PROGRESS OF NANOFILTRATION MEMBRANES

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OVERVIEW

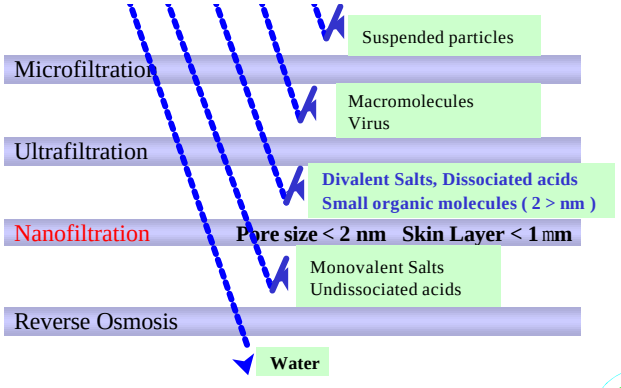
- **Introduction of Nanofiltration(NF)**
- **NF Application**
  - in Aqueous system
  - in Non-aqueous system
- **NF Membranes developed in KRICT**
  - Fouling resistant membrane
  - Solvent resistant membranes
- **Summary**

Application range of various membrane process

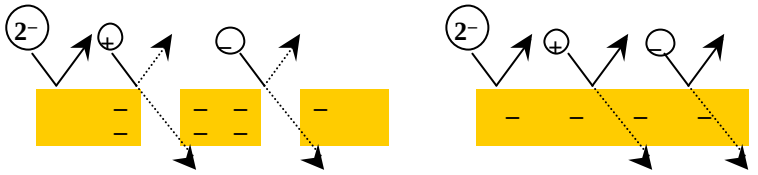
Particle size μm nm Molecular weight	atomic/ ionic range 100 200	low molecu- lar range 0.001 1.0 1000	high molecu- lar range 0.01 10 100,000 500,000	micro particle range 0.1 1.0 100 1000	macro particle range 10.0 10,000
Solute	aqueous salt metal ion sugar	microsolutes	colloidal silica virus proteins	bacteria	yeast cells
Mmebrane separation process	electrodialysis diffusion dialysis reverse osmosis nanofiltration gas separation pervaroration	dialysis	ultrafiltration	microfiltration	

NANOFILTRATION (NF) MEMBRANES

- **Membranes whose performance is in between those of UF and RO (MWCO: 200-1000 g/mole)**
- **Good rejection of multivalent ions or organic materials with low molecular weight**
- **Low Operating pressure**

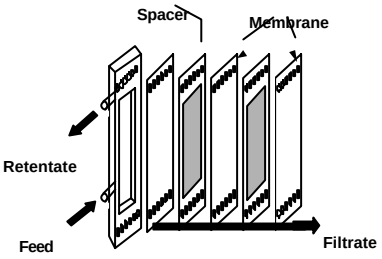


Schematic drawing of separation of ions by negative nanofiltration membranes

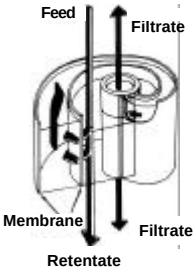


porous swollen

Membrane modules

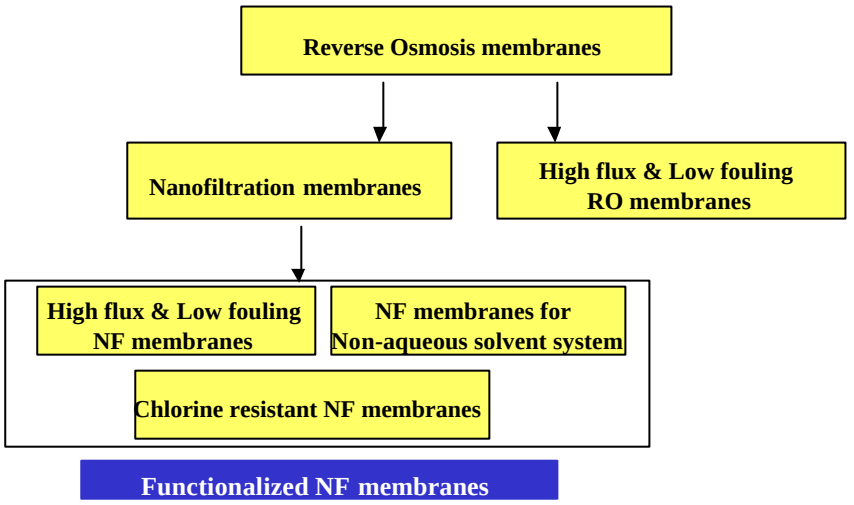


(a) Plate type module

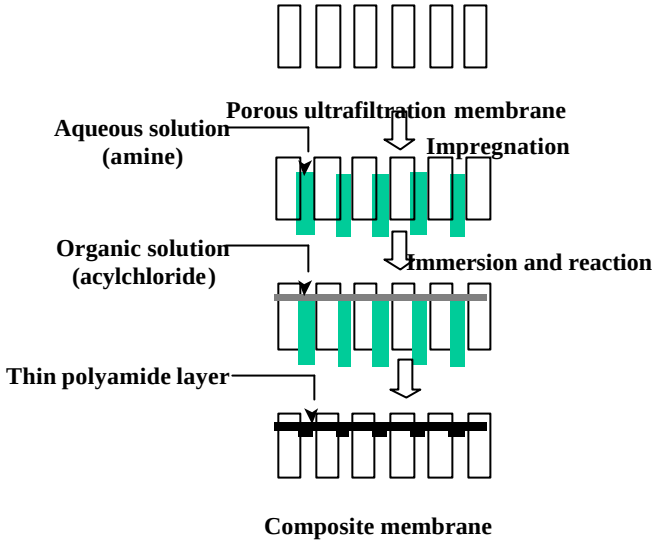


(b) Spiral-wound type module

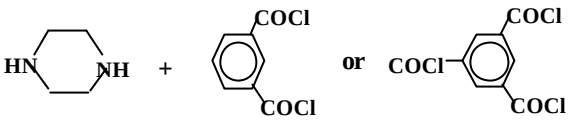
Progress in Nanofiltration Membranes



Preparation of composite polyamide membrane

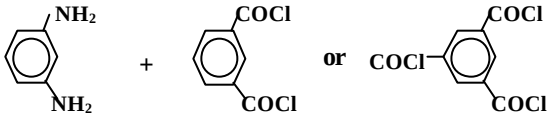


Polypiperazineamide; NF membrane

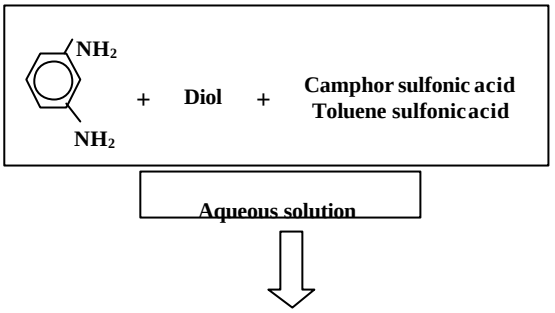


NF-40(FilmTec); NTR-7250, NTR-729(Nitto Denko); UTC-20/50/60(Toray)

Polyamide; RO & NF membrane



High flux RO & NF membranes



Significant flux enhancement due to the surface roughness increase

Low fouling RO & NF membranes

High flux RO & NF membrane

Coating neutral polymers or inorganic material

Fouling resistance due to the surface charge blocking

Solvent resistant NF membranes

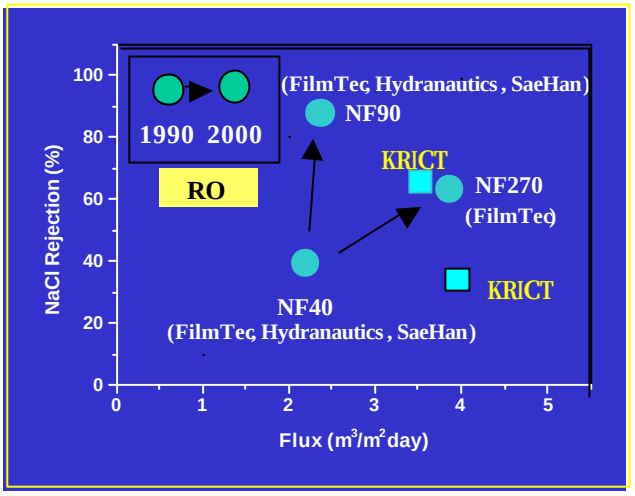
Cross-linked PAN UF membrane

Coating silicone

Kyriat weizmann; MPF series

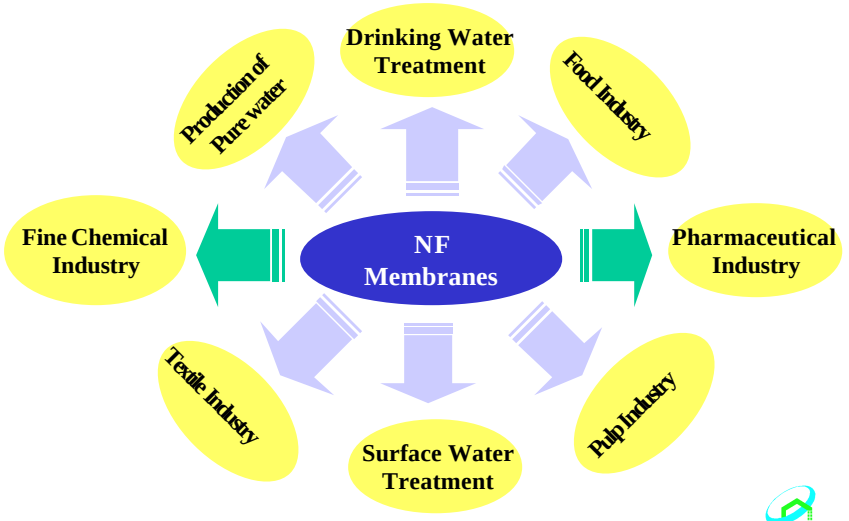
Solvent resistant against almost all solvents; Large pore (400 – 700Da)

Progress of NF membranes



225 psi; 2000 ppm NaCl

EXTENSION OF NF APPLICATION



NF for Aqueous System

A. Drinking and Process Water Treatment

- Water softening and Pure water production
- Potable Water Production_
- Surface and Ground water Treatment

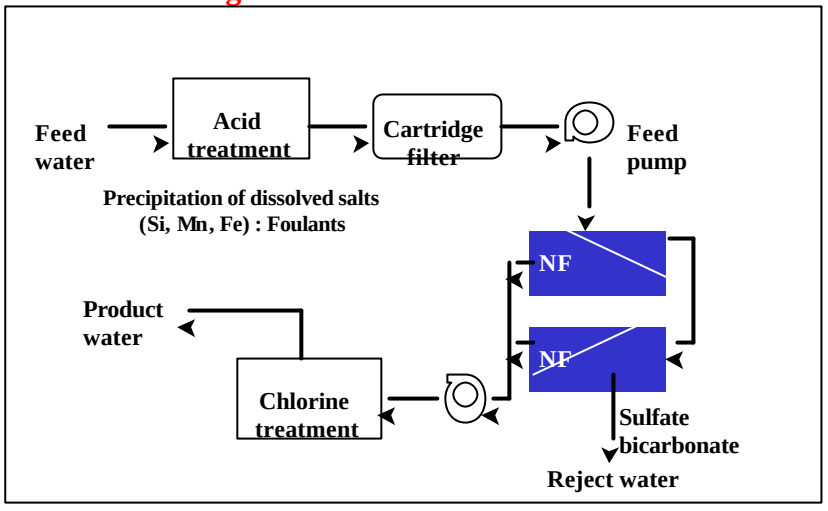
B. Wastewater Treatment

- Oily Wastewater
- Removal of Dye, VOC and Heavy Metals
- Chemical plant Wastewater
- Textile and Pulp Wastewater

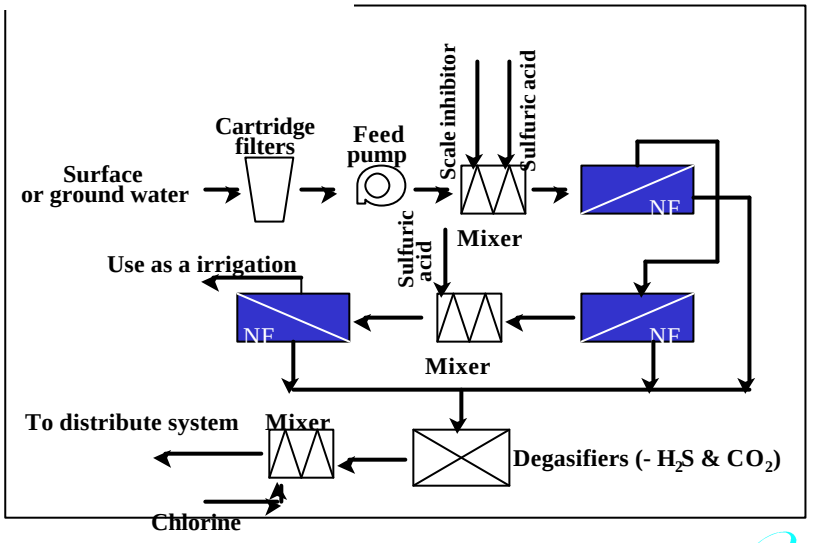
C. Food Industry

- Desalting of cheese whey and sea food processing
- Concentration of fruit juice
- Yeast Production

Water Softening



Potable Water Production



NF for Non-aqueous System

A. Fine Chemical Industry

- The separation of organometallic catalysts
- The separation of small molecular weight organics (300-1000Da) or residual reactants produced from the synthesis in an organic solvent-based systems

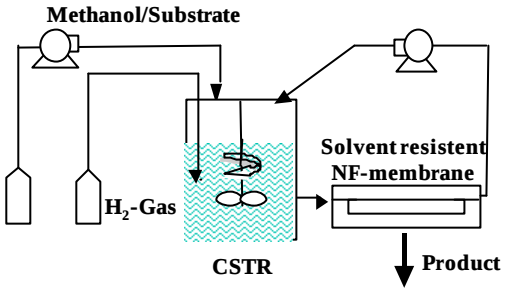
B. Pharmaceutical Industry

- The separation of pharmaceuticals (300-1000Da) synthesized in a variety of organic solvents via a multi-step synthetic route

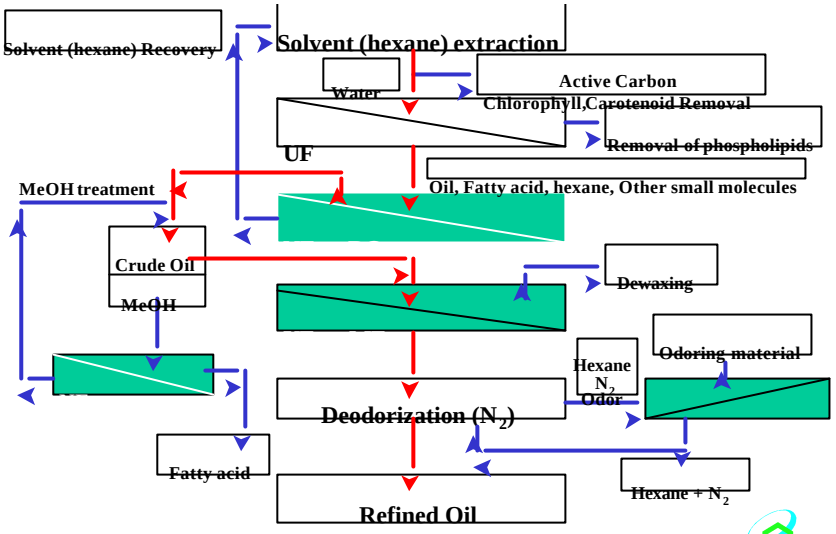
C. Vegetable Oil Industry

- The recovery of solvents used in the extraction of edible oil processing
- The concentration of edible oil
- The separation of denaturated oil (fatty acid)

NF Membranes for Catalytic Reactor



Membrane method for vegetable oil purification



NF membranes studied in KRICT

1. Polyamide NF membranes (interfacial polymerization)

NF-90 : > 90% rejection of NaCl; underground water treatment
NF-70 : > 70% ; underground water treatment
NF-40 : > 40% ; surface water treatment
NF-20 : > 20% ; surface water treatment
Development trend : High flux and low fouling

2. Organic solvent-resistant NF membranes

Low swelling and high flux in organic solution
High separation of small molecular solute in organic solution

3. PVA & Integrally skinned NF membranes

Low fouling and chlorine resistant

Fouling-Resistant NF Membrane

- **Fouling**

A. Foulants

- Humic acid
- Colloids
- Surfactants
- Proteins
- Mineral salts
- Silica

B. Problems

- Increasing operation and maintenance costs
- Deteriorating membrane performance
- Shortening membrane

C. Properties influencing fouling

- Surface structure (roughness, pore size)
- Electrokinetic characteristics (ξ-potential)
- Chemical property (hydrophobic-hydrophilic interaction)

PVA-coated polyamide composite membrane

- **Polyamides**
  Piperazine & m-phenylene diamine
  Trimesoyl chloride
- Poly(vinyl alcohol)
  Poly(vinyl alcohol) 0.05 wt%
  Glutaraldehyde
- **Interfacial & Dip coating Method**
- **Support membrane**
  Polysulfone MWCO 50kDa
- Other NF membranes
  NF 70
  NF 70/PVA

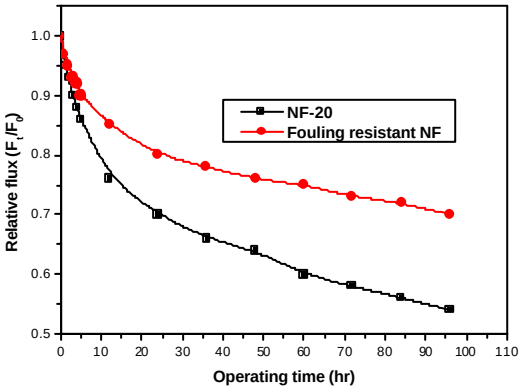
Change of membrane performance by PVA coating

	PWF (m^3/m^2day)	Rejection rate (%)	
		PEG 200	NaCl
PA	2.9	60	8
PA/PVA (1)	2.6	72	13
NF-70	1.7	81	75
NF-70/PVA (3)	1.4	88	83

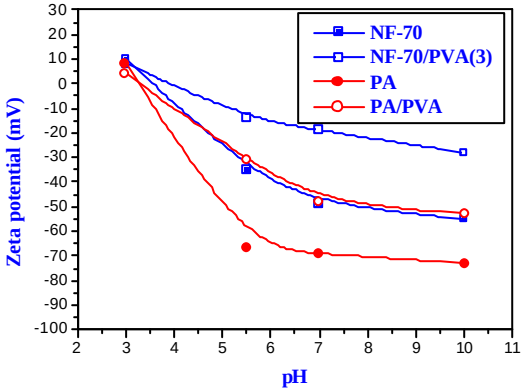
25 ℃; 200 psi

Neutral polymer- or nano particle-coated polyamide composite membrane

– Surface water treatment after microfiltration

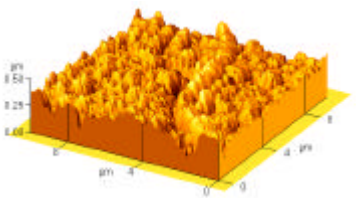


x-potential of PVA-coated NF membranes

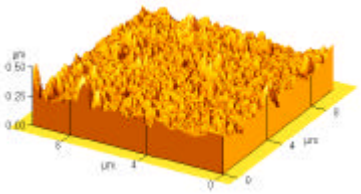


Electro-phoretic method; pH 7.0; 0.01M NaCl

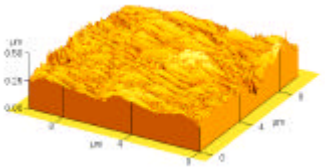
AFM images of NF-70 & PVA/NF-70 membranes



NF-70



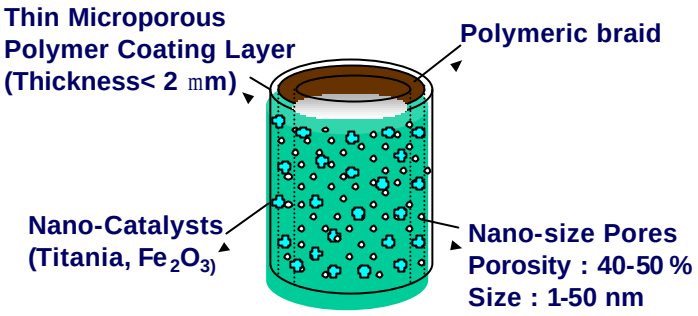
NF-70/PVA(1)



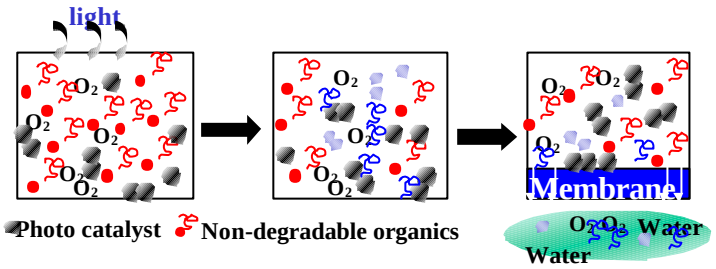
NF-70/PVA(3)

Nano catalysts coated NF membranes

Integral multifunctional antifouling nano-complex- membranes that would be efficient for the treatment of the waste-water through nano-catalytic-reaction and separation



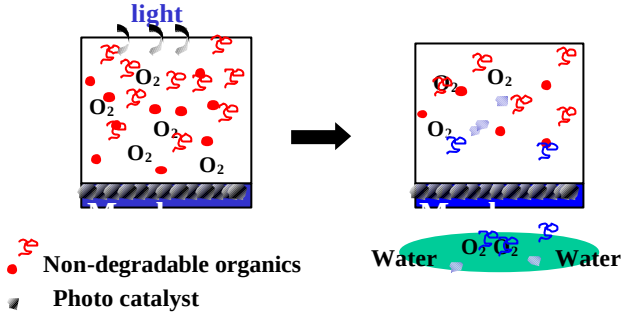
NF membrane-coupled Photo Catalyst Reactor



· Easy to recover the catalysts

· Need low-fouling NF membrane

Nano catalysts-coated NF membrane reactor



- No need to recover the catalysts
- Low fouling by catalytic degradation of organics

Solvent Resistant NF Membranes

Commercial NF membrane for non-aqueous system

MPF series (Kyriat Weizmann): MWCOs of 700 and 400Da
made with silicone

Advantage: high flux to organic solvent

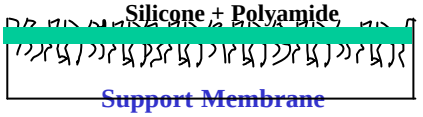
Disadvantage: difficult to reduce pore size

Objectives of the present work

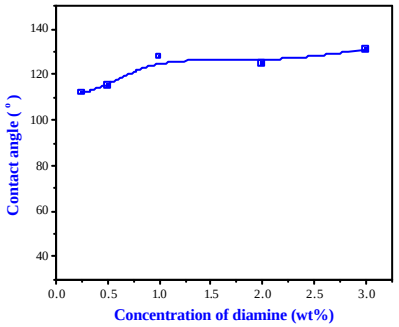
- **Develop various types of NF membranes which is stable in organic solvents**
- **Investigate the possibility to separate fatty acid in methanol and acetone solution**

Silicon Contained Polyamide NF Membranes

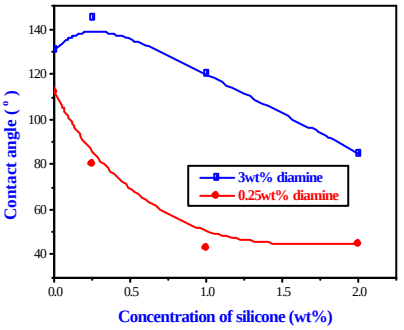
- **Polyamides**
  Piperazine & m-phenylene diamine
  Trimesoyl chloride
- **Silicones**
  Polydimethylsiloxane (prepolymer A & cross-linker B)
- **Interfacial & Dip coating Method**
- **Support membrane**
  Phase inversion
  PAN/NMP (15/85 wt%)
  Coagulated in water



Contact angle of polyamide and silicone-contained polyamide NF membranes



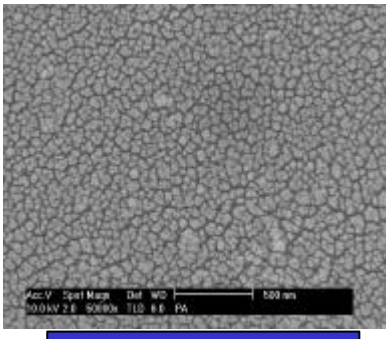
Polyamide



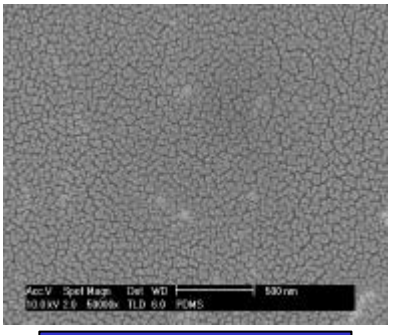
Silicone-based polyamide

Advanced angle of droplet formed by CCl4 in water

SEM photographs of membrane surfaces

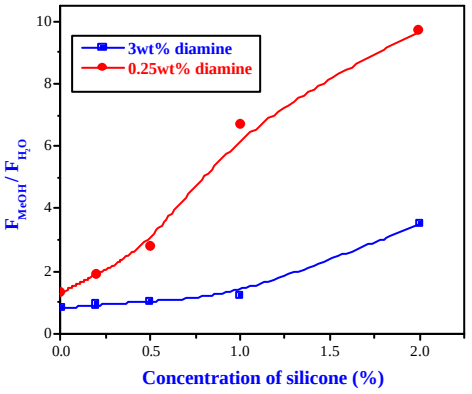


Polyamide

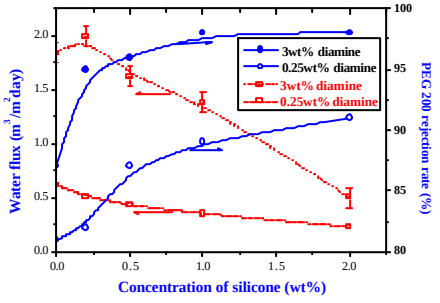


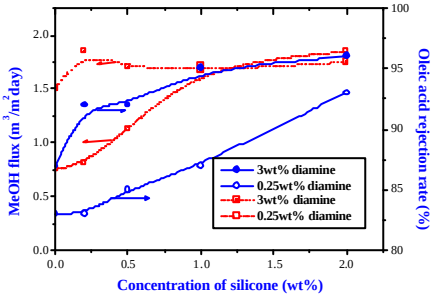
Silicone-based Polyamide

Flux ratio of MeOH to water of polyamide membrane



Performance of silicone-contained PA NF membranes in aqueous and MeOH solution





Concentrations of Diamines, 0.25 wt%

Silicone Conc. (wt%)	Solvent flux (TMD)						
	H2O	MeOH	EtOH	IPA	acetone	MEK	Hexane
0	0.54	0.68	0.41	0.11	1.09	0.20	-
0.2	0.44	1.09	0.56	0.39	1.62	0.36	0.25
0.5	0.31	1.44	0.85	0.44	2.03	0.68	1.12
1.0	0.12	1.85	1.09	0.79	2.41	1.82	2.85
2.0	0.09	1.75	1.29	0.88	2.58	1.85	2.89

25 ℃; 200 psi

SUMMARY

- Nanofiltration (NF) is rapidly growing in liquid phase separation for the removal of natural organic matter(NOM), multivalent salts, dyes, and small organic molecules.

- NF membranes with high flux, solvent resistance, and low fouling have been developed for the extension NF application range

- Membrane fouling is influenced by the membrane surface properties, such as surface roughness, charge and hydrophobic-hydrophilic properties and the PA membranes coated with a thin PVA layer or nano particles show very good fouling resistance

- For a non-aqueous NF system, solvent resistance of the membrane materials, and solvent fluxes are key issues. NF membranes prepared by blending of polyamide and silicone polymer show high solvent flux and high rejection to small organic molecules.