2023年度 一般社団法人先端膜工学研究推進機構 膜工学春季講演会
2024年3月27日，神戸大学

溶解性有機物によるファウリング現象の理解とファウリング抑制膜の開発

工学院大学 先進工学部 環境化学科

赤松 憲樹

E-mail : akamatsu@cc.kogakuin.ac.jp
http://www.ns.kogakuin.ac.jp/~wwb1051/index.html

KOGAKUIN UNIVERSITY 工学院大学

研究室紹介(所在地：東京都八王子市)

構成員 (2024年3月27日現在)

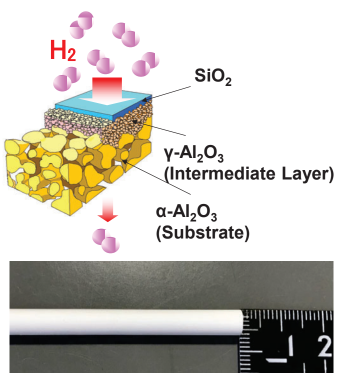
教授：赤松憲樹，特任教授：Xiao-lin Wang
大学院生 6名，卒論生 9名，客員研究員 1名，事務補佐員 1名

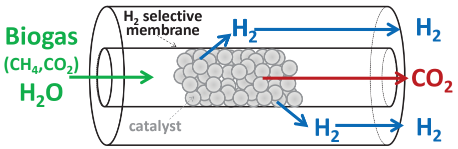
研究内容

1) 水処理用各種分離膜の開発と，これを用いた省エネ型水処理システムの開発
2) ガス分離シリカ膜の開発と，これを用いた各種膜反応器の開発
3) 新規膜利用プロセス/システムの開拓
4) マイクロフルイディック乳化技術を利用した機能性マイクロカプセルの開発

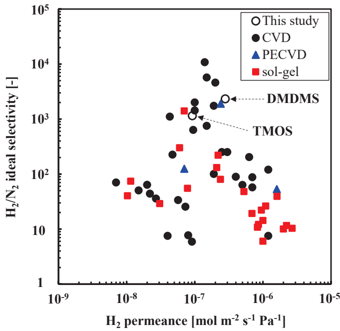
ガス分離シリカ膜，および各種膜反応器の開発

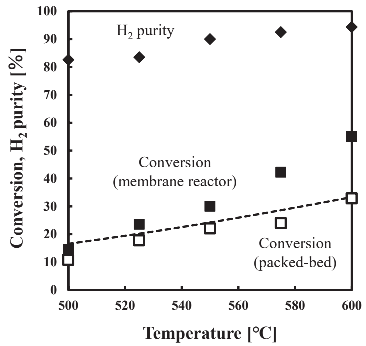
$CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2$





- High purity H_2
- High purity CO_2
- Conversion enhancement

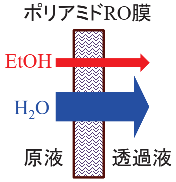


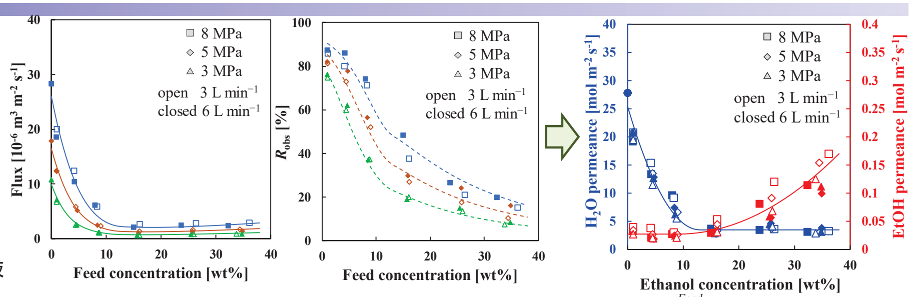


J. Membrane Sci., **580**, 268-274 (2019), *J. Chem. Eng. Japan*, **55**, 255-261 (2022) など

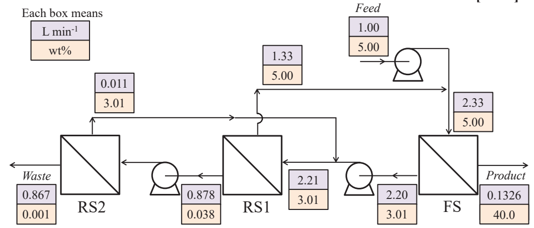
新規膜利用プロセス/システムの開拓

(例)
EtOH aq 濃縮





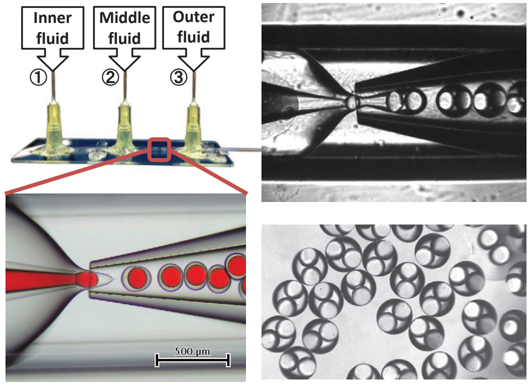
$$J = \frac{DC^m}{l\gamma^m}\left[\gamma_1^s x_1^s - \gamma_2^s x_2^s \exp\left\{\frac{v(p_2 - p_1)}{RT}\right\}\right]$$



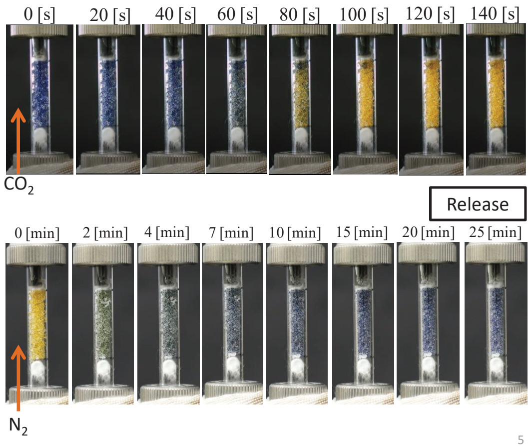
J. Chem. Eng. Japan, **57**, 2294934 (2024)

マイクロフルイディック乳化技術を用いた機能性マイクロカプセル

Microfluidic emulsification



CO_2 adsorptive microcapsules



本日の内容

1. 溶解性有機物によるファウリング現象の理解

2. ファウリング抑制膜の開発
   - ・低ファウリングポリマーを膜面および細孔内部に修飾する手法
     →促進酸化水浸漬とAGET-ATRP
   - ・低ファウリングポリマー含有膜を作製する手法
     →Non-solvent induced phase separation (NIPS) 時にブレンド

3. まとめ

Possible fouling mechanisms

Feed × Membrane × Operation

Feed
Organic substances/
Colloids, Concs.
×
pH，temp.
etc.

Membrane
Structure(pore size,
surface roughness)
×
Material
×
Hydrophilicty
etc.

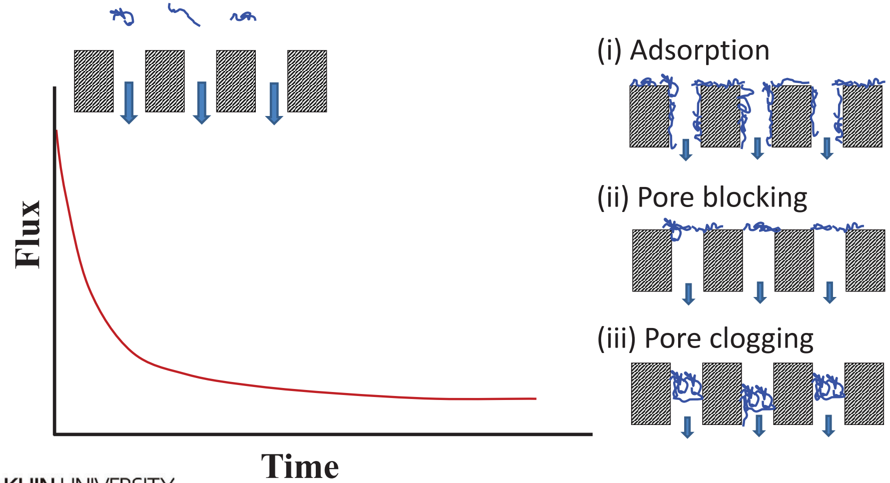
Operation
Dead-end or Crossflow
×
Module geometry
×
Pressure，Flowrate
etc.

・No two feeds are exactly alike.

・Impossible to change only one parameter

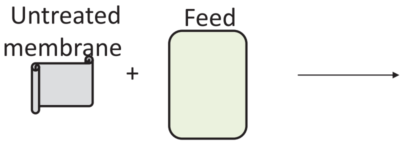
・No unified standard

Possible fouling mechanisms



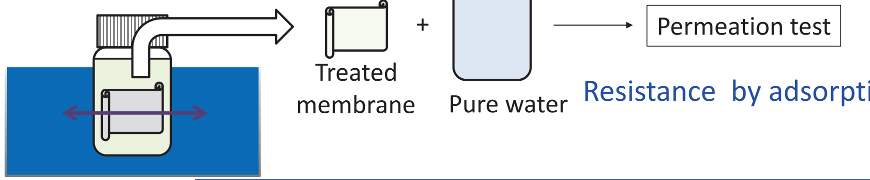
If “adsorption” is the dominant factor to decrease flux

(1) Closed-loop cross-flow filtration tests



Resistance overall

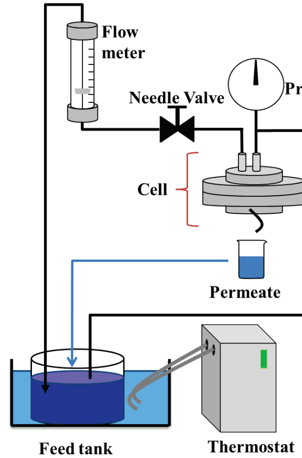
(2) Pure water flux tests with membranes that are immersed in solutions of the same fouling substances



Resistance by adsorption

The concentrations of the fouling substances and the pressure being equal, the fluxes in both tests should be comparable to each other.

Experimental: filtration tests & pure water flux tests



Material : Polyethylene (PE)

Ave. pore size : 0.06 [μm]

Porosity : 41 [%]

(1) Closed-loop cross-flow filtration tests

Filtration conditions

Solute : BSA, Sodium alginate (SA)

Conc. : 10 ～ 5000, 50～1000 [ppm]

Flow rate : 2 [L min^{-1}]

Temp. : 25±0.5 [℃]

(2) Pure water flux tests after immersion

Immersion Conditions

Solute : BSA, Sodium alginate (SA)

Conc. : 10 ～ 5000, 50～1000 [ppm]

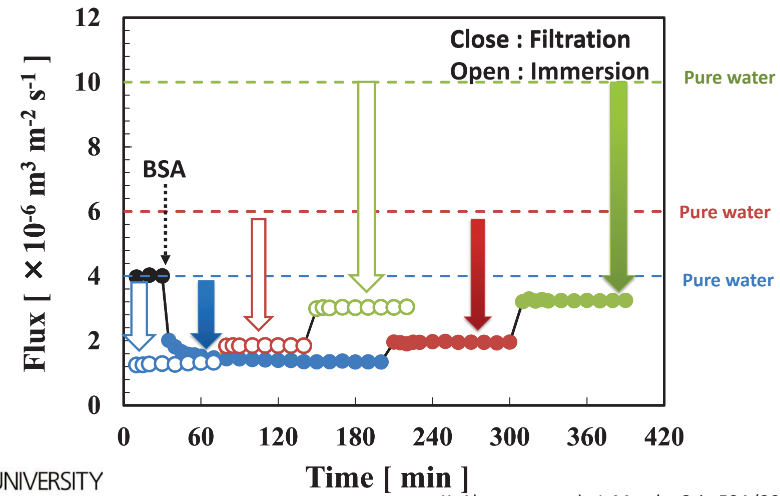
Time : 5, 20 [h]

Pure water test conditions

Flow rate : 2 [L min^{-1}]

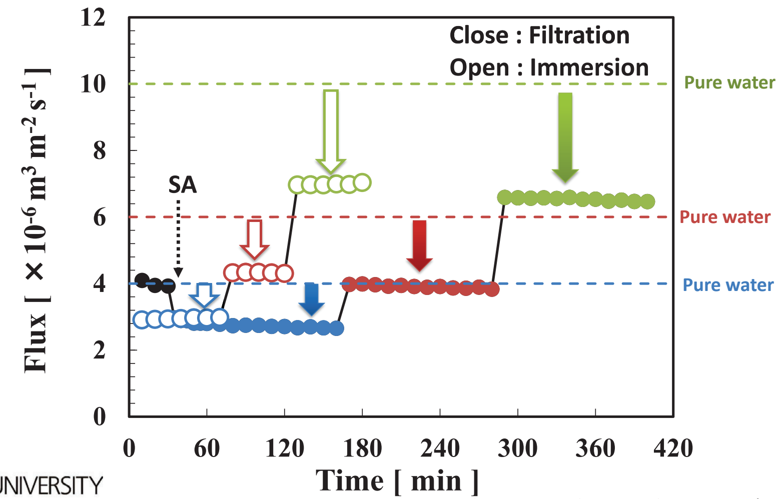
Temp. : 25±0.5 [℃]

Comparison (BSA 500ppm)



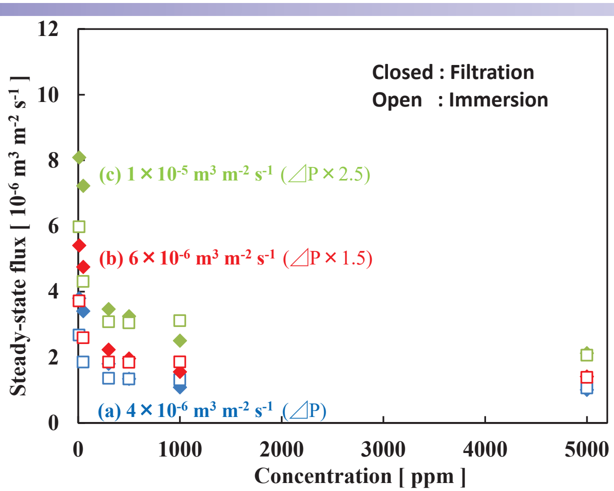
K. Akamatsu et al., J. Membr. Sci., 594 (2020) 117469

Comparison (SA 500ppm)



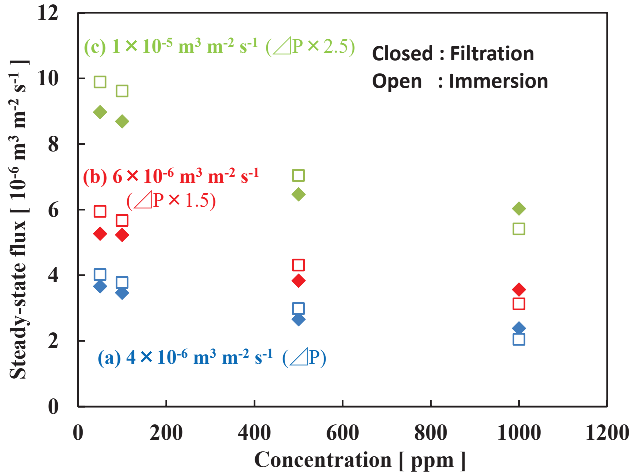
K. Akamatsu et al., J. Membr. Sci., 594 (2020) 117469

Comparison (BSA)



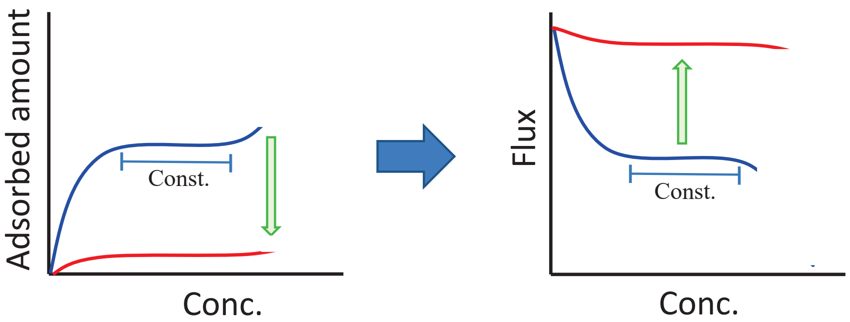
K. Akamatsu et al., J. Membr. Sci., 594 (2020) 117469

Comparison (SA)



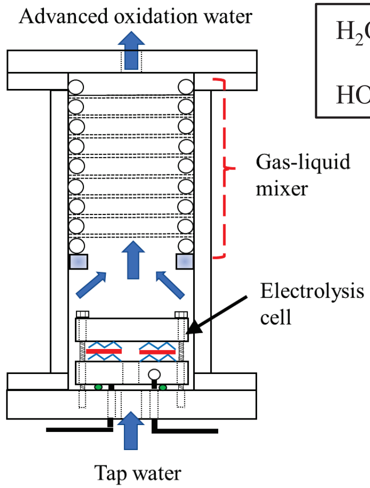
K. Akamatsu et al., J. Membr. Sci., 594 (2020) 117469

Relationship between adsorbed amount and flux



Adsorption is the dominant factor to decrease filtrate flux, which indicates us to develop membranes with adsorption-free surface.

Experimental: Production of an advanced oxidation water



$H_2O_2 \rightarrow HO_2^- + H^+$

$HO_2^- + O_3 \rightarrow \cdot OH + O_2^- + O_2$

Water flow rate [L/min]	1
Voltage [V]	100
Current [A]	2
Ozone [ppm]	2
H_2O_2 [ppm]	0.3

Experimental: Surface modification via the novel method

【Surface modification】

①-OH generation	
Immersion in AOW [h]	0.5

①-OH generation via Fenton[1]	
Pure water [mL]	20
Ethanol [mL]	20
N_2 bubbling [min]	15
$FeCl_2$ [g]	0.04
H_2O_2 [ml]	2.2
Reaction at 50℃ [h]	1

②Bromination	
Super-dehydrated dichloromethane [mL]	40
Triethylamine [mL]	3.5
BIBB [mL]	3.3
Reaction time at 0℃ [h]	1
Reaction time at RT [h]	24

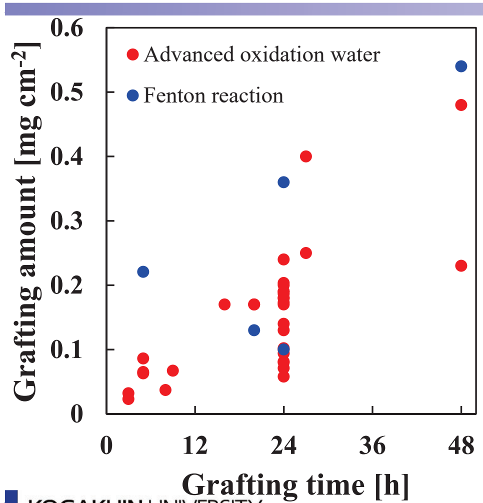
③AGET-ATRP	
MEA [mol L^{-1}]	1.0
Pure water [mL]	20
Ascorbic acid [mol L^{-1}]	0.20
PMDETA [μL]	140
$CuBr_2$ [g]	0.020
Reaction time [h]	1～48

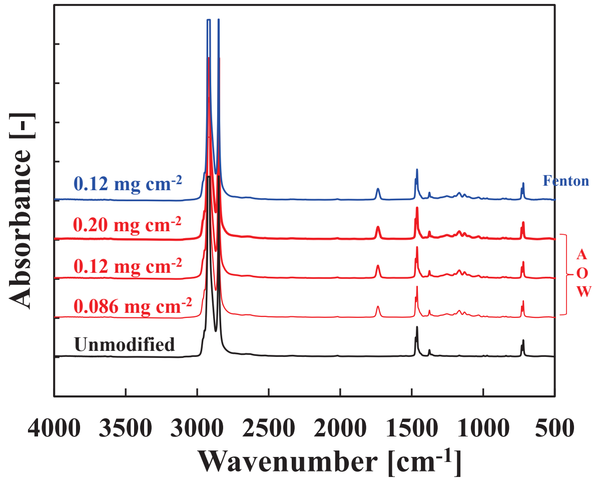
【Characterization】

FT-IR, FE-SEM, mechanical strength

[1] K. Akamatsu *et al*, *Ind. Eng. Chem. Res.* 60 (2021) 15248.

Relationships between AGET-ATRP time and grafting amount



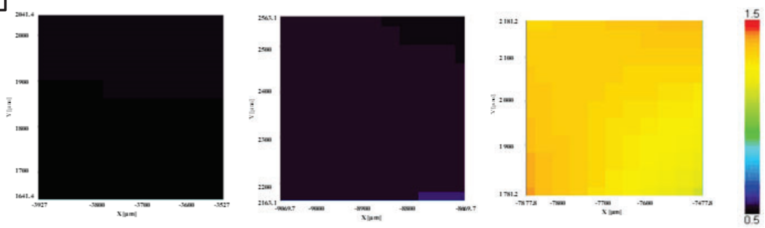


K. Akamatsu *et al*, *Ind. Eng. Chem. Res.* 62 (2023) 10611.

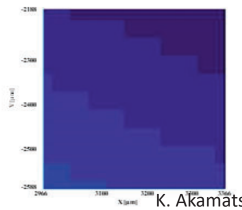
Surface uniformity analyzed with FT-IR mapping (400 μm × 400 μm)

I1735 / I1472

(a) 0.086 mg cm^{-2} (b) 0.12 mg cm^{-2} (c) 0.20 mg cm^{-2}

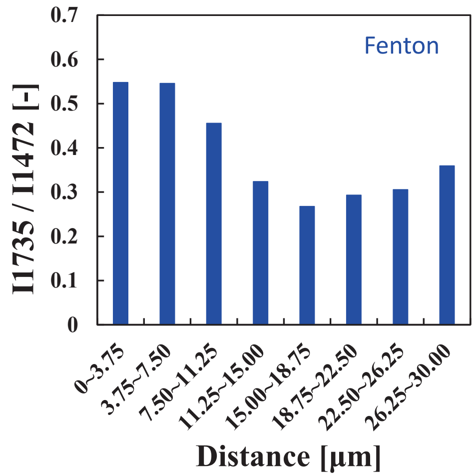


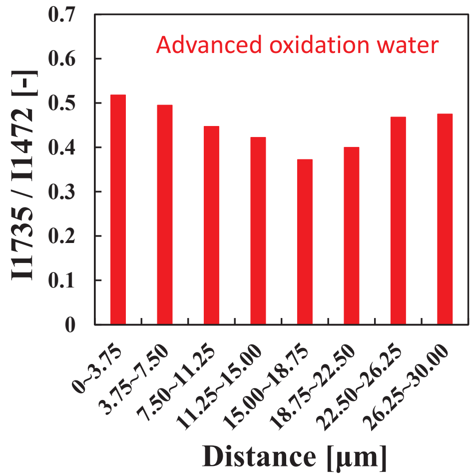
(d) 0.12 mg cm^{-2} (Fenton)



K. Akamatsu *et al*, *Ind. Eng. Chem. Res.* 62 (2023) 10611.

Uniformity in thickness direction (grafting amount: 0.10 mg cm^{-2})

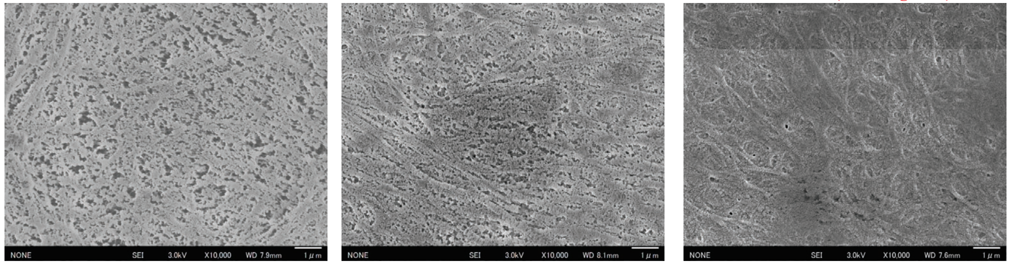




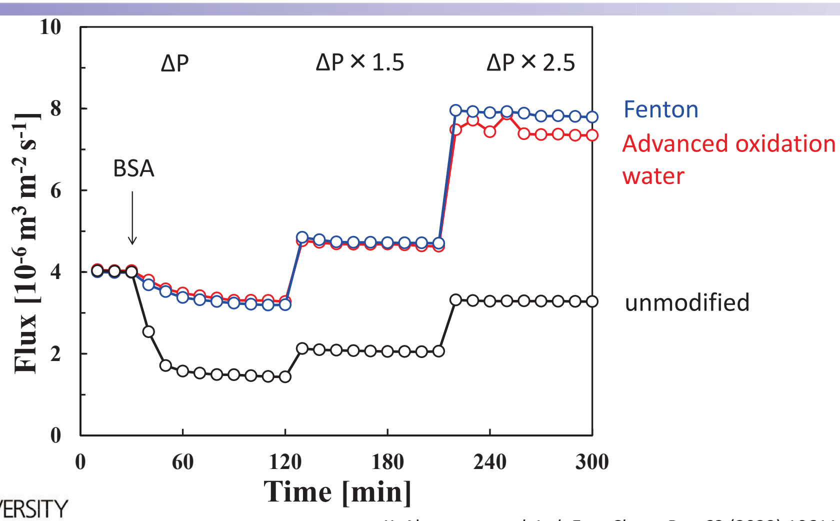
K. Akamatsu *et al*, *Ind. Eng. Chem. Res.* 62 (2023) 10611.

FE-SEM (magnification × 10,000)

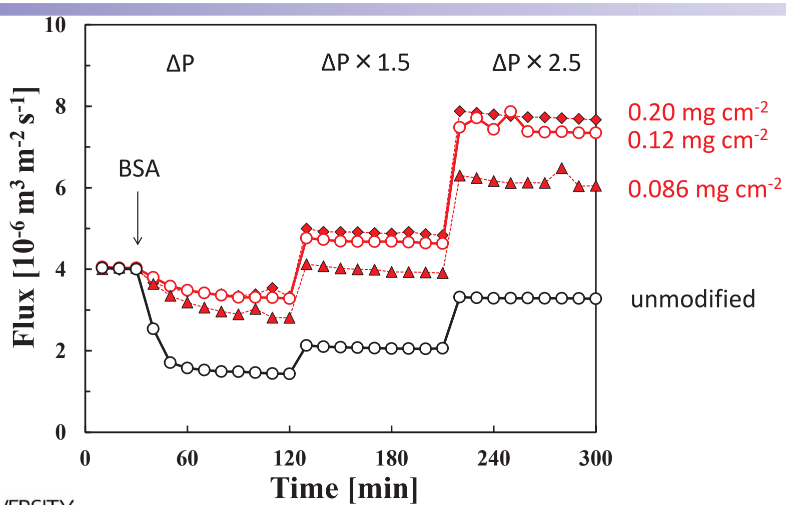
(a) unmodified | (b) Fenton (0.10 mg cm^{-2}) | (c) Advanced oxidation water (0.094 mg cm^{-2})



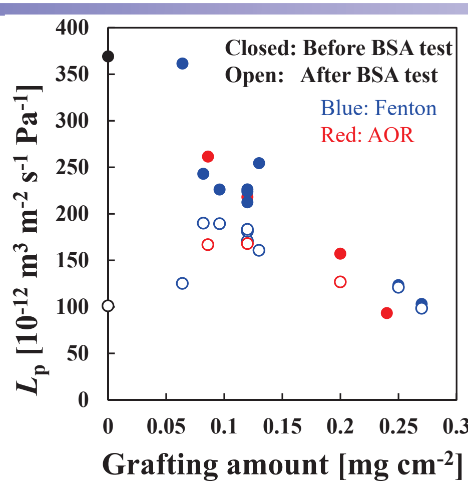
BSA filtration tests (grafting amount 0.12 mg cm^{-2})

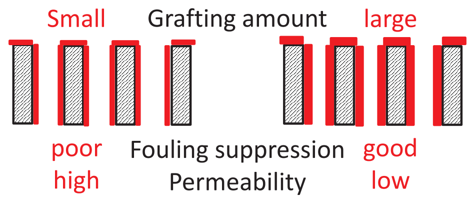


Effect of the grafting amount on the low-fouling properties



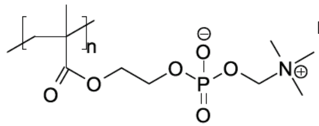
Relationship between grafting amount and L_p



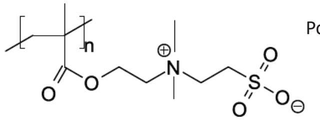


Low-fouling polymers: betaine polymers

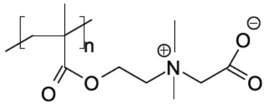
Betaine polymers (soluble in water)



Poly(2-(methacryloyloxy)ethyl phosphorylcholine) : MPC



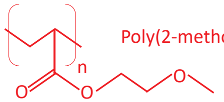
Poly(2-(methacryloyloxy)ethyl dimethyl-(3-sulfopropyl) ammonium hydrixide)



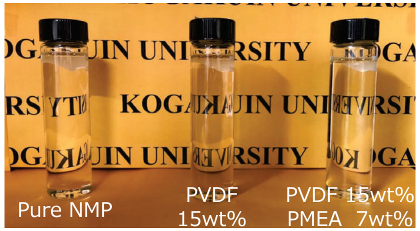
Poly(1-Carboxy-N, N-dimethyl-N-(2'-methacryloyloxyethyl) methanaminium inner salt)) : CMB

→ Blending with PVDF is difficult.

PMEA (insoluble in water)



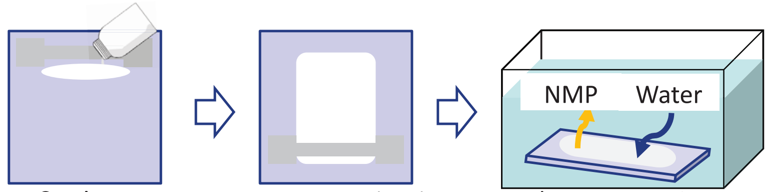
Poly(2-methoxyethyl acrylate)



→ Blending with PVDF is easy.

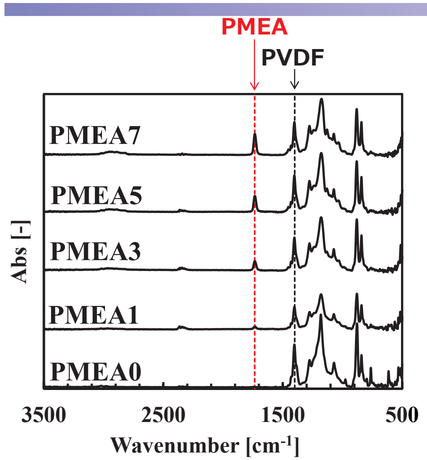
Experimental: Preparation of PVDF/PMEA blend membranes via NIPS

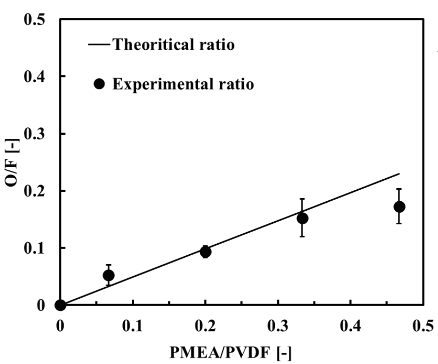
Membrane	PVDF [wt%]	PMEA [wt%]	NMP [wt%]
PMEA0	15	0	85
PMEA1	15	1	84
PMEA3	15	3	82
PMEA5	15	5	80
PMEA7	15	7	78

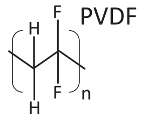


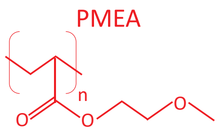
<Characterization>
- Viscosity (dope sol.)
- FT-IR
- FE-SEM

FT-IR and XPS





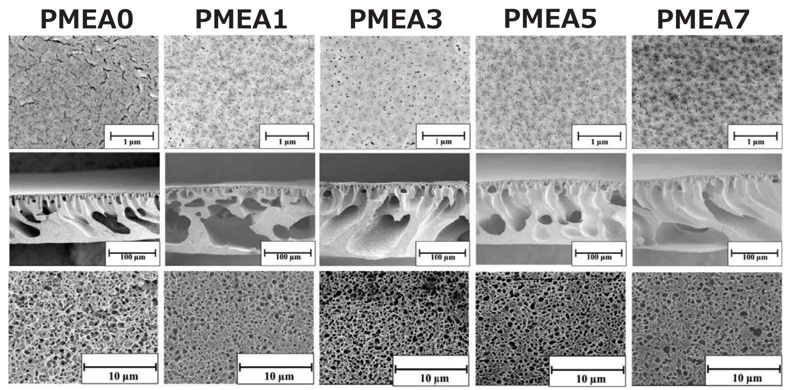




PMEA composition at the membrane surface can be tuned by the composition of the dope solution.

S. Ohno *et al*, Sep. Purif. Technol., 276 (2021) 119331

FT-SEM observation

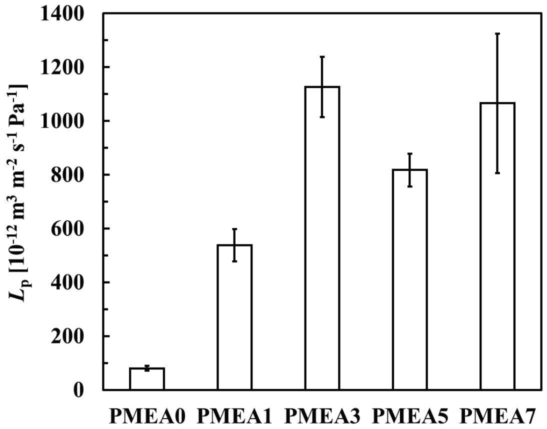


Thickness: 97±1 [μm] 136±4 [μm] 138±5 [μm] 155±5 [μm] 144±5 [μm]

Macrovoids of the blend membranes were larger than that of PDVF membrane.

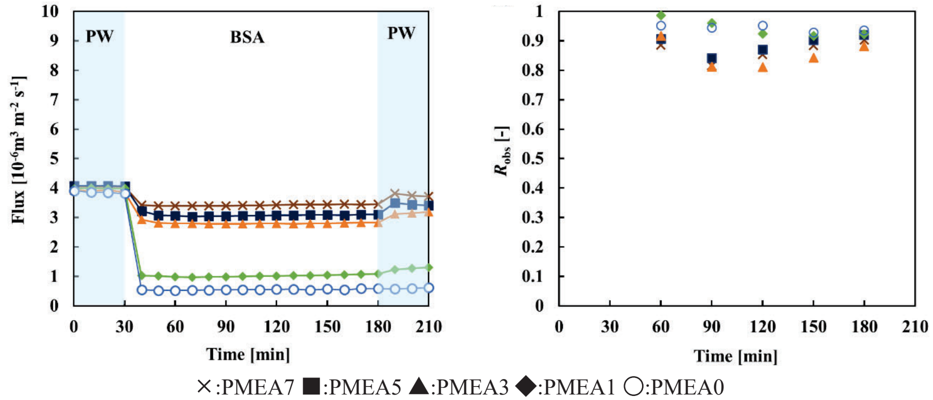
S. Ohno *et al*, Sep. Purif. Technol., 276 (2021) 119331

Pure water permeability L_p



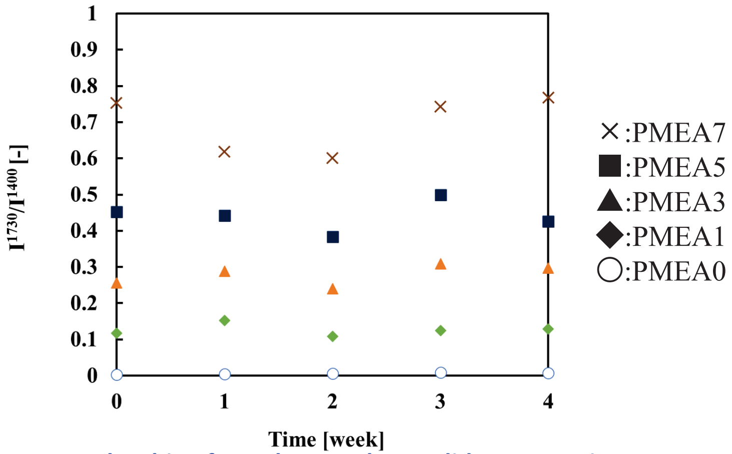
L_p becomes around 10 times larger in the blend membranes.

Low-fouling property



The blend membranes exhibited low-fouling properties against BSA .

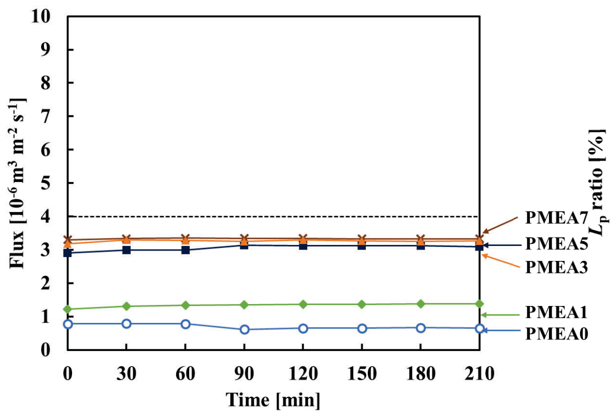
Stability in water



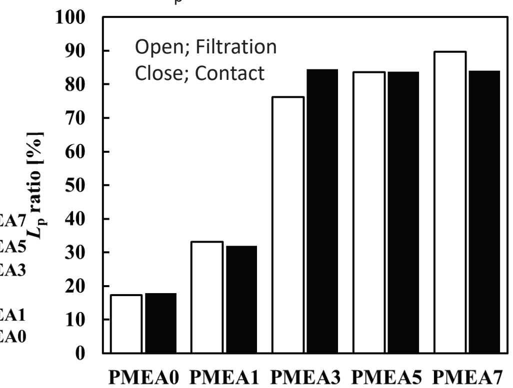
PMEA leaching from the membrane did not occur in water.

Effect of BSA adsorption (without pH control)

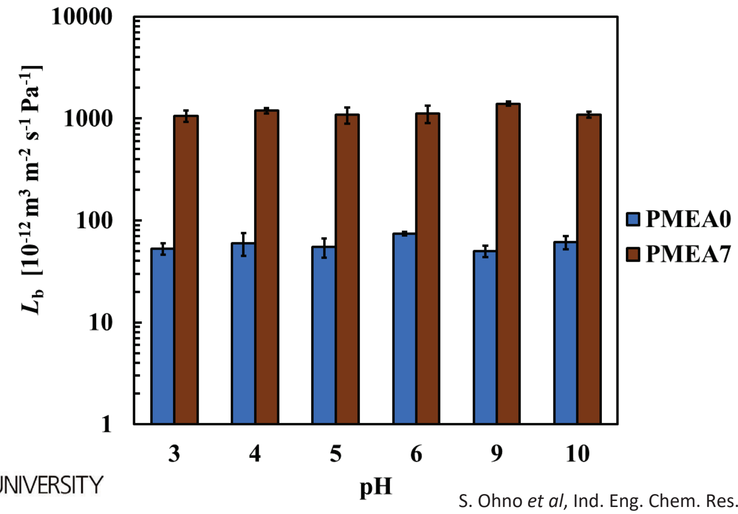
Pure water flux after the contact on feed side



Comparison of L_p in filtration and contact tests

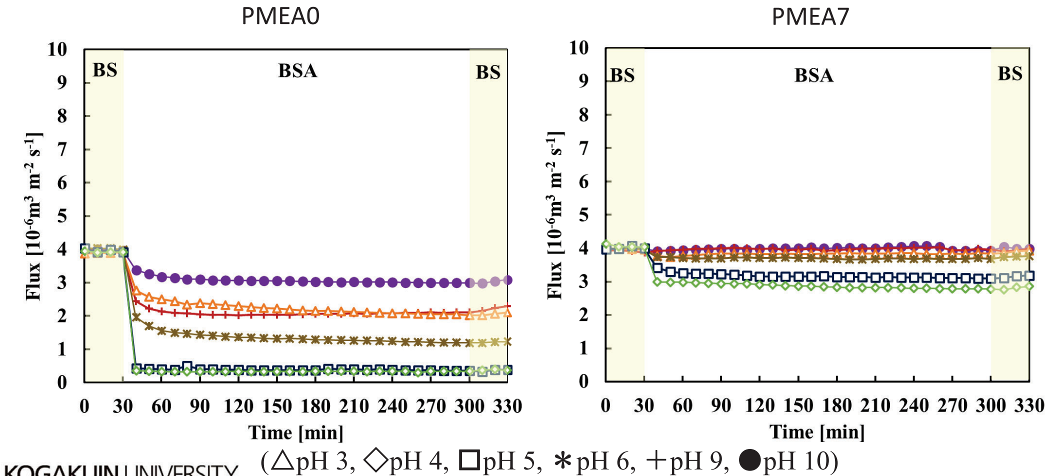


Effect of pH on L_p



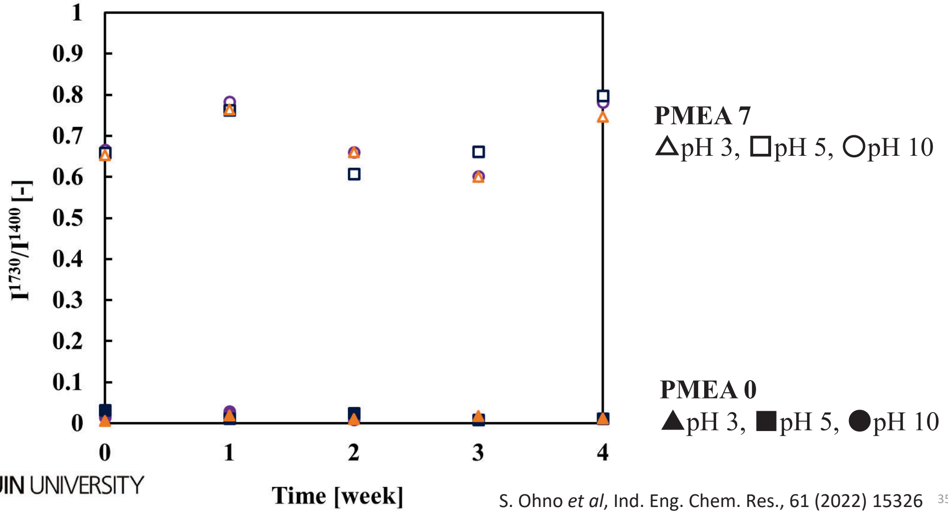
S. Ohno *et al*, Ind. Eng. Chem. Res., 61 (2022) 15326

Effect of pH on low-fouling property



S. Ohno *et al*, Ind. Eng. Chem. Res., 61 (2022) 15326

Stability of the membranes



S. Ohno *et al*, Ind. Eng. Chem. Res., 61 (2022) 15326

Summary

- ✓ 溶解性有機物の吸着が膜抵抗増大の主要因であるか見極める手法として，透過試験と浸漬試験の比較が有効である
- ✓ 溶解性有機物の吸着を抑制する高分子の 1 つである poly(2-methoxyethyl acrylate) を膜面および細孔内部にグラフトするため，促進酸化水処理後に AGET-ATRP を行う手法が有効である
- ✓ Poly(2-methoxyethyl acrylate) と PVDF の親和性の高さを利用してブレンド膜を作製でき，高透水性と優れたファウリング防止性を兼ね備えた精密ろ過膜となる