Inorganic Membranes for Treatment of Produced Water

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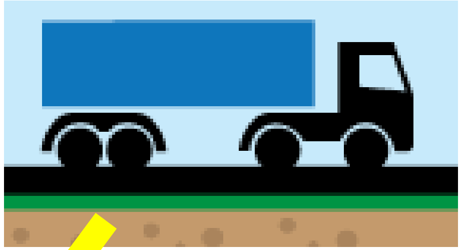
Background

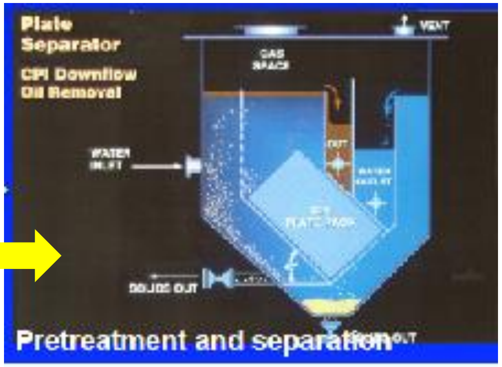
Produced Water (PW)

Silt and particulates
Dissolved salts
Chlorides
Heavy metals
Organic contaminants (hydrocarbons)
Radioactive materials ….

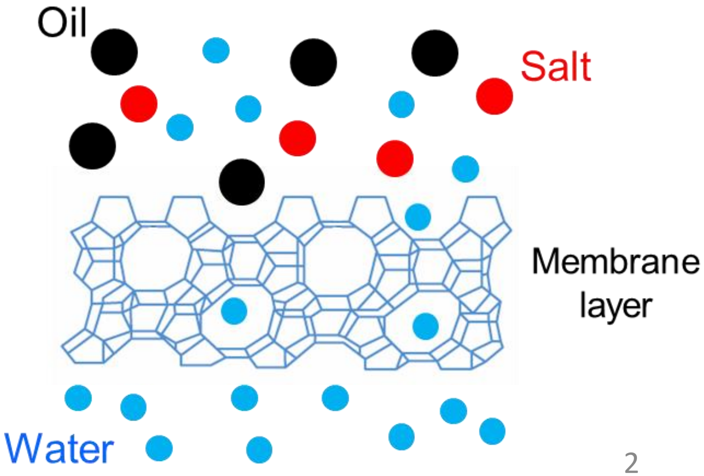
<u>Disposal</u> (energy intensive)

Trucking Cost
$108,240/well





<u>Membrane Process</u>
(energy efficient)



Background

Table. Example U.S. Water Cost Analysis.

4,626 active disposal wells in Oklahoma as of April 2017	
Average water required per well	120,000 bbl (barrel)
Typical load recovery (30%)	36,000 bbl
Typical water truck holds	110 bbl/load
Each well requires	328 truck trips
Average trucking time	3 hours
Average cost of trucking	$110/hours
Estimated trucking costs	$108,240/well
Freshwater costs	$90,000/well
Estimated disposal costs	$108,242/well
Total cost per well	$306,482/well

- Including fresh water and disposal costs, the total average cost for water in completion can exceed <u>$306,482 per well</u>.

Background

Table. Average Water Costs for Bakken Shale Stimulation Operations

Acquisition Costs (Cost, $/bbl)	
Raw Water	0.25-1.75
Transportation	0.63-5.00
Disposal Costs (Cost, $/bbl)	
Deep-Well injection	0.50-1.75
Transportation	0.63-9.00
Average Total Costs	2.00-16.80

-- Source: University of North Dakota's Energy and Environmental Research Center

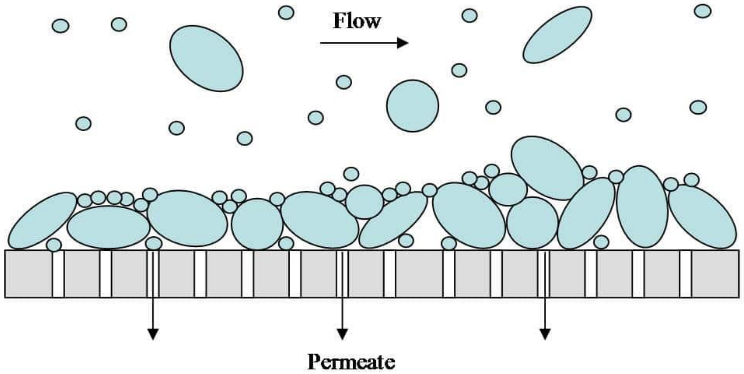
- Disposal costs increase exponentially as the trucking distance from the well site to the disposal site increases.

- The advanced "onsite" water filtration system enables PW to be reused without delivering freshwater to the wellsite, and transporting PW off-site for treatment.

Background

- **Hydrocarbon removal from PW**
  - Chemical demulsifiers
  - Match with the specific chemical profile
  - Inefficient trial-and-error serial testing
  - Chemical treatments cause sludge

- **Ultrafiltration membranes**
  - Fabrication
  - Fouling, Flux loss
  - Damage by foulants or the chemicals
  - Acidic and basic solutions, high temperatures
  - Thermal, mechanical, and chemical stability



Literature review of inorganic membranes for oil-in-water emulsion separation

Membrane or material	Substrate	Supplied pressure (bar)	Feed temperature (℃)	Flux (L/m^2-h)	Oil rejection rate	Reference
Zeolite MCM-22	α-Al_2O_3	1.00	-	9	100%	Barbosa, 2015
nano-TiO_2-coated ceramic	α-Al_2O_3	1.60	40	385	99%	Chang, 2014
Mullite-TiO_2 composite ceramic hollow fiber	Mullite hollow fiber	0.25	-	150	97%	Zhu, 2016
ZrO_2-coated alumina	α-Al_2O_3	1.60	30	441	97.8%	Zhou, 2010
Carbon nanotubes	Yttria-stabilized zirconia	1.00	-	36	100%	Chen, 2012
TiO_2 layer	α-Al_2O_3	3.00	60	108	100%	Nakamura, 2013
Kaolin-quartz-$CaCO_3$ layer	-	2.07	-	79.7	98.52%	Emani, 2014
Silica Nanoparticles	α-Al_2O_3	2.00	40	1000	93%	This research

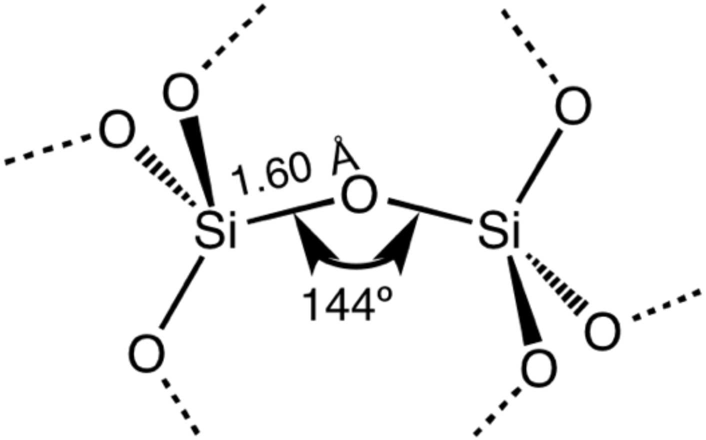
- Ceramic membranes are synthesized and coated on porous supports

Silica nanoparticles

- Silica is an oxide of silicon with the chemical formula SiO_2

- A compound of minerals and synthetic product: fused quartz, fumed silica, silica gel, and aerogels

- Silica nanoparticles (A200, 16 nm, 200 m^2/g) belong to the super-hydrophilic materials



Objectives

- Separate water from stable oil-in-water emulsion by using inorganic microfiltration membrane
- Increase membrane hydrophilicity to obtain high water flux and oil rejection
- Optimize conditions for membrane separation: different concentrations of silica NP solutions, pressures, and temperatures

Preparation of inorganic microfiltration membrane

Clean and dry the ceramic alumina membrane

↓

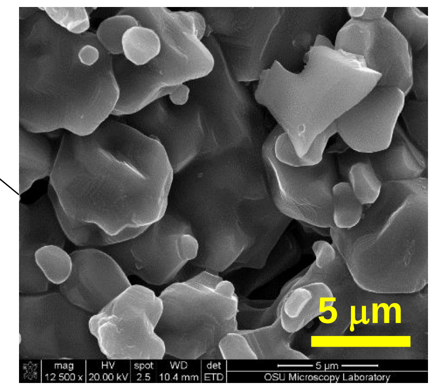
Immerse the above membrane into silica nanoparticles precursor solution at different concentrations (0, 0.05, 0.5, and 5 wt.%)

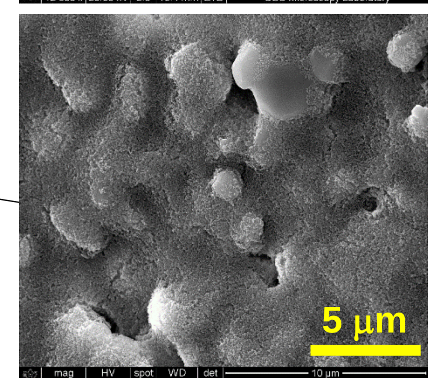
↓

Incorporate the silica nanoparticles uniformly on the membrane surface by using ultra-sonication for 15 min

↓

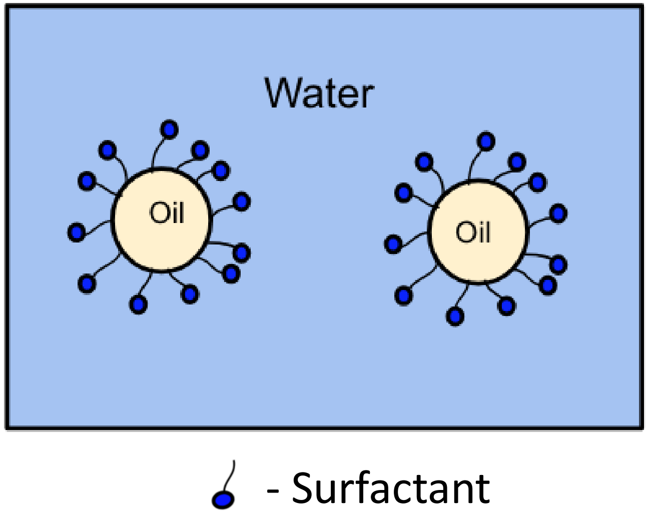
Calcine at 350 ^{o}C to integrate the silica nanoparticles firmly on the membrane surface

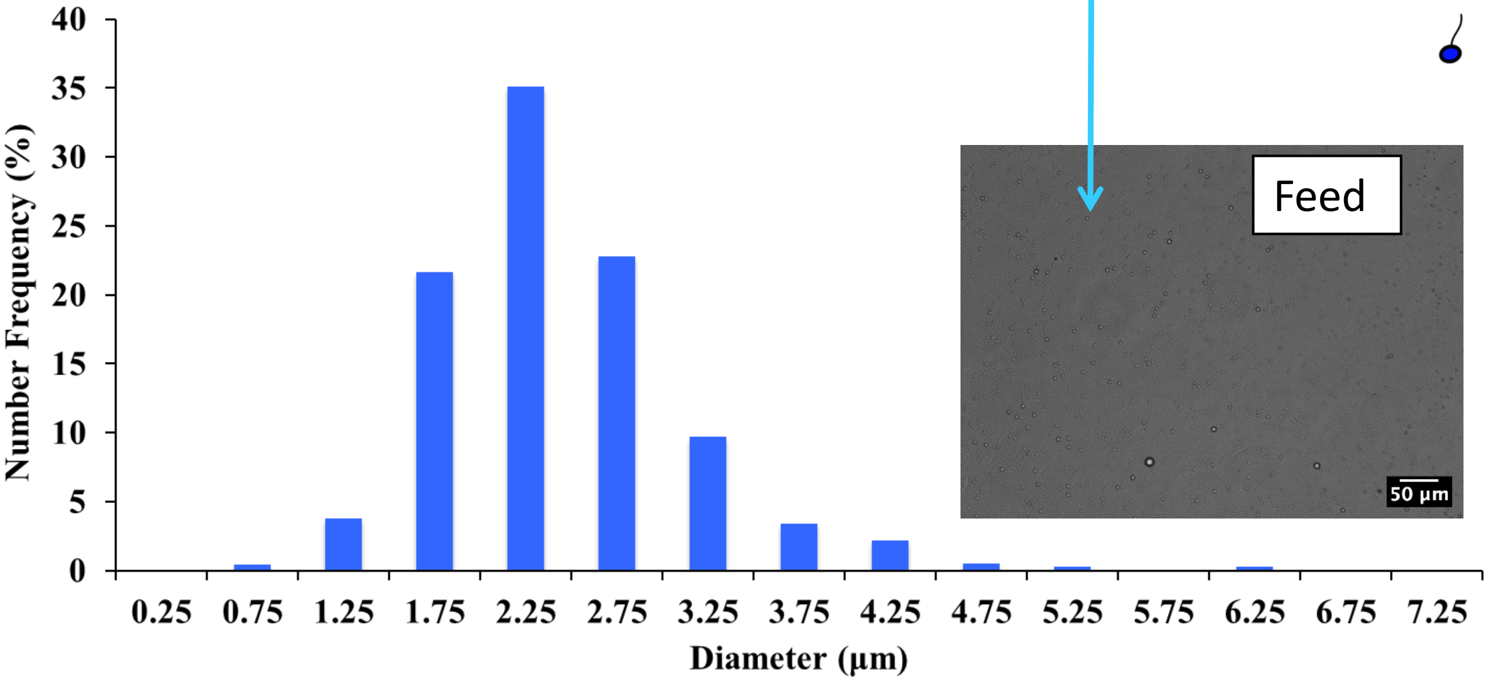




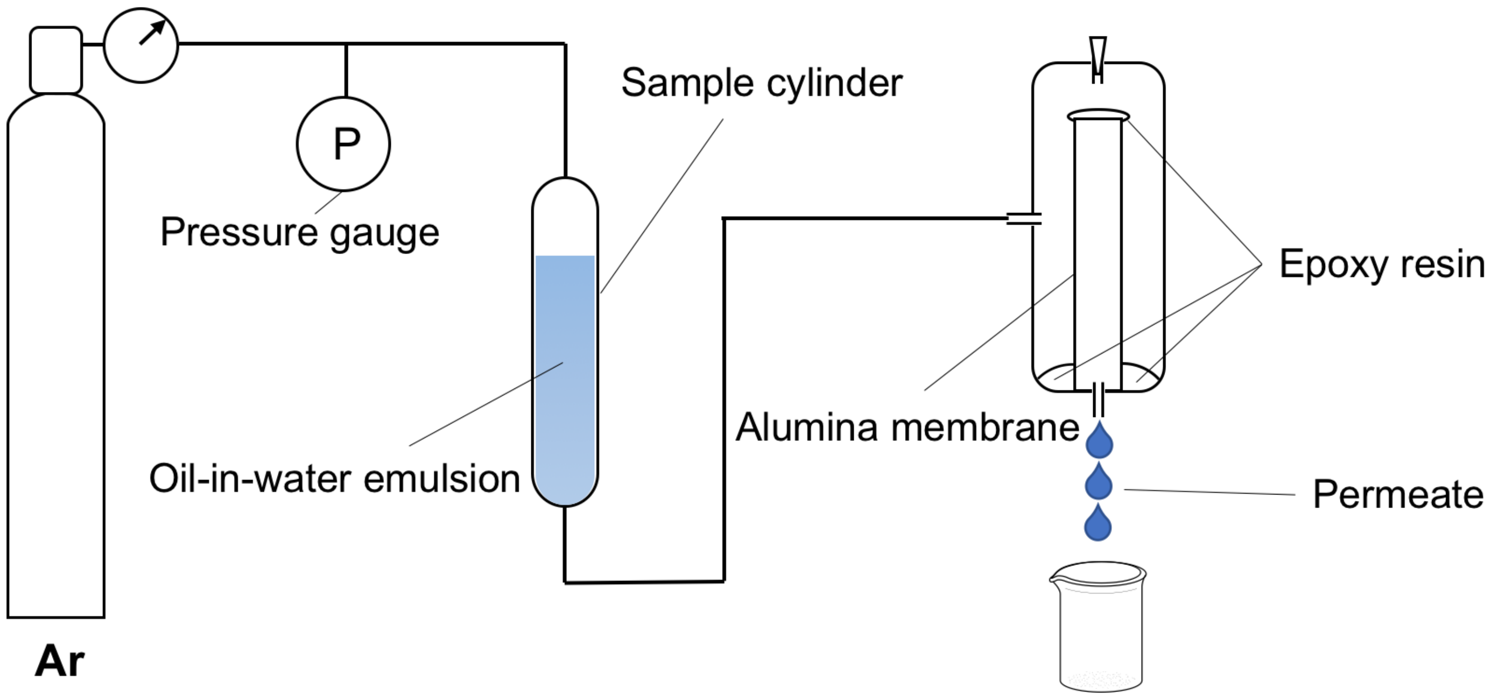
Oil-in-water emulsion

- Cyclohexane (500 ppm) + De-ionized water + sodium dodecyl sulphate (0.13 wt.%) – water soluble, anionic
- Average droplet size : 2.5 ± 0.7 μm





Experimental setup



- Oil rejection rate:
  $$\eta = (1 - C_i/C_0) \times 100\%$$
- The permeation flux:
  $$J = V/(A \times t)$$

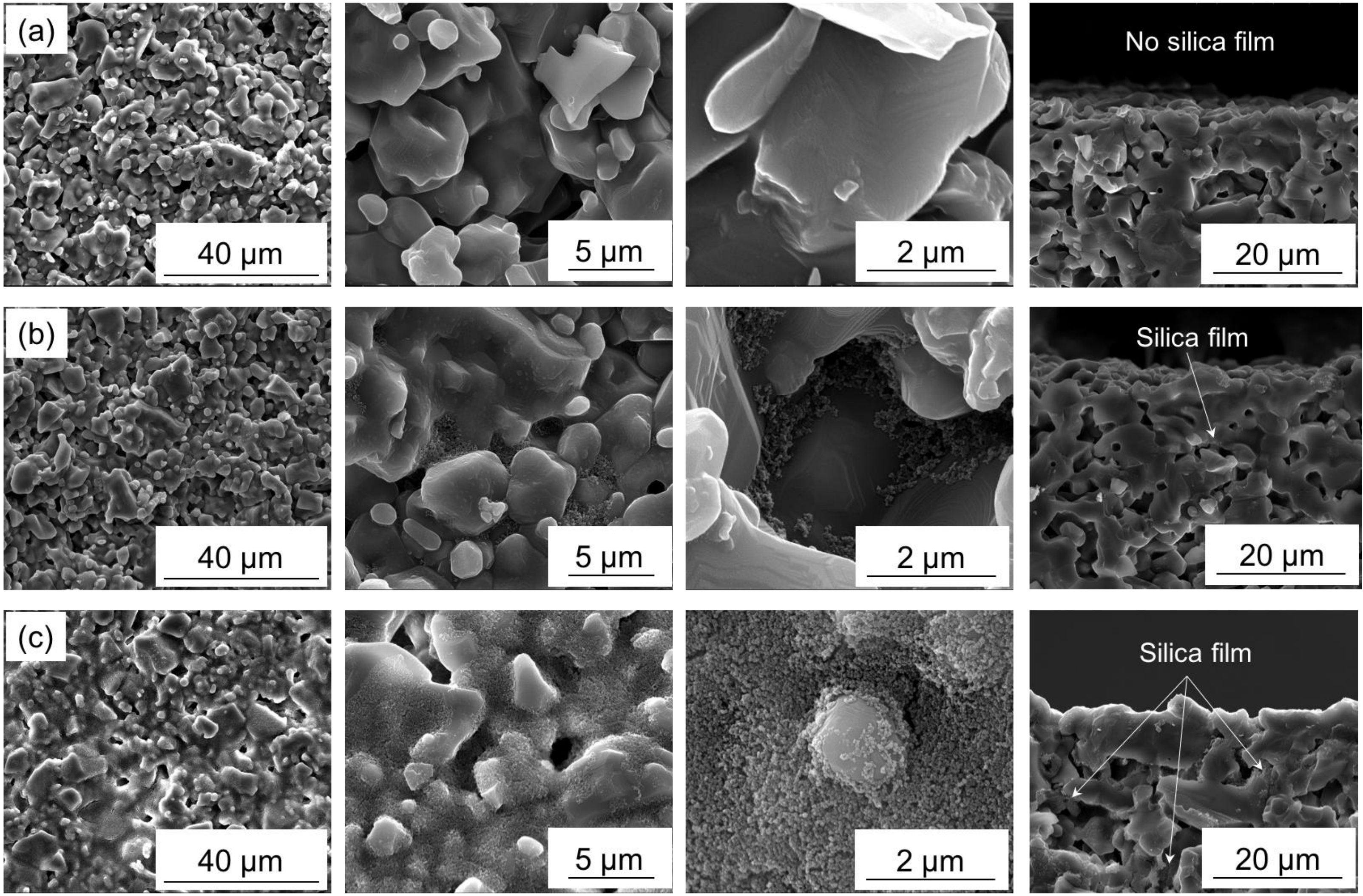
- Permeate oil concentration:
  - Cyclohexane was extracted
  - GC/MS QP2010
  - Automatic liquid sampler

SEM images of inorganic microfiltration membrane

M0
(0% precursor)

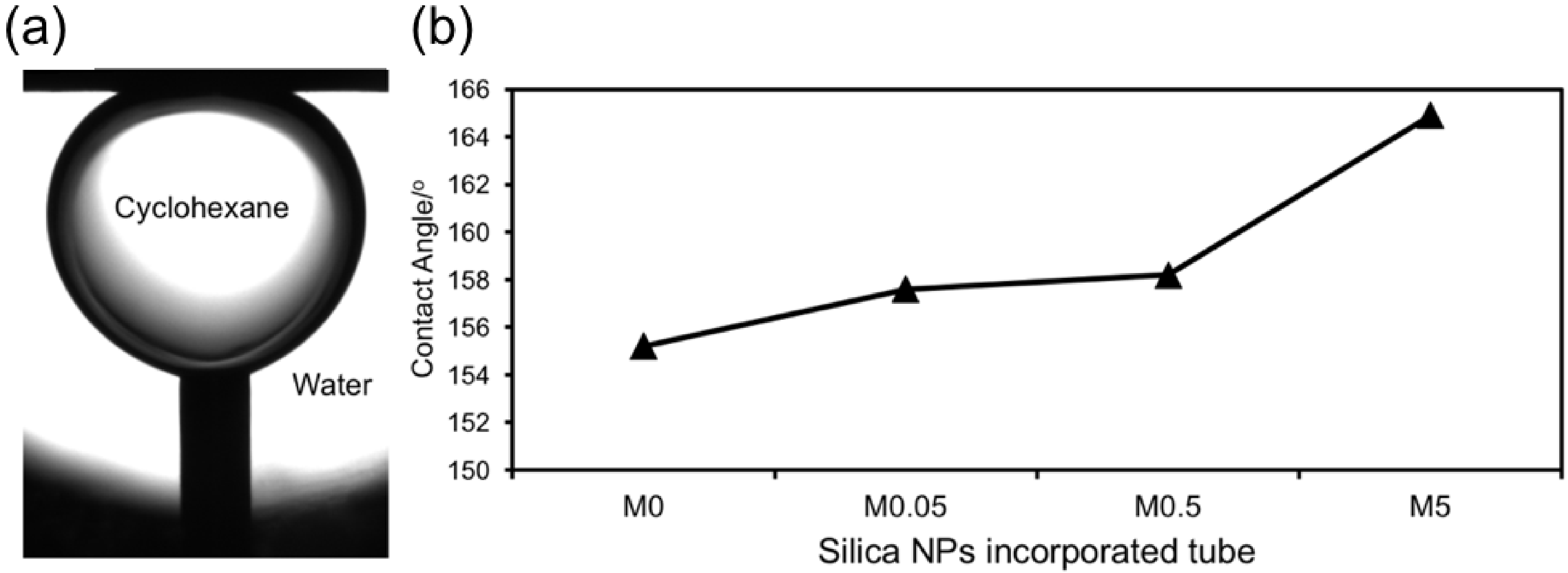
M0.5
(0.5%)

M5
(5%)



R. Liu, S.-J. Kim, C. Aichele, *Journal of Water Process Engineering*, 26 (2018).

Cyclohexane contact angle



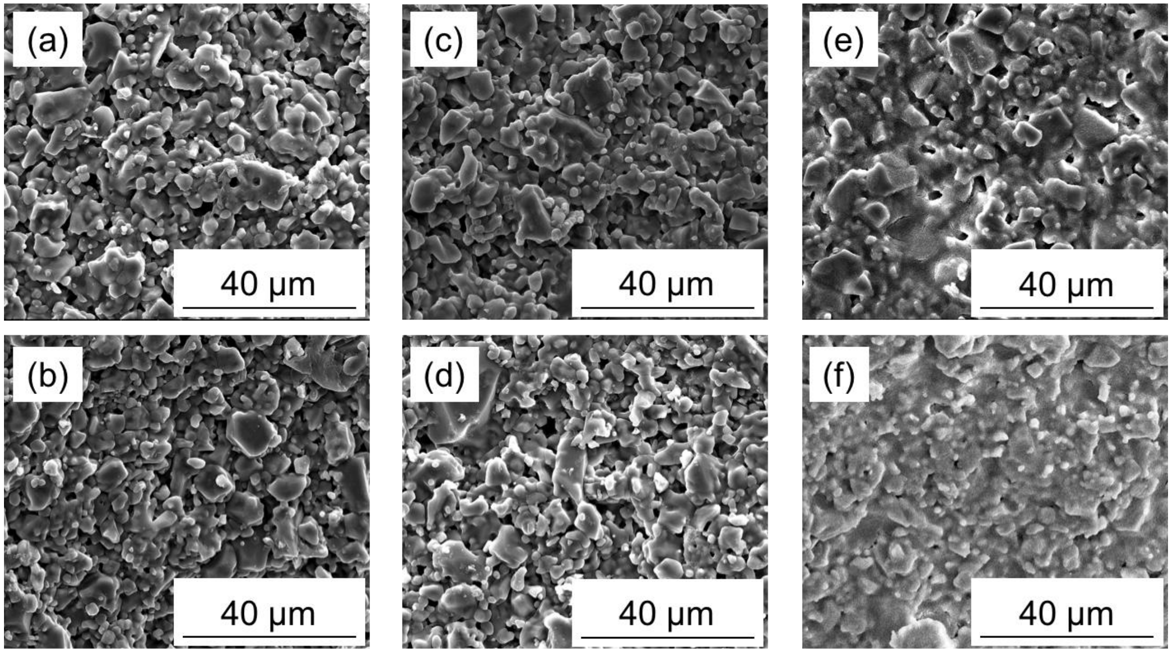
- The cyclohexane drop was repelled by the membrane
- Silica NPs enhanced hydrophilicity of the membrane

SEM images of inorganic microfiltration membrane

M0 M0.5 M5

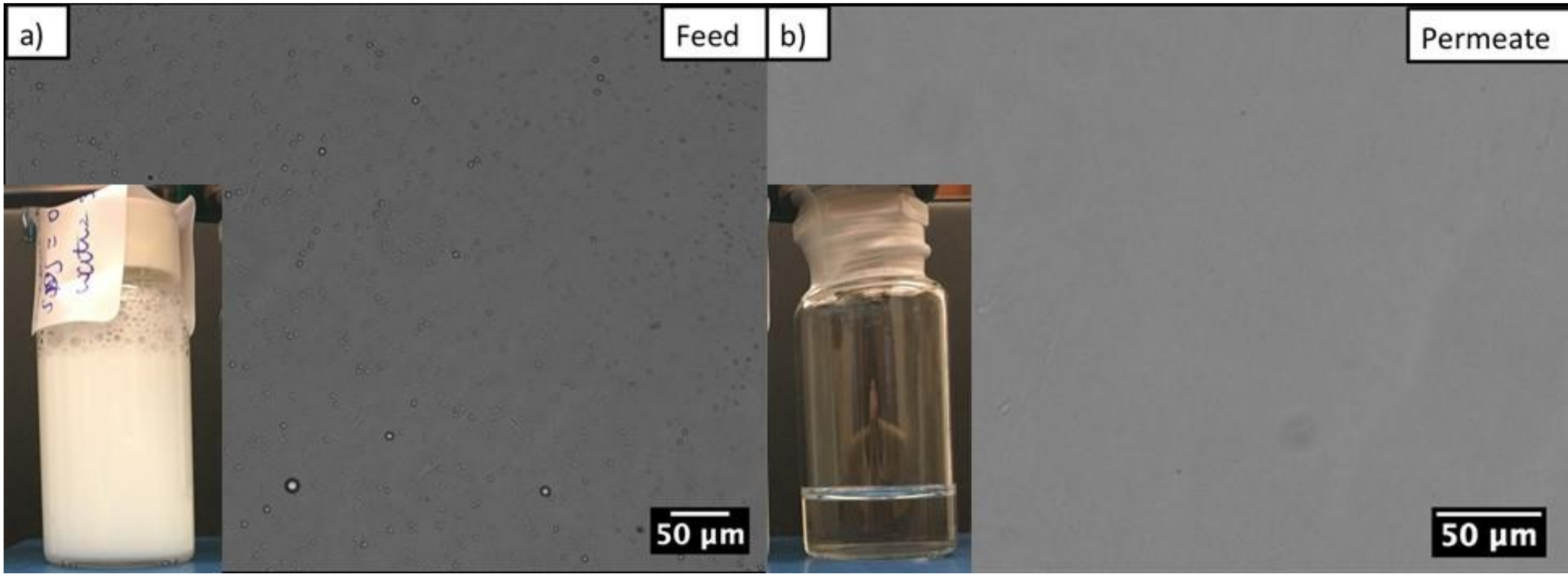
Before separation

After separation



		EDX atomic %		Si/Al
		Si	Al	
M0	Before separation	0	100	0
	After separation	0	100	0
M0.5	Before separation	0.59	99.41	0.0059
	After separation	0.45	99.55	0.0045
M5	Before separation	16.62	83.38	0.1993
	After separation	7.89	92.11	0.0857

Before and after separation with inorganic microfiltration membrane

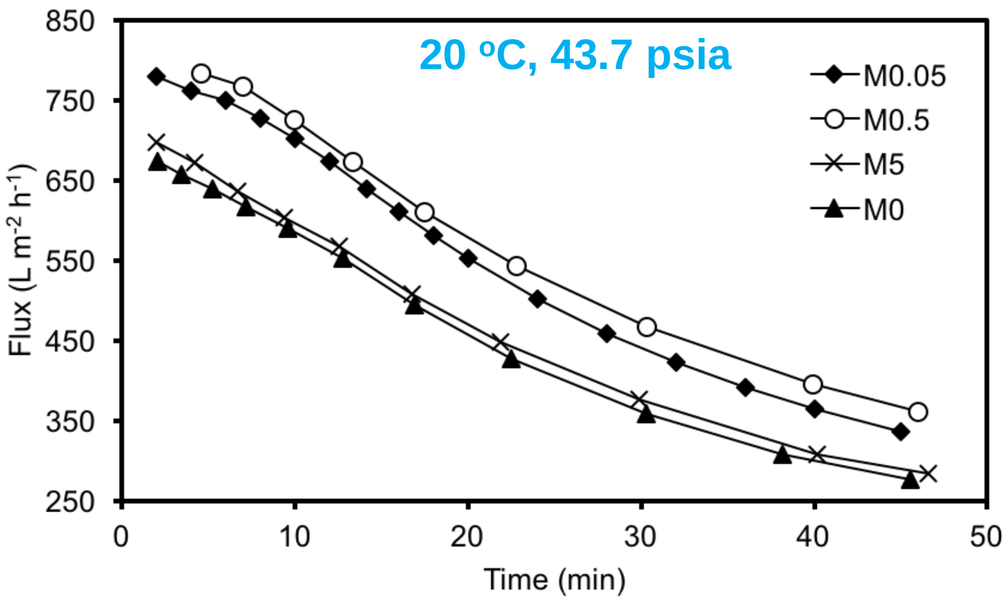


Microphotographs of the (a) feed and (b) permeate before and after microfiltration with M0.5 under the supplied pressure of 43.7 psia and the feed temperature of 20 ^{o}C.

R. Liu, S.-J. Kim, C. Aichele, *Journal of Water Process Engineering*, 26 (2018).

Effect of silica NPs concentration

- The silica NPs enhanced the membrane hydrophilicity
- The permeate cyclohexane concentration decreased
- The membrane flux diminished

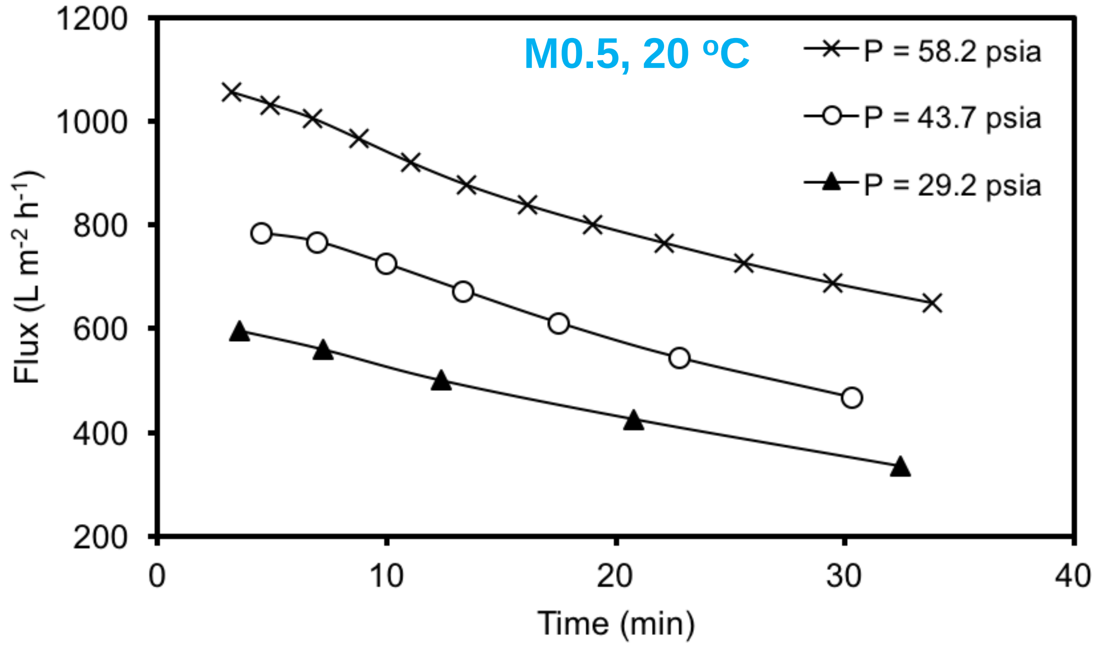


Membrane	Feed cyclohexane concentration (ppm)	Permeate cyclohexane concentration (ppm)	Oil rejection rate (%)	Initial average flux (0-5 min) (L m^{-2} h^{-1})
M0	500	60.42	87.92	640
M0.05	500	64.98	87.00	761
M0.5	500	33.89	93.22	784
M5	500	35.91	92.82	672

R. Liu, S.-J. Kim, C. Aichele, *Journal of Water Process Engineering*, 26 (2018).

Effect of feed pressure

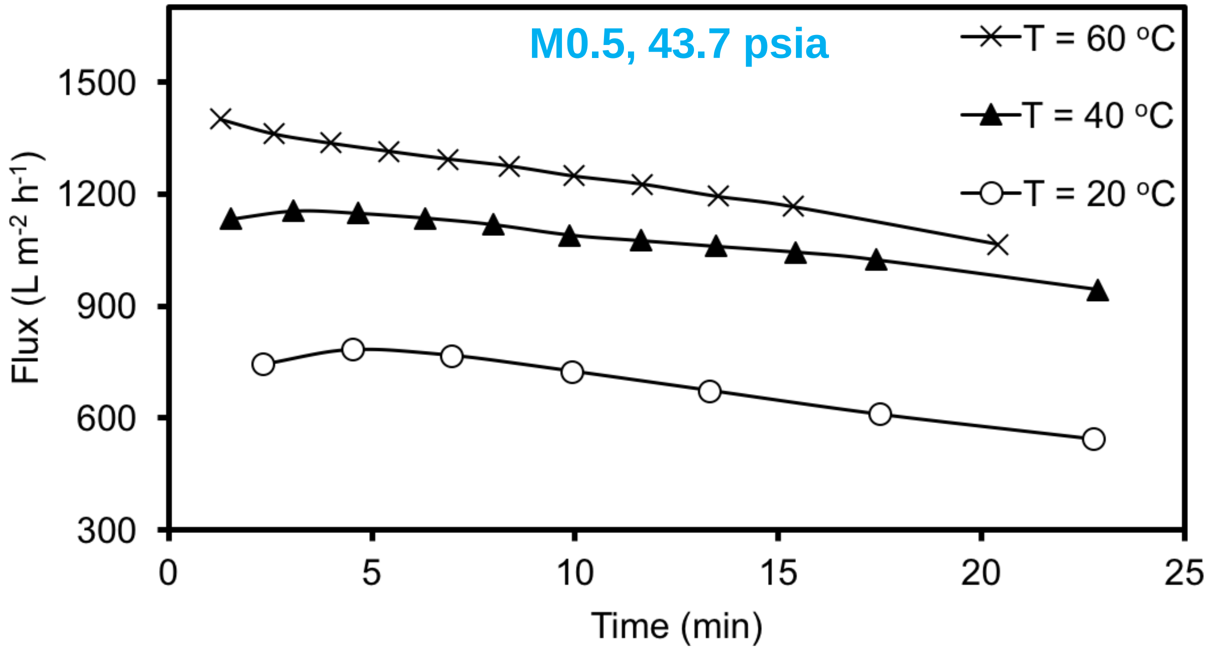
- The water flux increased and oil rejection decreased
- Higher flux worsen the fouling problem



Supplied pressure (psia)	Feed cyclohexane concentration (ppm)	Permeate cyclohexane concentration (ppm)	Oil rejection rate (%)	Initial average flux (0-5 min) (L m^{-2} h^{-1})
29.2	500	2.04	99.59	596
43.7	500	33.89	93.22	784
58.2	500	42.91	91.82	1032

Effect of temperature

- Water permeability increases with an increase in temperature
- The rejection rates varies < 2%
- Temperature did not affect the oil rejection performance



Feed temperature (°C)	Feed cyclohexane concentration (ppm)	Permeate cyclohexane concentration (ppm)	Oil rejection rate (%)	Initial average flux (0-5 min) (L m^{-2} h^{-1})
20	500	33.89	93.22	784
40	500	28.38	94.32	1149
60	500	39.54	92.09	1337

Conclusions

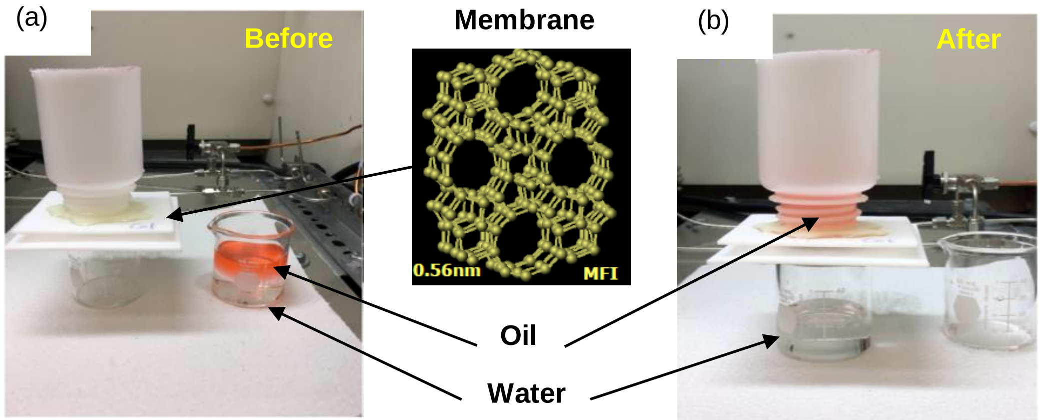
- We demonstrated a novel method to incorporate hydrophilic silica NPs into an α-alumina microfiltration tubular membrane for oil-in-water emulsion separation.

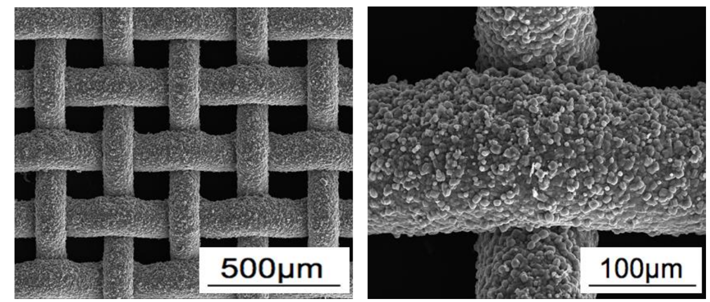
- The stable oil-in-water emulsion can be separated by using inorganic microfiltration membrane.

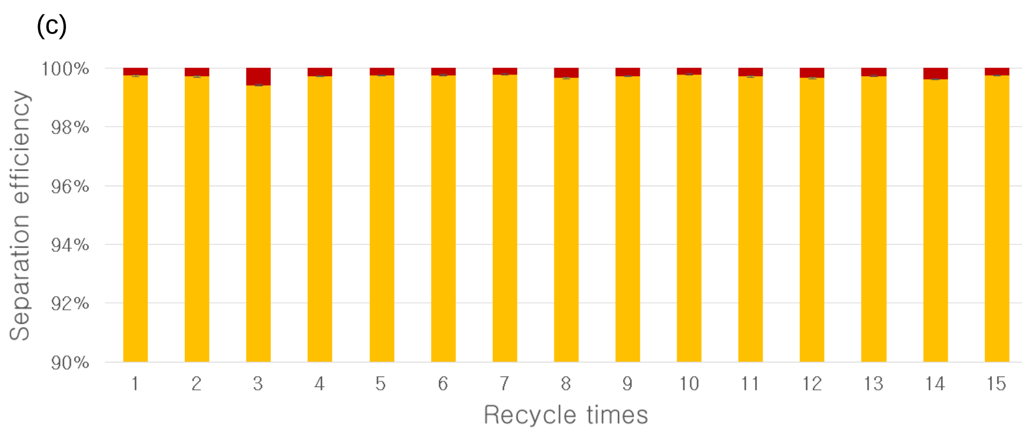
- The high water flux and oil rejection rate (>1000 L m^{-2} h^{-1} and >94% at 40 ^{o}C) was obtained by incorporating super-hydrophilic silica nanoparticles (0.5 wt.%)

Oil-water separation

Hydrophilicity-controlled MFI-type zeolite-coated mesh for oil-water separation







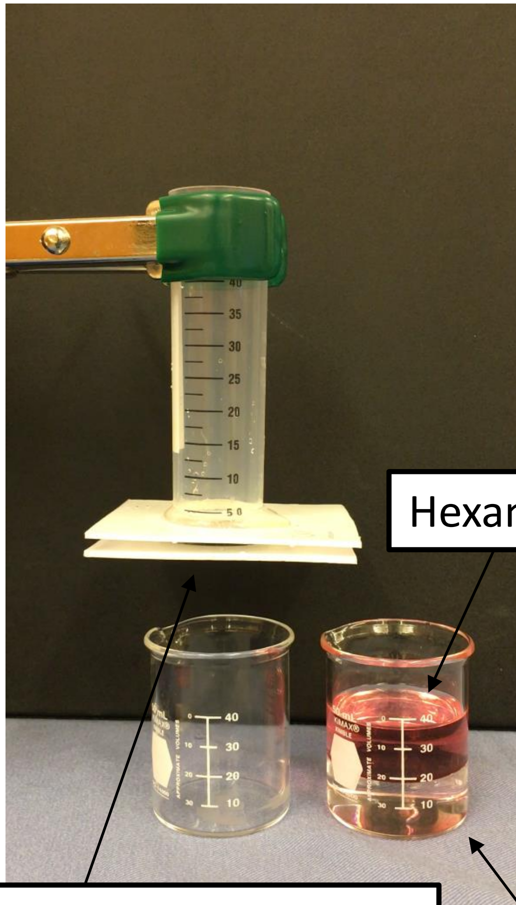
- Oil selectivity > 99% (15-times recycle)
- Membrane flux: ~90,000 L/m^2h
- Common targeting membrane flux :

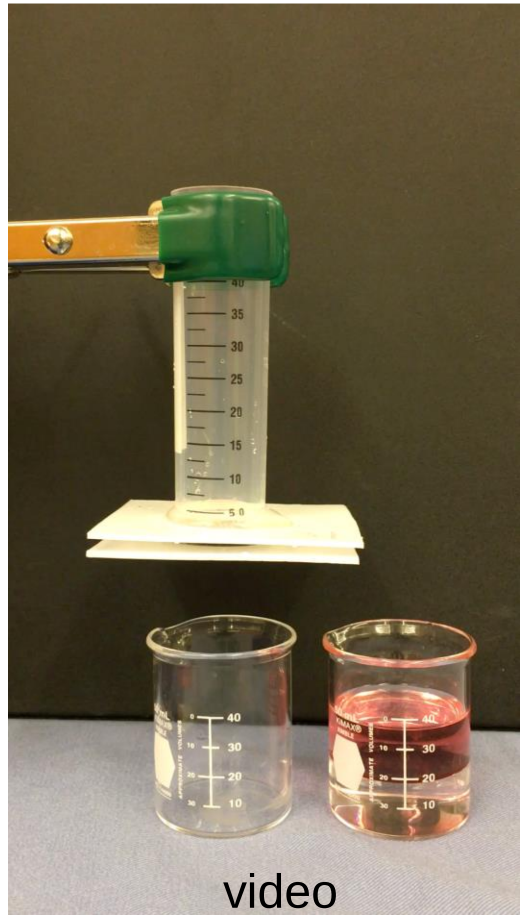
  20- 200 L/m^2h

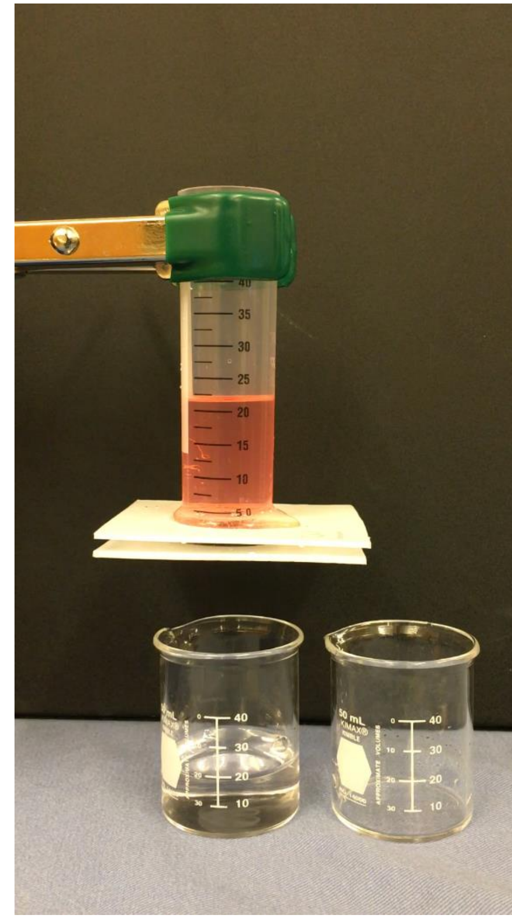
R. Liu, S.-J. Kim, *Sep. Purif. Technol.*, 195 (2018) 163-169.

Oil-water separation

Before | **After**



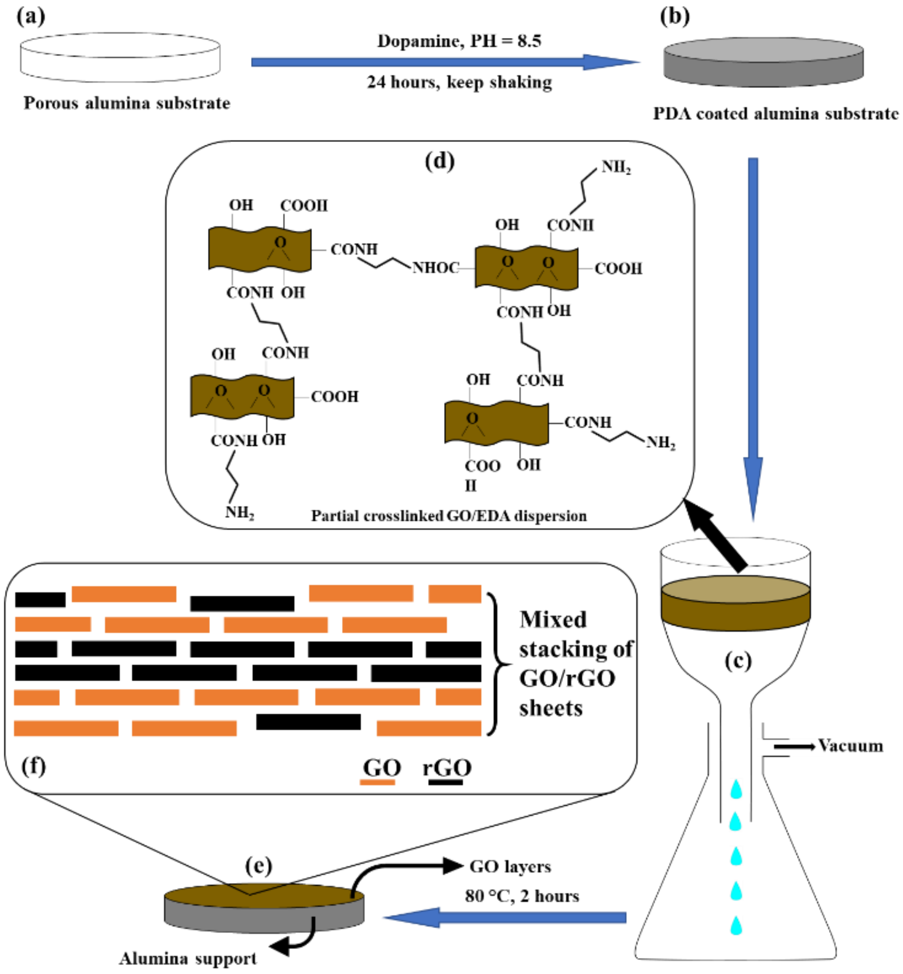




R. Liu, S.-J. Kim, D. N. McIlroy, *Colloids Surf., A,* 550 (2018) 108–114.

Desalination

Hybrid Graphene Oxide (GO/rGO) Membranes with Controlled Pre-crosslinking



H. Lin, R. Liu, S. Dangwal, S.-J. Kim, N. Mehr, Y. Li, J. Zhu, *J. Membr. Sci.* 563 (2018) 336-344.

Desalination

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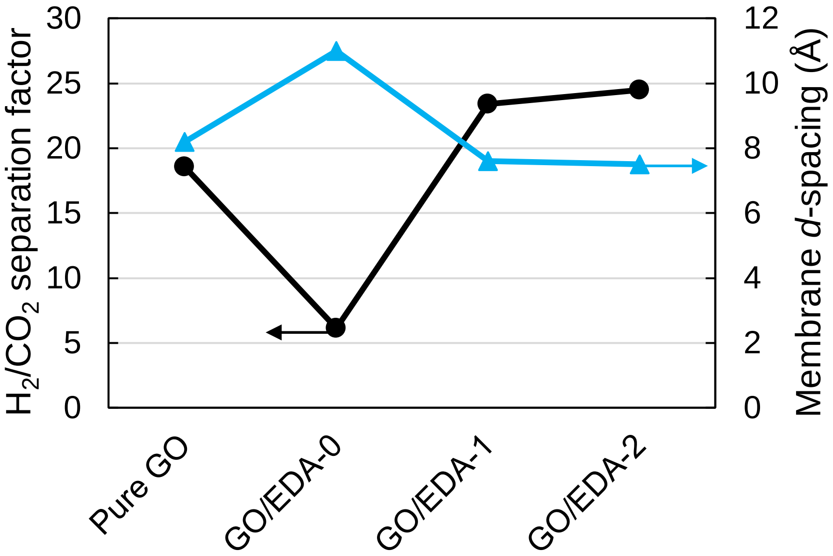


Ions	Feed (ppm)	Rejection rate (%)	Rejection rate (%)	Rejection rate (%)
		GO/EDA-0	GO/EDA-1	GO/EDA-2
Na^+	853.86	92.51	99.84	99.06
K^+	30.00	100.00	100.00	100.00
Mg^{2+}	103.90	86.37	94.82	99.56
Cl^-	1434.01	94.10	95.35	99.78
SO_4^{2-}	220.75	76.11	93.78	99.04

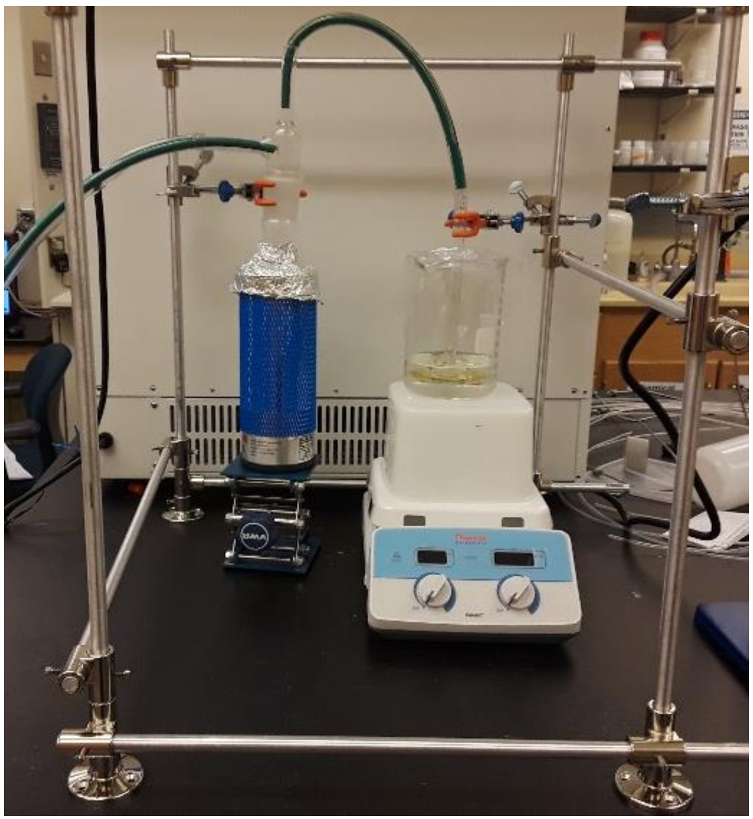
H. Lin, R. Liu, S. Dangwal, S.-J. Kim, N. Mehr, Y. Li, J. Zhu, *ACS Appl. Mater. Interfaces*. 10 (2018).

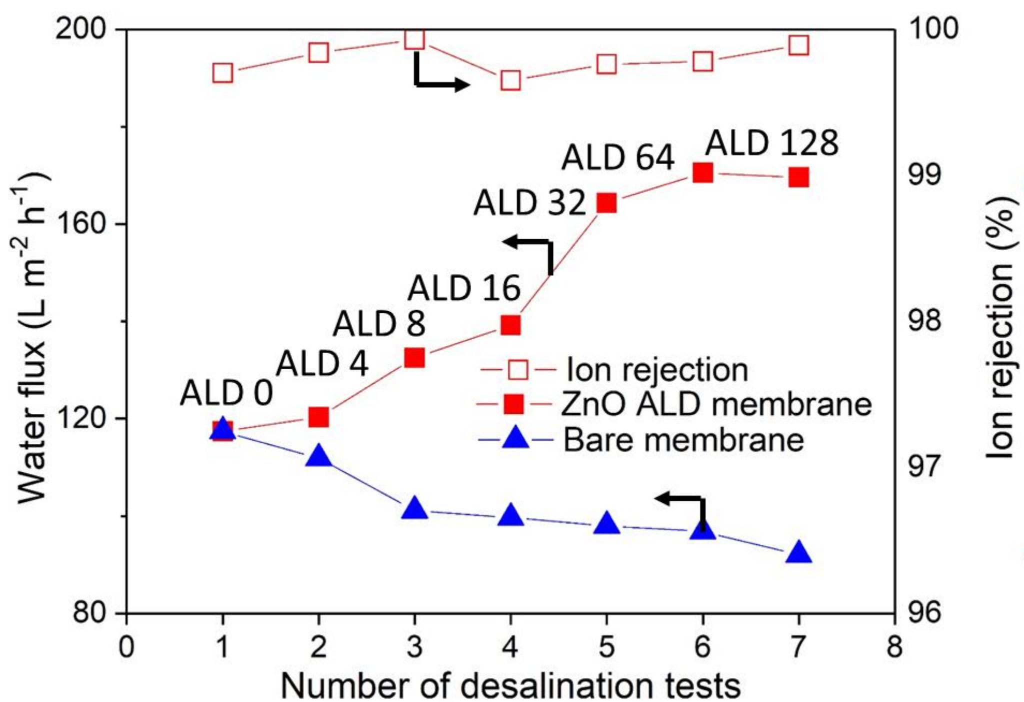
Desalination

Vacuum Flow Through Evaporation Method

Salt rejection > 99.9%

Flux ~100 L m^{-2} h^{-1}





S. Dangwal, S.-J. Kim, D. N. McIlroy, (under review).

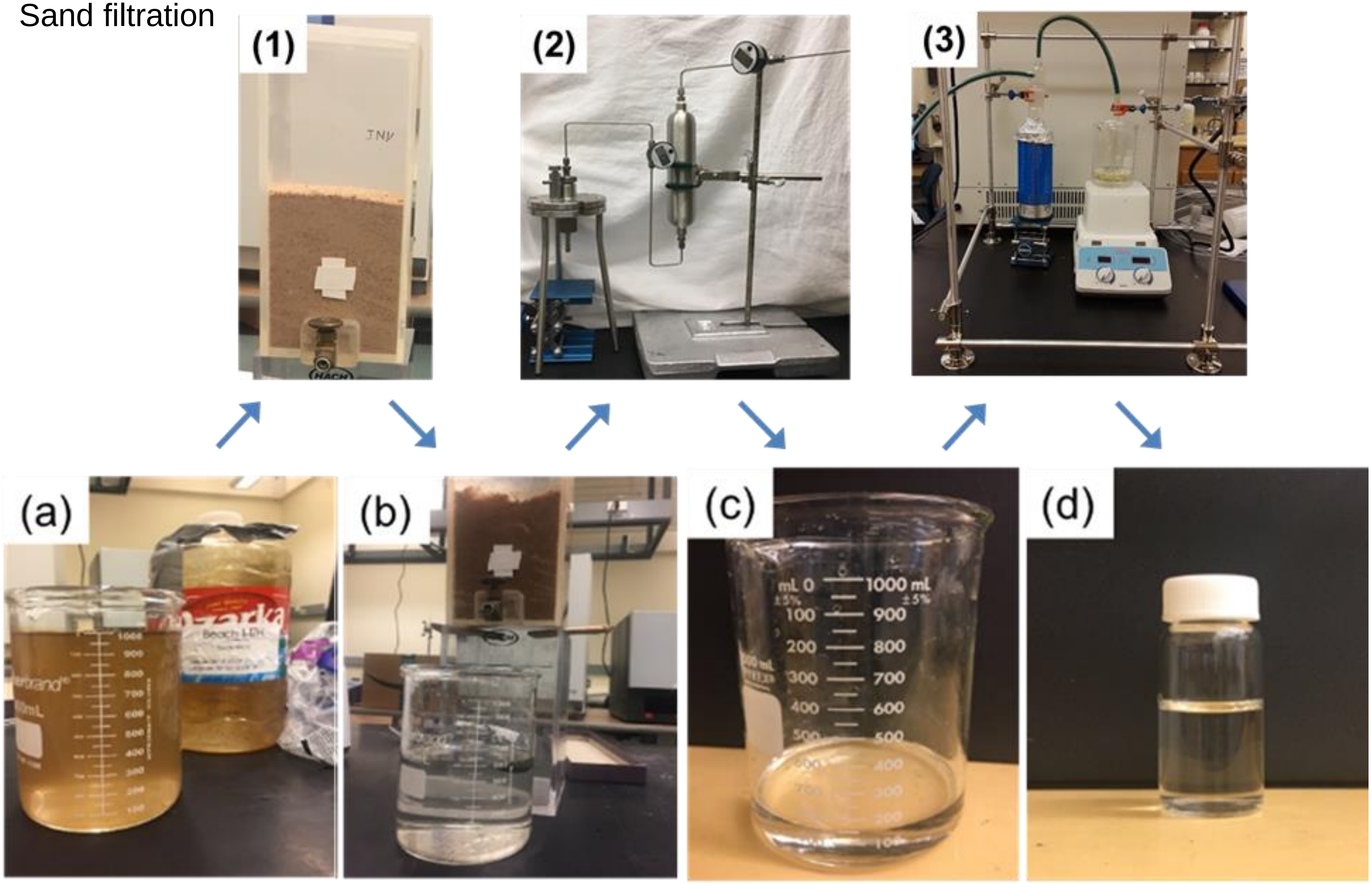
Preliminary results

Three-stage-system for PW treatment

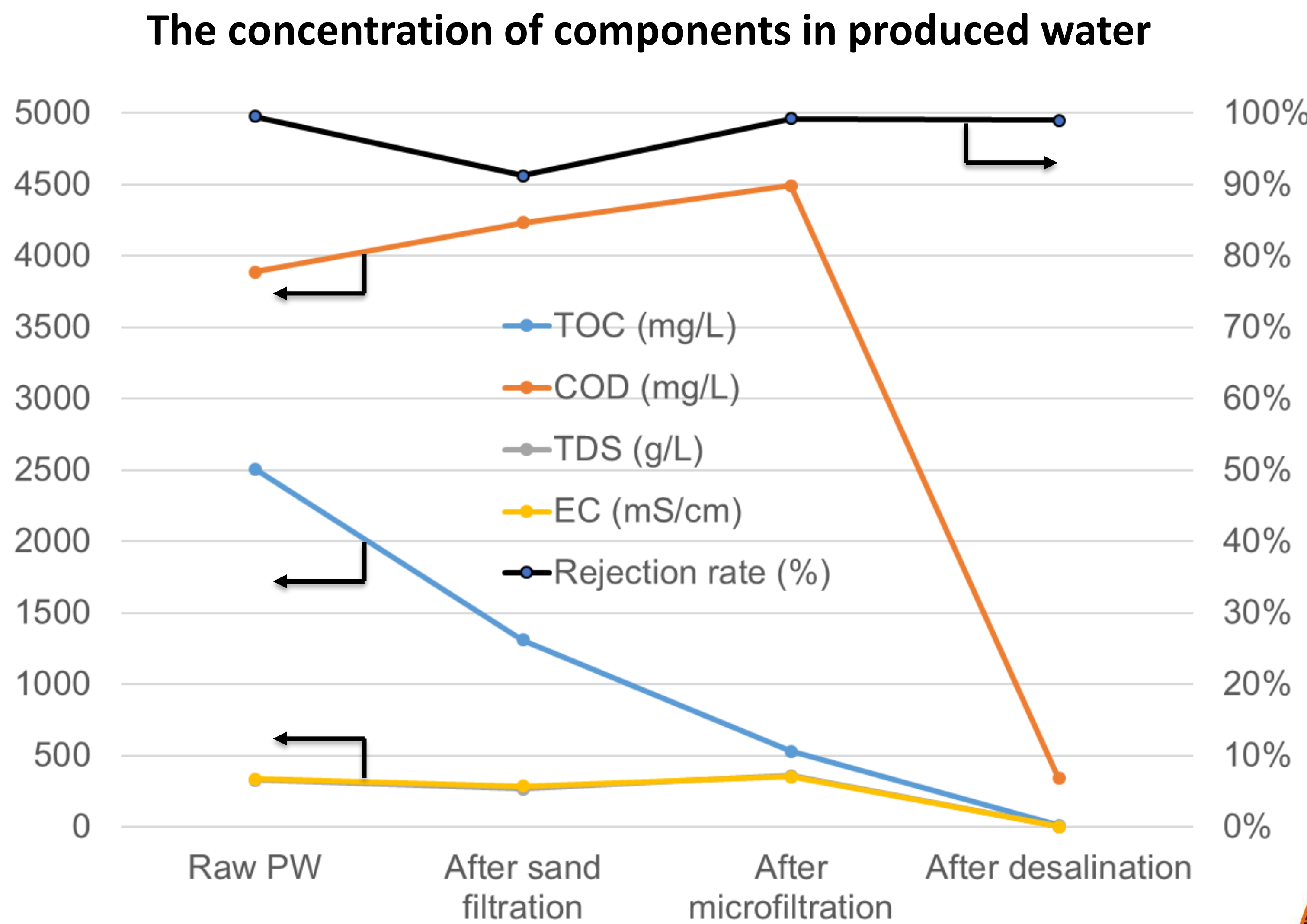
Chemical precipitation
Sand filtration

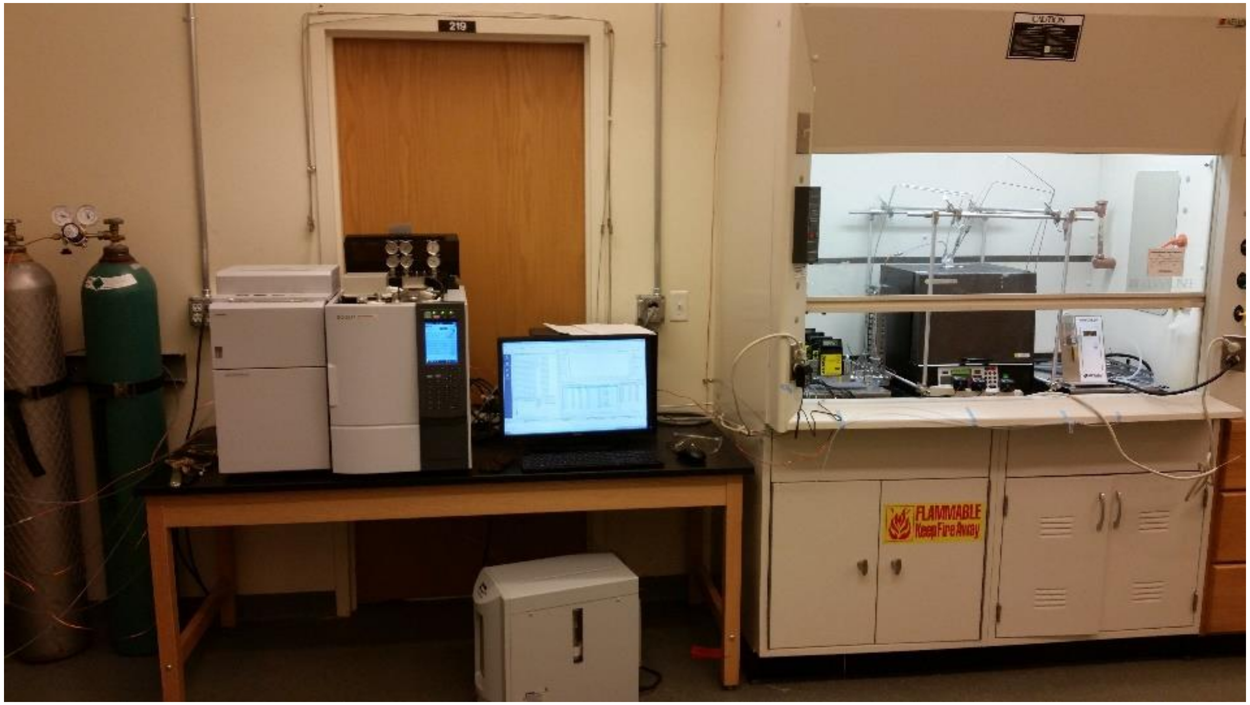
Microfiltration (oil rejection)
Flux ~1000 L m^{-2} h^{-1}

Desalination (salt rejection)
Flux ~100 L m^{-2} h^{-1}



Preliminary results

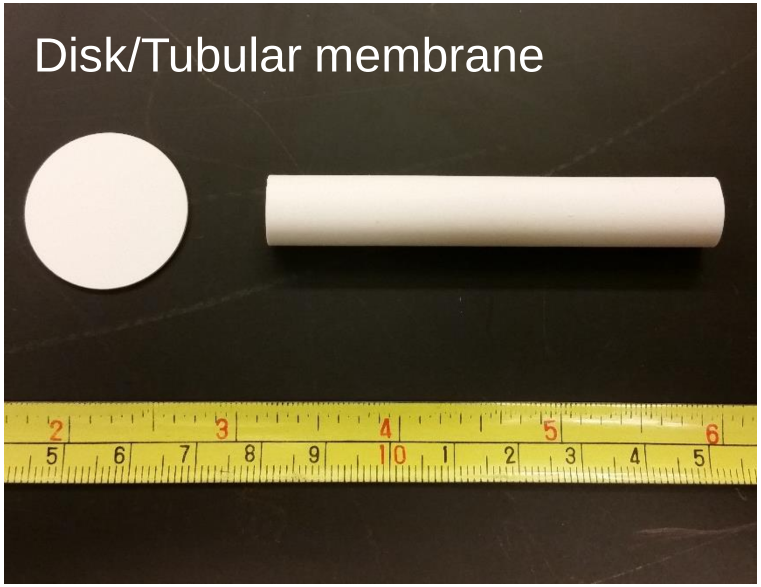


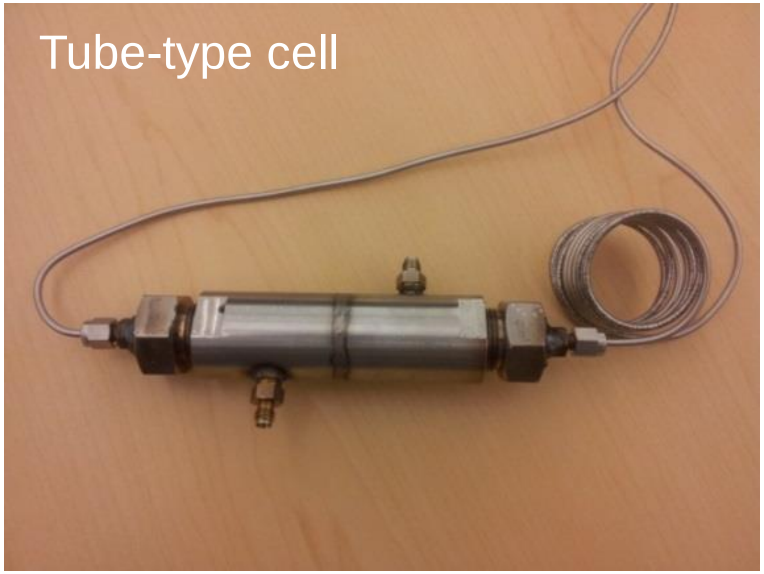


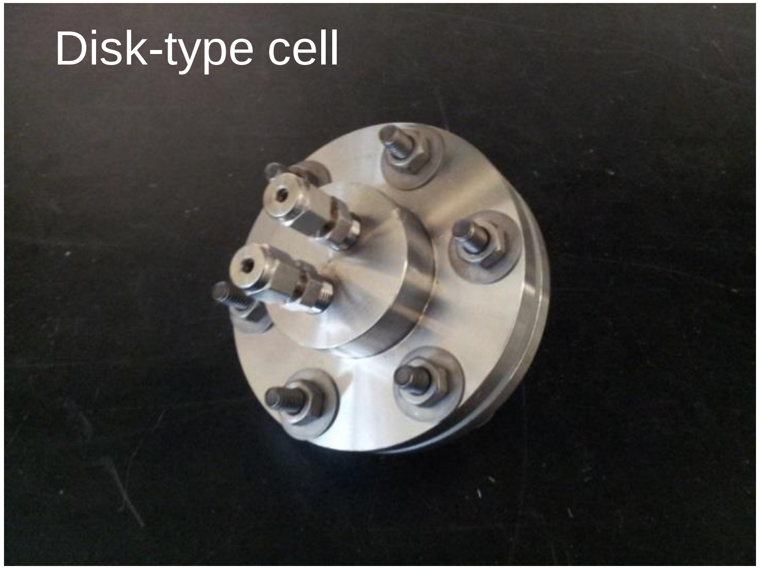
Membrane reaction and separation system and GC

Ovens and furnaces

Membrane Cells



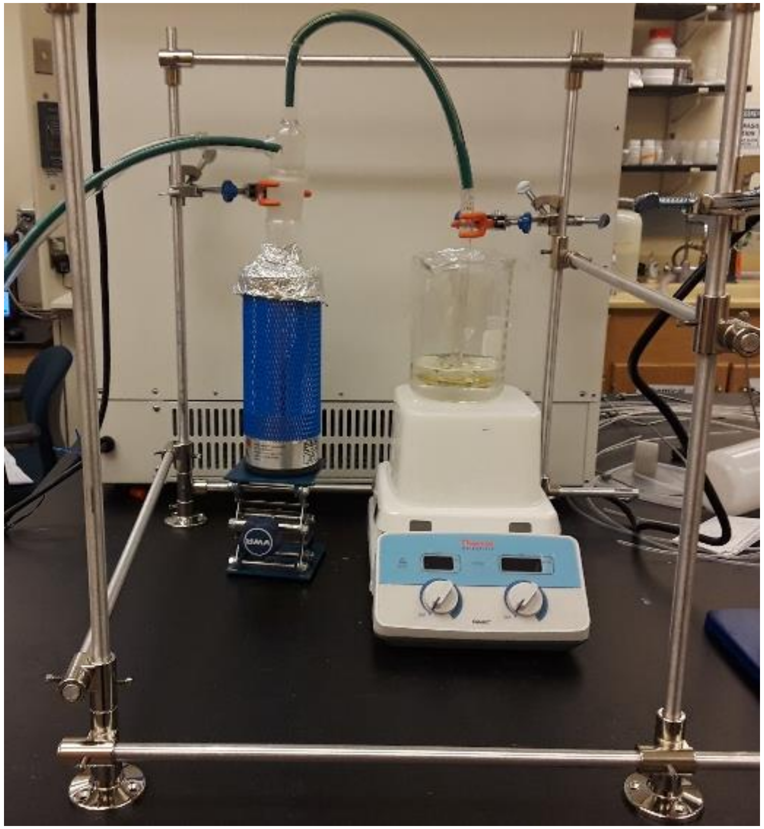




Water purification

MF filter equipment

Desalination



Thank you!