Membranes Technologies
For Water and Energy Applications

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June 8, 2011
Outline

• Background

• Ongoing membrane research works
  • Fouling
  • Trace organics
  • Membrane fabrication/characterization
  • Osmotic membrane processes

• Summary
What is a membrane?

A **selective barrier** that allows the **separation** of components in a mixture.

Energy input or driving force is required to separate components that otherwise mix spontaneously.

Driving forces:
- $\Delta P$ – pressure difference
- $\Delta C$ – concentration difference
- $\Delta T$ – Temperature difference
- $\Delta E$ – electrical potential difference
Membranes in the water cycle

**Uses:**
- Domestic
- Industrial
- Agricultural
- Ecological

**Sources**
- Raw Freshwater
- Raw seawater

**Water treatment**
- MF, UF, NF
- Conventional treatment
- RO, electrodialysis
- Distillation

**Wastewater treatment**
- Membrane Biological Reactor
- Conventional wastewater plant
- secondary wastewater effluent

**Water reclamation**
- RO
- MF/UF

**Legend:**
- Sources
- Membrane treatment
- Use
- Discharge

**Conventional treatment**
Singapore - a show case for membranes and the water cycle

- WTP 274ML/d
- Desal 136
- NeWater 500 *
- MBR 23
- Barrage

* Includes Changi. Target is 30% reuse by 2011, 45ML/d to indirect potable

Courtesy: Prof. Tony Fane
Newater to meet 40% of S’pore’s needs

2020 goal part of effort to be self-sufficient in water, says SM Goh

By Cassandra Chew

fields if unrolled, into the space of just two pitches.

Almost all this reclaimed water is consumed by industries, whose appetite for it has grown from four million gallons daily for about 20 firms in 2003, to 60 million now for over 360 companies.

Only 2 per cent of Newater produced.
Where are membranes used?

- Removal of CO₂ from natural gas
- Desalination & water treatment
- Dialysis
- Fabrics
- Drug delivery devices
- Fuel Cells
- Membrane Bioreactors (MBR)
- Removal of CO₂ from natural gas
CY’s background

• PhD, Stanford University (2002-2006), James O. Leckie’s “water chemistry” group
• Assistant Professor, (2006-current), Nanyang Technological University
  – School of Civil & Environmental Engineering
  – Singapore Membrane Technology Centre
• IDA Fellow
• FiDiPro Fellow
SMTC  A centre specialized in membrane technology for water and energy applications

http://smtc.ntu.edu.sg
CY’s ongoing research

- Membrane fouling and fouling control
- Trace organics removal
- Membrane synthesis
- Membrane characterization
- Osmotic membrane processes
Membrane Fouling

Pressurized vessel

Cross flow velocity

Feed Water

Concentrate

Insoluble salts
Inorganic colloids
Organic macromolecules
Microorganisms

membrane

Permeate Flux

\[ J = \frac{\Delta P}{\eta(R_m + R_f)} \]

- \( J \) – permeate flux
- \( \Delta P \) – differential pressure
- \( \eta \) – permeate water viscosity
- \( R_m \) – hydraulic resistance of membrane
- \( R_f \) – hydraulic resistance of foulant
Membrane fouling

**Membrane Properties**
- Roughness
- Charge
- Hydrophobicity

**Feedwater Composition**
- Foulant concentration
- pH, ionic strength, Ca$^{2+}$

**Hydrodynamic Conditions**
- Flux
- Cross flow velocity

Tang et al., Advances in Colloid and Interface Science, accepted 2010.
RO/NF membrane fouling

(a) Test conditions:
NF90, 5 mg/L PAHA, 10 mM NaCl, pH7

- 345 kPa (50 psi)
- 690 kPa (100 psi)
- 1034 kPa (150 psi)
- 1379 kPa (200 psi)
- 2069 kPa (300 psi)

Flux (m/day) vs. Time (hours)

Effect of initial flux

ESP3A membrane at increasing initial flux

A: 689.5 kPa 1.2 m/day
B: 1379 kPa 2.0 m/day
C: 2758 kPa 3.8 m/day

Accumulation of PAHA (µg/cm²)

Initial Flux (m/day)

5 mg/L PAHA, pH 7, 10 mM NaCl 4 days

Scale bar for all TEM images

500 nm
Limiting flux for protein

Flux (L/m².hr) vs. Time (hrs)

- P180
- P140
- P110
- P75
- P50
- P25

20 mg/L BSA, pH 7, IS=10mM, CF=9.5cm/s

Wang and Tang, JMS, 2011
Limiting flux for protein

20 mg/L BSA
pH 7,
IS=10 mM,
CF=9.5 cm/s

Wang and Tang, JMS 2011
Limiting flux for protein

Flux @ 96 hr (L/m$^2$.hr) vs. Protein zeta potential squared (mV$^2$)

Wang and Tang, JMS, 2011
Ongoing works on RO fouling control

Fouling Control
1) Use of chemicals to improve RO desalination
2) Membrane modification
3) Pretreatment
4) Optimization of operational parameter to minimize fouling

Spacer Design & Hydrodynamic in Spiral Wound Module
Spacer & hydrodynamics
Ultrasound
Vibration
Aeration
Micropollutants

Organic toxins
- Pharmaceuticals
- Endocrine disruptors
- Pesticides/herbicides
- Disinfection byproducts
- Other emergent contaminants
- ...

Inorganics
- Boron
- Bromide

N-nitrosodimethylamine (NDMA)

Boric acid
Micropollutants

- PFOS

XPS results
BW30 at different contact time

Test conditions: 10 ppm PFOS, 200 psi, 20 cm/s CF, 25C
Borate ion
\( \text{H}_2\text{BO}_3^- \)

Boric acid \( \text{H}_3\text{BO}_3 \)

\[ \text{H}_3\text{BO}_3 = \text{H}^+ + \text{H}_2\text{BO}_3^- \]

Fraction of Boron

**SWRO:** 88-95%

**BWRO:** 38-65%
Experimental and Predicted Boron Rejection

![Graph showing experimental and predicted boron rejection as a function of flux density.](image)

- **Experimental**
  - RO
  - AL-FW
  - AL-DS

- **Predicted**
  - RO: solid line
  - AL-FW: solid triangle
  - AL-DS: solid square

- Pressure conditions:
  - 200 psi
  - 260 psi
## Micropollutants

<table>
<thead>
<tr>
<th>PAEs</th>
<th>M.W. (Da)</th>
<th>Log Kow</th>
<th>Dipole Moment (D)</th>
<th>Volume (A³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl phthalate (DMP)</td>
<td>194.2</td>
<td>1.66</td>
<td>2.80</td>
<td>173.1</td>
</tr>
<tr>
<td>Diethyl phthalate (DEP)</td>
<td>222.2</td>
<td>2.65</td>
<td>2.90</td>
<td>206.7</td>
</tr>
<tr>
<td>Di-n-butyl phthalate (DnBP)</td>
<td>278.4</td>
<td>5.6</td>
<td>2.75</td>
<td>273.9</td>
</tr>
<tr>
<td>Di(2-ethylhexyl)phthalate (DEHP)</td>
<td>390.6</td>
<td>7.3</td>
<td>2.84</td>
<td>441.5</td>
</tr>
</tbody>
</table>

PAEs = Phthalate Acid Esters
Pharmaceuticals

Carbamazepine (CB)

Naproxen (NA)

Ibuprofen (IP)

Diclofenac (DI)
Next generation membranes

**FORWARD OSMOSIS**
Water molecules migrate by natural osmosis, without energy input, into an even more concentrated “draw solution,” whose special salt (green) is then evaporated away by low-grade heat.
*On the market: 2010-2012*

**CARBON NANOTUBES**
An electric charge at the nanotube mouth repels positively charged salt ions. The uncharged water molecules slip through with little friction, reducing pumping pressure.
*On the market: 2013-2015*

**BIOMIMETICS**
Water molecules pass through channels made of aquaporins, proteins that efficiently conduct water in and out of living cells. A positive charge near each channel’s center repels salt.
*On the market: 2013-2015*
Membrane Fabrication

Hollow Fiber Spinning Process

Dope fluid
Bore fluid
Water spray
Flushing bath
Coagulation bath
Syringe pump
Spinneret

Nonsolvent in-flow
Solvent out-flow

Membrane with Different Structures

Polymer
Dope formulation
Unstable region
Metastable
Metastable

Polymer

Solvent
Nonsolvent

K = \frac{D_{n2}}{D_{nl}}

very porous structure
open-cell structure
relatively dense structure

K < 1
K > 1
K < 1
Membrane fabrication

A thin film composite polyamide membrane for forward osmosis applications

Membranes fabricated using layer-by-layer method
Membrane Characterization

Microscopic characterization

AFM adhesion force

Electrokinetic characterization

Contact angle

Infrared

XPS

O (1S)  N (1S)  C (1S)
## Membrane chlorination

### Table. Elements by atomic percent of degraded membranes at 2000ppmhr Cl and pH4

<table>
<thead>
<tr>
<th>Membrane</th>
<th>O (%)</th>
<th>N (%)</th>
<th>C (%)</th>
<th>Cl (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF90</td>
<td>Avg</td>
<td>15.61</td>
<td>10.08</td>
<td>63.71</td>
</tr>
<tr>
<td></td>
<td>STD</td>
<td>0.83</td>
<td>0.58</td>
<td>0.78</td>
</tr>
<tr>
<td>LE</td>
<td>Avg</td>
<td>16.01</td>
<td>10.03</td>
<td>62.99</td>
</tr>
<tr>
<td></td>
<td>STD</td>
<td>1.19</td>
<td>0.64</td>
<td>1.35</td>
</tr>
<tr>
<td>XLE</td>
<td>Avg</td>
<td>15.46</td>
<td>10.23</td>
<td>63.51</td>
</tr>
<tr>
<td></td>
<td>STD</td>
<td>0.46</td>
<td>0.49</td>
<td>1.11</td>
</tr>
<tr>
<td>BW30</td>
<td>Avg</td>
<td>30.55</td>
<td>2.25</td>
<td>64.63</td>
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<tr>
<td></td>
<td>STD</td>
<td>0.79</td>
<td>1.05</td>
<td>1.07</td>
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<tr>
<td>LFC1</td>
<td>Avg</td>
<td>29.95</td>
<td>2.7</td>
<td>64.87</td>
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<tr>
<td></td>
<td>STD</td>
<td>0.77</td>
<td>0.57</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Alternative disinfectants? Alternative membranes?
Other membrane characterization works

1) Feed fouling monitor
   - Adaptation of Integrity Sensor (NTU patent)
   - Dual membrane based sensors to predict feed fouling propensity, *online* monitoring and more sensitive than SDI and MFI

2) Ultrasonic time domain reflectometry (collaboration with MAST, Colorado)
   Based on acoustic properties of medium, provides thickness & density information, *in-situ* method

3) Electrical impedance spectroscopy (collaboration with INPHAZE Australia)
   Based on electrical properties (conductance & impedance) of medium, provides structural information, *in-situ* method
Direct microscopic observation
Reverse osmosis vs. forward osmosis

- Reverse osmosis (RO)
  - Applied pressure $P > \Delta \pi$

- Forward osmosis (FO)
  - Applied pressure $P = 0$

- Pressure retarded osmosis (PRO)
  - Applied pressure $P < \Delta \pi$

Xu et al, JMS 348, 298-309, (2010)
FO desalination

Forward Osmotic Membrane Bioreactor

Advantages of FOMBR
- lower energy requirement
- better water quality for water reclamation
• To provide carbon-neutral biofuels and other useful product (e.g., fertilizer)
• To treat wastewater
• To sequester carbon dioxide
Major Challenges for FO Applications

- **Suitable draw solutions**
  - high osmosis pressure
  - good FO performance
  - easy regeneration
  - non-toxic
  - seawater, RO brine??

- **Optimized membrane**
  - high water flux
  - low solute passage
  - strength
  - stability
Pressure Retarded Osmosis

Figure 1: A simple PRO process for osmotic power harvesting

- Brine in a pressure vessel
- Water flow through PRO, $Q_p$
- PRO membrane
- Wastewater or impaired water
- Turbine generator or other energy recovery devices
## Bench scale PRO tests and optimization

PRO water flux and power density at various conditions

<table>
<thead>
<tr>
<th>Draw (M)</th>
<th>Feed (mM)</th>
<th>ΔP (Pa)</th>
<th>Jw (L/m²h)</th>
<th>Power density (w/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>10</td>
<td>0</td>
<td>7.70</td>
<td>0</td>
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<tr>
<td>0.5</td>
<td>10</td>
<td>3.52E+05</td>
<td>7.20</td>
<td>0.70</td>
</tr>
<tr>
<td>0.5</td>
<td>10</td>
<td>6.45E+05</td>
<td>5.61</td>
<td>1.00</td>
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<tr>
<td>0.5</td>
<td>10</td>
<td>1.15E+06</td>
<td>1.79</td>
<td>0.57</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>0</td>
<td>14.62</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>6.36E+05</td>
<td>12.22</td>
<td>2.16</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>1.19E+06</td>
<td>9.48</td>
<td>3.13</td>
</tr>
</tbody>
</table>
Summary

• Membrane fouling and fouling control
• Trace organics removal
• Membrane synthesis
• Membrane characterization
• Osmotic membrane processes
Thank You

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Acknowledgements

• FiDiPro Programme
  – Tekes
  – VTT
• Funding support from the Singapore Environment and Water Industry Programme Office (EWI), National Research Foundation
• Support from Singapore Membrane Technology Centre
• Students/Post-docs/Collaborators
**Microfiltration**

- Asymmetric structure
- Selective skin layer
- Porous substrate

**Ultrafiltration**

- Asymmetric structure
- Selective skin layer
- Porous substrate
Nanofiltration

- Water
- Monovalent ions
- Multivalent ions
- Organics
- NOM
- Colloids
- Viruses
- Bacteria

Reverse Osmosis

- Water
- Monovalent ions
- Multivalent ions
- Organics
- NOM
- Colloids
- Viruses
- Bacteria

Non-porous skin
Porous substrate