Membrane technologies for water purification

Mathias Ulbricht

Lehrstuhl für Technische Chemie II
and Center for Water and Environmental Research,
Universität Duisburg-Essen, 45117 Essen, Germany
Membrane technologies

- Microfiltration: > 0.1 μm
- Ultrafiltration: 100 - 2 nm
- Nanofiltration: < 2 nm
- Reverse Osmosis: < 0.8 nm

→ potential absolute barriers for water purification
Membrane technologies

**Advantages of membrane technologies**
- unique separation principle – perm-selective barrier
- low energy consumption
- mild conditions
- no additives (chemicals)
- continuous processes easy
- scale up (or scale down) easy

**Organisation / integration of more complex processes**
- hybrid separation processes
- membrane reactors,…

**Limitations**
- often low selectivity or flux („trade-off“) of available membranes
- concentration polarization
- membrane fouling
- up-scaling more or less linear
Porous membranes

... with meso- or macroporous barrier

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<table>
<thead>
<tr>
<th>Pore or particle size (nm)</th>
<th>NF</th>
<th>UF</th>
<th>MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10000</td>
<td></td>
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</tbody>
</table>

- **NF** (Nanofiltration)
- **UF** (Ultrafiltration)
- **MF** (Microfiltration)

- **viruses**
  - "cut-off" of standard hemodialysis
  - removal of smallest viruses
  - standard sterile filtration

- **proteins**
- **bacteria**

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Polymer membranes

... via nonsolvent-induced phase separation (NIPS)
... established large-scale industrial processes
Composite membranes

... with microporous barrier

... via interfacial polymerization → very thin barrier layer (< 50 nm)

→ highly efficient in industrial scale: < 10 EUR/m²
Membrane technologies

Sea water desalination with reverse osmosis

currently:

*total >25.000 Mio m$^3$/year*

all recent installations RO (except Gulf c.)

Membrane technologies

Sea water desalination with reverse osmosis

\[-d(\Delta G_{\text{mix}}) = -RTlna_w dn_w = \Pi_s \overline{V} dn_w\]

reduced energy consumption:
- higher-permeability membranes
- energy recovery devices
- more efficient pumps

very large scale RO
\[\rightarrow < 0.5 \text{ EUR} / \text{m}^3\]

Sea water desalination with reverse osmosis - Pretreatment

**Intake**

- **Screen**
  - Disinfection
  - Coagulation / flocculation agents
  - pH adjustment

**Flocculation**

- **Multimedia filtration**
  - Dissolved air flotation (+ filtration)
  - Ultrafiltration

**Cartridge filtration**

**Alternative**

- Antiscalant agents
- Dechlorination
- RO

**Membrane technologies**

- Sea water desalination with reverse osmosis
- Pretreatment
- Coagulation / flocculation agents
- pH adjustment
- Dissolved air flotation (+ filtration)
- Ultrafiltration
- Antiscalant agents
- Dechlorination
- RO
Integrated membrane system: „UF in – RO out“

Source: KINDASA Water Services, Jeddah
Membrane technologies

Membrane bioreactor (MBR)

ZW-500a (1997)
- Packing Density 153 m²/m³
- Avg. Daily Flux 20 L/m²/h
- Capacity 180 m³/d

ZW-500c (2000)
- Packing Density 183 m²/m³
- Avg. Daily Flux 22 L/m²/h
- Capacity 270 m³/d

ZW-500d (2003)
- Packing Density 162 m²/m³
- Avg. Daily Flux 27 L/m²/h
- Capacity 960 m³/d

ZW-500d (2008)

Increasing Performance
Decreasing $/m³

Waste water recycling:
Options for integrated membrane technologies

MBR
Using microfiltration or ultrafiltration (or nanofiltration?)

RO

Disinfection (UV or visible?)

Potable water

e.g.: NewWater, Singapore

efficient and safe removal of:
- micropollutants
- viruses
- bacteria

Nanofiltration

... for removal of micropollutants

Fig. 7 – Influence of NOM alginate on permeate flux of nanofiltration membrane SR3 (transmembrane pressure 10 bar, pH = 7.5, feed concentration of pharmaceutical 500 µg/L).

→ limited selectivity
→ significant reduction of flux and selectivity by fouling

Membrane technologies

Challenges

- higher permeability
- higher selectivity
- higher stability

- minimize concentration polarization
  (i.e., accumulation of rejected species close to membrane surface)
- minimize fouling
  (i.e., reversible or irreversible deposition on membrane)
- minimize cleaning

→ smaller foot-print → lower investment cost
→ less material
→ less energy → lower operating cost
→ less/no cleaning chemicals
Advanced membranes

... via nanotechnology

- permeability,
- selectivity,
- robustness,

- material cost,
- scalability,
- compatibility with existing manufacturing infrastructure

Graft copolymerization of anti-fouling layers on UF membranes

UV wavelength: > 300 nm
UV intensity: 35 ± 5 mW/cm²

monomer (PEGMA)
PES UFM (100 kDa)
grafted ultrathin
hydrophilic, flexible
polymer layer

PES-based thin-layer hydrogel composite membrane

PES-based thin-layer hydrogel composite membrane (MWCO 10 kDa)

Thin-layer hydrogels as “protective“ layer on the outer UF membrane surface reduce adsorptive fouling tendency, specific cake resistance and strength of cake adhesion, and contribute to barrier (sieving) properties. “Fine-tuning“ of anti-fouling efficiency and barrier properties is possible via choice of functional monomer (high degree of swelling in water) and cross-linking.

- similar results with proteins, polysaccharides and mixtures thereof.

Hydrogels for antifouling

... from surface grafting to thin-layer composite membranes

common sense: kosmotropic surfaces (PEG, zwitterionic, ...) are best suited, but there are also specific requirements:

with respect to foulants:

biofouling
→ maximize swelling degree

organic fouling
→ exclude biomacromolecules

+ mechanical strength

Initial deposition of *P. fluorescens* F113 on different hydrogels at varied cross-linking

Hydrogels for antifouling

... on polyamide composite NF membranes (NF 270)

after protein filtration (1 hour)

Water permeability reduction

<table>
<thead>
<tr>
<th>Permeability reduction(%)</th>
<th>BSA(pH4.8)</th>
<th>Lys(pH7.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base membrane</td>
<td>0</td>
<td>-10</td>
</tr>
<tr>
<td>BEE-TH/PEGMeMA 12.6%CL</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>BEE-TH/PEGMeMA 1.3%CL</td>
<td>-5</td>
<td>0</td>
</tr>
</tbody>
</table>

➔ largely reduced organic fouling (but function of solute size!)

after biofilm growth (P. fluorescens F113; 2 days)

➔ almost eliminated biofouling

unmodified

polyPEGMeMA

Magnetically activated micromixers for separation membranes

Controlled surface-initiated polymerization and subsequent covalent coupling of Fe$_3$O$_4$ NPs

**Visualization of macromixing**

<table>
<thead>
<tr>
<th>Base membrane (NF 270)</th>
<th>NP functionalized NF 270</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 Hz</td>
<td>![Images for 0 Hz]</td>
</tr>
<tr>
<td>9 Hz</td>
<td>![Images for 9 Hz]</td>
</tr>
<tr>
<td>22 Hz</td>
<td>![Images for 22 Hz]</td>
</tr>
<tr>
<td>30 Hz</td>
<td>![Images for 30 Hz]</td>
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</tbody>
</table>

**PIV:** turbulence only for NP functionalization and medium rotation frequency!

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**Functional hybrids**

Stimuli-responsive nanofiltration membrane

micromixing at the surface reduces concentration polarization

**Table 1. Average Fluxes and Salt Rejections for Control and Modified Membranes at 45 psig (3.1 bar)**

<table>
<thead>
<tr>
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<th>500 ppm CaCl₂</th>
<th>2000 ppm MgSO₄</th>
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<tbody>
<tr>
<td></td>
<td>control</td>
<td>modified</td>
</tr>
<tr>
<td>with field</td>
<td>34.4 ± 0.2</td>
<td>40.4 ± 0.2</td>
</tr>
<tr>
<td>without field</td>
<td>32.5 ± 0.2</td>
<td>34.2 ± 0.2</td>
</tr>
<tr>
<td>Salt Rejection (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filtrate Flux (L/m²·h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>with field</td>
<td>13.4 ± 0.6</td>
<td>9.6 ± 0.7</td>
</tr>
<tr>
<td>without field</td>
<td>12.8 ± 0.6</td>
<td>7.8 ± 0.7</td>
</tr>
</tbody>
</table>

**NF:** significant improvement of flux and salt rejection only for NP functionalization and rotating magnetic field (~ 10 Hz)
Conclusions

Membrane technologies for water purification and recycling are very well established and rapidly growing.

Further efficiency improvements are achieved by integrated membrane processes.
... to the group

Thank you very much for your attention!

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