Natural Organic Matter (NOM) Fouling of NF Membranes

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Graduate Students/PDFs

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Outline

- Background and Objective
- Materials and Methods
- Fouling Behavior and Mechanisms
  - Effect of divalent (calcium) ions
  - Effect of initial permeate flux
  - Effect of crossflow velocity
  - Coupled effects of chemistry and hydrodynamics
- Concluding Remarks

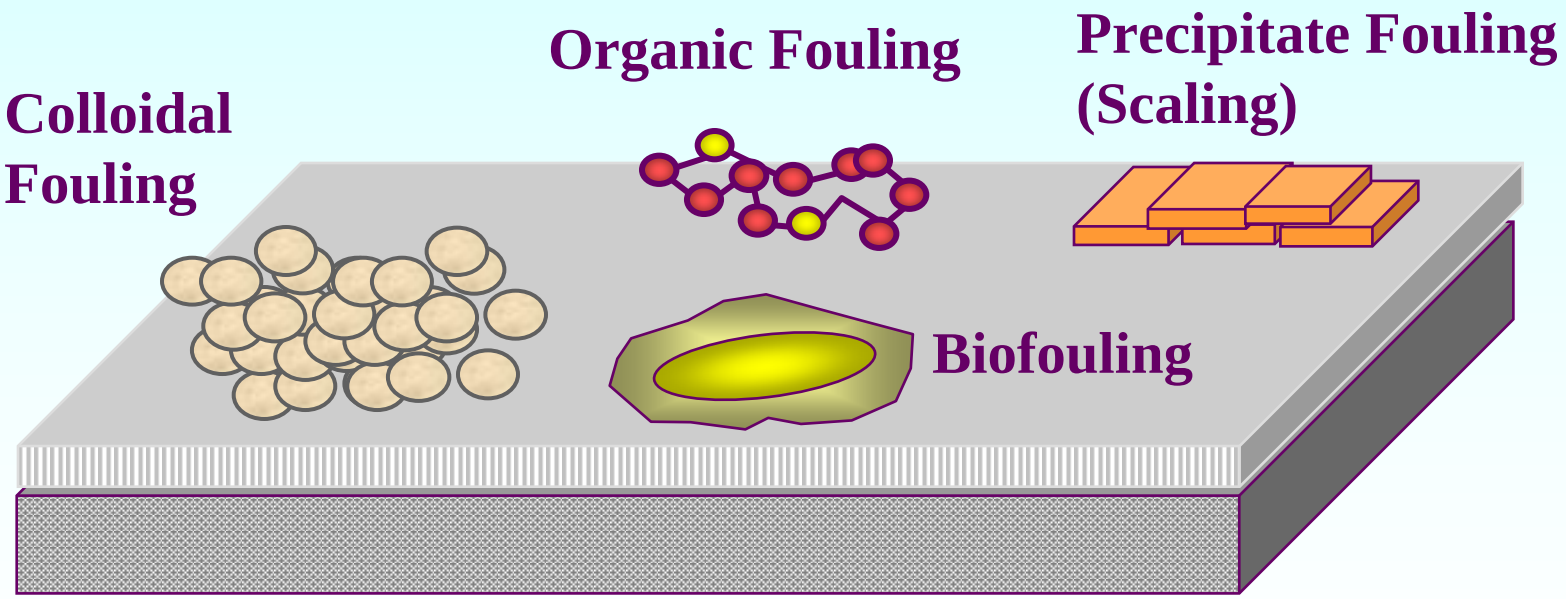
Nanofiltration (NF) Membranes

- NF membranes can meet multiple water quality objectives. Examples include:
  - Removal of hardness (softening)
  - Removal of THM precursors from surface waters (Disinfection/Disinfection By-products Rule)
  - Removal of inorganic contaminants such as arsenic (Arsenic Rule)

Membrane Fouling

- A major obstacle for efficient operation of membrane systems
- Fouling refers to the deterioration of membrane performance (reduced flux and selectivity) due to accumulation of substances on the membrane surface and/or within the membrane pores

Foulants in Natural and Waste Waters



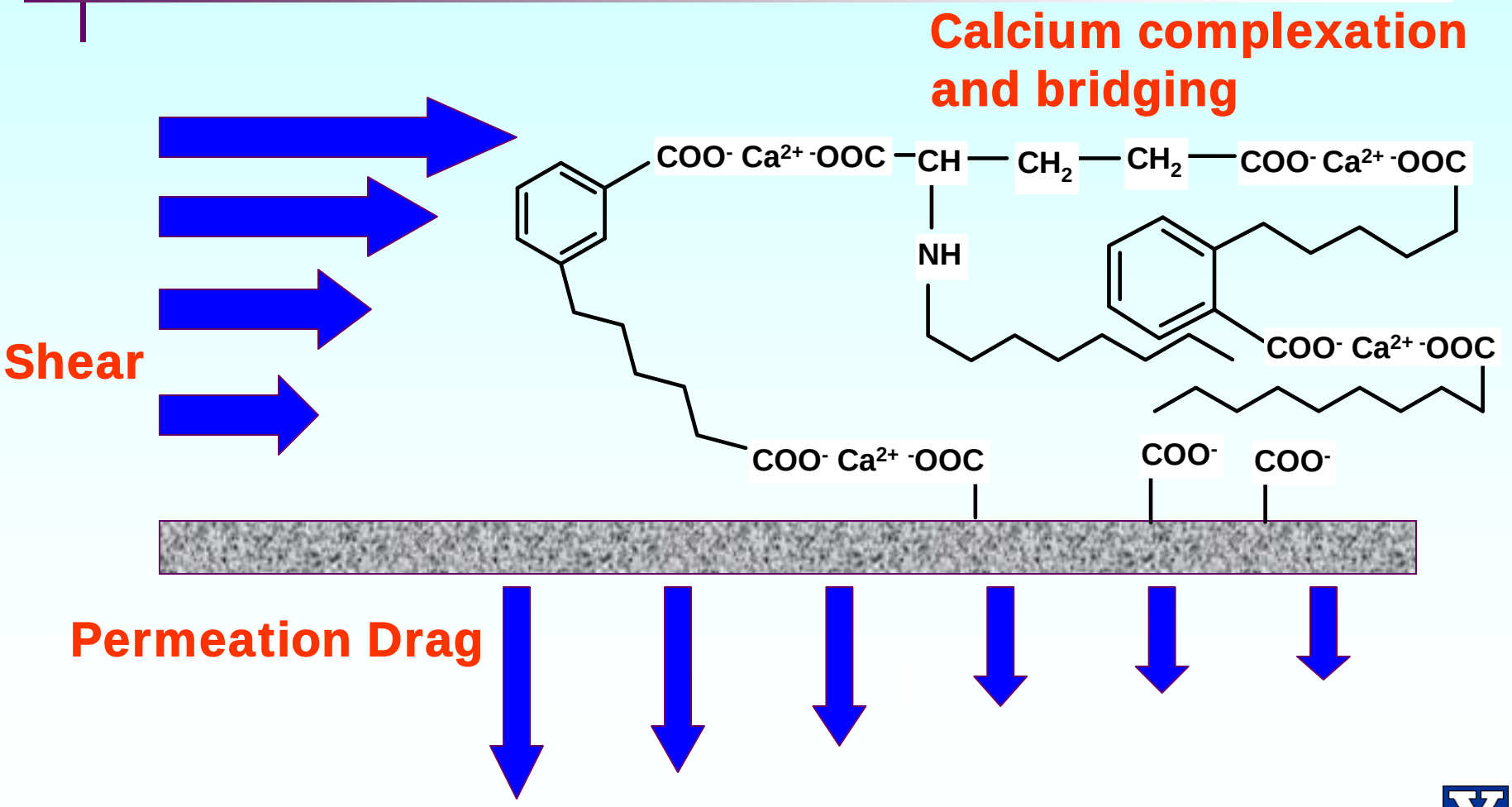
Natural Organic Matter (NOM)

- Ubiquitous in natural waters (lakes, reservoirs, rivers, seawater, groundwater)
- Comprised of mostly humic and fulvic acids
- Complex, heterogeneous anionic macromolecules with mostly carboxylic functional groups
- Molecular weight < 10,000 Da

Motivation

- Natural organic matter is a major foulant in natural waters
- Fouling is influenced by hydrodynamics and solution chemistry and, therefore, may be reduced by optimizing operational conditions.

Overview of NOM Fouling



Objective

To investigate the combined (coupled) influence of

- solution chemistry (divalent calcium ions)
- permeation drag (permeate flux)
- shear rate (crossflow velocity)

in controlling NF membrane fouling by NOM

Model NOM and NF Membrane

- Model NOM: Aldrich humic acid; purified via repeated precipitation by HCl
- NF Membrane: NF-70; fully aromatic thin-film composite; negatively charged

Characterization of NOM and NF Membrane

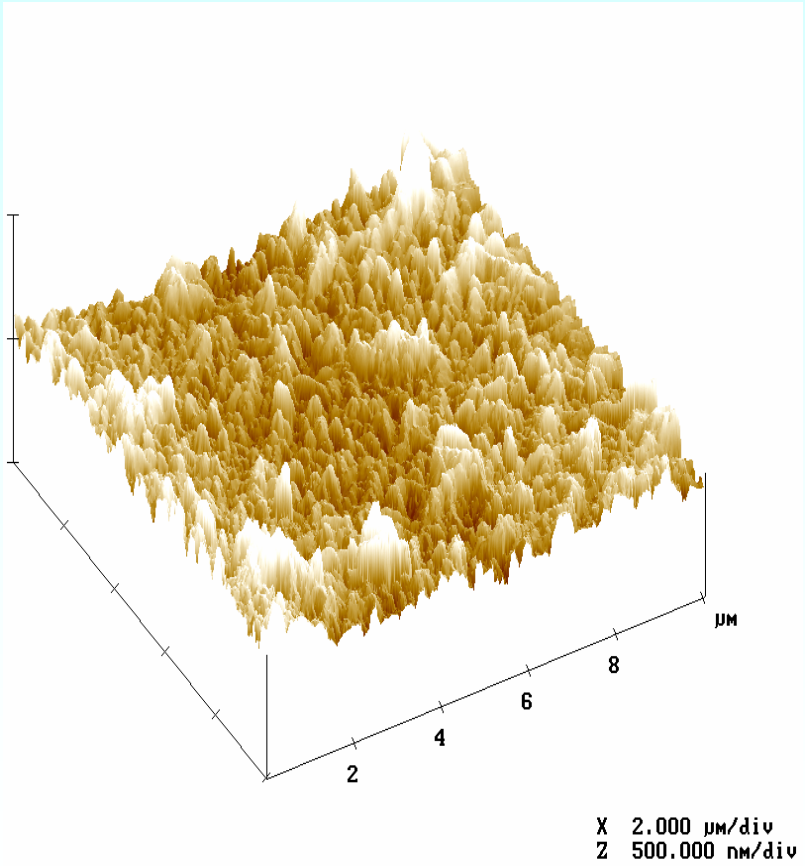
NOM:

- Carboxylic acidity (titration)
- Complexation of Ca^{2+} with NOM

NF Membrane:

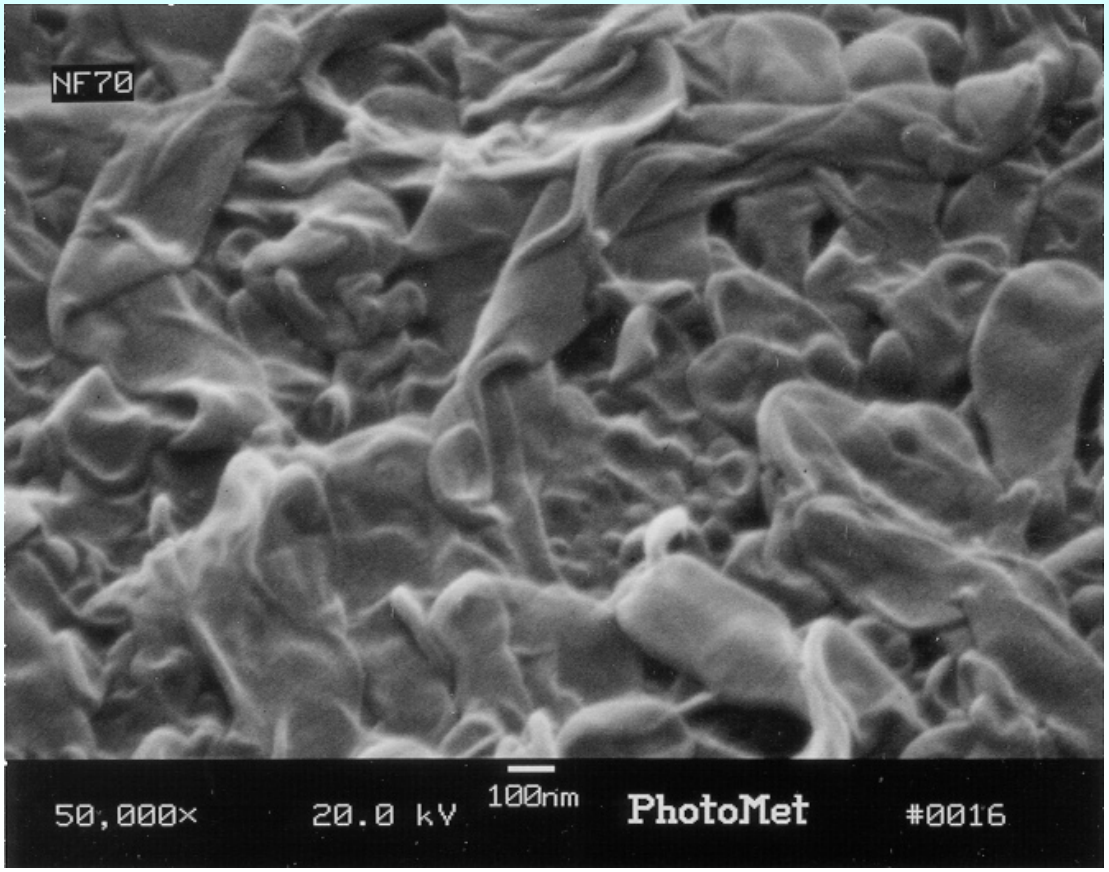
- Permeability and selectivity
- Surface charge (zeta potential with NOM and Ca^{2+})
- Surface morphology (AFM and SEM)
- Hydrophobicity (contact angle)

NF Membrane Surface Morphology (via AFM)

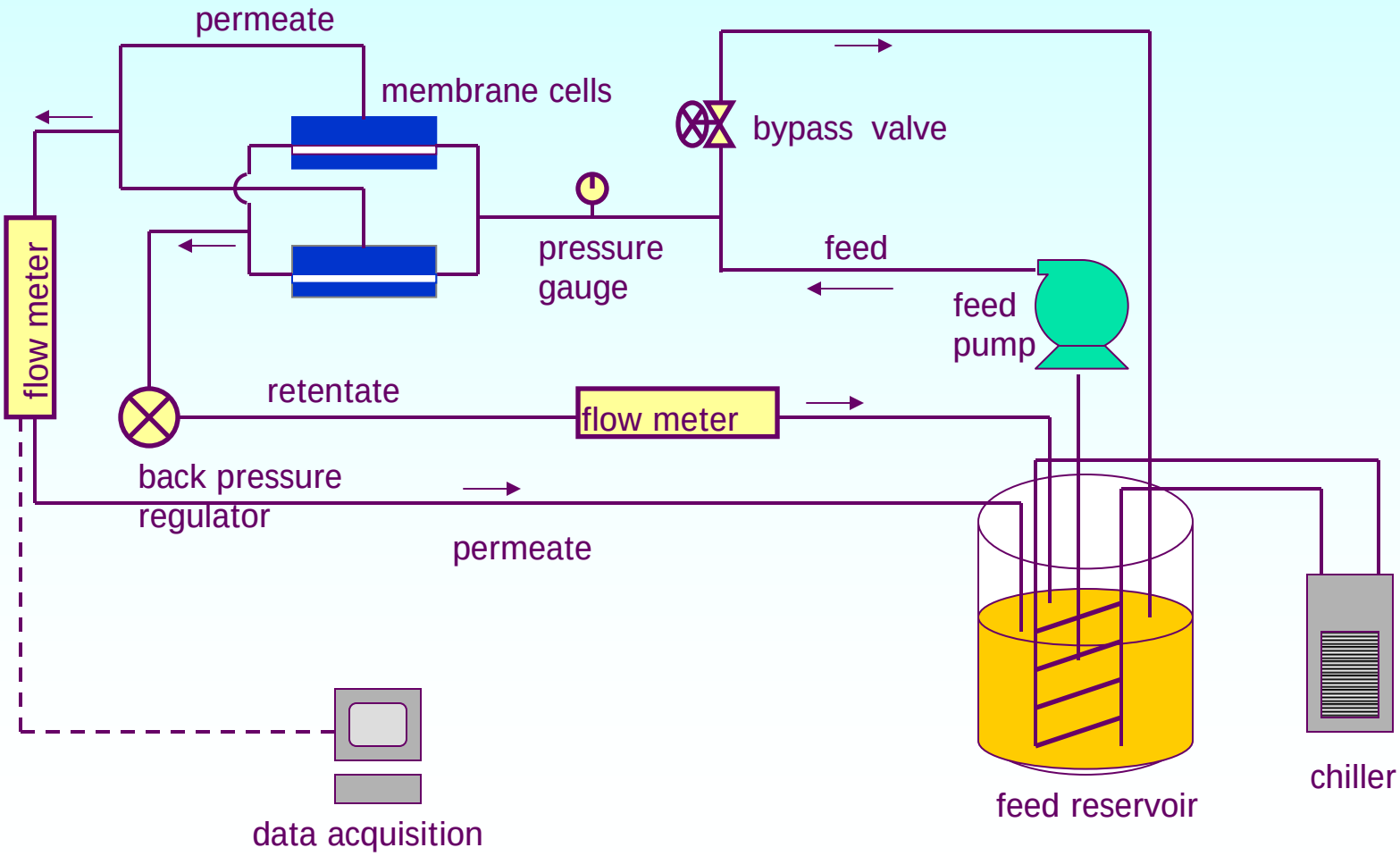


Parameter	Average
RMS (nm)	56.5
Surface Area Difference (%)	20.7
Peak Count	210

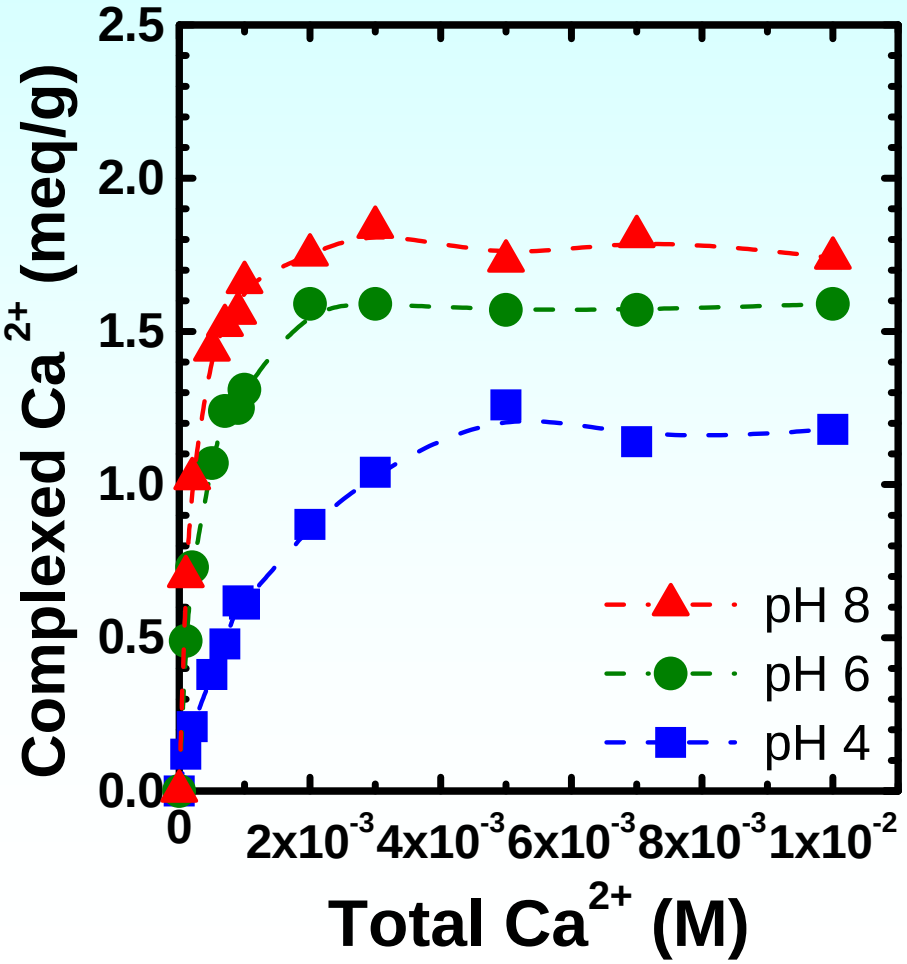
NF Membrane Surface Morphology (via SEM)



NF Test Unit


permeate
membrane cells
bypass valve
pressure gauge
feed
feed pump
flow meter
retentate
flow meter
back pressure regulator
permeate
data acquisition
feed reservoir
chiller

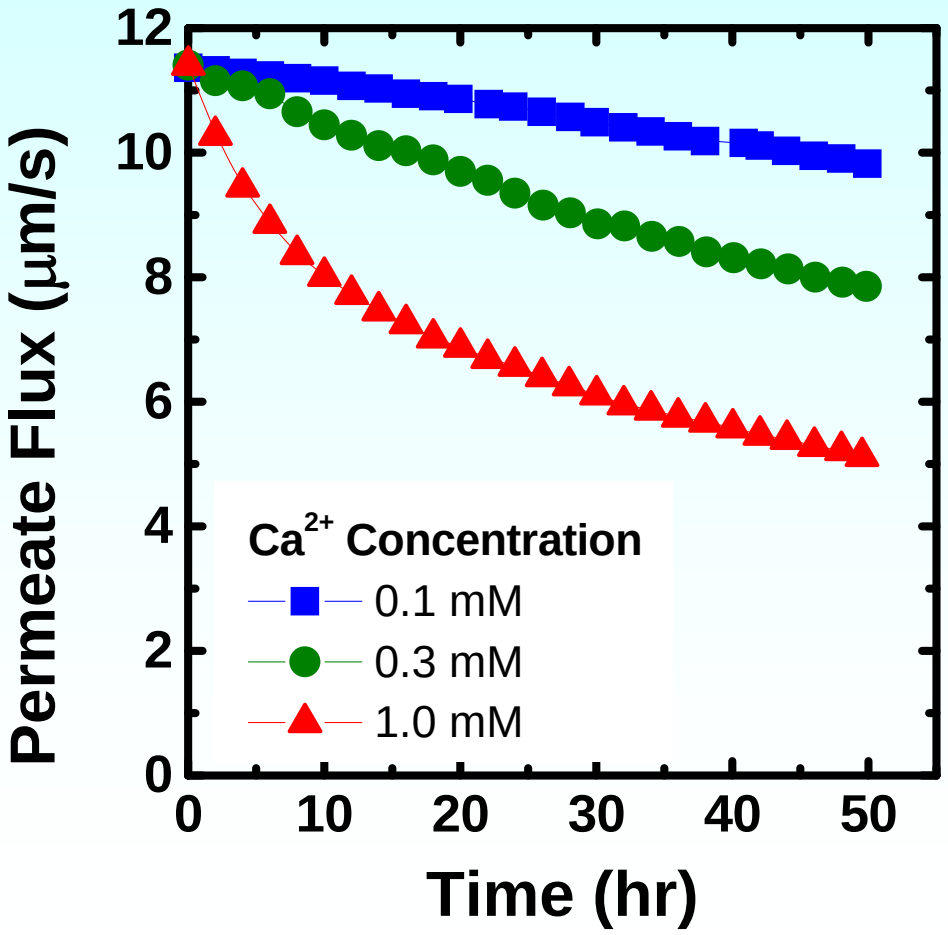
Calcium Complexation with NOM



Conditions

- 0.1 g/L humic acid
- 0.01 M NaCl

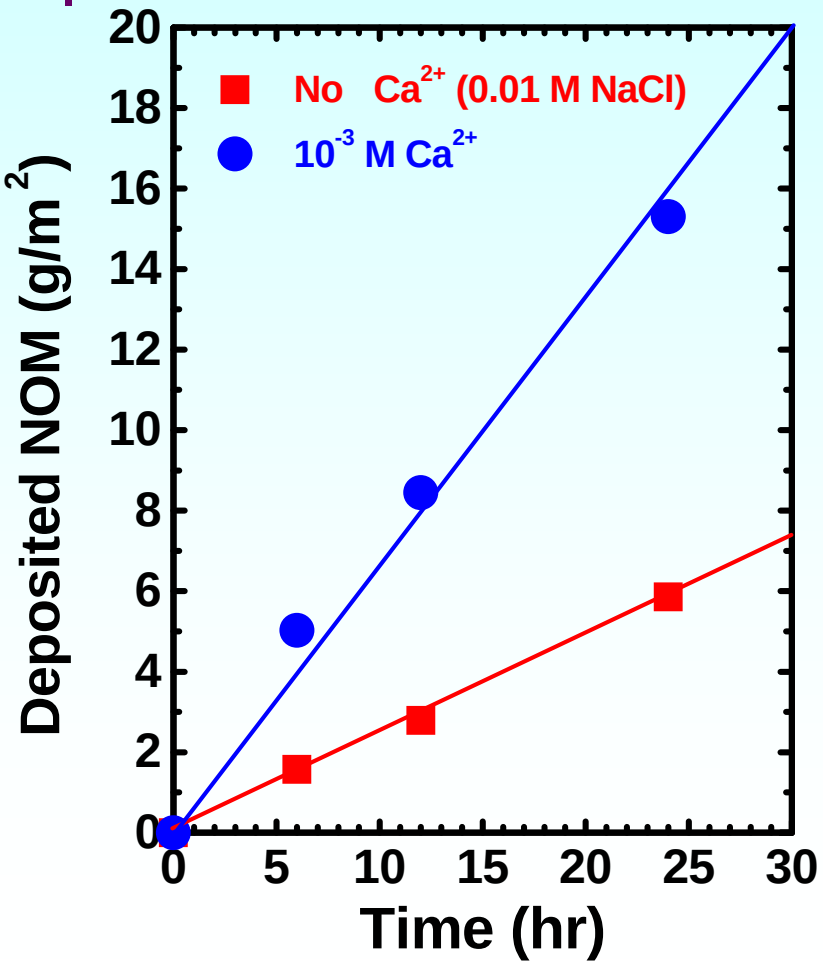
Effect of Divalent Cations (Calcium)

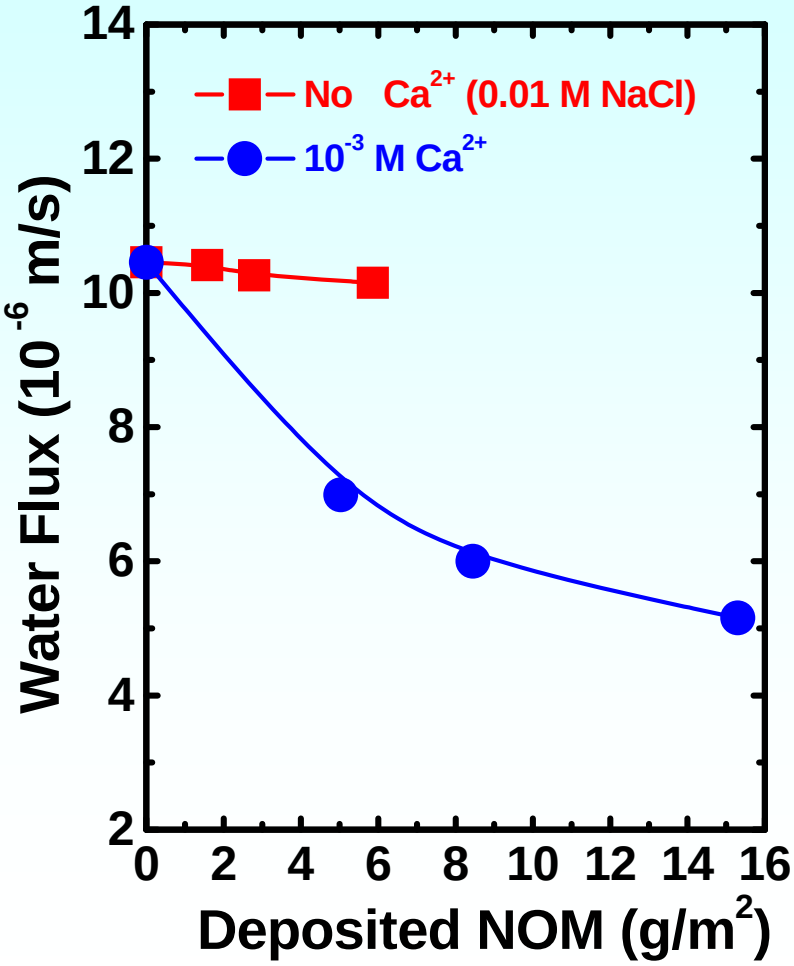


Conditions

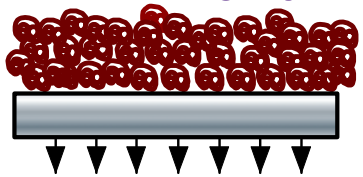
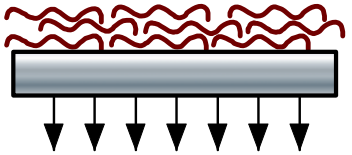
- Initial Flux:
  11.3 μm/s (24 gfd)
- Crossflow Velocity:
  12.1 cm/s
- pH 8.0
- Total Ionic Strength:
  0.01 M (adjusted by NaCl)
- 20 mg/L HA

Effect of Divalent Cations

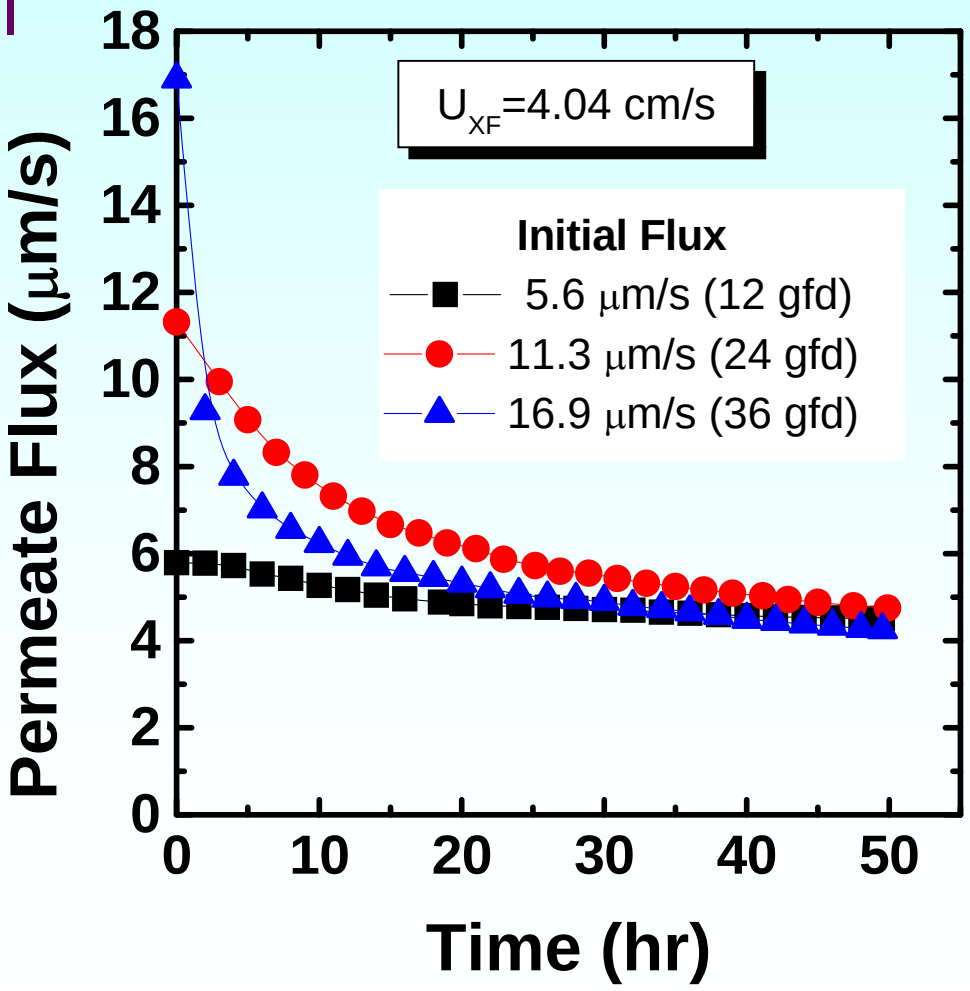




NOM Fouling Mechanisms

Chemical Conditions	NOM in Solution	NOM on Membrane Surface
High ionic strength, low pH, or presence of divalent cations	 Coiled, compact configuration	Compact, dense, thick fouling layer  Severe permeate flux decline
Low ionic strength, high pH, and absence of divalent cations	 Stretched, linear configuration	Loose, sparse, thin fouling layer  Small permeate flux decline

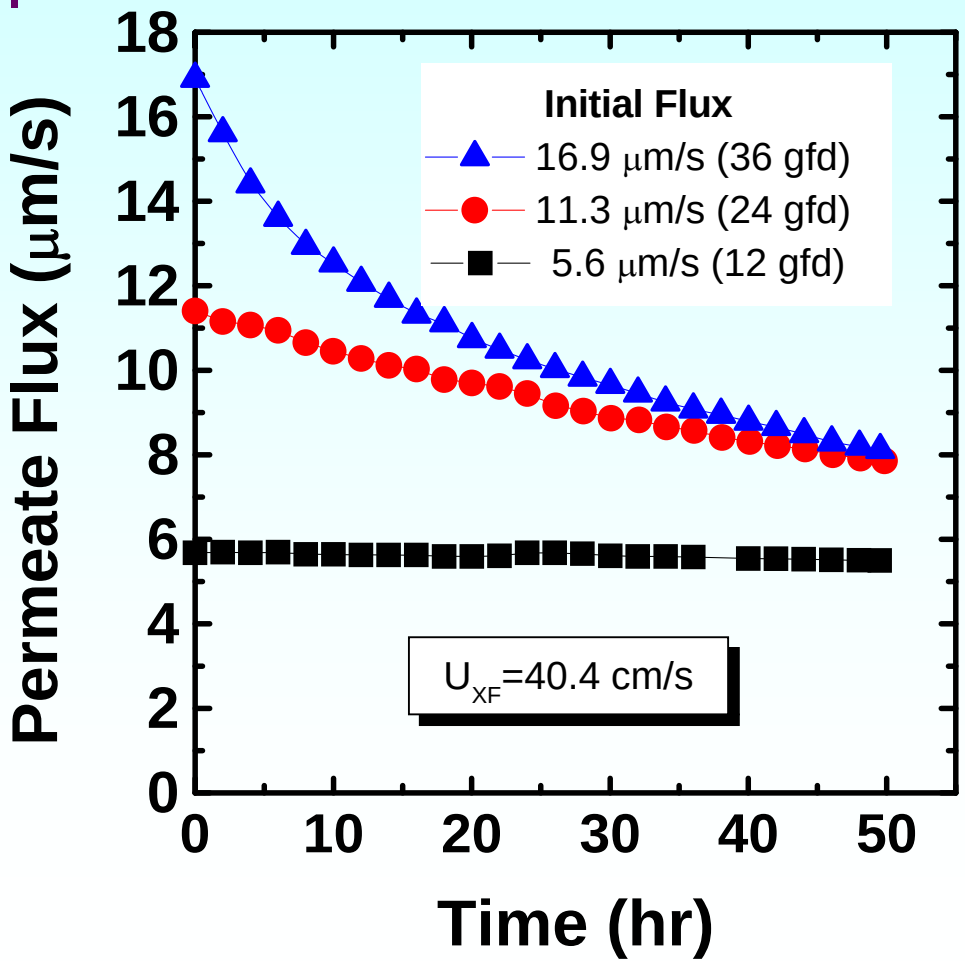
Effect of Initial Permeate Flux (low crossflow rate, U_{XF})



Solution Composition

- NOM : 20 mg/l
- Ionic Strength: 10 mM (adjusted by NaCl)
- $CaCl_2$: 0.3 mM
- pH 8

Effect of Initial Permeate Flux (high crossflow rate, U_{XF})



Solution Composition

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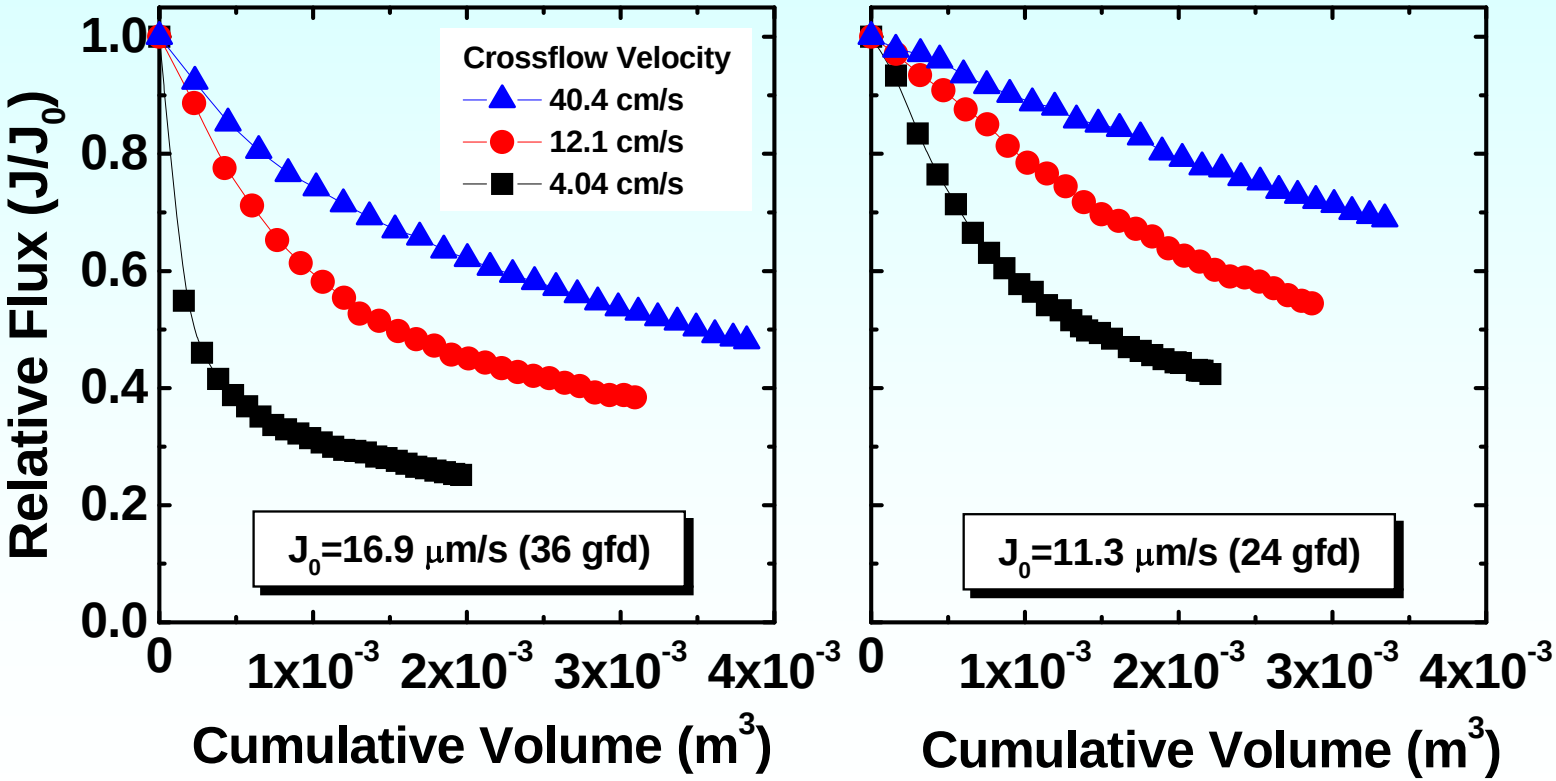
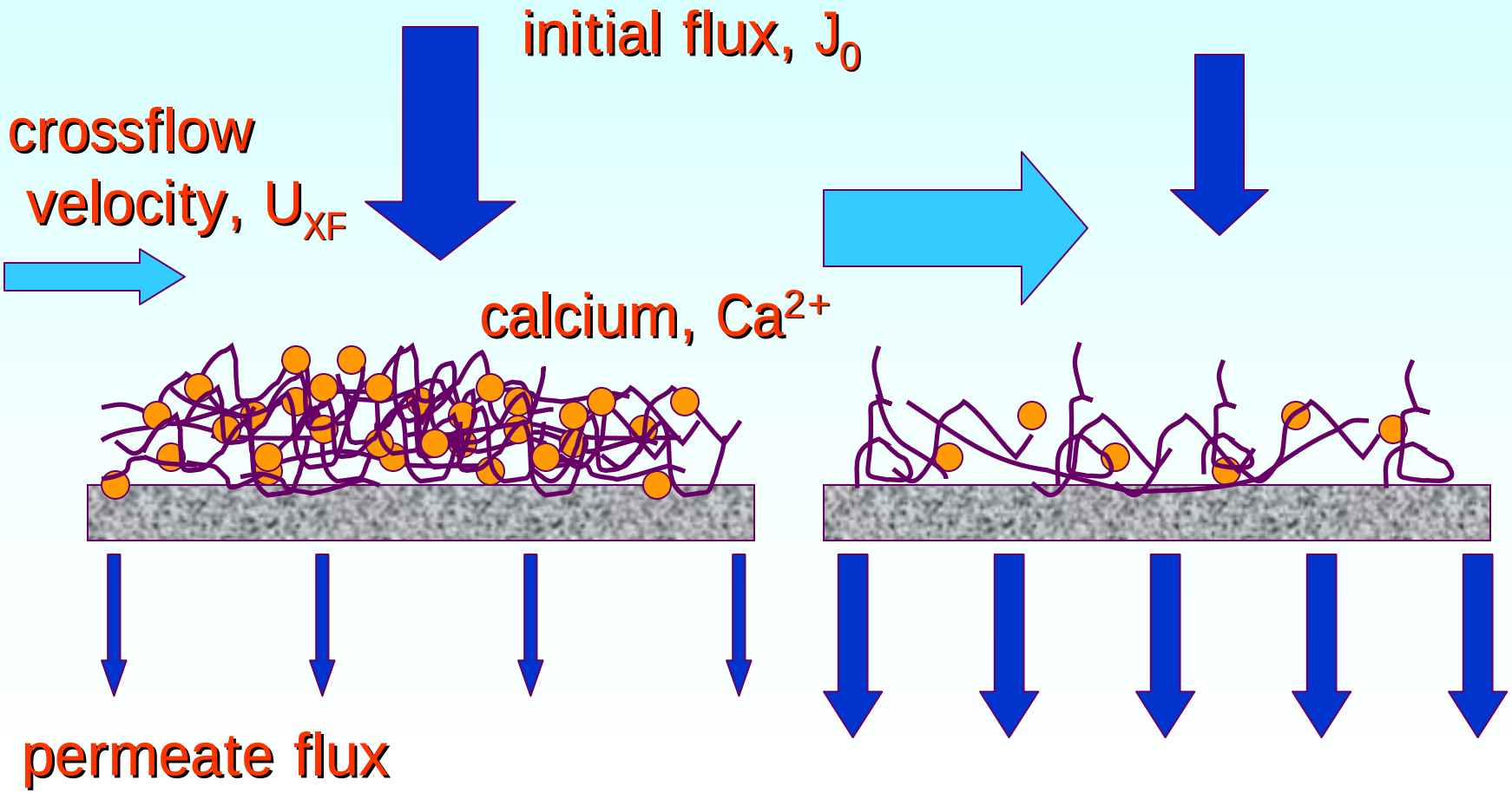
- pH 8

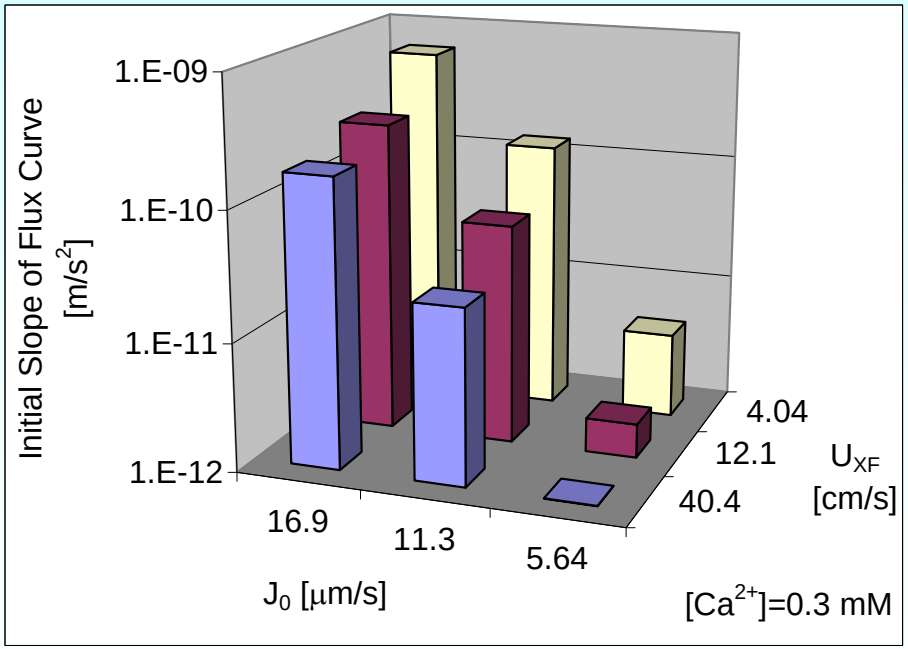
Effect of Crossflow Velocity

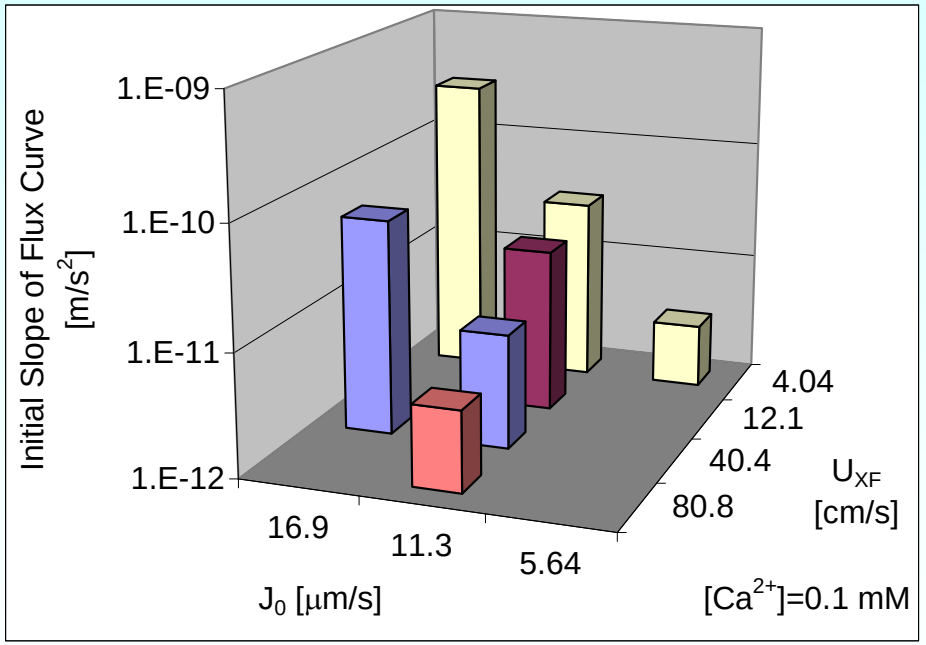


Combined (Coupled) Influence of Hydrodynamics and Chemistry



Coupled Influence of Hydrodynamics and Chemistry





Fouled Membranes

J_0=16.9 μm/s (36 gfd)

U_{XF}=4.0 cm/s; 1 mM Ca^{2+}

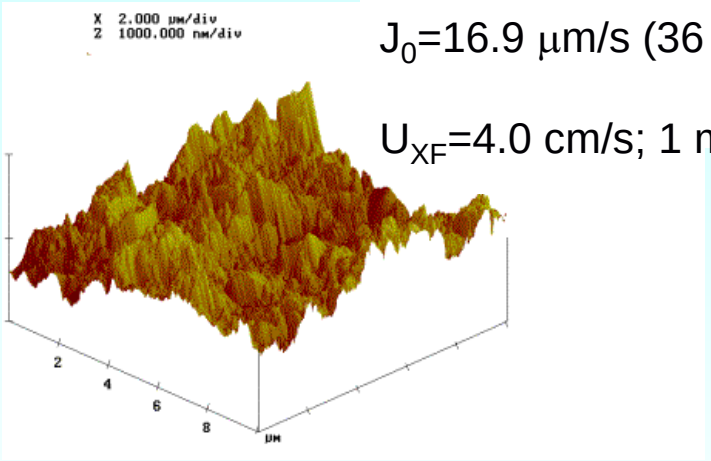
J_0=11.3 μm/s (24 gfd)

U_{XF}=12.1 cm/s; 0.3 mM Ca^{2+}

J_0=5.6 μm/s (12 gfd)

U_{XF}=40.4 cm/s; 0.1 mM Ca^{2+}

Fouled Membranes and Fouling Layer



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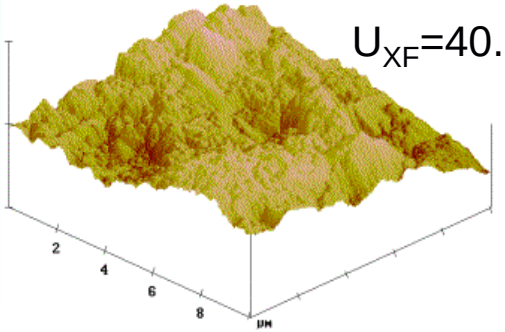
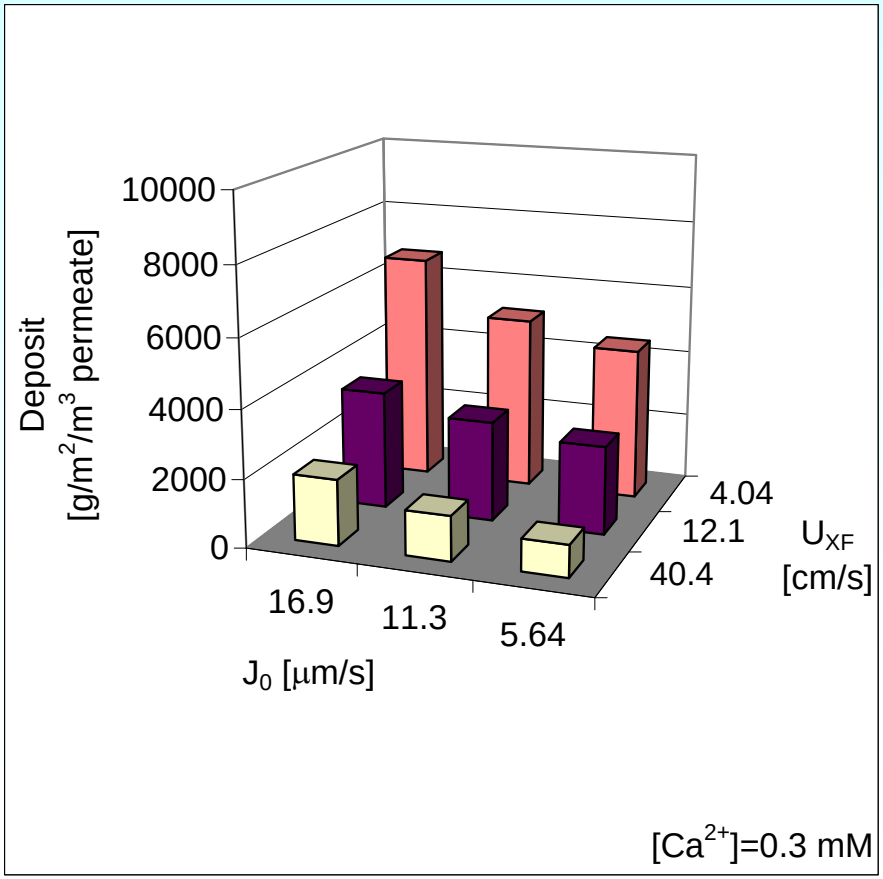
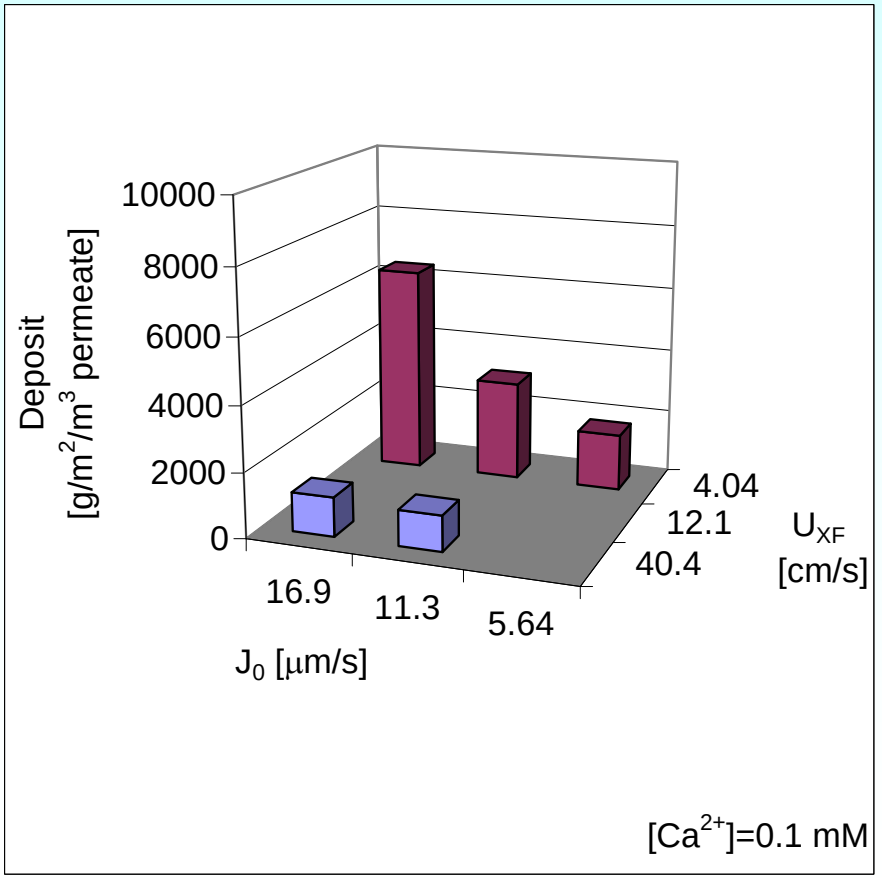


J_0=5.6 µm/s (12 gfd)

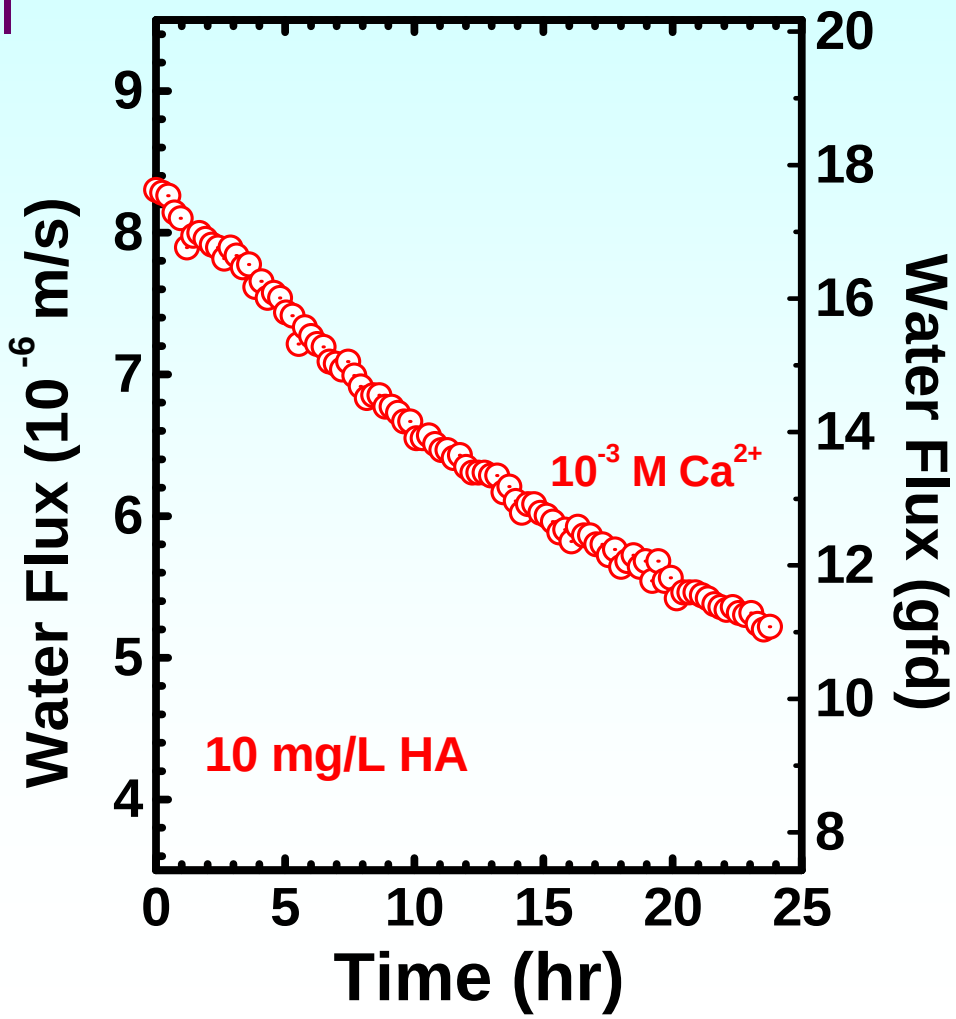
U_{XF}=40.4 cm/s; 0.1 mM Ca^{2+}

NOM Fouling Layer Weight





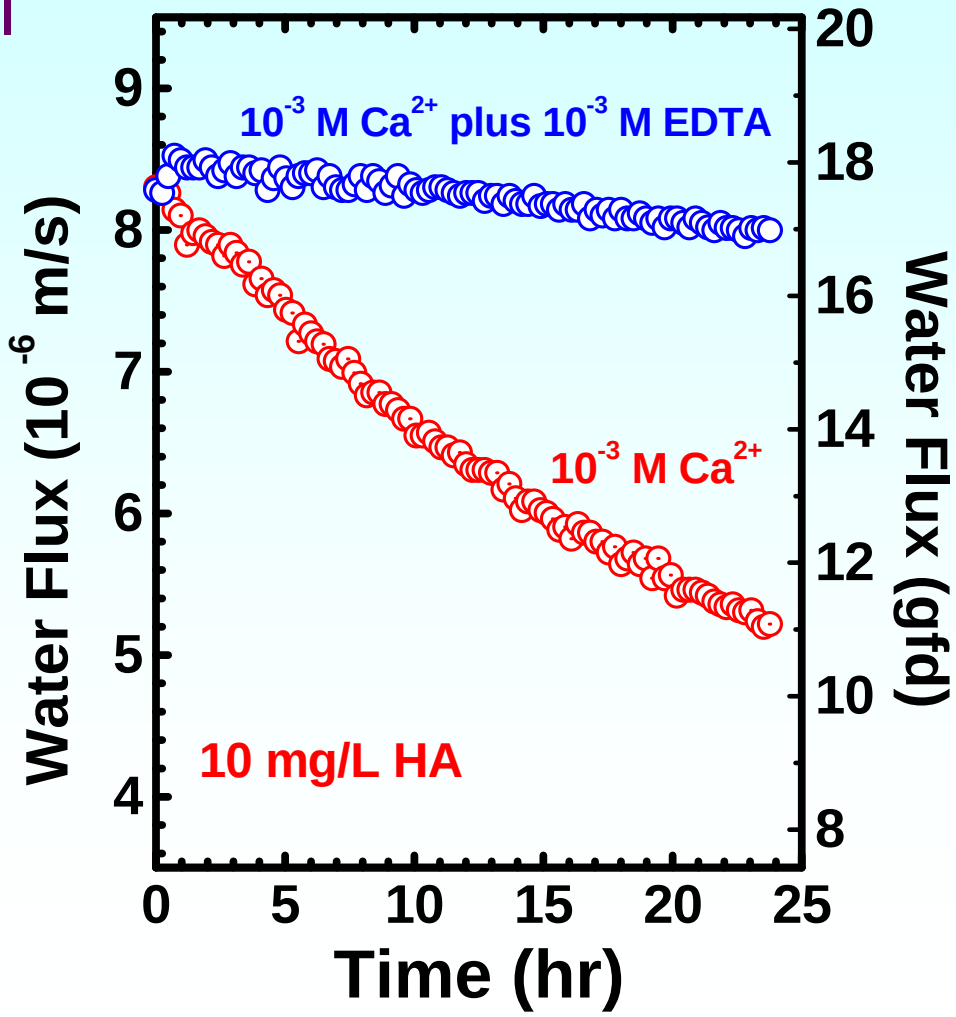
Pre-Treatment



Conditions

- Initial Flux:
  8.2 μm/s (17.5 gfd)
- Crossflow Velocity:
  3.5 cm/s
- pH 8.0
- Ionic Strength: 0.01 M
- 10 mg/L HA

Pre-Treatment



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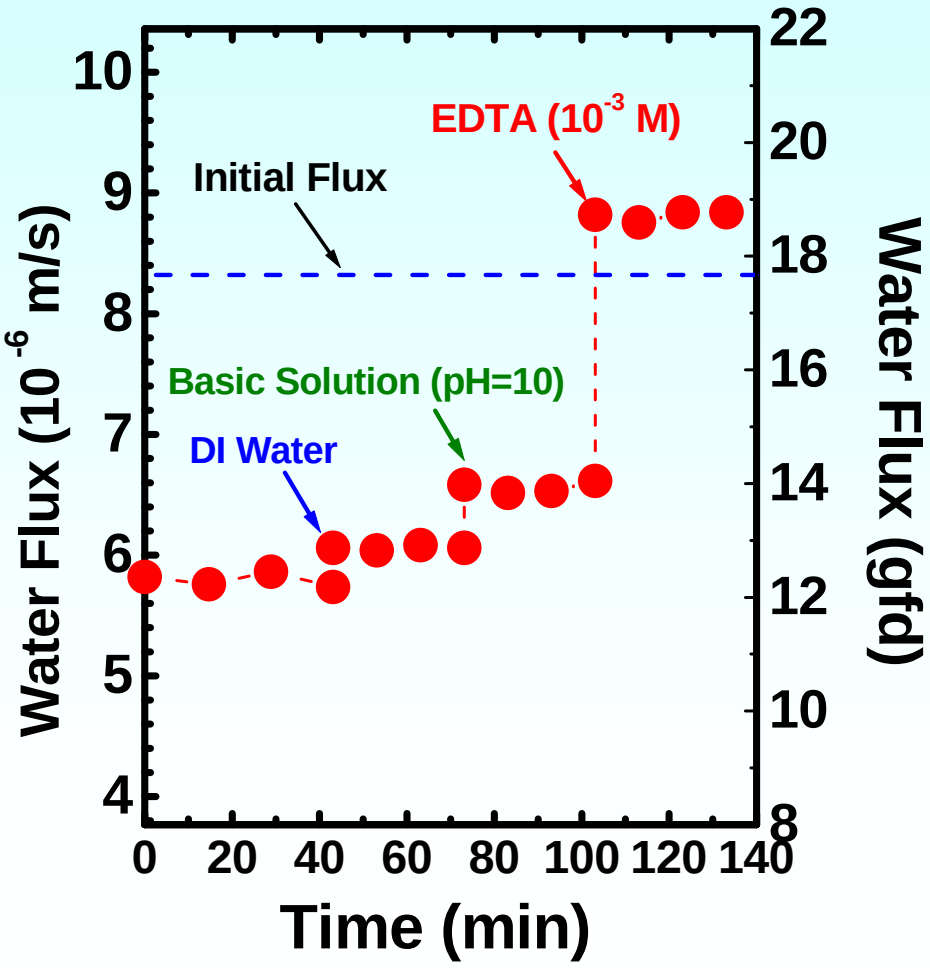
Post-Treatment



Concluding Remarks

- NOM fouling is determined by **coupling** between **chemical** and **physical** (hydrodynamic) interactions.
- Membrane fouling can be minimized by **optimization** of operational parameters (applied pressure and crossflow)