Studies on Separation Performance of Interfacially Formed Membranes

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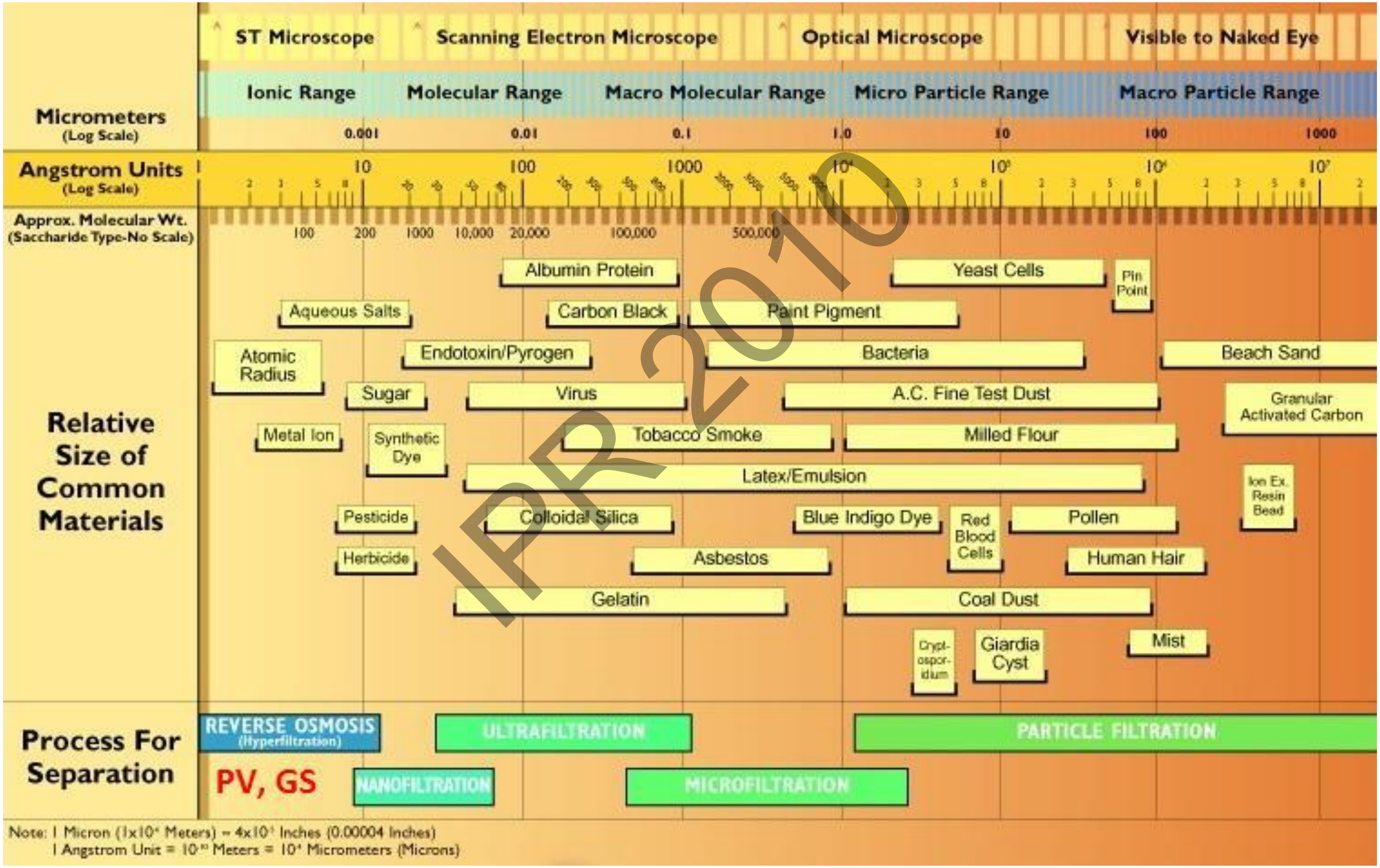
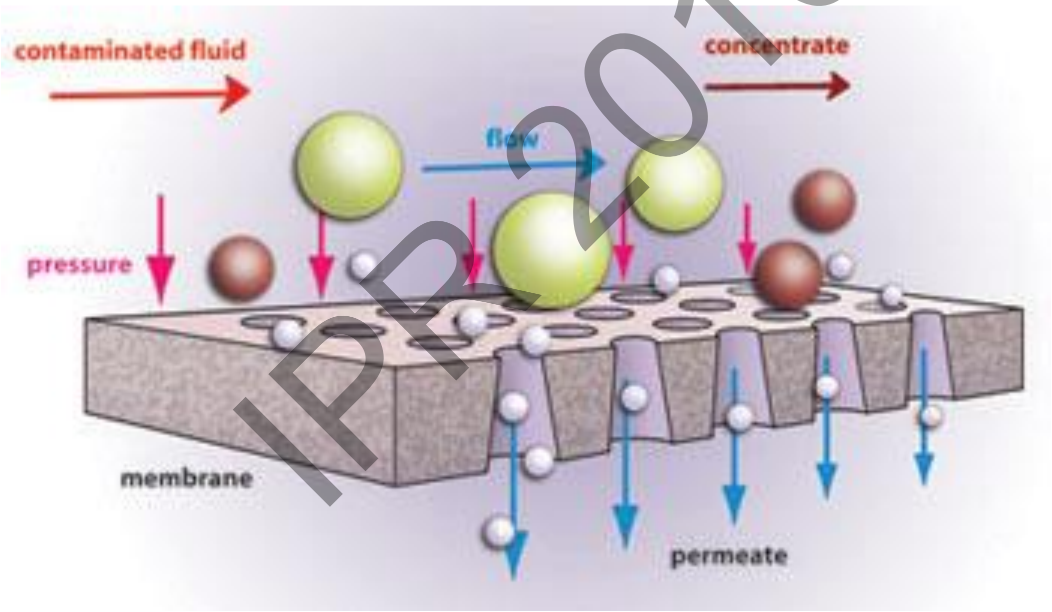
Outline

- Basic principles of membrane separation
- Interfacially formed membranes
- Separation performance in CO_2 capture, natural gas dehydration, desalination, and drinking water treatment

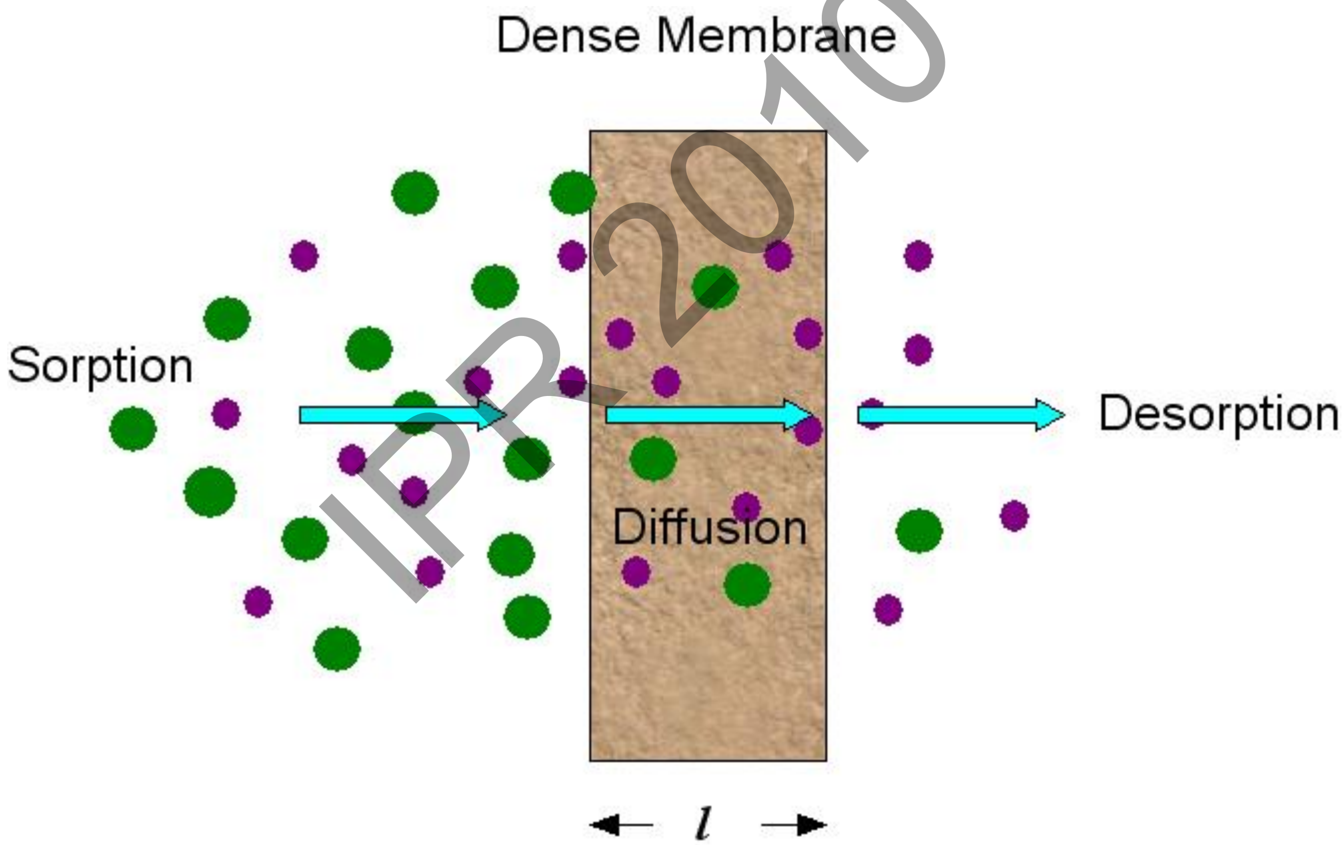
Separation Spectrum



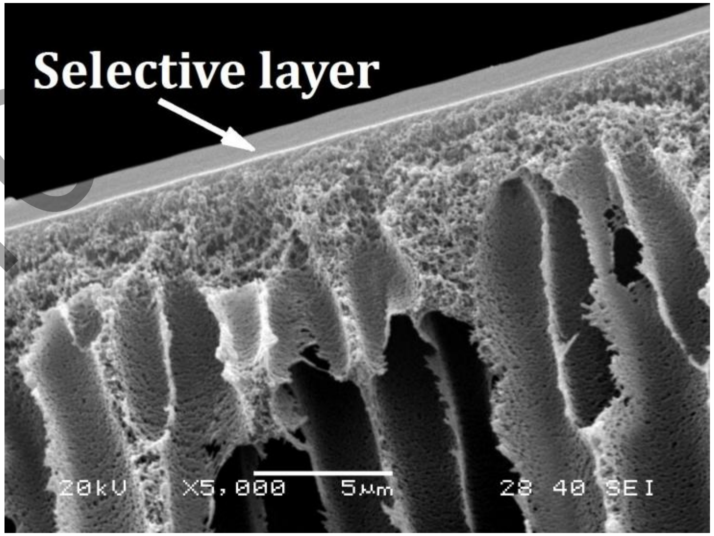
Sieve Mechanism of Porous Membranes



Solution-Diffusion Mechanism of Nonporous Membranes



3 Key Elements to Determine the Performance (flux/selectivity)



1. Material Chemistry

- Film-formation and mechanical property
- Inherent hydrophilicity, fouling tendency
- Intrinsic permeability & selectivity
- Bio-compatibility
- Chemical resistance

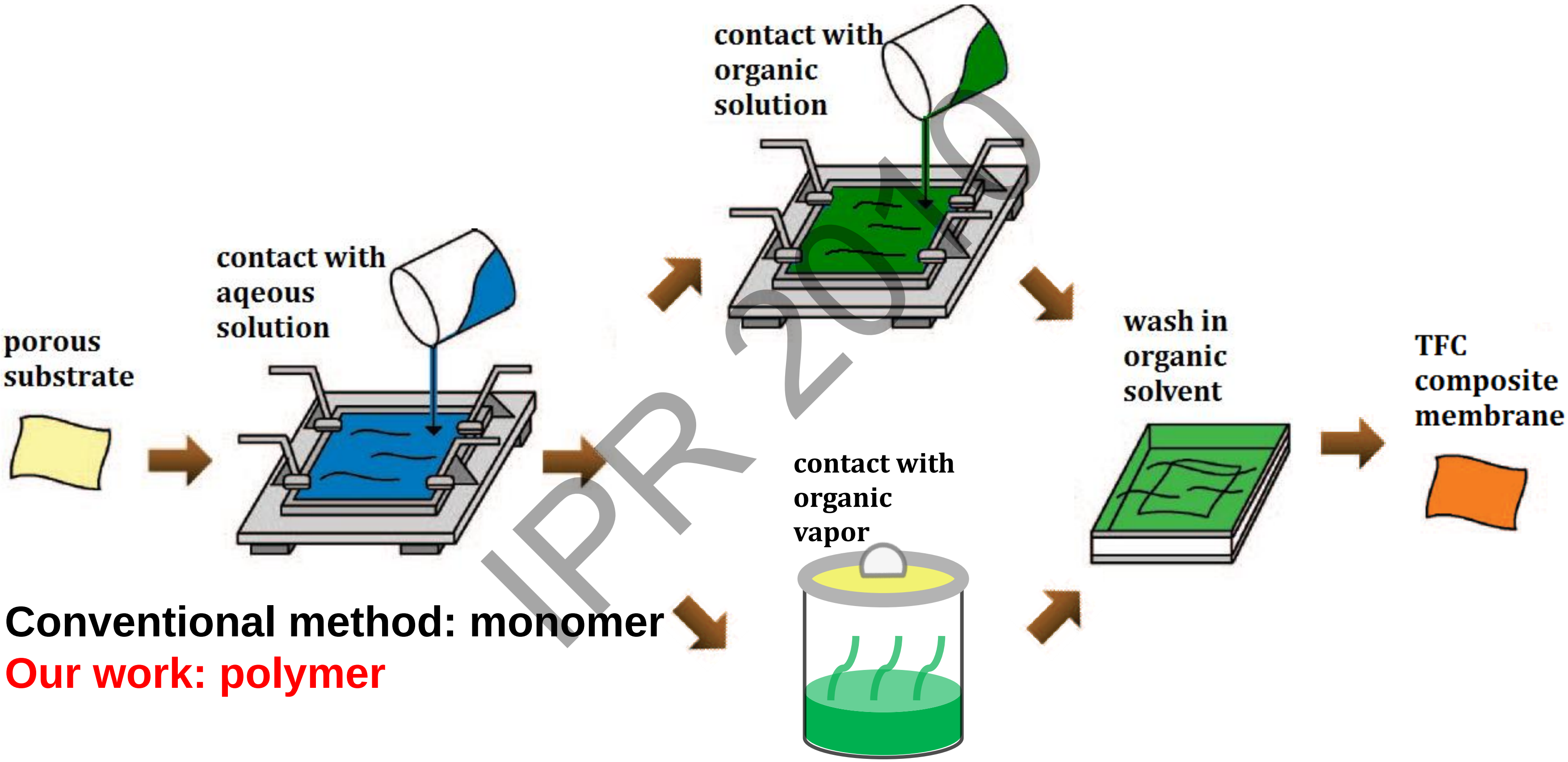
2. Pore Size

- 0.3-0.5 nm for GS, PV
- 0.4-1.2 nm for desalination, separate low MW solutes
- 2-200 nm for UF, separate high MW solutes
- 50-1000 nm for MF

3. Selective Layer Thickness

- Controls the flux (productivity)
- As thin as possible

Interfacially Formed Thin-film-composite (TFC) Membranes

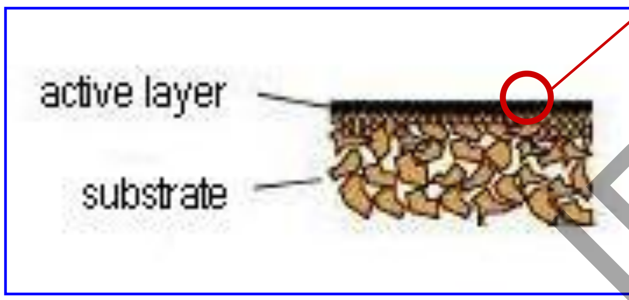


Conventional method: monomer
Our work: polymer

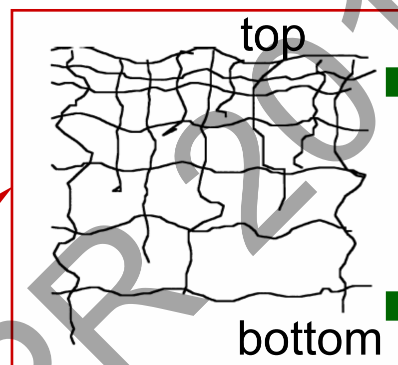
Conventional method: liquid-liquid interfacial reaction
Our work: solid-liquid or solid-vapor interfacial reaction

Conventional method: limited to RO or NF of liquid mixtures
Our work: good for GS, PV, NF, and UF processes

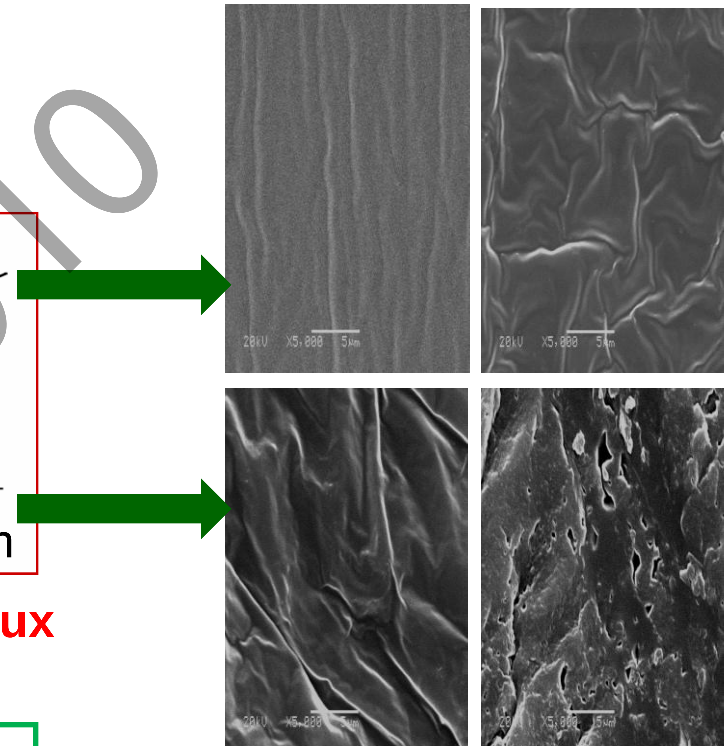
Interfacially Formed Asymmetric Structure



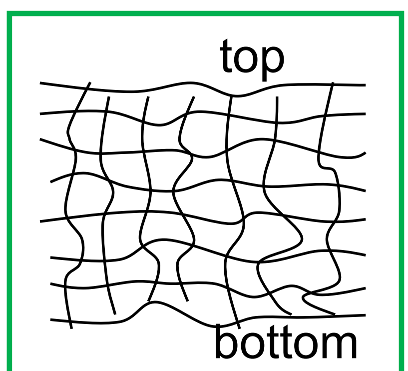
Interfacial crosslinking



ideal for high flux



Bulk crosslinking

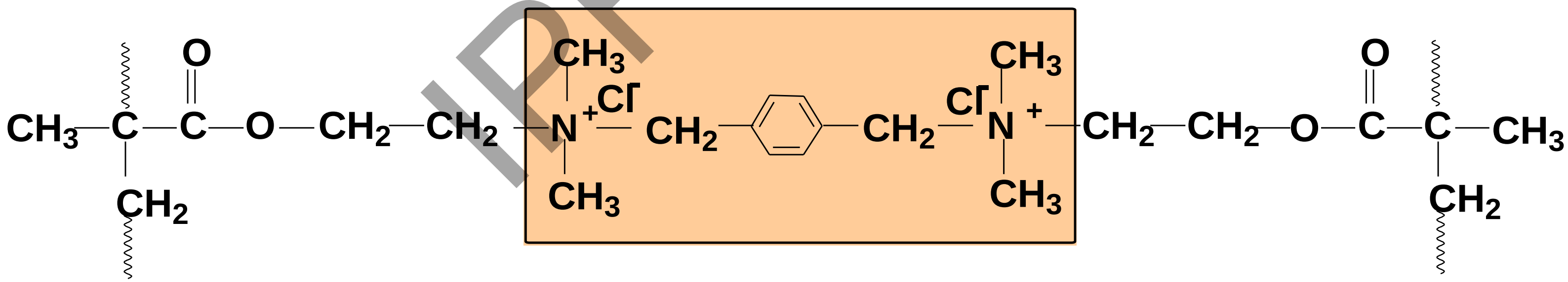


Before water rinsing

After water rinsing

Interfacially Formed PDM membranes

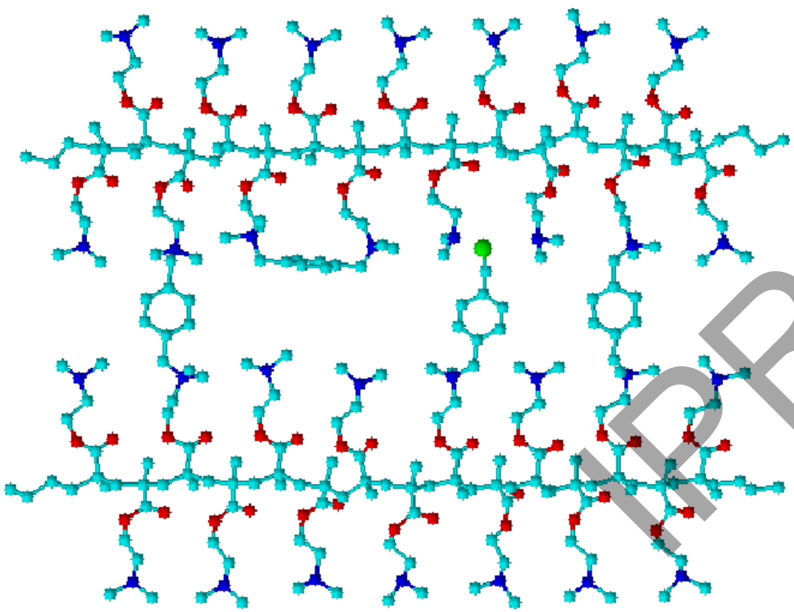
Poly(*N*,*N*-dimethylaminoethyl methacrylate)
PDM



Crosslinked PDM

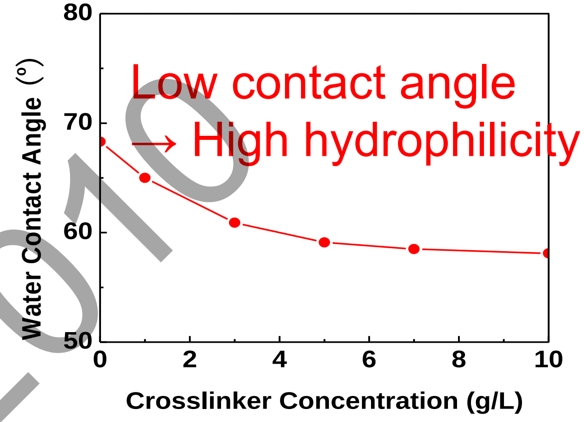
Chemical Properties of PDM Membranes

1. Weak alkalinity



1% PDM aqueous solution: pH 7.7

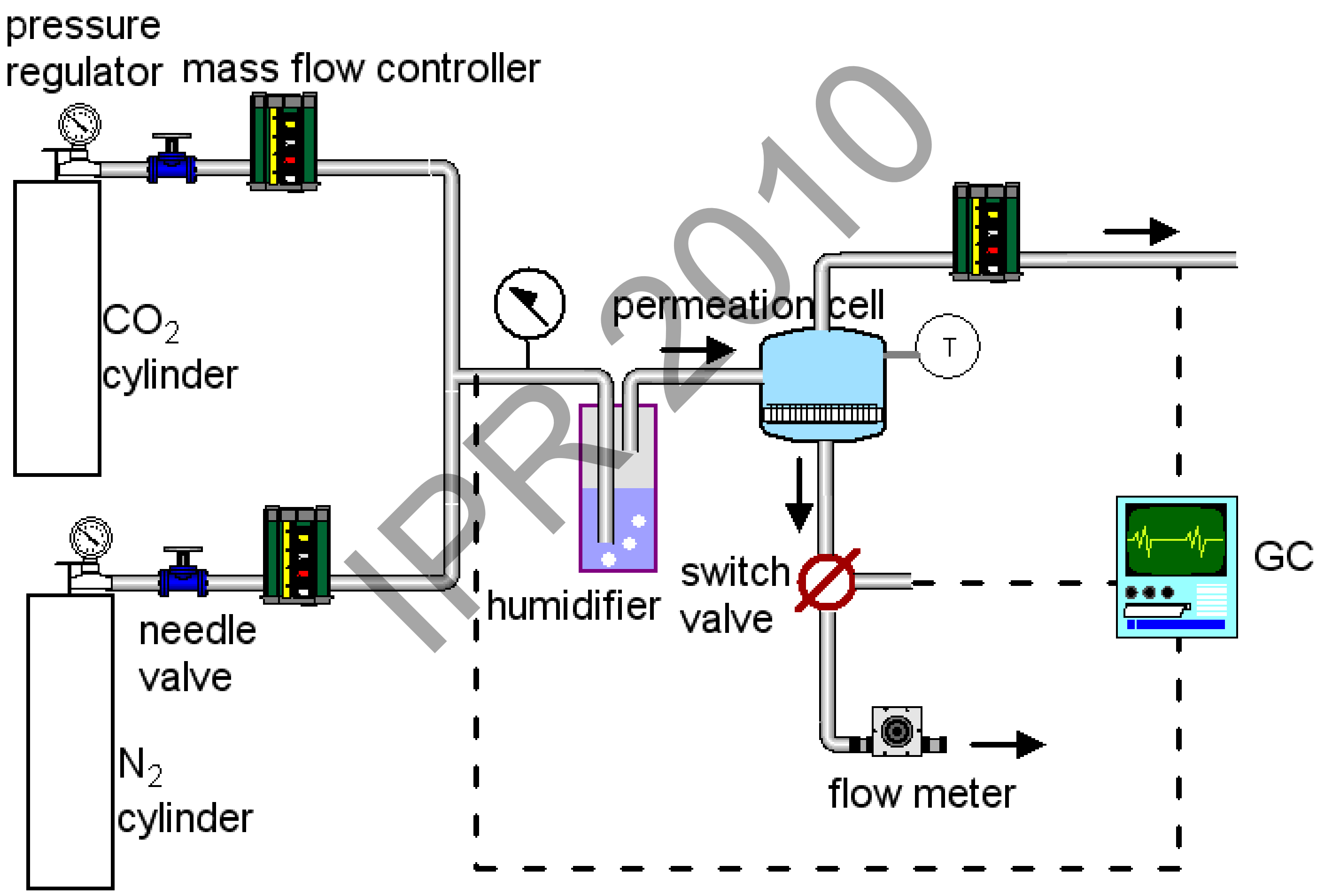
2. High hydrophilicity



3. Strong polarity

Du et al. *J. Appl. Polym. Sci.* 91 (2004) 2721-2728

Flue Gas (CO_2/N_2) Separation



Comparison with Other Membranes for CO_2 Separation

Membrane	α (CO_2/N_2)	J_{CO2} (GPU)
Poly(4-vinylpyridine-co-acrylonitrile)	9	0.001
Poly(DMAEMA-co-acrylonitrile)	90	0.2
Plasma-grafted DMAEMA on polyethylene	130	5
Polyethylenimine/Polyvinyl alcohol	230	4
PDM/PSF (Bulk crosslinked) (our work)	50	30
PDM/PSF (Interfacially formed) (our work)	50	85

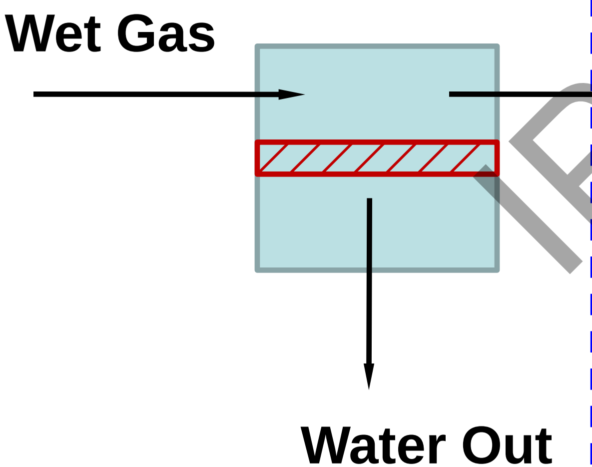
low

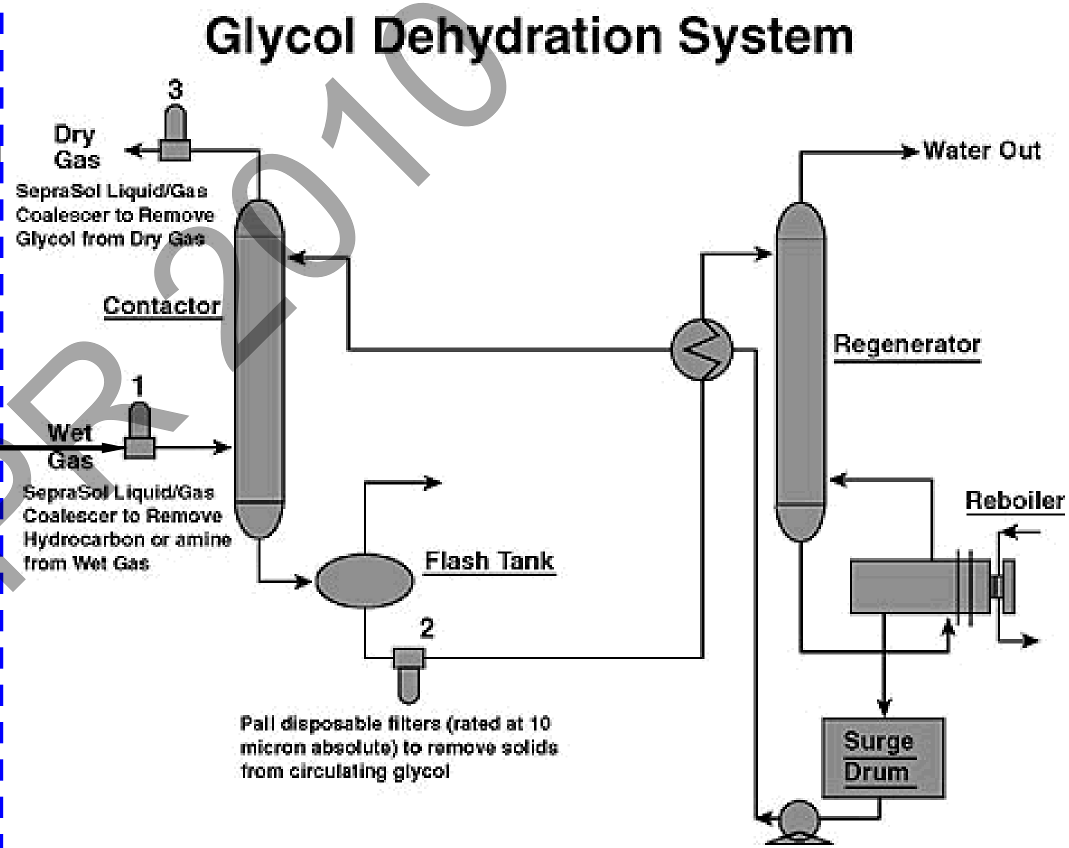
$J = \frac{V}{At\Delta p}$ Unit: GPU= $10^{-6}cm^3(STP)/cm^2.s.cmHg$ $\alpha = \frac{J_{CO2}}{J_{N2}}$

Du et al. *J. Membr. Sci.* 279 (2006) 76-85; 290 (2007) 19-28

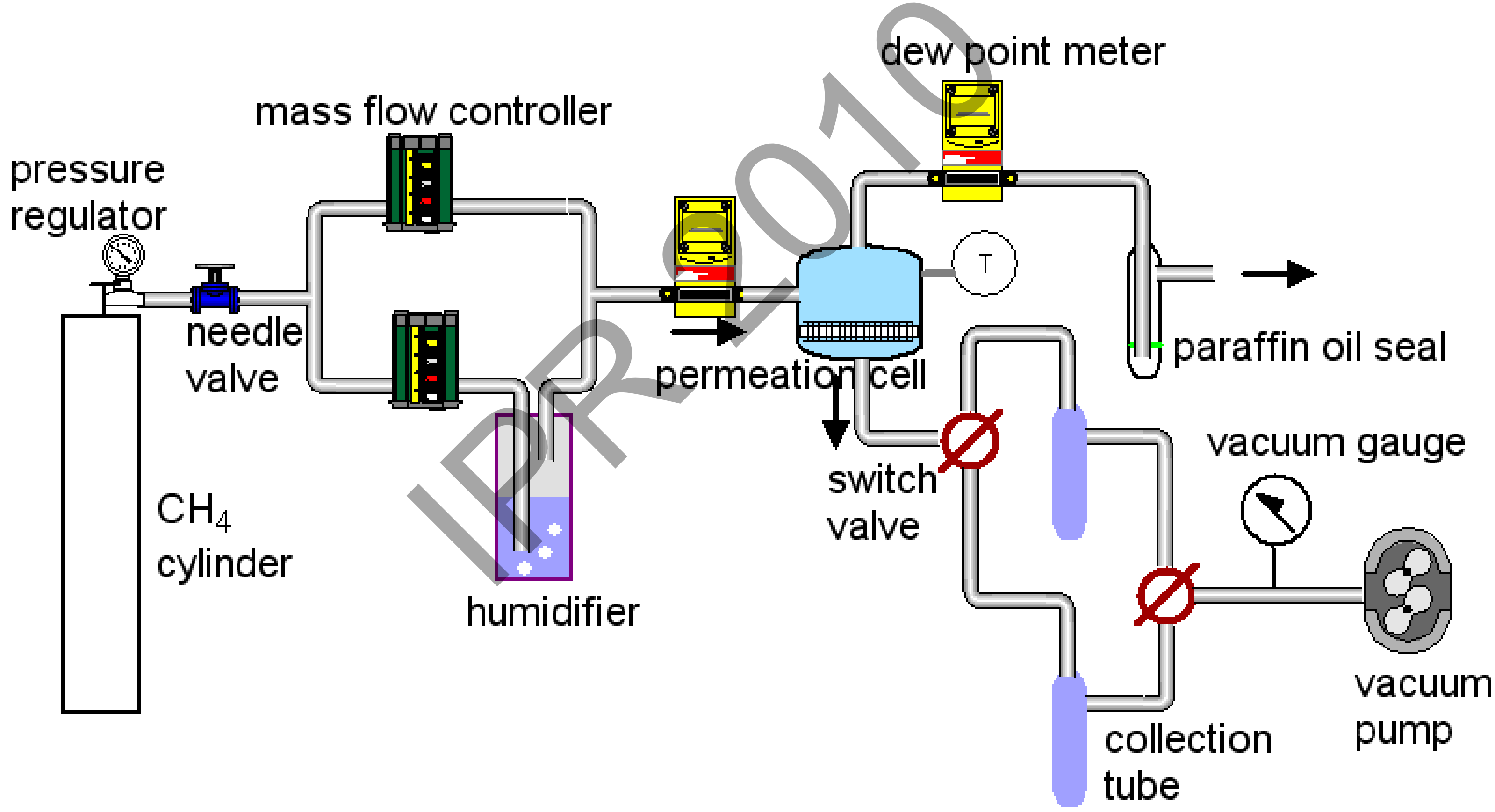
Natural Gas Dehydration

Membrane Dehydration System

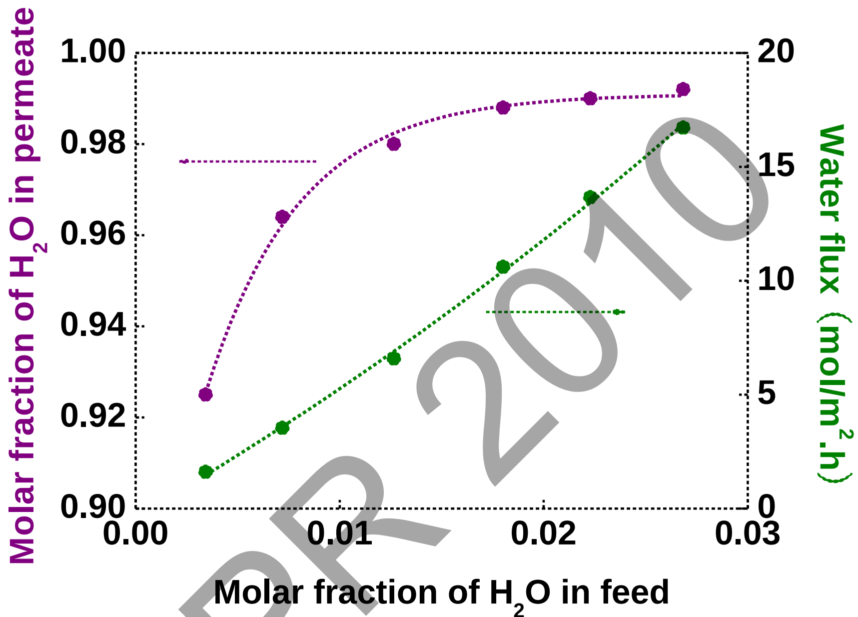




Membrane Dehydration System



Gas Dehydration Performance

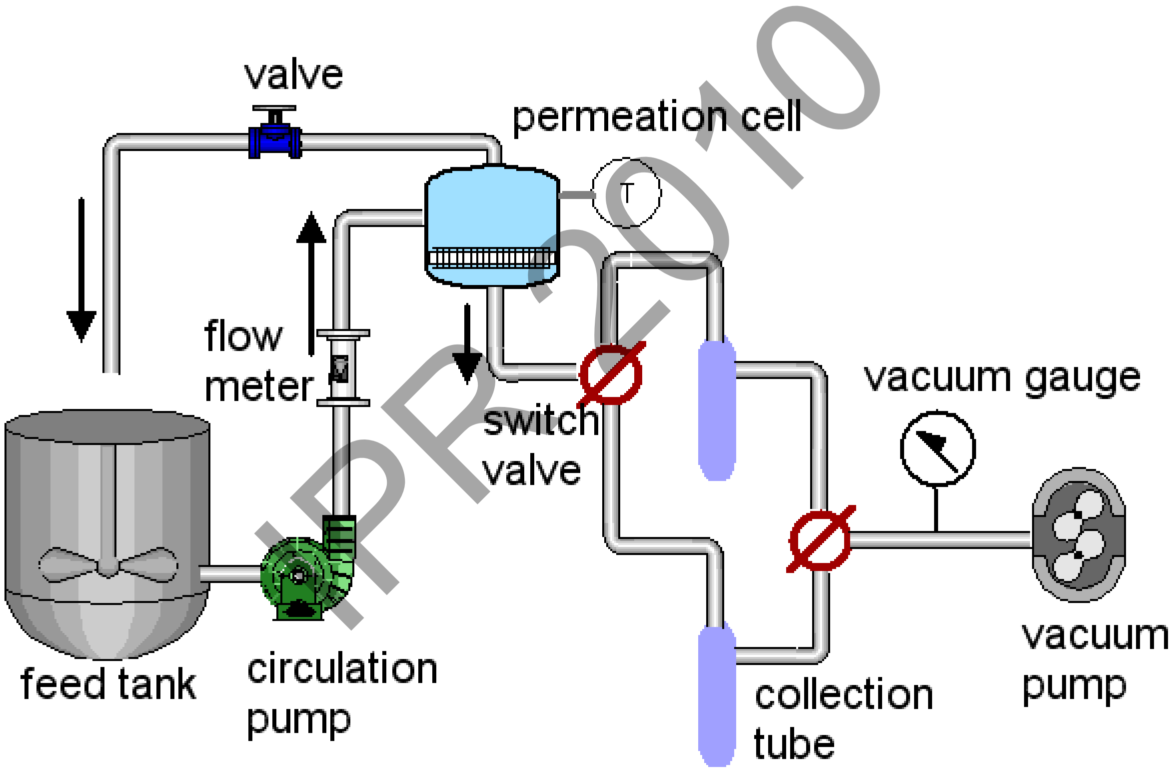


	J_{H2O} (GPU)	α (H_2O/CH_4)
PDM/PAN (our work)	4000	3500
Pilot test * (other polymer)	45	100

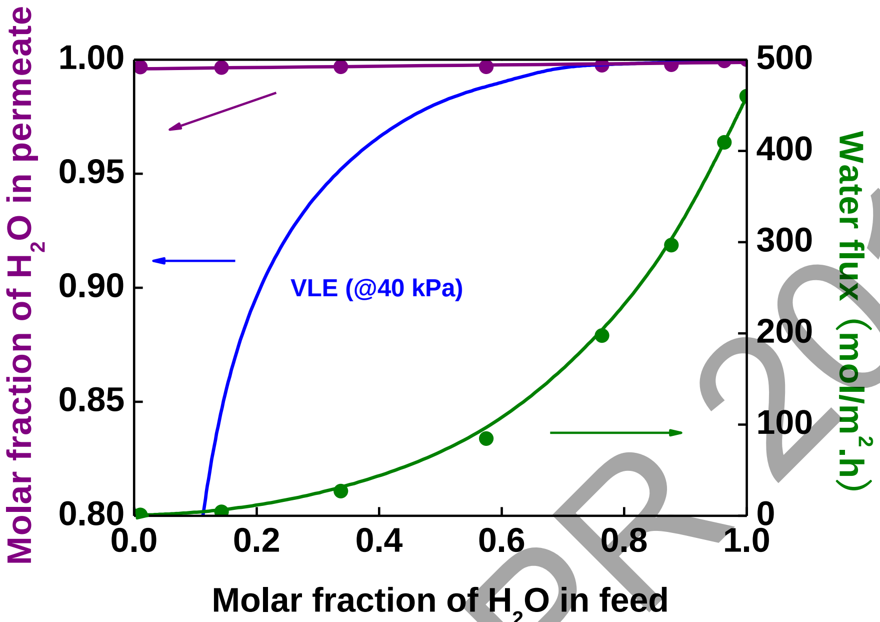
Du et al. *Chem. Eng. Sci.* accepted

* Liu et al. *Chem. Eng. Technol.* 24 (2001) 1045-1048.

Glycol Regeneration System - Pervaporation



Glycol Regeneration Performance

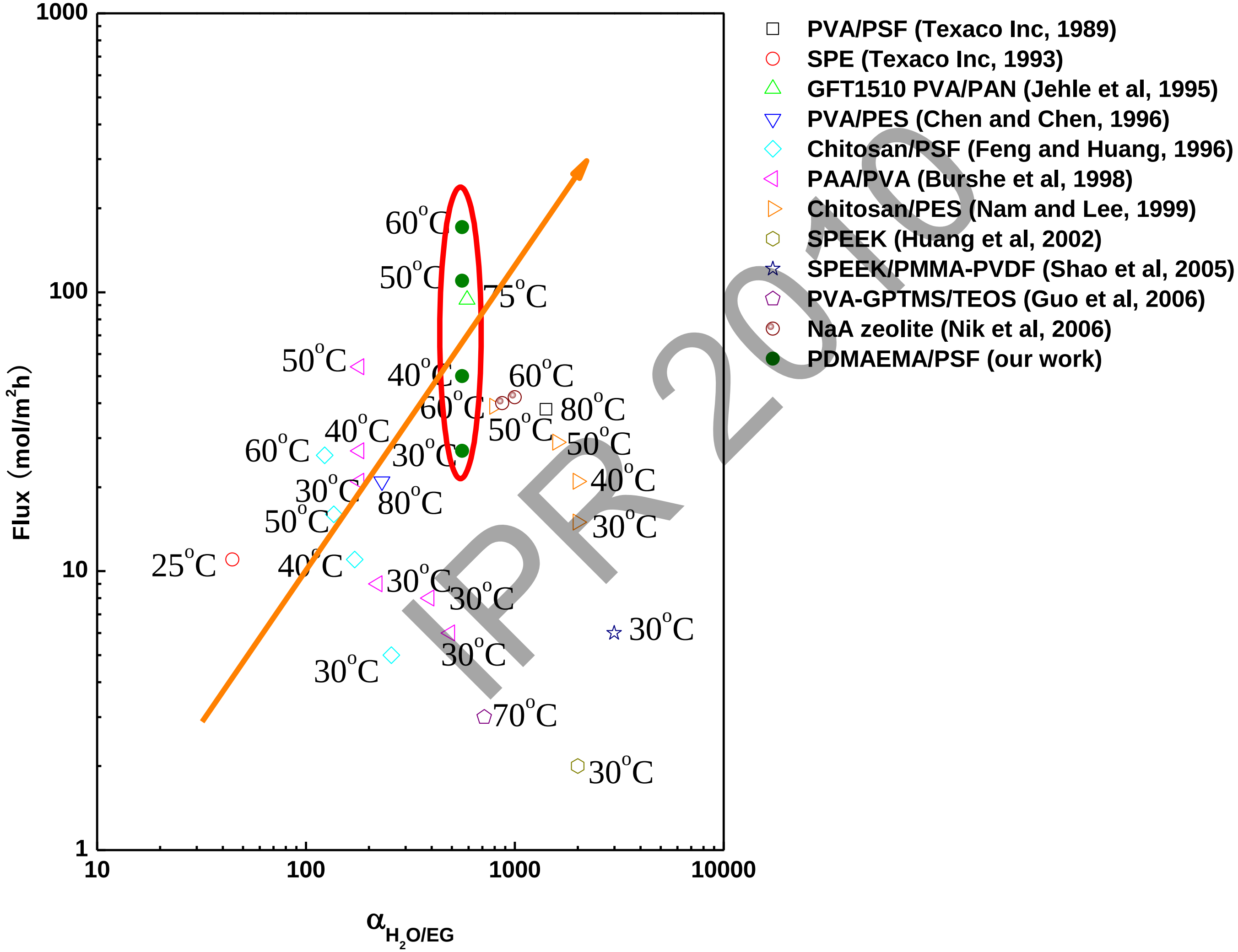


30°C
Downstream pressure 1.3 kPa

- **Selectivity of PV is much higher than that of distillation at low feed water concentration**

Du et al. *Sep. Purif. Technol.* 64 (2008) 63-70

Comparison with Other Membranes for Glycol Regeneration



Nanofiltration

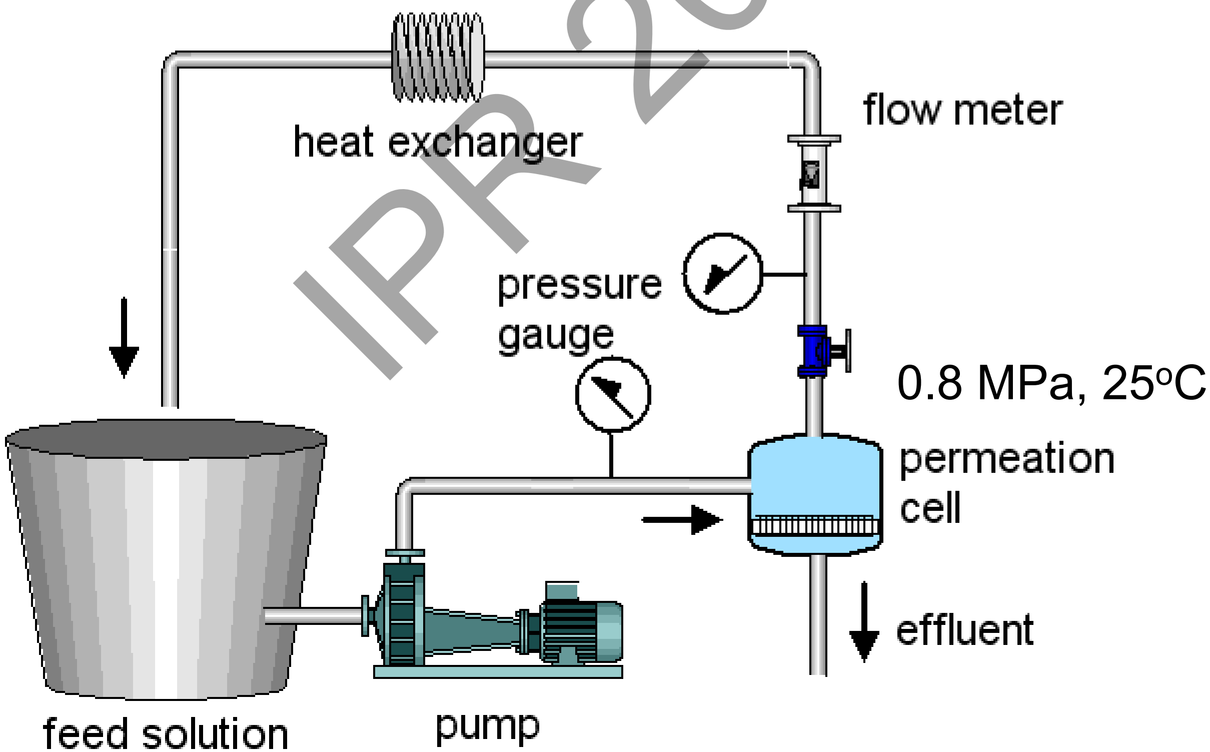
- **Commercially available**

  mostly negatively charged (aromatic polyamides, sulfonated polysulfone)

- **Separation mechanism**

  Physical sieving – neutral organics (i.e., polysaccharide)

  Electrostatic repulsion/attraction – ions (i.e., salts, dyes)



Desalination Performance

Salt	Rejection (%)	
	PDM	NTR-7450 (Nitto Denko)*
$MgCl_2$	98	13
$MgSO_4$	91	32
NaCl	77.8	51
Na_2SO_4	66	92

*NTR-7450 (Hydranautics/Nitto Denko): sulfonated polysulfone

Chemical Resistance

Solution	ΔR (%)	ΔF (%)
NaClO (5 ppm)	-2	4
H_2O_2 (5 ppm)	-8	-4

$MgSO_4$ 1g/L; 3 weeks storage in solutions

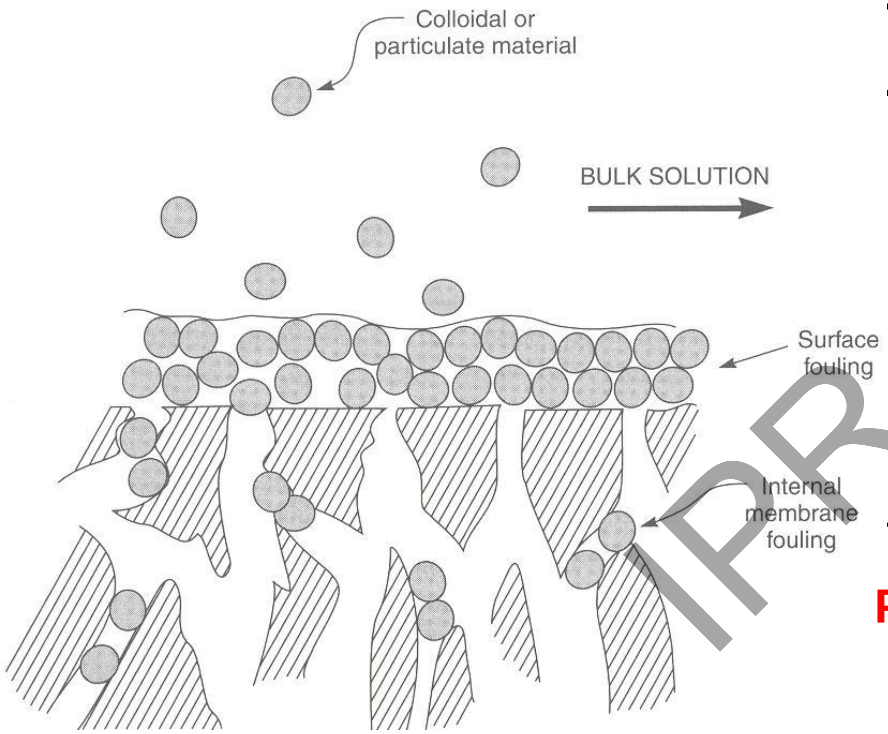
$$F = \frac{V}{At} \qquad R = \frac{C_F - C_P}{C_F} \times 100\%$$

Resistant to oxidants

N.B.- Commercial aromatic polyamide NF membranes are very sensitive to chlorine

Du et al. *J. Membr. Sci.* 239 (2004) 183-188

Fouling Control in Water Treatment



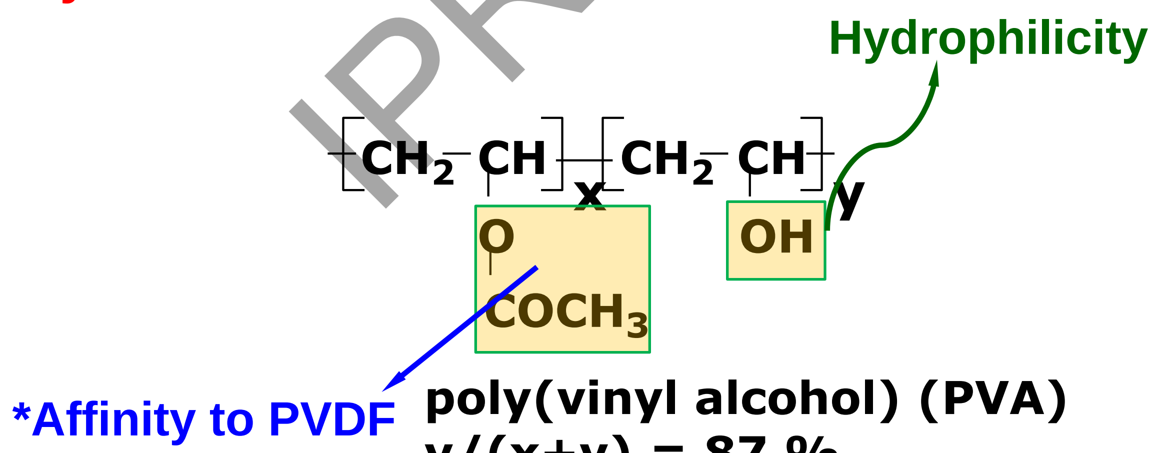
Morphology	Surface Chemistry
roughness	hydrophilicity
porosity	charge
tortuosity	
thickness	
pore size distribution	

PVDF (polyvinylidene fluoride) membranes:

- Good film-forming property
- Good chemical, thermal resistance
- High hydrophobicity
- Rough surface

Material Selection for Modification - PVA

- Good film-forming property
- Good physical and chemical resistance
- Non-toxic
- Highly hydrophilic (active layer material for commercial PV)
- Smooth surface (protective layer material for commercial NF, RO)
- Affinity to PVDF

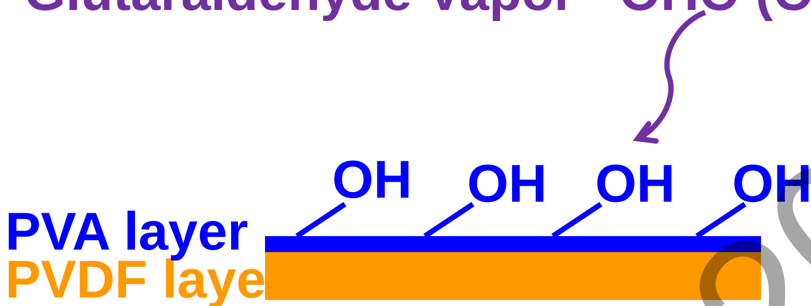


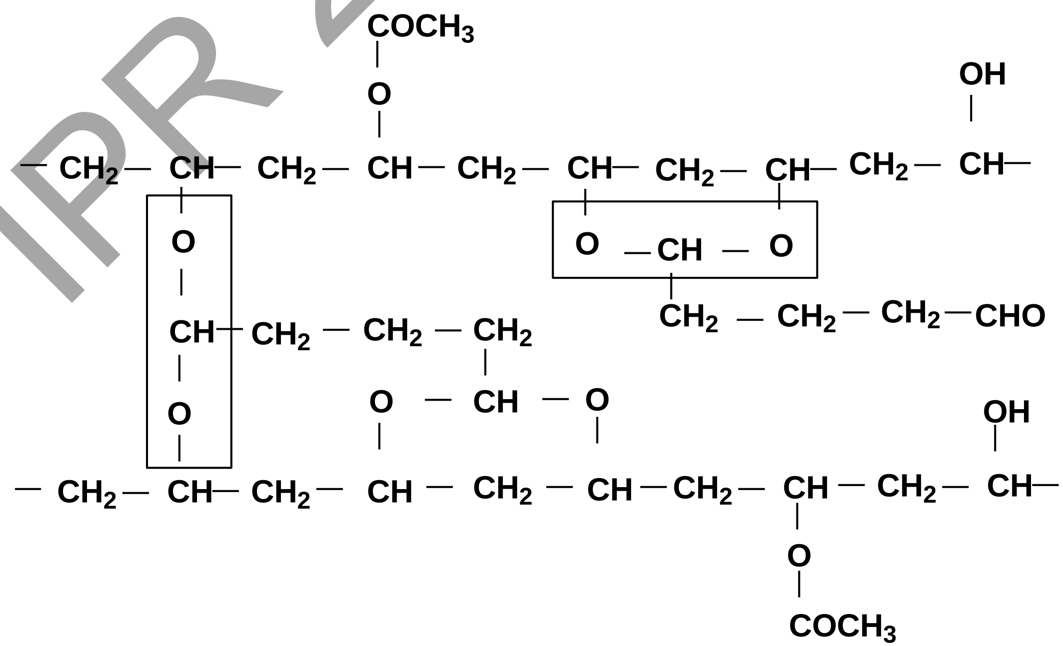
poly(vinyl alcohol) (PVA)
$y/(x+y) = 87\ \%$

*Gholap and Badiger, *J. Phys. Chem. B* 109 (2005)13941-13947

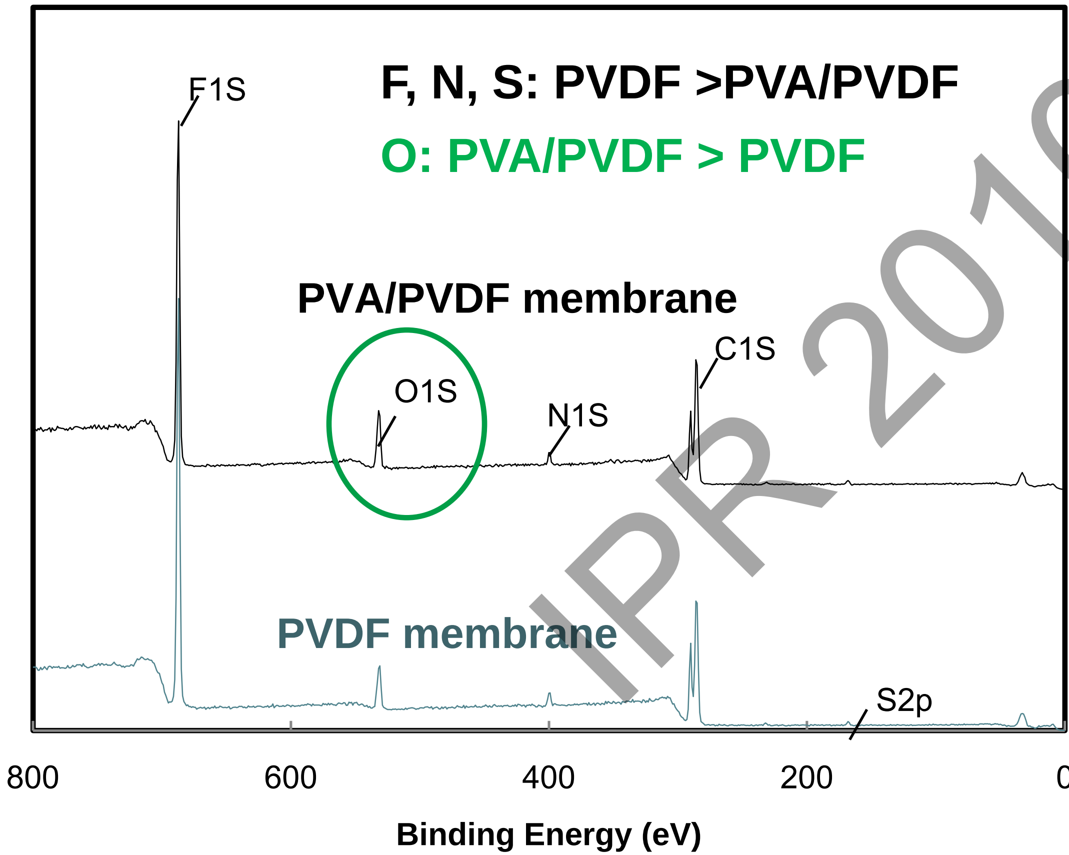
Interfacially Formed PVA Membrane

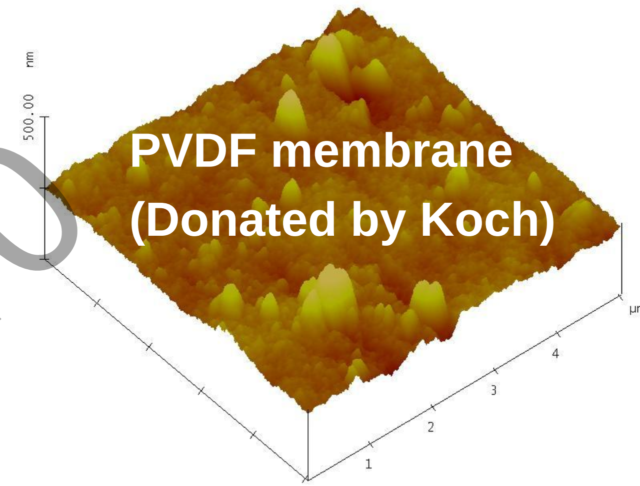
Glutaraldehyde Vapor $OHC\text{-}(CH_2)_3\text{-}CHO$



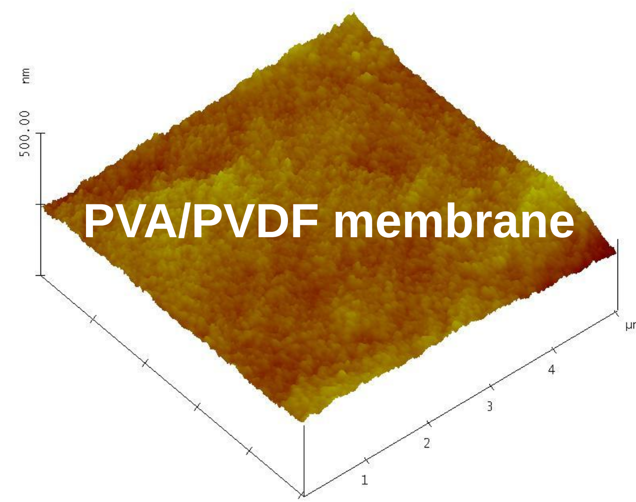


Surface Comparison of PVDF and PVA/PVDF Membranes





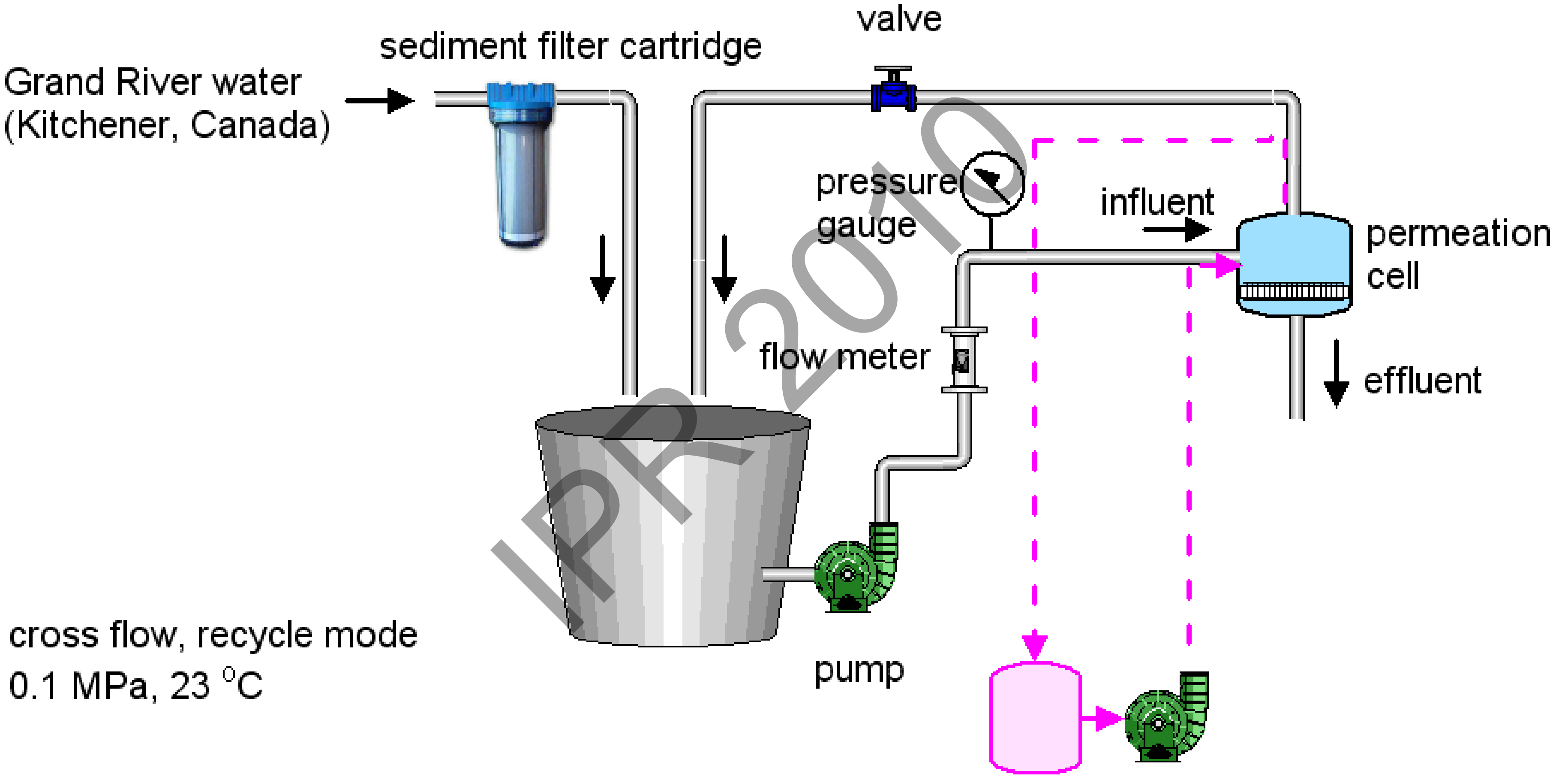
Roughness reduced



Contact angle reduced ~ 10°, 16%

Du et al. *Water Res.* 43 (2009) 4559-4568

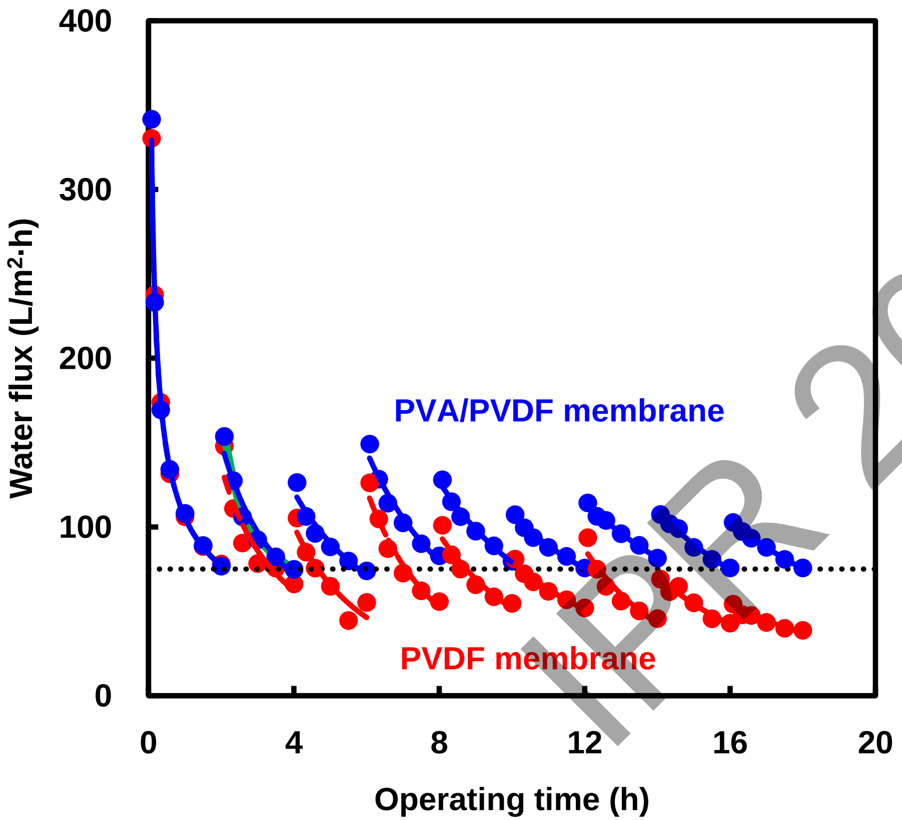
Ultrafiltration Setup

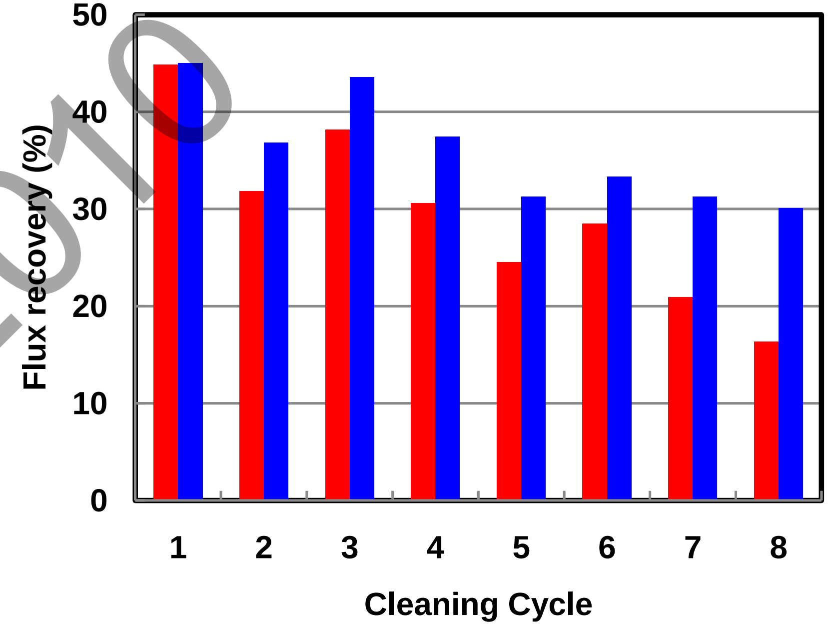


cross flow, recycle mode
0.1 MPa, 23 °C

chemical cleaning system
NaOH (1 g/L)
every 2 hr for 20 min

Fouling Resistance

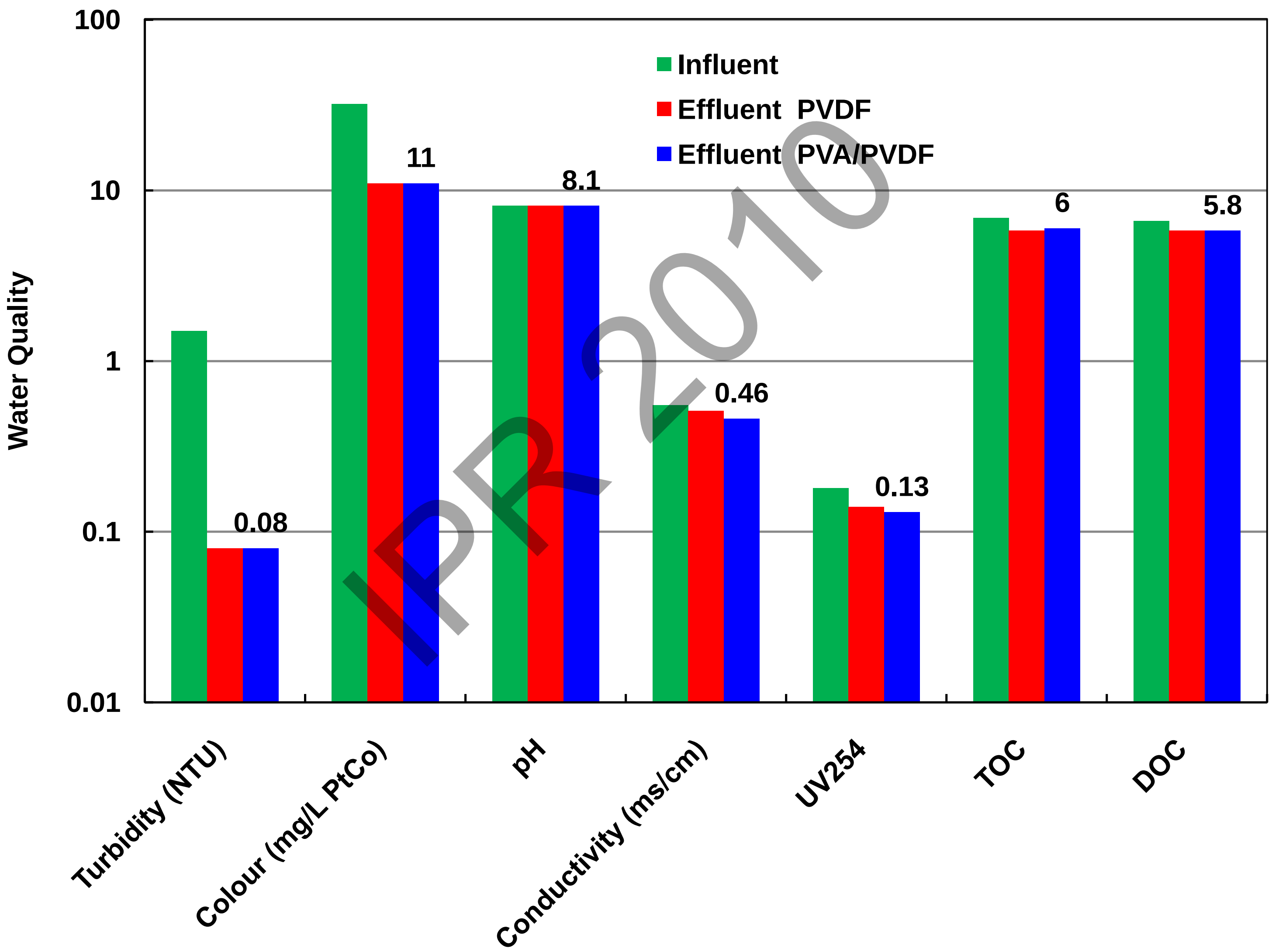




PVA/PVDF membrane:

- **ease of cleaning**
- **flux stability**
- **95% higher flux than PVDF membrane**

Effluent Quality



Summary

- Porous/nonporous selective layers via solid-liquid or solid-vapor interfacial reaction
- Good permselectivity for gas separation, pervaporation, nanofiltration and ultrafiltration processes

Acknowledgements

- **Dr. Amit Chakma, Dr. Xianshe Feng, Dr. Peter M. Huck, Dr. Sigrid Peldszus, Dr. Jiasen Zhao**
- **Membrane Separation Processes Research Lab @UW**
- **NSERC Chair in Water Treatment @UW**
- **Industrial Research Partners**