Separation and purification techniques

I. Membrane processes in electric potential gradient

II. Application of membrane separation processes in food industry and biotechnologies

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7. Membrane separation in electric potential gradient

Principle:
1. Motion of charged particles (dissociation in water) in an electric field (one of the compounds must be electrolyte)

2. Particle transport through the membrane called ion-exchange membranes

Membrána usually contains only one type of ions
**Counter-ion** – carries the opposite charge than the one fixed in the membrane
**Coion** – carries the same charge as the one fixed in the membrane

Driving force:
Electric potential difference
Ion-exchange membranes

- **Cation-exchange** – motion of cations (sulfite group –SO$_3^{2-}$, carboxyl group –COO$^-$)
- **Anion-exchange** – motion of anions (tertiary amines N+ (CH$_3$)$_3$)
- **Bipolar (amfoteric)** – contain ionogenic groups of both types; compartment or mosaic structure

**Heterogenous** – older, polymer + ion-exchanger, higher thickness – resistance

**Homogenous** – newer, polymer containing ionogenic groups, thin, high capacity ⇒ high ion selectivity

**Membrane properties:**

- High ion selectivity (capacity – number of bounded ion groups)
- High electrical conductivity
- Mechanical properties: cross-linked polymer, swell (in water)
- Membrane fouling – membrane poisons (irreversible bound between the molecule and the membrane)
**Ion transport principle**

Concentration of ions in the membrane

Donnan equilibrium:

\[ c_{\text{FIX}} + \bar{c}_- = \bar{c}_+ \]

\[ \bar{c} = \text{mobile ions} \]

Non ideal membrane contains also mobile ions

\[ \bar{c}_- \times \text{ideal membrane} \]

**Electroneutrality principle must be maintained**

Coulometric efficiency of the membrane is given by transport numbers: Penetration of co-ions \( \rightarrow \) lower separation effectiveness

\[ \bar{t}_+ = 1 - \bar{t}_- \]
Flow Q on ion-exchange membrane

Limiting current:
High $\dot{Q}$ (due to high potential)
Transport of ions towards the membrane is faster than the diffusion and convection flow:

$I > I_{\text{lim}} \Rightarrow$ increased $R$

higher resistance – dissipative energy (high temperature, water decomposition (electrolysis))
Electrodialysis - Industrial application

- Low-molecular weigh charged substances (desalination - potable water, soil desalination - $\text{Na}_2\text{SO}_4$, salt production, regeneration of rinsing solution from industry – Ni, sea water desalination)
- Separation of inorganic and inorganic acids, reducing of acidity of fruit juices and concentrates
- Protein purification (serum, vaccine, enzymes)
- Regeneration of chemical agents

http://w3.bgu.ac.il/ziwr/desalination/images/electrodialysis.gif
Electrodialysis - principle:

NaCl feed

Anode

Cl\(^-\)

KA

KA

Desalinated solution

Concentrate

AA = Anion-exchange membrane

KA = Cation-exchange membrane
Membrane electrolysis (ME)

- **Electrochemical process using membranes**
- **Anodic and cathodic compartments divided by membrane**
- **Redox reactions run directly with electrons from electrode:**
  - No redox agents (chemicals) are used
  - No waste redox agents are formed
- **Reaction kinetics is managed and operated by the electric current**
- **Usually mild reaction conditions**
- **Energetically demanding processes run at higher potential**

**Applications:**

- Production of concentrated solutions (eg. NaOH from NaCl)
- Production of organic acids from their salts present in the fermentation broth (lactic acid, acetic acid, citric acid, gluconic acid, etc.)
- Production of inorganic acids from their salts (HCl, HNO₃, H₂SO₄)
Membrane cell for electrolysis

Production of Cl₂, H₂ and NaOH from NaCl:
- **Anode** – Cl⁻ ions oxidised to Cl₂
- **Cathode** – water hydrolysis – formation of H₂ and OH⁻ ions

\[ \text{Na}^+ \text{ passes through the membrane to the cathodic compartment – reaction with OH}^-\]

**Reactants:** NaCl and water

**Products:** gases Cl₂, H₂, NaOH and depleted NaCl

http://wps.prenhall.com/wps/media/objects/602/616516/Chapter_18.html
Membrane electrolysis

Cl\textsuperscript{-} ions come to **anodic compartment**: high concentration of Cl\textsuperscript{-} provided by addition of salt - CaCl\textsubscript{2}.

**Cathodic compartment**: even low concentration of HCl is sufficient as a source of Cl\textsuperscript{-} ions

Anion-exchange membranes destroyed by oxidising agents ➜ **BUT** new chlorine resistant membranes are developed recently.
Salt recyclation and their distribution among acids and bases

Example:
Closed loop of chemical processes:

Sodium sulphate comes to the solution of sulphuric acid and sodium hydroxide

A combination of electrolysis and electrodialysis in anion-exchange membrane

http://www.bci.uni-dortmund.de/tca/web/de/textonly/content/mitarb/akad_oberrat/akad_oberrat.html
8. Preparative separation in electric field gradient

Processes using membranes:
- Transport depletion
- Electroosmosis
- Forced-flow electrophoresis

Electrokinetic processes:
- Capillary zone electrophoresis
- Elektrophoresis
- Isoelectric focusing
- Isotachophoresis
Transport depletion

**Principle:**
- Electrodialysis – anion exchange membrane replaced with electroneutral ones
- AE membranes cannot be used $\Rightarrow$ fouling, low effectiveness

**Application:**
- Separation of organic substances, colloids

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Electroosmosis

Motion of liquid due to applied potential:
- Cation-exchange membranes – e.g. fused silica, silanol groups (Si-OH), negatively charged (Si-O⁻).
- Electrical double layer is formed (positively charged)
- Potential over the membrane – cations attracted by the cathode – motion through the membrane
- Membrane surface – solvation – molecules of water move as well
- Low pH → the capillary loses its negative charge → the electric double layer is thinner
- Applications – micropumps (low fluxes)

http://www.stanford.edu/~dlaser/electrokinetics_and_eof/electrokinetics_and_eof.htm
Forced-flow electrophoresis

Several membranes of different cut-off
Arrange according to cut-off (sieving effect)
Usually three-compartment cell

Zone electrophoresis

Different ion mobility in electric field $\mu_i$
Electric field – driving force, increases the speed
Mobility – charge size, molecule size, molecule shape, temperature and concentration
Anticonvective medium: paper, gel (polyacrylamide)
**Electrophoresis**

Condition of separation: different mobility $\mu_L > \mu_A \ldots > \mu_i > 0$

L – leading electrolyte

Quantitative and qualitative analysis – bend width, distance of the zone

**Isoelectric focusation**

Separation of polyamfolytes – gradient of pH and electric field

Sample dispersed in the cell

Separation according to the isoelectric point

Alcaline pH

Acidic pH
Isotachophoresis

Similar to capillary electrophoresis
Two electrolytes: leading L and terminal T
Capillary
Quantitative and qualitative analysis
Motion of ions in a constant electric field
Constant velocity

Applications:
- Inorganic ions (anions, cations – heavy metals)
- Organic acids (long-chain fatty acids, amino acids)
- Amines
- Others: aspartame, fertilizers, pesticides, preservatives, colorants, medicine, alkaloids.
Izotachophoresis - analysis

Detection: Electric conductivity, UV, temperature
Izotachophoresis - apparatus
9. Application of membrane processes in food industry and biotechnologies

General applications:

- Removing of high molecular compounds
- Purification and decolourization
- Primary purification and concentration before following technological steps
- Separation of products and valuable substances from wastes or outlets that can be consequently processed
- Cold sterilization of products
- Waste water treatment
- Replacement of conventional filtration techniques using filtration aids (e.g. diatomaceous earth – kieselguhr)

Advantages:

- No or mild changes of sensory properties
- The activity of biological active substances is maintained
- Nutrition values unchanged
- Reduced operating costs during food production (elimination of heat processes; e.g. distillation, evaporation)
Dairy industry

- The biggest application possibilities of membranes among food technologies
- Approximate estimation of a filtration area: 300,000 m² worldwide
- UF and RO most common, MF occasionally

Particle and molecule size profile of milk and whey

Possible application of MF and UF in dairy

- Fat and bacteria removing from milk and whey
- Separation and concentration of high-molecular components of milk and - UF (retentate - proteins, fat and salts bound on proteins)


*Figure 8.5. Processing options with UF and MF membranes in the dairy industry (adapted from Cheryan and Alvarez 1995).*
Possible application of MF, UF and RO in dairy

- Production of whey protein concentrate – defatted whey is concentrated by UF; membrane retains proteins, remaining fat. Lactose, salts and other low molecular components pass into permeate.

Concentration of liquid fractions: milk, whey (WPC = Whey Protein Concentrate; 82-85%, WPI = Whey Protein Isolate; 90%)

- Desalination of whey by NF

- Lactose isolation

Figure 8.8. Sequential membrane processing in the dairy industry (adapted from Cheryan and Alvarez 1995).
Possible application of membranes in dairy

**Profitable:** to use UF before milk coagulation and precipitate retentate only – reduced consumption of milk, lactic culture and rennet.

**Drawbacks:**
- Higher protein-content – higher milk viscosity – worse addition of rennet and lactic culture – worse cheese texture
- Retentate recirculation – partial homogenization of fat – worse texture of hard cheese

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*Figure 8.8. Comparison of traditional and UF methods of manufacturing cheese (adapted from Maubois 1989; Maubois et al. 1969).*
Filtered milk can be used for production of many other products – condensed milk, dried milk, cheese, cottage, yogurt, ice cream, etc.

UF basic process for cheese production

Standardization of protein and fat content using UF – stable quality

**Figure 8.9.** Possible options for incorporating UF in the manufacture of various types of cheese (adapted from Koch Membrane Systems product literature).
## Beverage industry – fruit and vegetable juices

### Manufacture of apple juice by traditional and UF process

<table>
<thead>
<tr>
<th>UNIT OPERATION FOR FRUIT JUICE</th>
<th>CONVENTIONAL PROCESS</th>
<th>ULTRAFILTRATION PROCESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUSPENDED SOLIDS REMOVAL</td>
<td>Centrifugation</td>
<td>None</td>
</tr>
<tr>
<td>PECTIN/STARCH HYDROLYSIS</td>
<td>Enzyme Treatment</td>
<td>Not critical</td>
</tr>
<tr>
<td>COLLOID AND HAZE REMOVAL</td>
<td>Fining Treatment</td>
<td></td>
</tr>
<tr>
<td>FINING AGENT REMOVAL</td>
<td>Diatomaceous Earth Filtration</td>
<td>Membranes</td>
</tr>
<tr>
<td>FINAL FILTRATION</td>
<td>Polish Filtration</td>
<td></td>
</tr>
</tbody>
</table>

**CLARIFIED JUICE**

<table>
<thead>
<tr>
<th>Yield</th>
<th>80 - 94%</th>
<th>95 - 99%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process time</td>
<td>12 - 36 hours</td>
<td>2 - 4 hours</td>
</tr>
</tbody>
</table>

*Figure 8.78. Manufacture of apple juice by traditional and UF processes.*

Beverage industry – production of fruit and vegetable juices

- UF:
- Cold sterilization and juice fining
- Pectinase filtration
- Haze removing

**Example:** apple juice; ceramic membranes


*Figure 8.79.* Typical schematic for producing clear fruit juices. Operations on the left side are used in the conventional method. The membrane method is depicted on the right side.
Production of fruit juice concentrate

- Combination of UF and RO:
  - UF – cold sterilization and juice fining
  - RO – concentration before evaporation; permeate from UF can be consequently concentrated using RO
- Concentration of liquid fractions: fruit juices, coffee extract (RO)

Figure 8.85. Producing high-strength fruit juice concentrates by ultrafiltration and reverse osmosis (adapted from Cheryan and Alvarez 1995).
Meat processing and food preservation

- UF – animal blood serum concentration
- UF of protective atmosphere for meat product packaging (removing of microorganisms, moisture, solids)
- Removing of oxygen and its replacement by nitrogen (permeation) – increasing of durability of packed meat products
- Purification and isolation of proteins from brines
- Concentration of egg whites and whole eggs
- UF – concentration and desalination of gelatin protein before evaporation


Figure 8.51. Membrane process in gelatin manufacture (adapted from Koch 1984).
Starch industry

- Processing of starch syrups (starch hydrolysis to glucose and enzymatic glucose isomerisation to fructose)
- UF – separation and concentration of enzymes – reutilization.
- Purification of hydrolysates - decolourization, fat removing (corn syrups), separation of proteins, colloids and suspended solids.
- Waste water treatment

Possible application of membranes for starch syrup clarification

MF in starch hydrolysate clarification

Parameters:
Starch syrup of 95 DE filtration area 2 x 442 m²
Investment costs: 2,08 mil.


Operating cost comparison

<table>
<thead>
<tr>
<th></th>
<th>MF</th>
<th>RVPF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane replacement cost</td>
<td>282,624</td>
<td>0</td>
</tr>
<tr>
<td>Diatomaceous earth</td>
<td>0</td>
<td>136,0779</td>
</tr>
<tr>
<td>Disposal cost of diatomaceous earth</td>
<td>0</td>
<td>204,117</td>
</tr>
<tr>
<td>Power consumption</td>
<td>186,121</td>
<td>160,355</td>
</tr>
<tr>
<td>Labor</td>
<td>25,200</td>
<td>63,000</td>
</tr>
<tr>
<td>Cleaning</td>
<td>3,533</td>
<td>0</td>
</tr>
<tr>
<td>Maintenance</td>
<td>19,930</td>
<td>40,000</td>
</tr>
<tr>
<td>Total operating cost</td>
<td>517,408</td>
<td>1,828,251</td>
</tr>
</tbody>
</table>
Membrane reactor for starch hydrolysis

Drawbacks of conventional (batch) technology:
- Low yields
- High volumes of reaction mixtures (high investment costs)
- Product variability (every batch is different)
- Low exploitation of enzyme

Membrane reactor – production of HFCS (high fructose corn syrups) hollow fibres
α-amylase and glucoamylase added into substrate and filtered

Isolation and concentration of proteins from soya, oats and wheat

Gluten production:

Gluten = a mixture of proteins in cereal kernel

Gluten of low quality (containing salts, colorants or aroma from cereals) – undesirable products need to be removed by extraction in alkali solution

Extract → UF (low molecular compounds pass into permeate).


Figure 8.49. Separation of corn proteins by solvent extraction and membrane technology (Cheryan 1992, 1994).
Sugar industry

- Sugar production = demanding process (technology and energy) – membranes might bring high energy savings
- BUT the limitations: high viscosity, density and osmotic pressure of sugar juices
- UF – purification of thin juice (sterility, low colorant content)
- RO – concentration of thin juice before evaporation (energy savings)
- RO – of water obtained by pressing of extracted sliced beet (so called press water) – sterility, removing of beet tissue, colloids and proteins
Possible membrane application in the sugar industry

1. Pressed pulps
2. Molasses
3. Thin juice
4. Extracted pulps

Diagram:

- Beets
- SLICER
- EXTRACTOR
- PRESSING
- EVAPORATION
- DECOLORIZATION
- CRISTALLIZATION and CENTRIFUGATION
- REGENERATION
- FILTRATION
- HEATING
- LIMING
- CLARIFICATION
- EPURATION
- CO₂ FIRST CARBONATION
- 2nd CARBONATION
- SO₂

Flowchart details:

- Press water
- Raw Juice
- Extracted pulps
- HEATING
- LIMING
- CLARIFICATION
- EPURATION
- CO₂ FIRST CARBONATION
- 2nd CARBONATION
- SO₂
- HEATING
- FILTRATION
Purification and concentration of press water

Extracted pulps

PRESSING

Pressed pulps

Press water

PURIFICATION

RO 1

RO 2

Retentate to low grade sugar crystallization

Permeate to extraction

R_{NF}

R_{NF}

To low grade sugar crystallization

R_{RO}

To waste

P_{NF}

P_{RO}

Permeate to extraction
The scheme of non-waste technology

Connection of sugar technology with fermentation
Brewing and wine making technologies

- **UF** – juice fining before fermentation (= removing of colloids, high molecular substances, tannin, suspended solids, polyphenols, and microorganisms)
- Cross-flow filtration of hopped wort (a supplement to vortex separators)
- **MF** – after fermentation (= yeast separation, replacement of candle filters and filtration using filtration aids, diatomaceous earth)
- **UF** of wine and beer – improving of the product stability (replacement of candle filters and filtration using filtration aids, diatomaceous earth)
- Pervaporation - non-alcoholic beer
Removing of CO\textsubscript{2} from beer
Purification, drying and storage of CO\textsubscript{2}
Aeration of hopped wort

gas permeation (dense polymeric membranes)

Membrane applications in wine production

There are several potential benefits of MF and UF in winemaking (Figure 8.86). UF can be used either before the fermentation (i.e., for clarifying

Figure 8.86. Membrane applications in wine production. The first UF step removes microorganisms, colloids, and high molecular weight materials. The second membrane step (MF) removes yeast. The third membrane step is a final filter; it could also be a sterilizing microfilter.
Biotechnologies, medicine and biochemistry

Large potential for membrane processes!

Expectant growth of membrane application market in natural sciences within 2002-2009 (millions of $)
Biotechnologies

- Bioreactors – enzymatic and microbial conversion (immobilization)
- Tissue culture reactors
- Production of high purity water (so-called ultrapure water)
- Filtration of gases entering the bioreactors (sterility)
- Filtration of exhaust gases from bioprocesses
- Sterilisation of media for cell cultures

Cell immobilization in the hollow fiber reactor

Figure 8.66. Schematic of plug flow membrane reactors: Top: hollow fiber beaker reactor; the biocatalyst can be trapped either in the shell side or the tubes; Bottom: tubular type hollow fiber bioreactor. The biocatalyst is loaded into the shell side through the permeate ports. Feed is pumped through the tube under pressure and the product stream removed through the retentate outlet. The reverse (i.e., tube-side loading of biocatalyst) is less common.
Biotechnologies a pharmaceutical industry

Separation of microorganisms and proteins (MF, UF):
- Isolation of cells from fermentation broth

Purification of products after fermentation (MF, UF, NF, RO, membrane electrolysis = removing of organic acids, ED):
- Isolation of metabolites from medium – antibiocs production (Penicillin, Bacitracin, Cephalosporin, Streptomycin, Tetracycline; replacement of rotary vacuum filters – improved yields, reduction of processing costs)
- Industrial enzyme production (Celullase, peroxidase, protease; concentration of enzymes before further downstream processes)
- Purification and concentration of amino acids
- Production and purification of proteins
- Production of organic acids (lactic, butyric, citric and acetic acids)
- Vitamin production, vaccines, monoclonal antibodies and pharmaceuticals
- Removing of viruses during pharmaceutical production
- Concentration and demineralization of blood plasma
- Concentration of peptides

Next membrane applications:
- Sample immobilization for microscopy
- Transfer, immobilization and detection of DNA, RNA and proteins