane is lower, which causes evaporation followed by condensation of vapours.

Separation mechanisms: different diffusivity

Separation of volatile compounds (hexane, toluene, ethanol) from liquid mixtures (dehydration of organic solvents), separation of azeotropic mixtures, pollutants and impurities removal, solution concentration

PV membrane:

Composite membranes (active layer)

Hydrophobic membranes – separation of organic solvents (polysulfone, polydimethylsiloxane, polyamide)

Hydrophilic membrane – polar solutions (water, water vapours) – glass, crystalline polymers of hydrophilic nature)
Pervaporation set-up

Modules - membranes: Capillary, hollow fibre, planar, spiral wound, tubular

Minimal $p_{ip}$:
1. Permeate side – maintain a vacuum (20 – 30 mbar)
2. Permeate side purified by sweeping gas – removal of desorbed compounds
3. Temperature reduction on permeate side – lower $p_i$ of component i (-20 °C, opt. $\Delta T = 50$ °C)

The effect of temperature
- Permeate side - latent heat of vaporization causes cooling
- Isothermal separation ($t_F = t_P$) the flow profile through the membrane is shorter – faster process.
Gas permeation

An analogue of pervaporation, but uses **non-porous membranes**

The same phase on both size of the membrane (gas)

Concentration gradient is provided - sweeping gas

Separation mechanism:
- different velocity of gas permeation (sorption, diffusion, sieving effect, desorption)

Feed (higher pressure)

Permeate (lower pressure)
Membranes for gas permeation

Composite structure
Porous PS (polysulphone) coated by thin layer of rubber (PDMS; polydimethylsulphoxan) placed on macroporous support
  PDMS – low selectivity, high permeability
  PS – reversal

Applications:
- Separation of CO$_2$, CH$_4$ from natural gas and biogas
- H$_2$S removing from natural gases
- N$_2$ – O$_2$ separation
- Gas drying (water removing)
- Separation of organic pollutants from air
Membrane distillation (MD)

Uses both distillation and membrane separation – porous hydrophobic membrane (permeable for water vapours but not for liquid water)

Driving force: temperature and pressure gradient

Principle:
- One side of the membrane: liquid is heated – evaporation, vapors pass through
- Other side: cooling – vapor condensation – water removing

The separation is influenced only by the equilibrium liquid-vapours (the membrane has no effect):
- Limit – unsuitable for azeotropic mixture separation (azeotropic point = identical composition of gas and liquid phase)
- Necessary requirement – the membrane must not be sodden – pore blocking, application for hydrophobic solutions

Velocity of permeation is given by $\Delta t$ – high $\Delta t$ ensures speed and selectivity
Membranes for the membrane distillation

- Hydrophobic (non-polar)
- Microporous
- Material: PTFE (polytetrafluoroethylene = teflon)
  PP (polypropylene)

Applications

Separations
- Mixtures EtOH – water (up to 30 - 40 vol. %)
- Water solutions of salts – desalination (e.g. water for heating systems)
- Sea water desalination

Drawbacks
- Low selectivity
- Limited application