Electrically Conducting Carbon Nanotube - Polymer Composite Membranes for Fouling Prevention

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Membrane Fouling

- Membrane fouling – a major problem in water treatment processes
  - Organic/colloidal deposition
    - NOM and polysaccharides (alginate acid)
  - Mineral scaling
    - CaSO₄
    - CaCO₃
  - Biofilm formation

Kim et al., 2010
Electrofiltration

- Electrically charged surfaces have been demonstrated to...
  - Prevent biofilm growth
  - Slow down/eliminate mineral scale formation
  - Induce electrostatic repulsive forces

The challenge:
- Create an electrically conducting, semi-permeable surface, which maintains the necessary transport properties needed in water treatment processes
  - High salt rejection, high flux, robust, cheap

The solution:
- CNT – polymer composites combine the selectivity and flexibility of polymers with the electrical conductivity of CNTs
Electrically Conducting RO Membranes

Contact angle = 77° ± 3°

Ester bond linking TMC to hydroxyl group on CNT

"Plain" PA
Scaling Inhibition

- Scaling – the formation of salt crystals on the membrane surface
  - Salt concentrations increase along membrane surface (concentration polarization) leading to supersaturated conditions, nucleation and crystal growth
- $\text{CaSO}_4$ (gypsum) scaling is a serious challenge while desalinating certain inland brackish waters
- Difficult to control due to insensitivity to pH conditions
- Requires the addition of anti-scaling agents to prevent precipitation
Scaling Inhibition – CaSO₄

- In our experiments:
  - Scaling solution – CaCl₂, MgSO₄, Na₂SO₄
  - Ionic strength = 0.134 M
  - Saturation index = 1.01
  - Cross-flow velocity = 2 cm/s
  - No bulk crystallization outside of membrane module
  - Feed water was recirculated through the membrane module and back to the feed tank with no filtration
  - **Voltage applied as DC**
  - Three distinct regions on membrane
Scaling Inhibition – CaSO₄

- Applying a DC voltage had a significant impact on scale formation.
- Charge sign was determined to be critical for membrane performance.
  - Membrane as anode (positive charge) inhibited scaling.
  - Membrane as cathode (negative charge) encouraged scaling.
Scaling Inhibition – CaSO₄

- The application of a positive DC potential changed crystal morphology
  - In controls, crystals appear small, needle-like, and tightly packed
  - When membrane is used as an anode (1.5V), crystals are much larger and loosely packed
Scaling Inhibition – CaSO$_4$

• The electric double-layer structure forming along the electrically charged membrane surface exhibits non-stoichiometric conditions in the diffuse layer, with regards to Ca$^{+2}$ and SO$_4^{-2}$ ion concentrations

• Non-stoichiometric conditions lead to longer induction times

• Away from the membrane, stoichiometric conditions are re-established and nucleation takes place in the bulk

Alimi and Gadri, *Desalination*, 2004
Scaling Modeling – CaSO₄

- We use a modified Poisson-Boltzmann equation to predict the potential distribution as a function of distance from the membrane surface.
- We calculate ion concentrations as a function of potential.

\[
\frac{d^2}{dx^2} e = -eN_A \sum_{i=1}^{m} \frac{z_i c_i \exp \left( \frac{z_i e}{kT} \right)}{1 + \sum_{i=1}^{m} \frac{c_i}{c_i^{\max}} \exp \left( \frac{z_i e}{kT} \right)}
\]

\[
c_i = \frac{c_i \exp \left( \frac{z_i e}{kT} \right)}{1 + \sum_{i=1}^{m} \frac{c_i}{c_i^{\max}} \exp \left( \frac{z_i e}{kT} \right)}
\]

\[
c_i^{\max} = \frac{p}{3} R_i^3 N_A
\]
Organic Fouling on UF Membranes

- UF Membranes are composed of a PVA-CNT-COOH thin film deposited on a PSF support.
- PVA and COOH (on CNTs) groups cross-linked with gluteraldehyde.

![Image of membrane surfaces and rejection graphs]

- PSF only: 49°
- CNT only: 81°
- PVA+CNT: 32°
Organic Fouling on UF Membranes

- We used high concentrations of alginic acid (5 g/L) as a model organic foulant
- Cross-flow membrane system operated with constant flux (20 LMH, 10 cm/s)
- Surface hydrophilicity reduces organic fouling
- Ionic strength has significant impact of electrostatic repulsion (not surprising)
- Neutral organic foulants (PEO) are not impacted by electric fields
Conclusions

- By combining electrically conducting CNTs with appropriate polymers (such as PA or PVA), membranes can maintain their critical transport properties, e.g. salt rejection and water permeability, with the addition of electrical conductivity.
- Electrically charged membranes can reduce membrane fouling.
  - Scaling inhibition on RO membranes
  - Organic fouling (molecules and biofilms)
- Ionic strength greatly impacts system performance.
- Modeling of electrostatic phenomena in these systems require a different approach (simple DLVO doesn’t work).
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