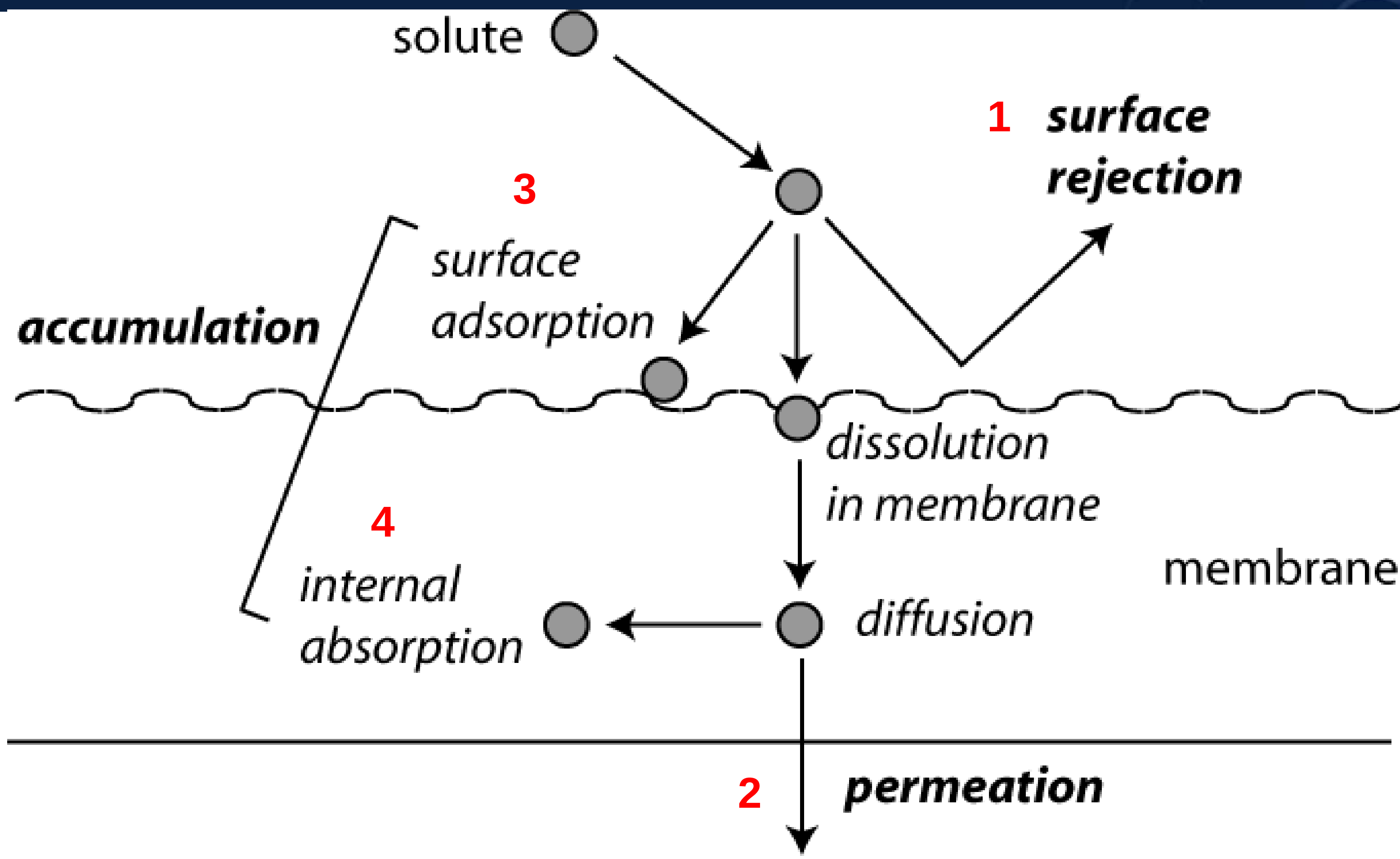
Organic Contaminant Removal and Membrane Fouling

Martin Reinhard
Eva Steinle-Darling, Megan Plumlee, Federico Pacheco, Yi-li Lin
Civil and Environmental Engineering
Stanford University

Kennedy/Jenks Consultants
Engineers & Scientists
National Water Research Institute

Idealized membrane separation



Solute-membrane-feedwater matrix interactions

Membrane
- Type
- Surface charge
- Surface roughness
- Cross-linking
- Contact angle
- Pore size/MWCO
- Performance indicator
-

Rejection mechanisms
Size exclusion
Charge repulsion

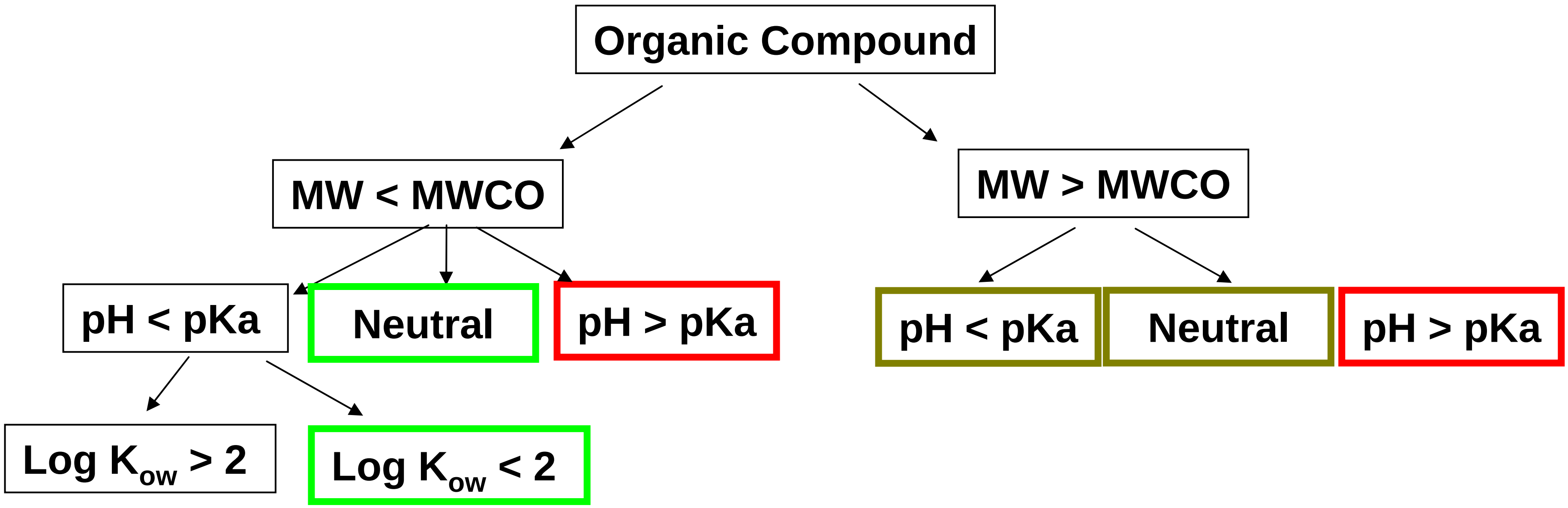
Membrane modifications
Charge neutralization
Adsorption, fouling

Solute
- Structure
- Molecular size/mass
- Shape/diameter
- Charge/pK_a
- Hydrophilicity

Solute reactions
Ionization
Coiling
Complexation

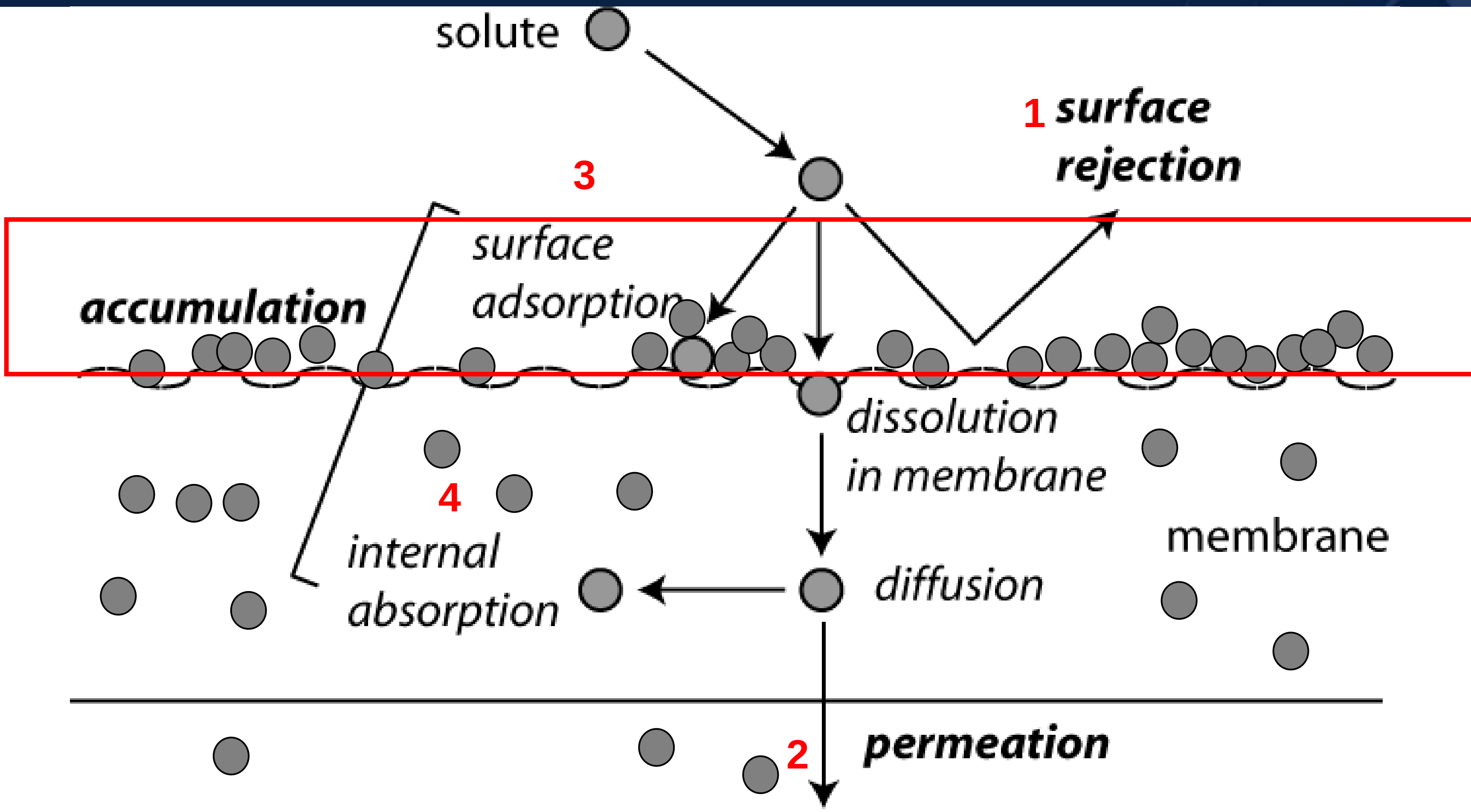
Feed water
- pH, cations
- Salt content
- Foulants, bacteria
- Organic matter
- Hardness

Simplified solute-matrix-membrane interaction scheme

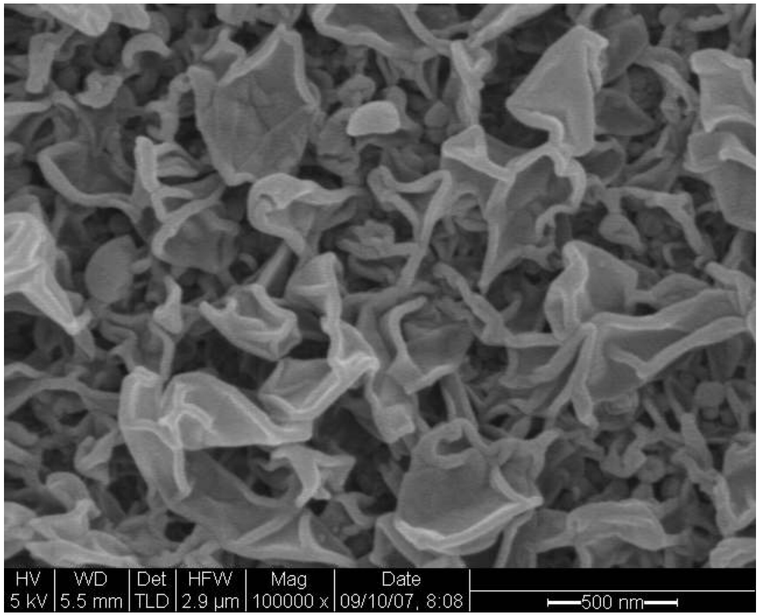


Transmission | Rejection | Sorption + transmission | Sorption + fouling

Rejection and fouling, formation of cake layer



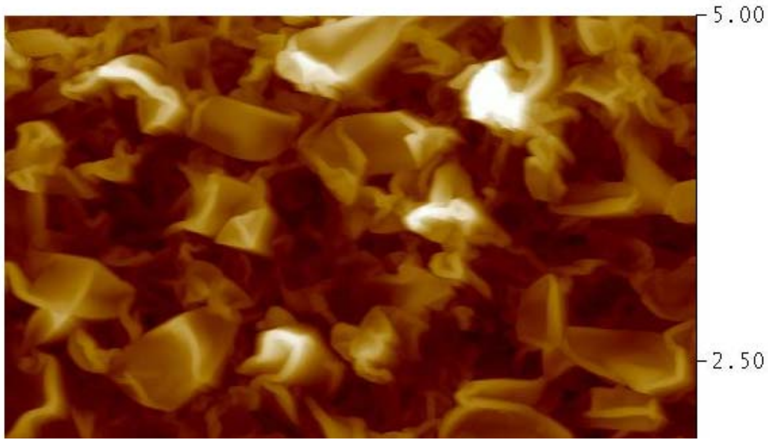
Surface roughness virgin ESPA-3

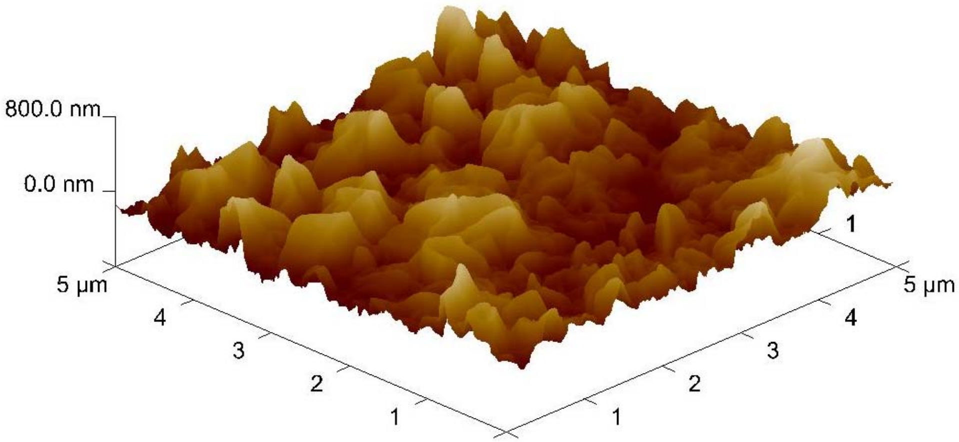


SEM

Scale bar: 500 nm

AFM

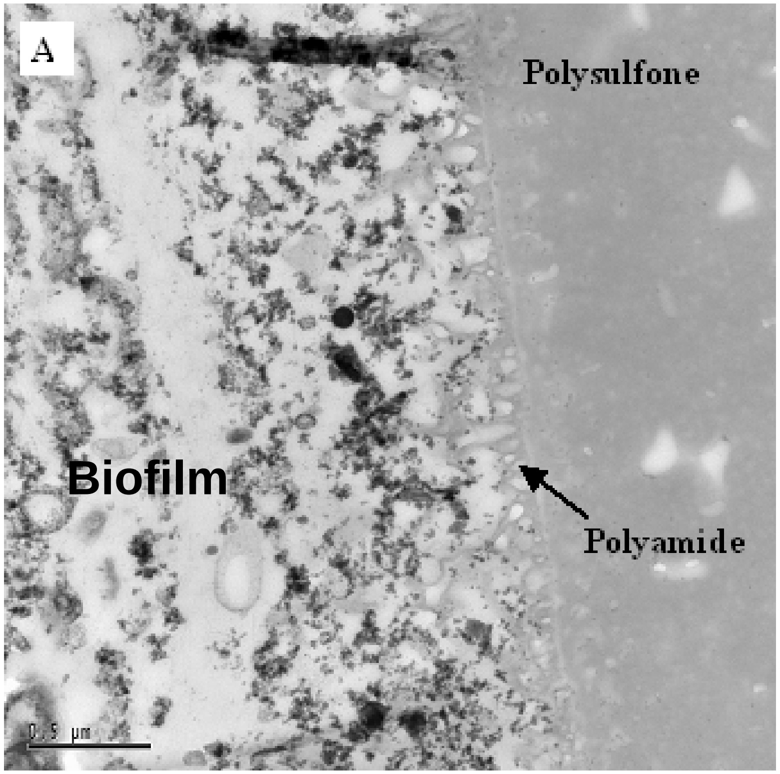




Surface roughness increases surface area and causes cavities – both promote sorption.

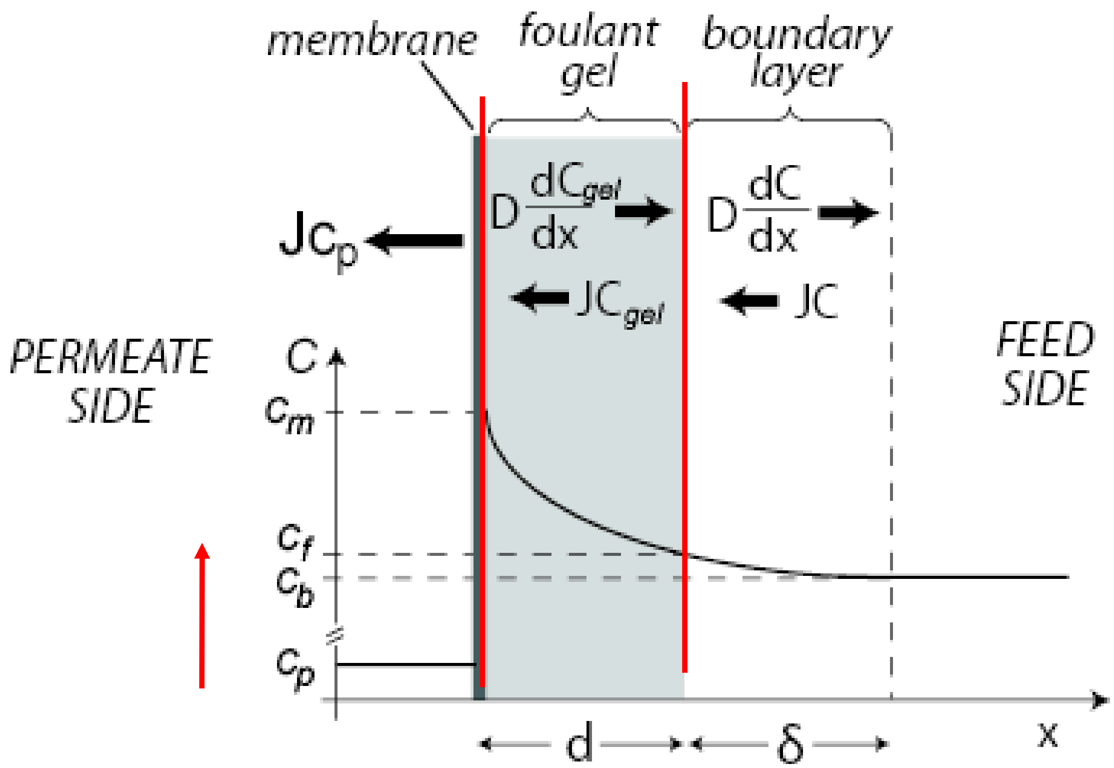
Fouling processes

Colloids, polymers, inorganic precipitates and bacteria form a cake at the membrane surface.



Kennedy/Jenks Consultants
Engineers & Scientists
National Water Research Institute

Concentration polarization with permeable foulant layer



D = alginate layer

D inside fouling layer is same as D in water.

Concentration at the membrane surface, C_m increases.

Gradient driving diffusion increases

Permeate concentration increases

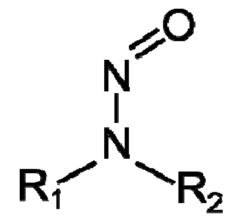
Steinle-Darling et al. Water Research. 41, 3959 - 3967 (2007)

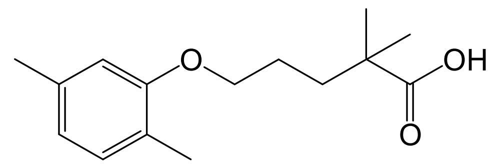
Investigative approach

1. Select test chemicals
2. Characterize membranes
3. Quantify solute rejection
4. Study solution conditions
5. Observe rejection in fouled membranes
6. Infer rejection mechanisms
7. Compare laboratory with treatment plant data

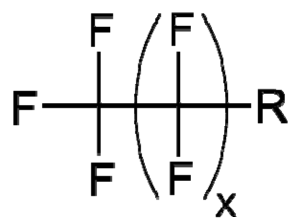
Test chemicals

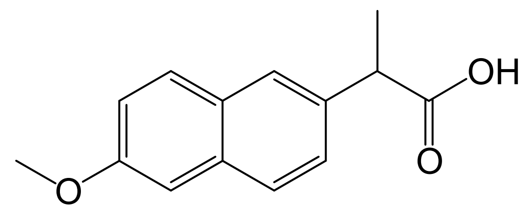
Nitrosamines

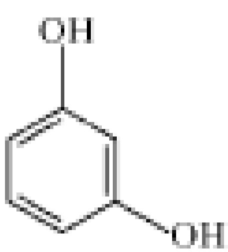


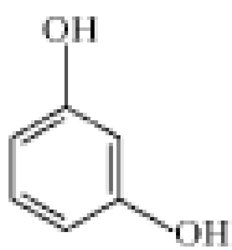


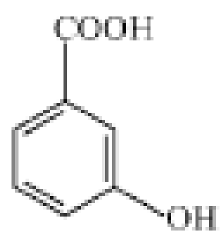
Perfluorocompounds

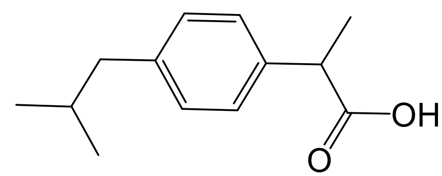








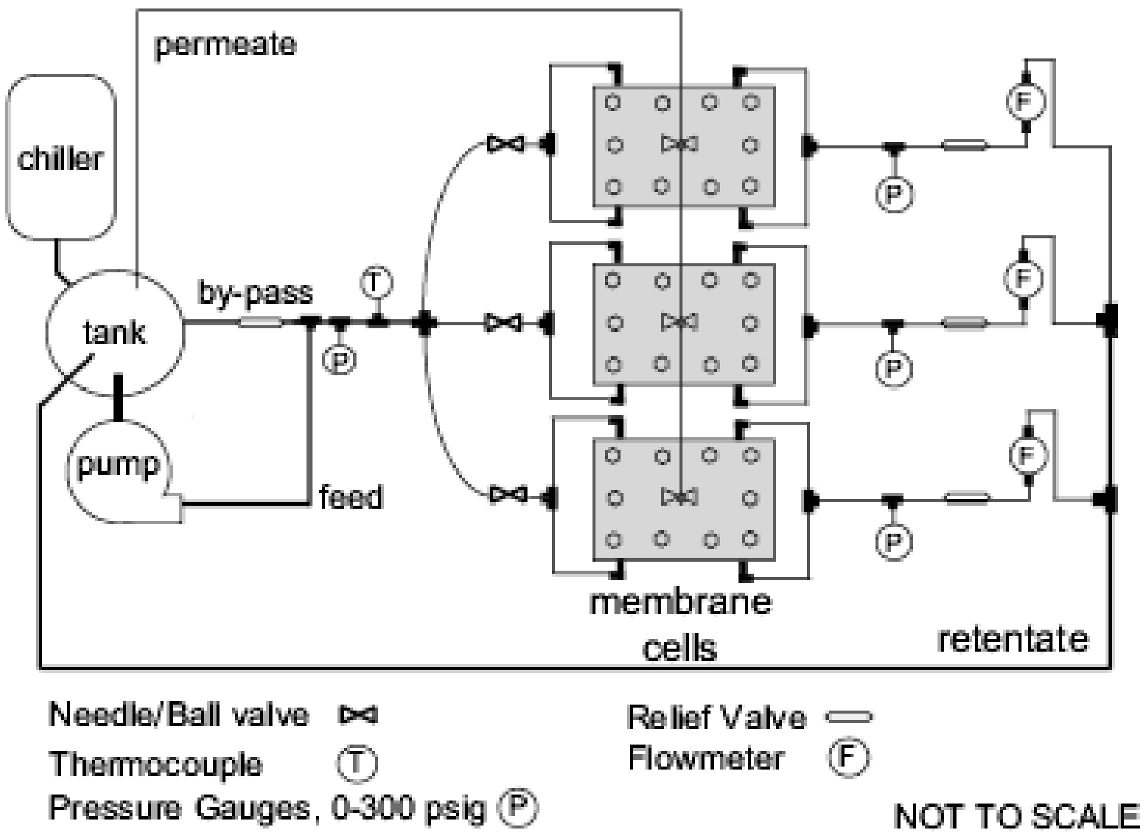




Pharmaceuticals

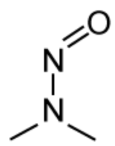
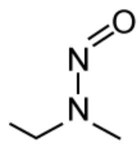
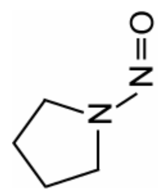
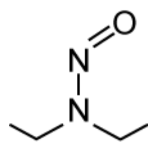
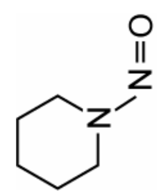
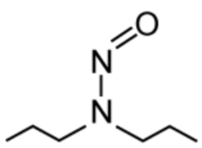
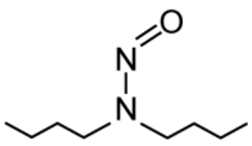
THM precursors + tannic acid (MW 1700

Experimental approach



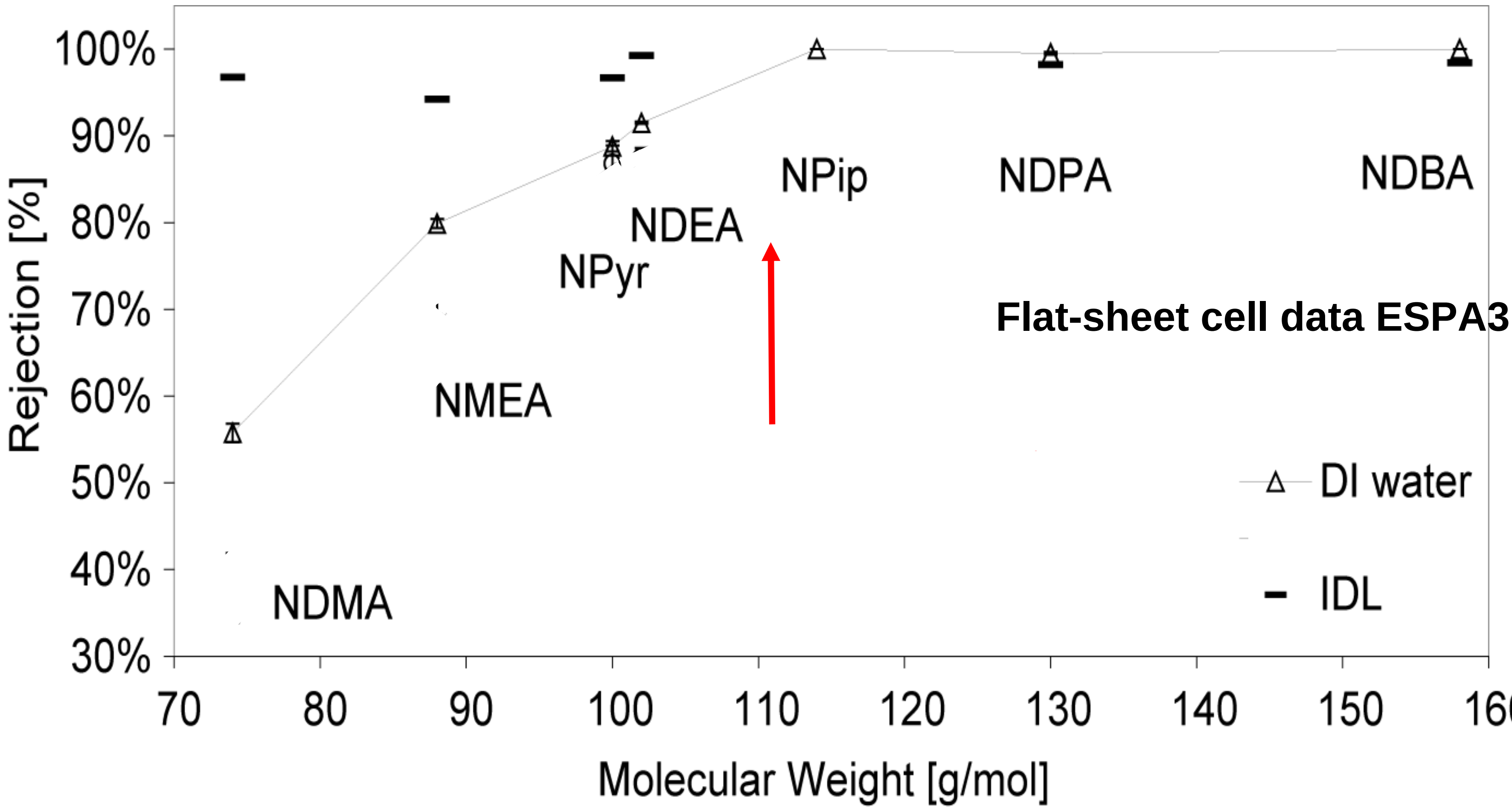
1. **Adjust solution conditions and pre-compact membrane**
2. **Spike compound into feed tank.**
3. **Measure compound in feed, concentrate, and permeate, and membrane**
4. **Evaluate mass balance**

Nitrosamines

Name	NDMA	NMEA	NPyr	NDEA	NPip	NDPA	NPBA
Structure							
MW	74	88	100	102	114	130	158
$\log K_{ow}$	- 0.57	0.04	- 0.19	0.48	0.36	1.36	2.63

- small
- hydrophilic
- uncharged
- NDMA 2 ng/L reporting limit

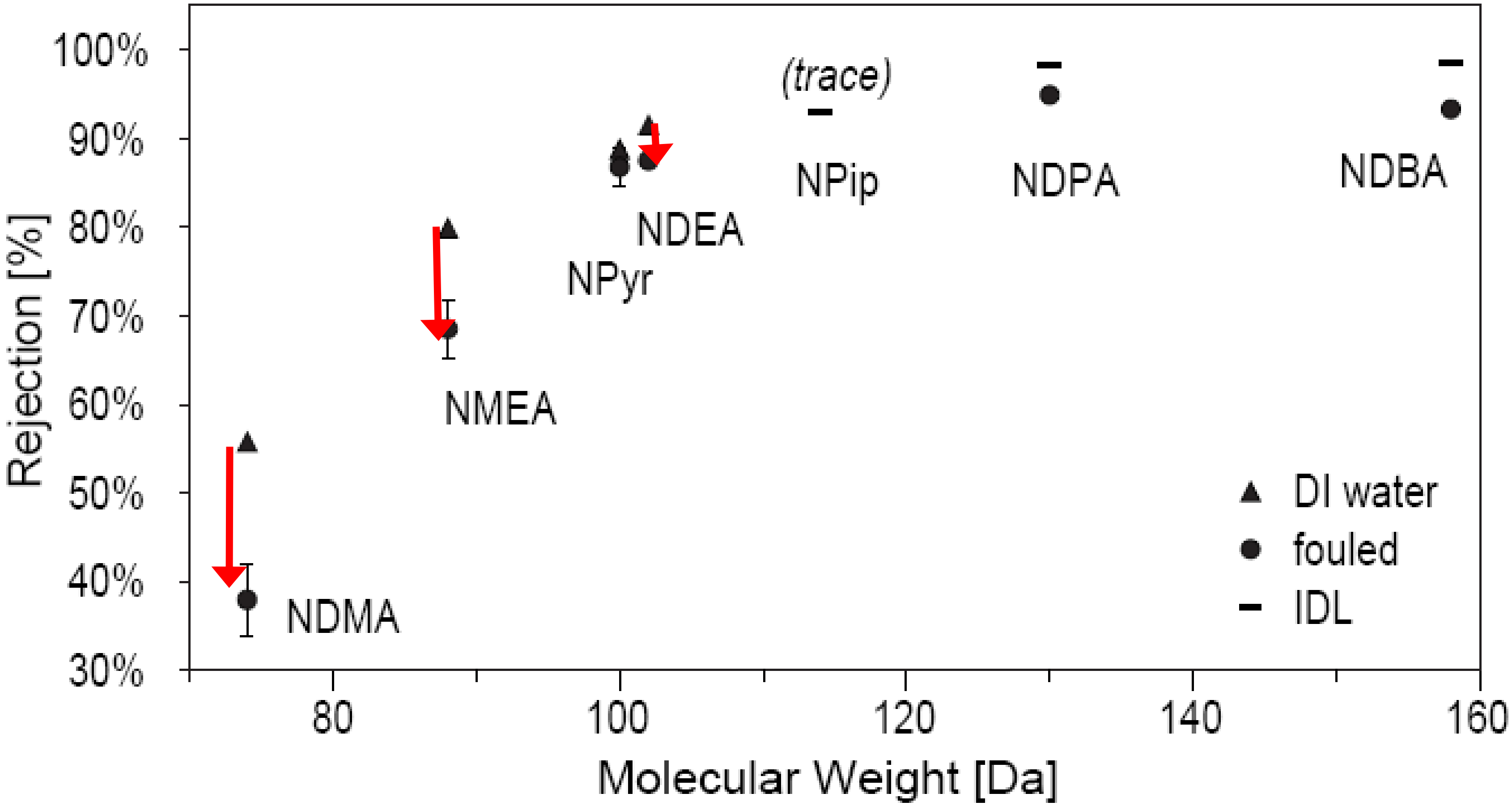
Nitrosodialkylamine rejection in DI water: MW dependence



Steinle-Darling et al. Water Research. 41, 3959 - 3967 (2007)

Kennedy/Jenks Consultants
Engineers & Scientists
National Water Research Institute

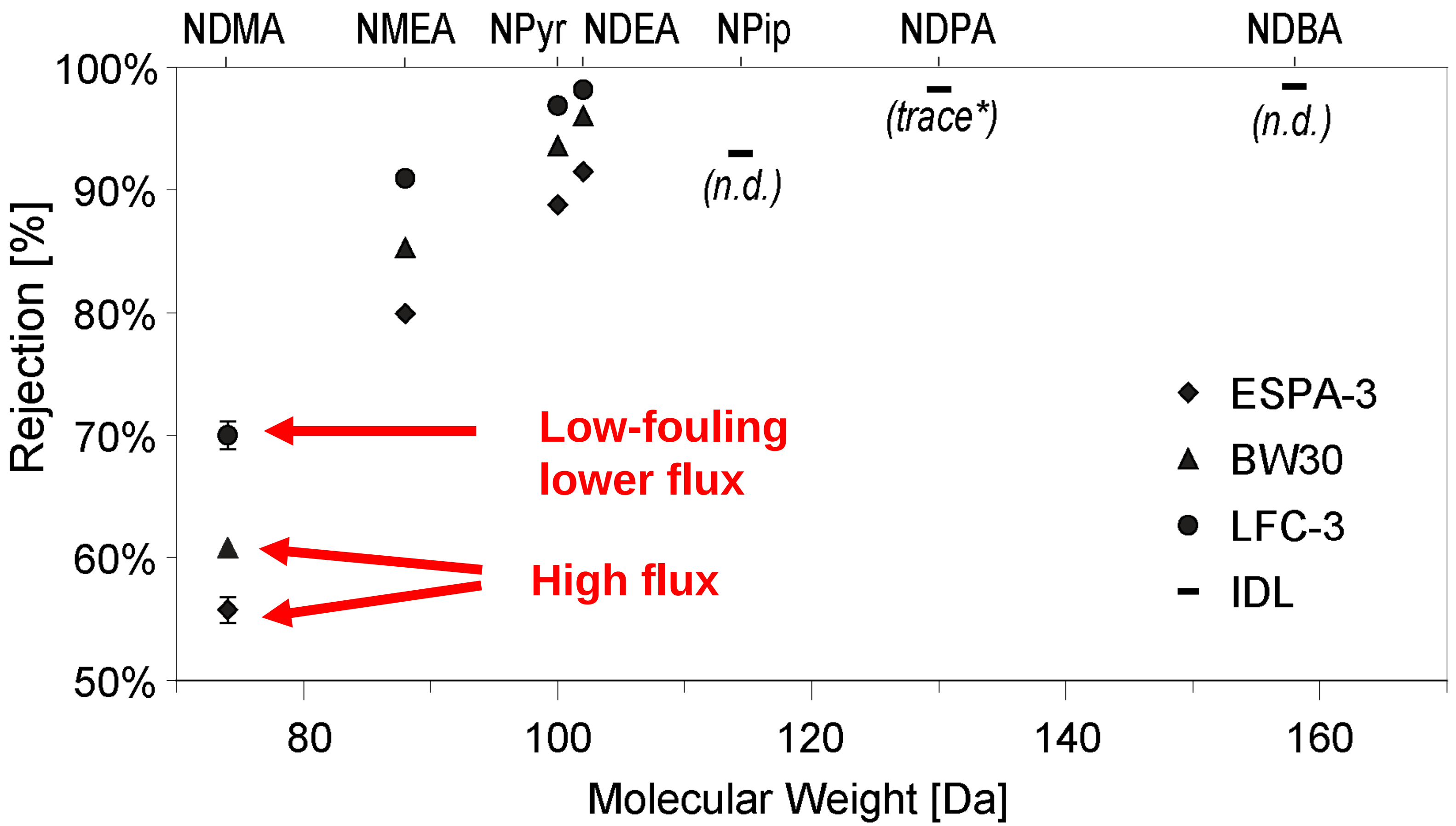
Artificially deposited alginate lowers rejection



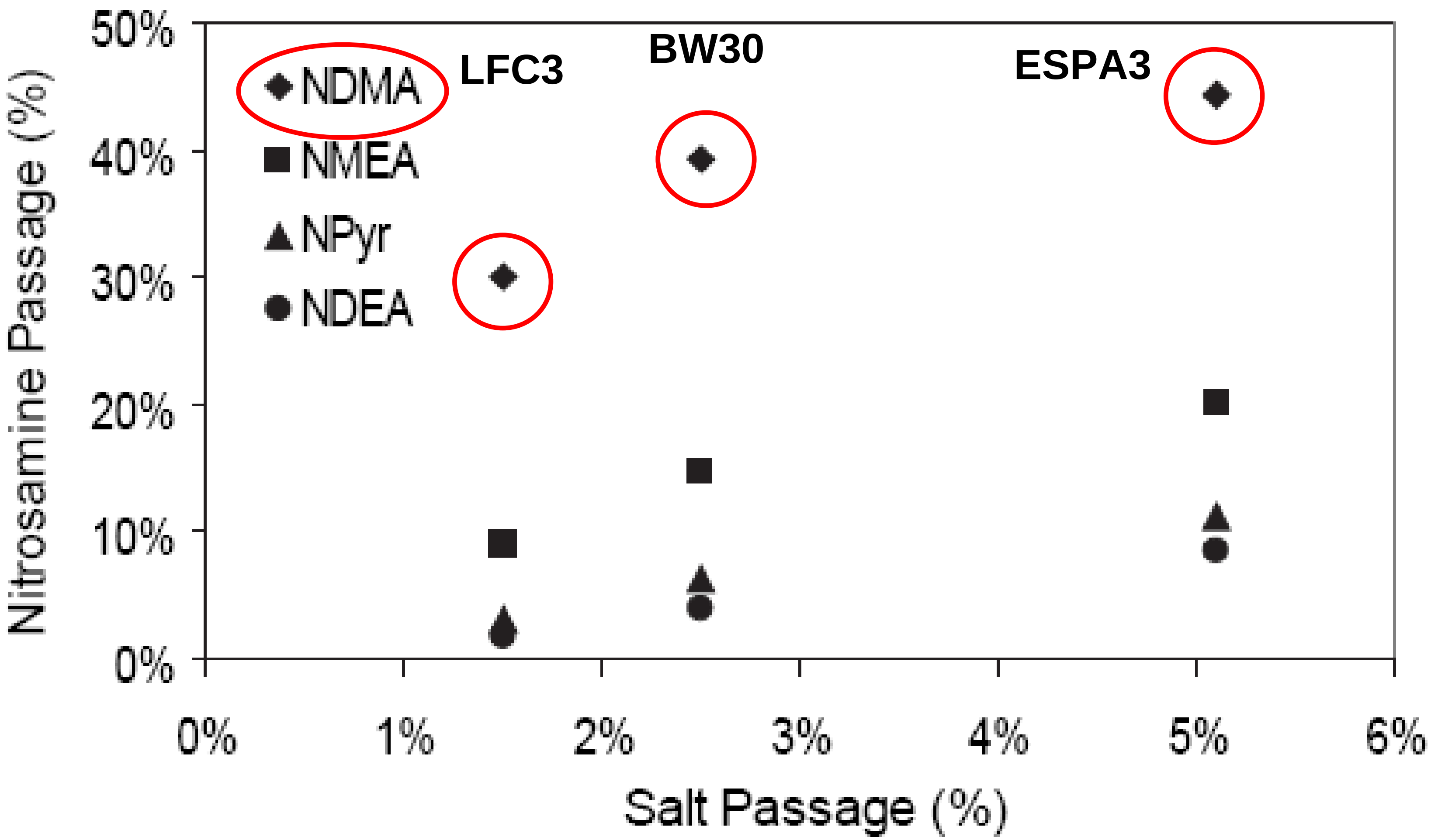
Steinle-Darling et al. Water Research. 41, 3959 - 3967 (2007)

Engineers & Scientists
National Water Research Institute

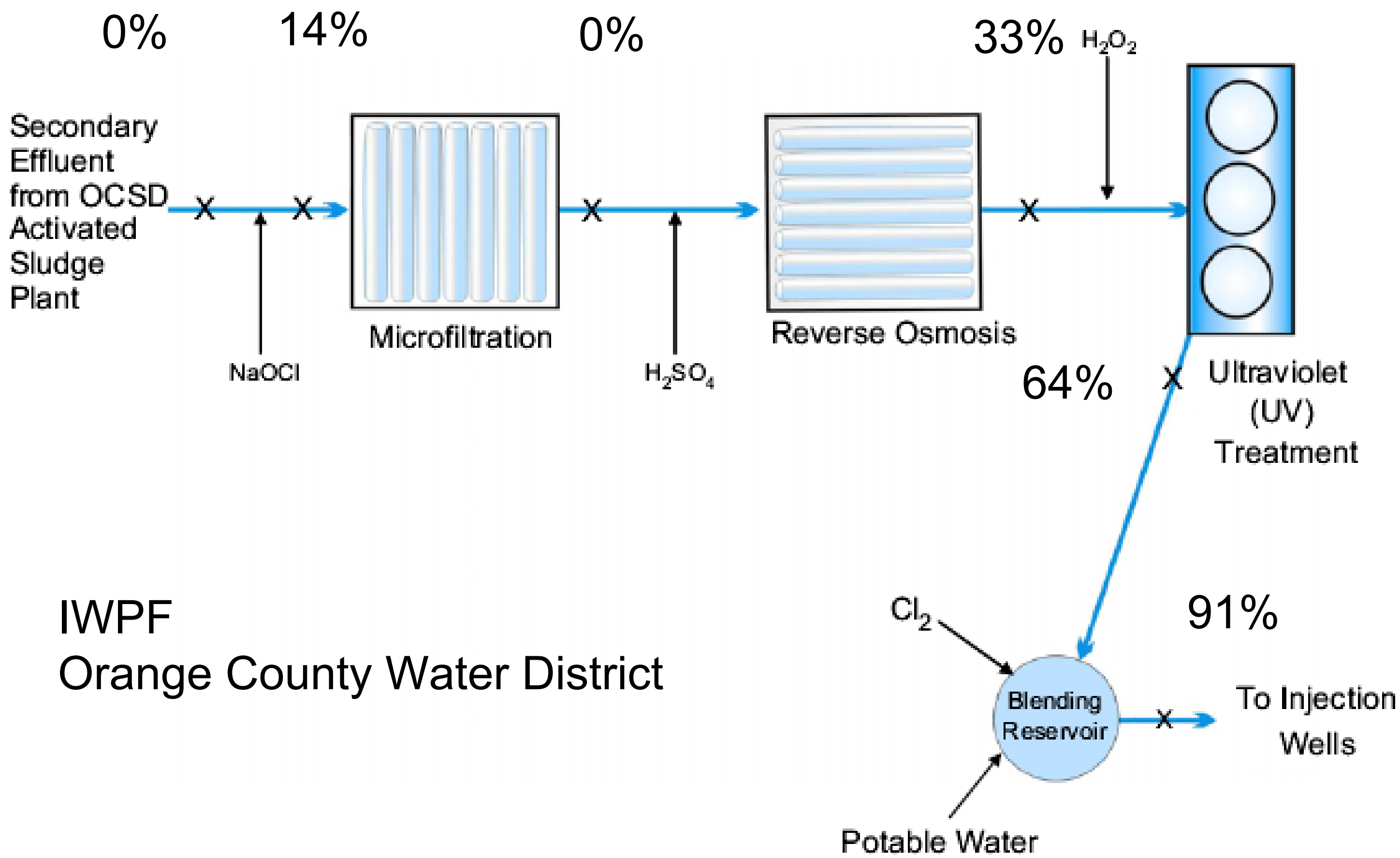
Rejection below MWCO varies with membrane type



Transmission of Nitrosamines increases with salt passage



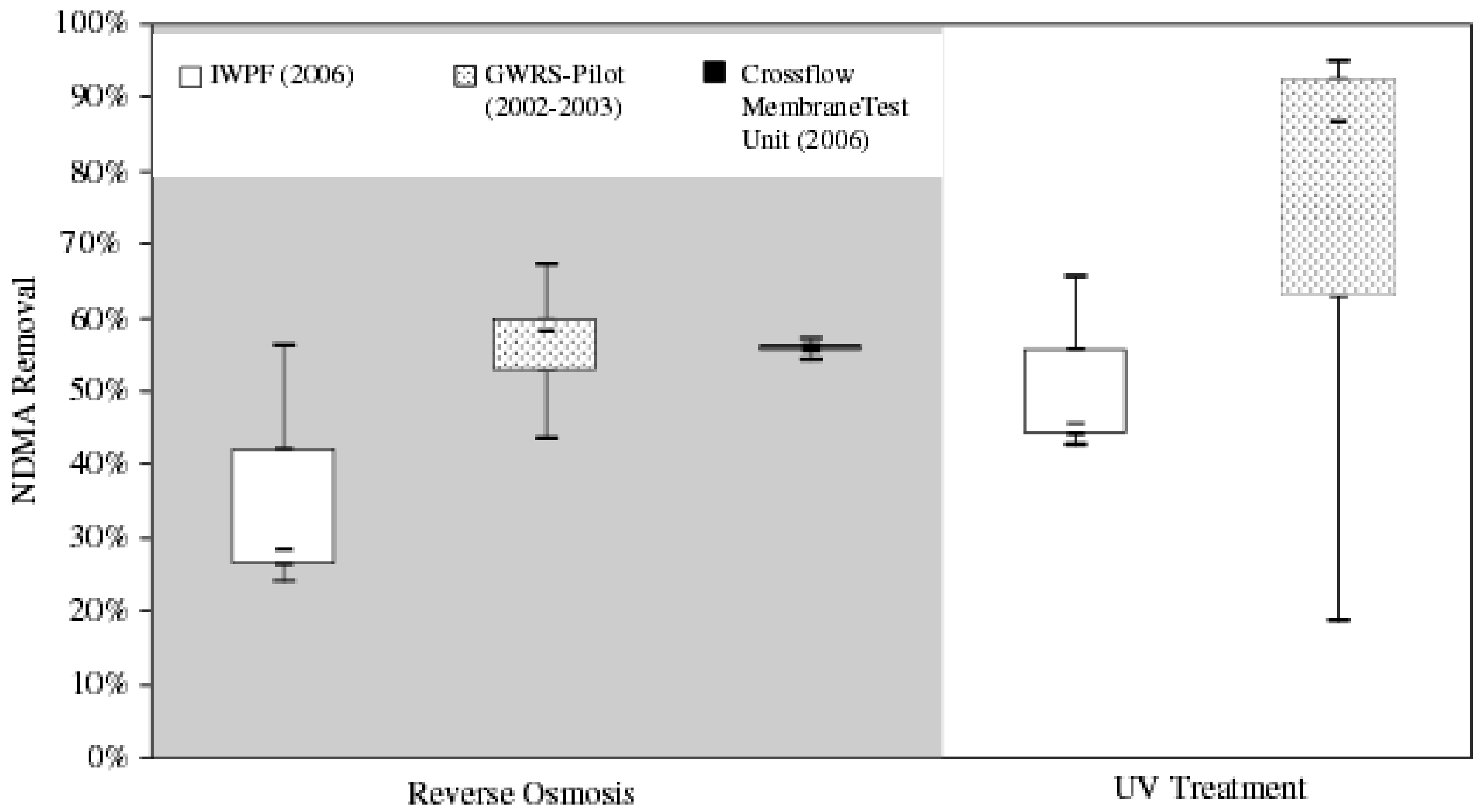
NDMA Removal at Interim Water Purification Facility



IWPF
Orange County Water District

Plumlee et al. Water Research. 42, 347 - 355 (2008)

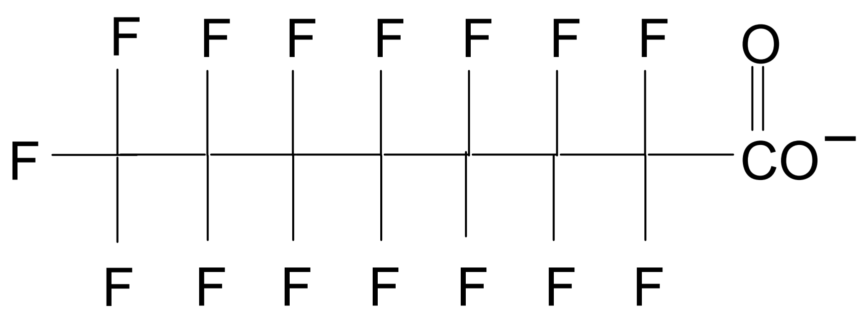
NDMA removal by RO and UV



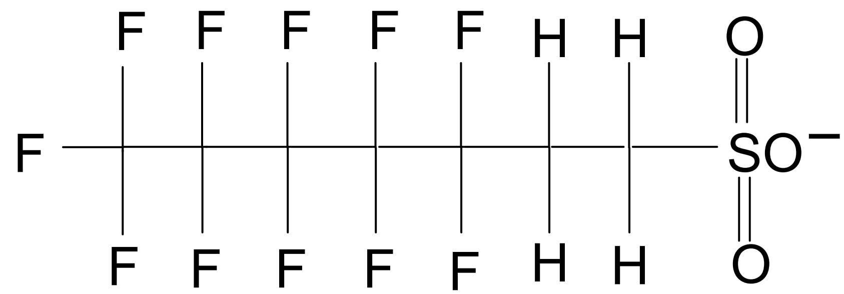
Plumlee et al. Water Research. 42, 347 - 355 (2008)

PFC compounds

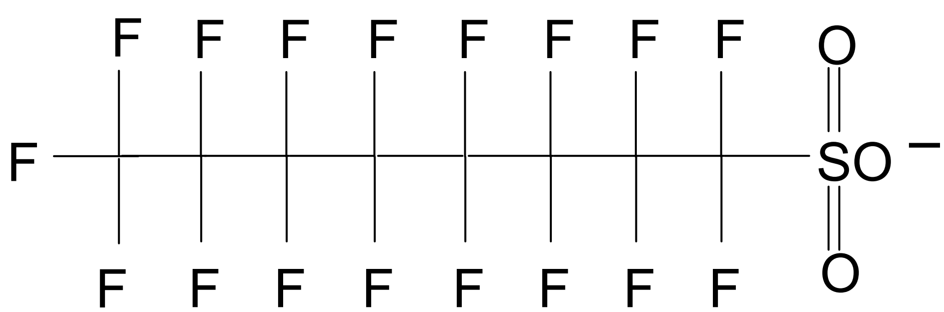
Perfluorooctanoic acid (PFOA)



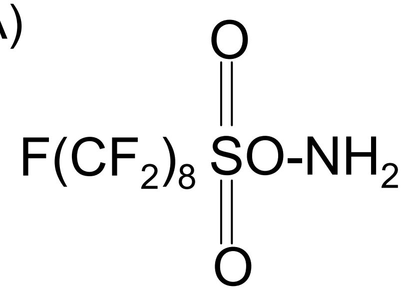
1H,1H,2,H,2,H-perfluorooctane sulfonate
6:2 FtS



Perfluorooctane sulfonate (PFOS and C_4 to C_8)

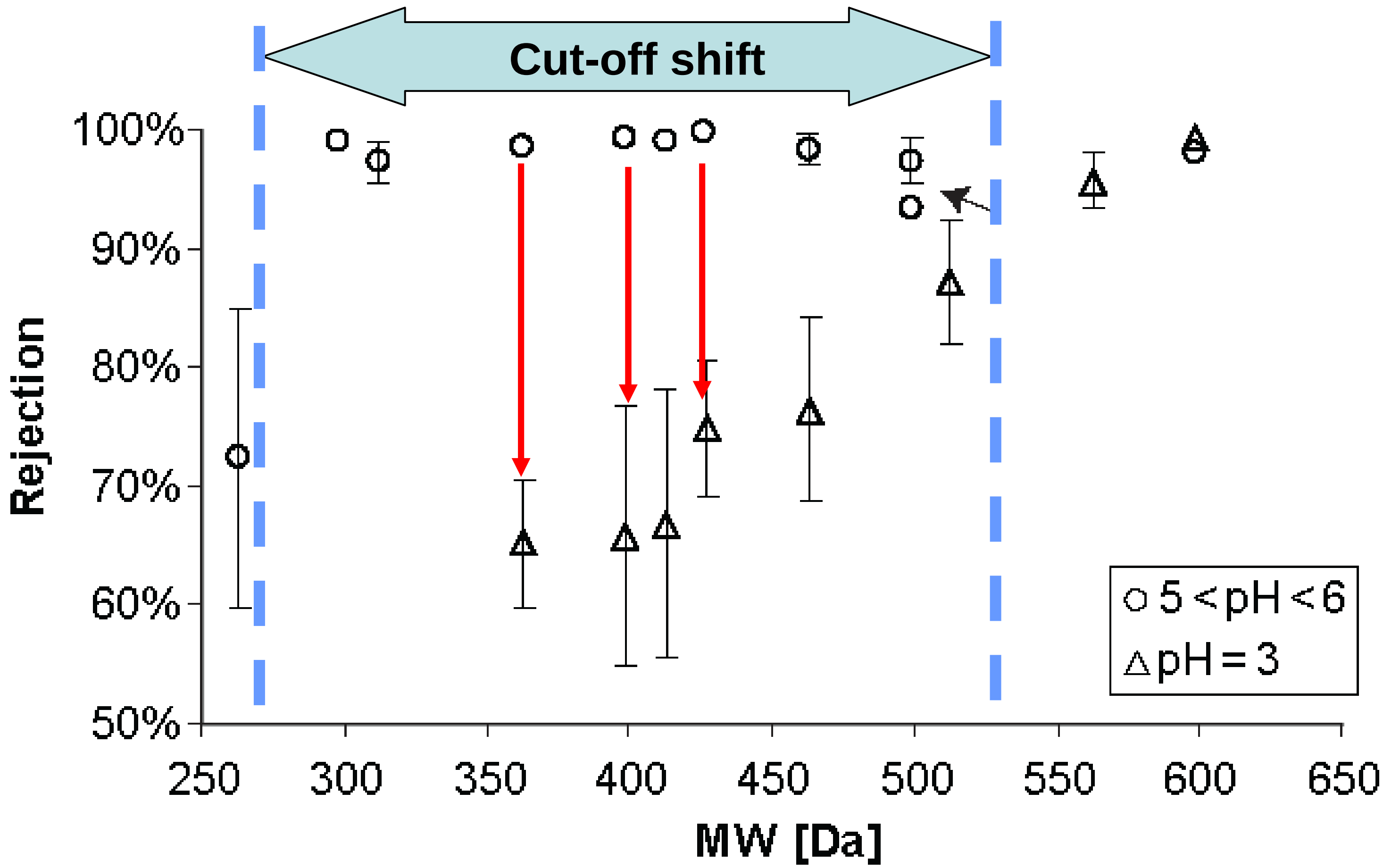


Perfluorooctane sulfonamide
(FOSA)



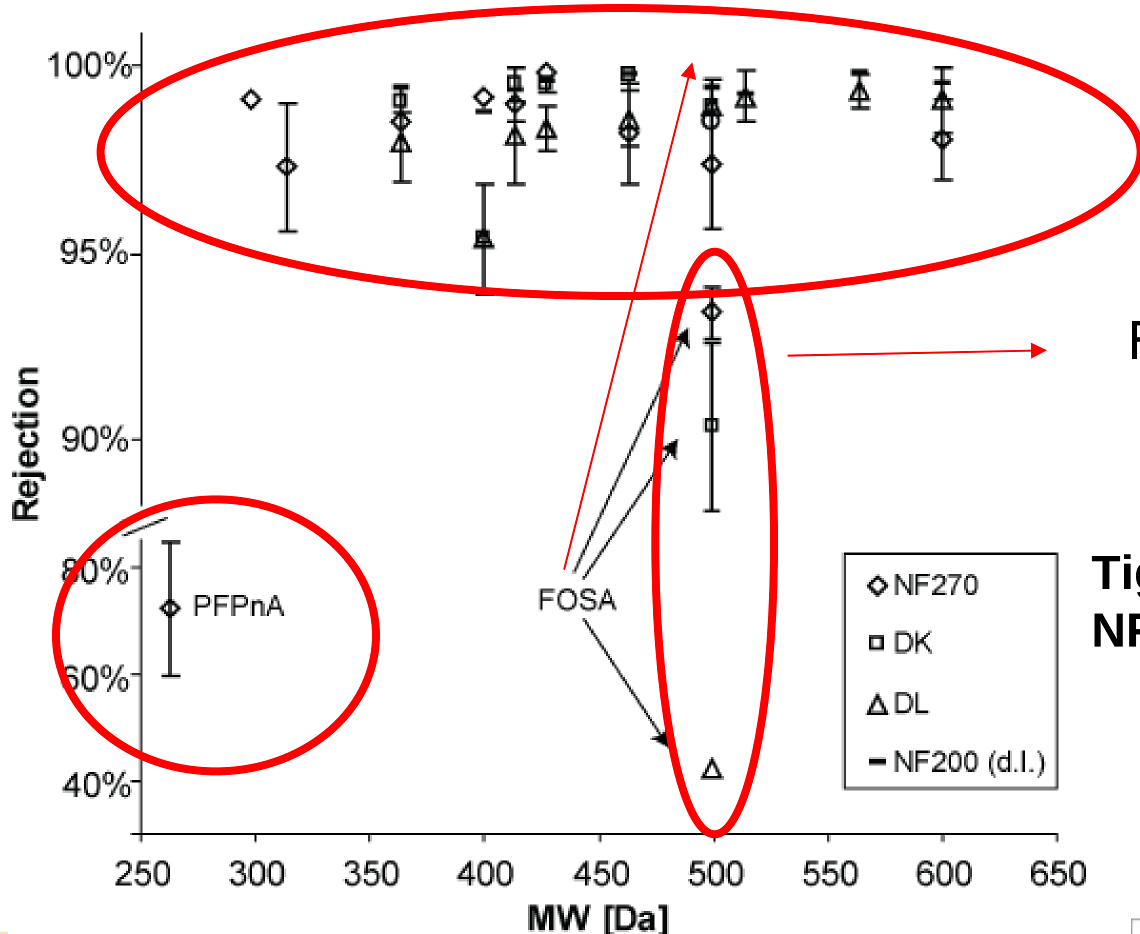
MW range 150-600 Da, surface active, all charged, except FOSA

Neutralization of membrane charge reduces rejection



Kennedy/Jenks Consultants
Engineers & Scientists
National Water Research Institute

PFC rejection: size and charge



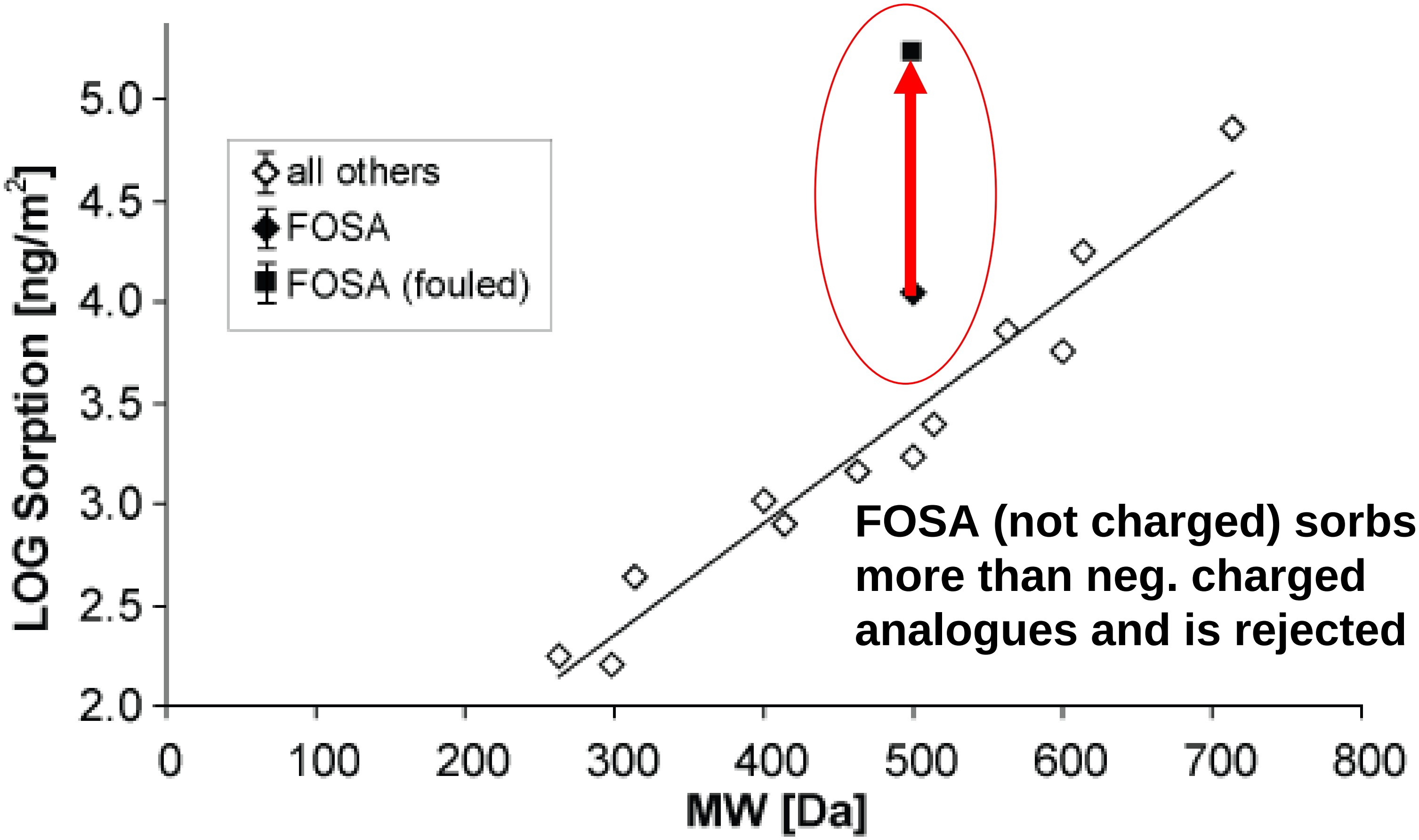
$F(CF_2)_8SO_2-NH_2$

Pentyl

Tightness
NF200>NF>270>DK>DL

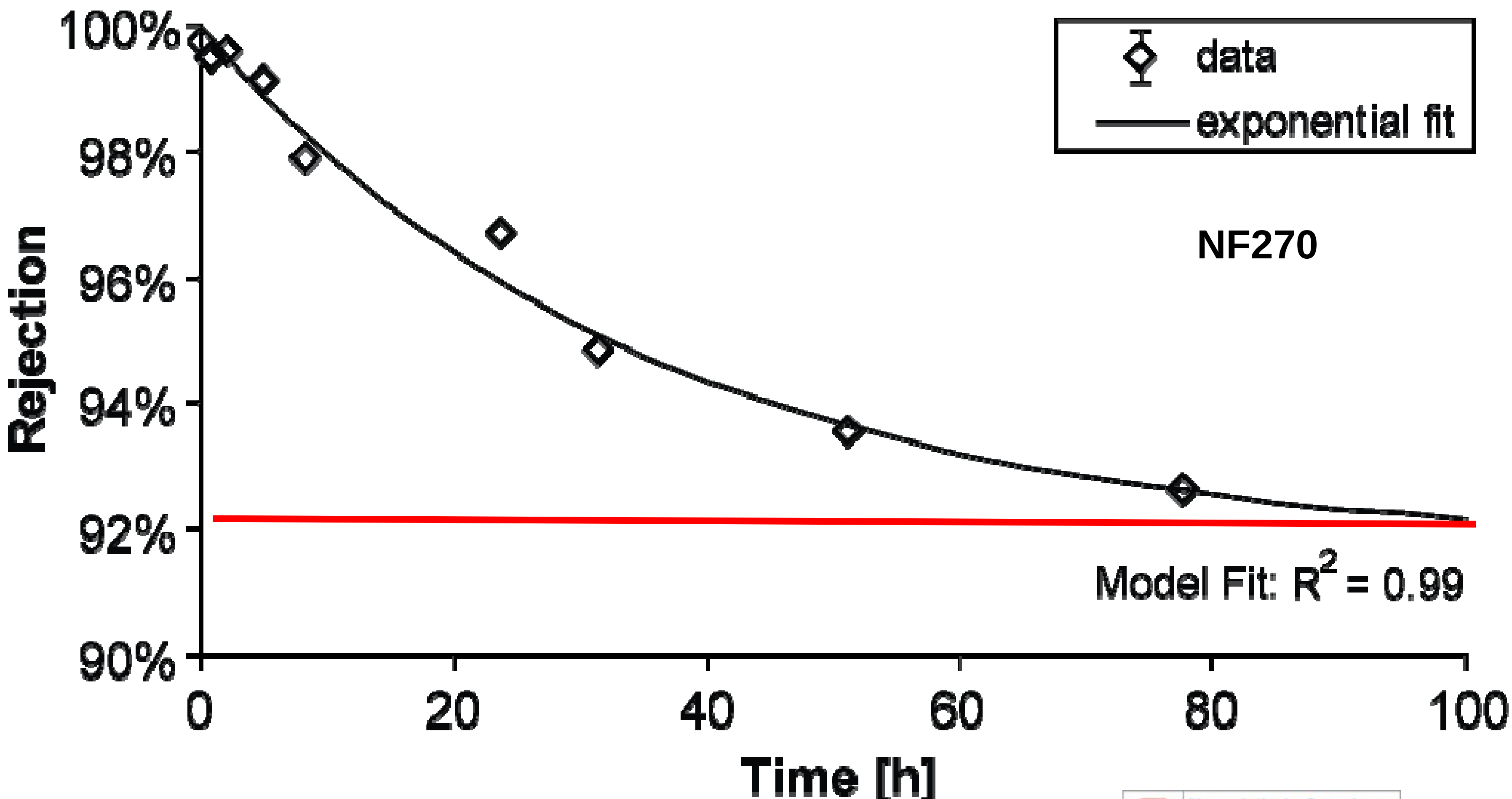
Kennedy/Jenks Consultants
Engineers & Scientists
National Water Research Institute

Sorption dependence of PFCs and FOSA on NF270



FOSA (not charged) sorbs more than neg. charged analogues and is rejected less.

Approach to steady-state rejection of FOSA



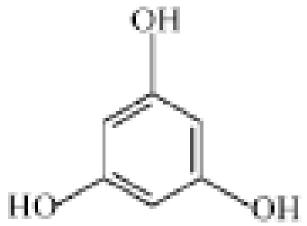
PFC: Salt and PFC Transmission

looseness

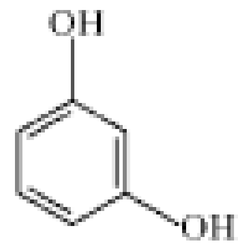
	NF200	NF270	DK	DL
$MgSO_4$ transm.	n.a.	<3% [8]	2% [8]	4% [29]
MWCO*	360 [30]	430 [31]	n.a.	n.a.
Avg. PFC transm.	n.d.	1.2%	1.3%	2.1%
FOSA transm.	1.5%	7%	10%	58%

High jump in FOSA transmission is not accompanied by proportional increase PFC transmission

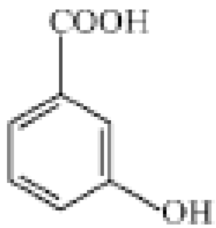
Polyphenols and hydroxy acids



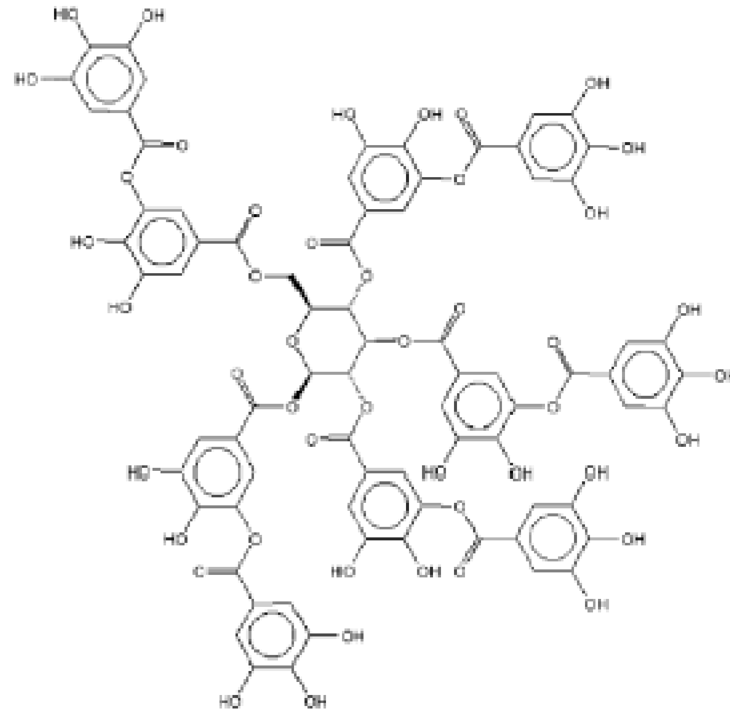
Phloroglucinol
MW 126 Da
Radius 0.343 nm
pK_1= 8.0



Resorcinol
MW 110 Da
Radius 0.349 nm
pK_1=9.4



3-Hydroxybenzoic acid
MW 138 Da
Radius 0.366
pK_1= 4.0

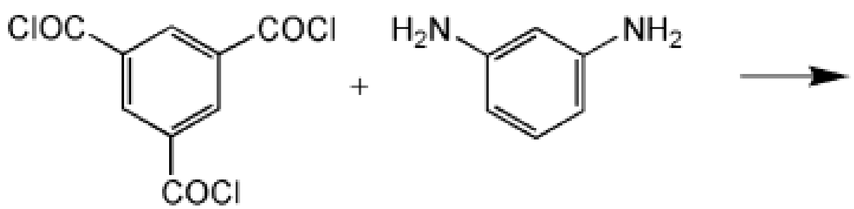


Tannic acid
MW 1701 Da
Radius 0.858 nm

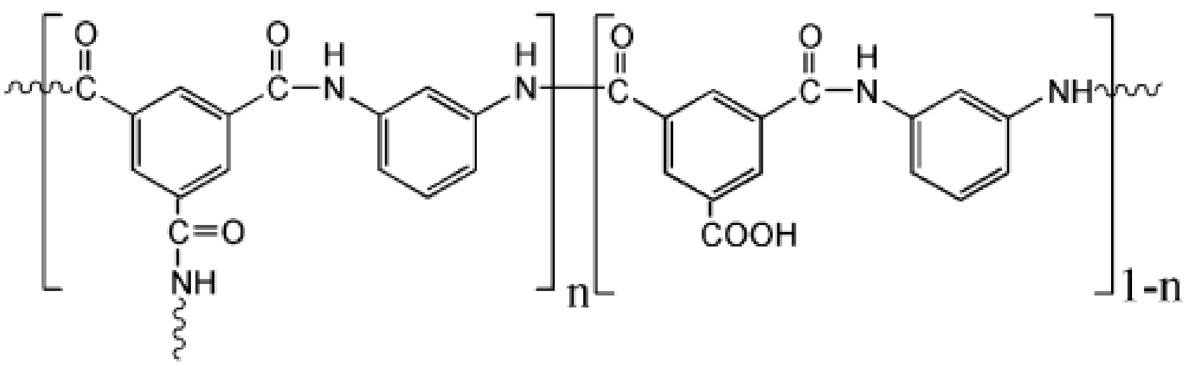
Yi-Li Lin et al. J. Haz. Mat. 146, 20-29 (2007)

O/N ratio, cross-linking and charge

Cross-linking determines surface charge, polymer rigidity, and MWCO



trimesoyl chloride 1,3-benzenediamine

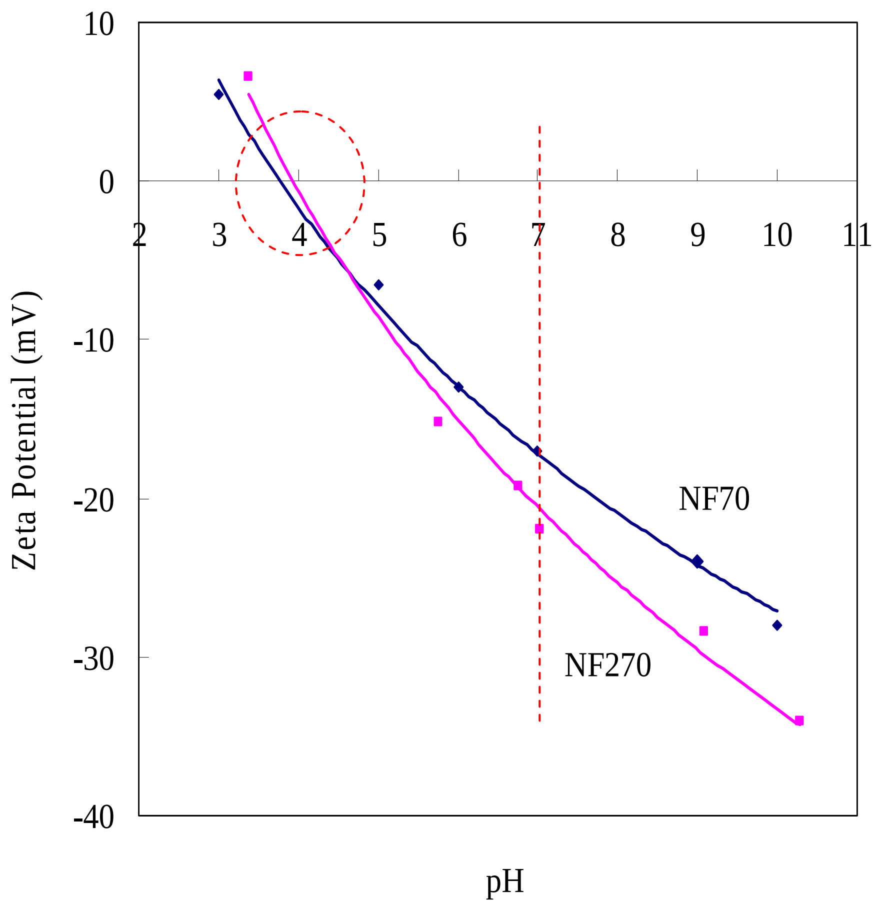


- n = 1
  - Fully cross-linked
  - Charge low
  - O/N ratio = 1
- n = 0
  - Linear
  - Charge high
  - O/N ratio = 2

NF 70 1.2
NF 270 1.5

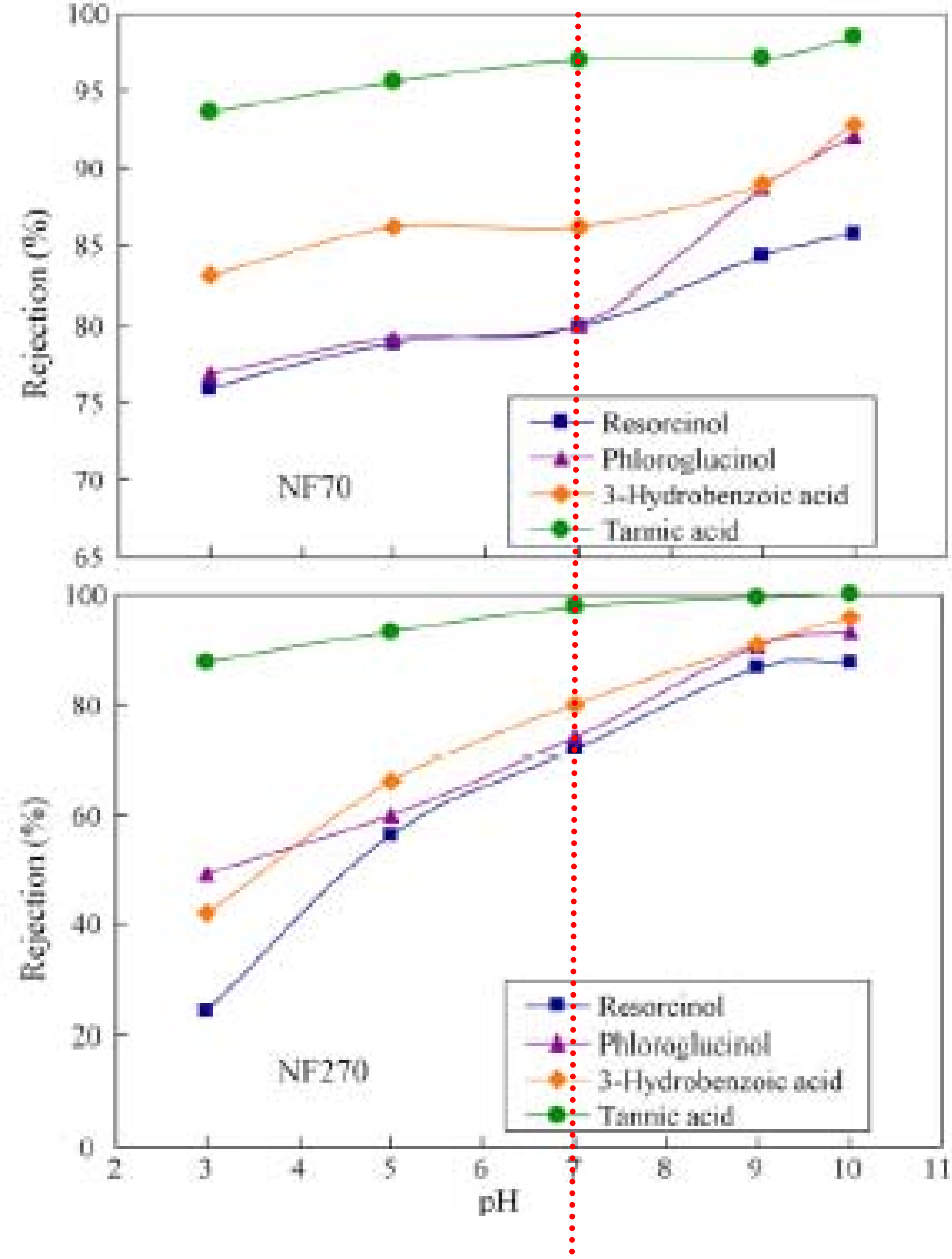
XPS analysis: elemental composition in surface layer (1 to 5 nm)

NF70 and NF270 Properties



Property	NF70	NF270
Type	arom.	semi-ar.
Flux (70 psi) L h^{-1} m^{-2}	32	71
O/N (cross-linking)	1.2	1.5
$CaCl_2$ rejection %	85-95	40-60
MWCO	250	300
Pore radius	0.48	0.54
Roughness (rms) nm	21	10
Zeta potential at pH 7	lower	higher

Yi-Li Lin et al. J. Haz. Mat. 146, 20-29 (2007)



Property	NF70	NF270
Organic removal	high	low
Type	arom.	semi-a
Flux	low	high
Cross-linking	high	low
$CaCl_2$ rejection	high	low
MWCO	low	high
Pore radius	small	high
Roughness (rms) nm	high	low
	lower	higher
Zeta potential at pH 7	lower	higher

Yi-Li Lin et al. J. Haz. Mat. 146, 20-29 (2007)

Kennedy/Jenks Consultants
Engineers & Scientists
National Water Research Institute

Removal of pharmaceuticals and EDCs by NF

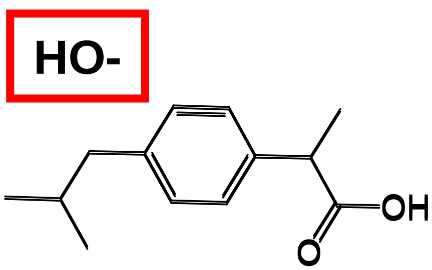
Kimura et al.
JMS
245 71-78 2004

Name	Manufacturer	Materials	MWCO[a]	Salt rejection (%)[a]
XLE	Dow-FilmTec	Polyamide	<200	90
SC-3100	Toray	Cellulose acetate	200–300	94

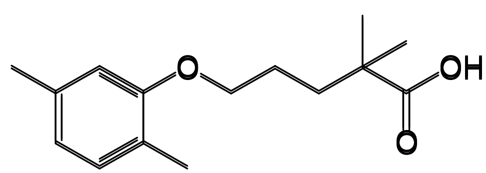
aa	XLE	SC-3100
2-Naphthol	57	0
4-Phenylphenol	61	11
Phenacetine	74	10
Caffeine	70	44
NAC standard	79	0
Primidone	87	85
Bisphenol A	83	18
Isopropylantipyrine	78	69
Carbamazepine	91	85
Sulfamethoxazole	70	82
17β-Estradiol	83	29

Removal of selected PhACs in pilot MF-RO system (μg/L)

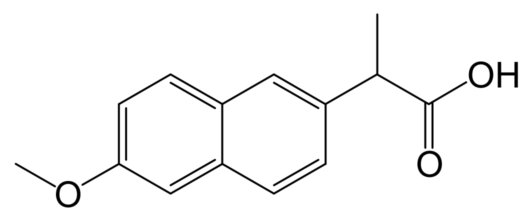
Compound	Inf.	MF	RO	% removal
Ibuprofen	3.4	2.0	0.005	99.75
OH-Ibuprof	24.1	8.4	0.008	99.9
Gemfibrozil	0.82	0.7	0.003	99.6
Naproxen	8.3	1.7	0.009	99.5



Ibuprofen MW 206.3



Gemfibrozil MW 250.3



Naproxen MW 230.3

Summary and conclusions

1. The MWCO of a membrane depends on compound structure and solution properties (pKa, solution pH).
2. The membrane type influences passage of small compounds.
3. Increasing pH increases rejection of acidic compounds; effect is stronger with the highly cross-linked membranes.

Summary and conclusions

4. Some trace organics sorb - uncharged solutes more than charged solutes.
5. Sorbing compounds are rejected less.
6. Fouling deepens polarization layer and decreases organics rejection.
7. Pharmaceuticals are removed by

   RO 70 to >99%

   NF 60 to 99%.