Selected Membrane Applications : Arsenic (As), Perchlorate(ClO_4^-), Natural Organic Matter(NOM), and Effluent Organic Matter(EfOM)

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Part 1
Treatment of Arsenic in Drinking Water via Membrane Technology

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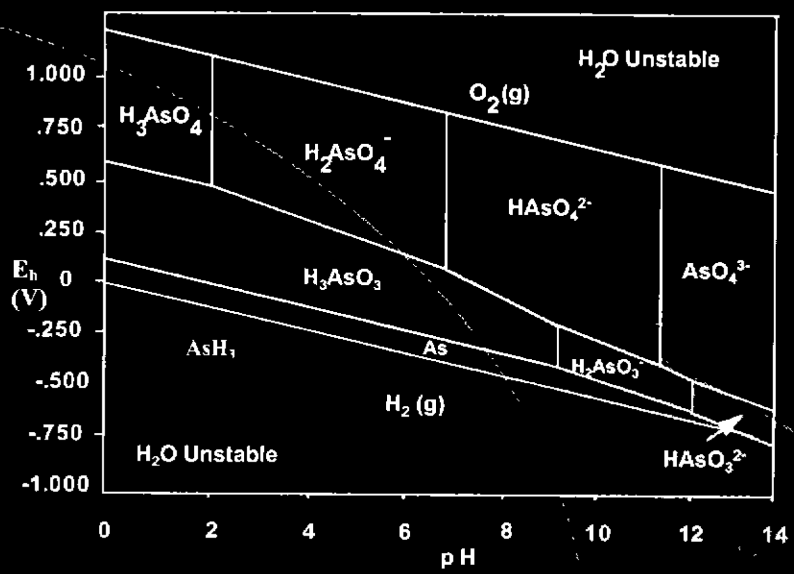
Outline

- Arsenic Chemistry
- Performance of (Spiral Wound) RO/NF/UF
  - Factors Influencing Performance
- Performance of Coagulation/Microfiltration
  - Factors Influencing Performance

Arsenic E_h - pH Diagram in Pure Water

Ferguson and Garvis (1972)



RO/NF/UF Performance - 20 to 50 μg/l As Spike

MQ Water

Class	# Tested	As(V) Removal	As(III) Removal
NF	3	85 - 96 %	5 – 40 %
UF	3	5 – 63 %	0 – 5 %

Groundwaters (2)

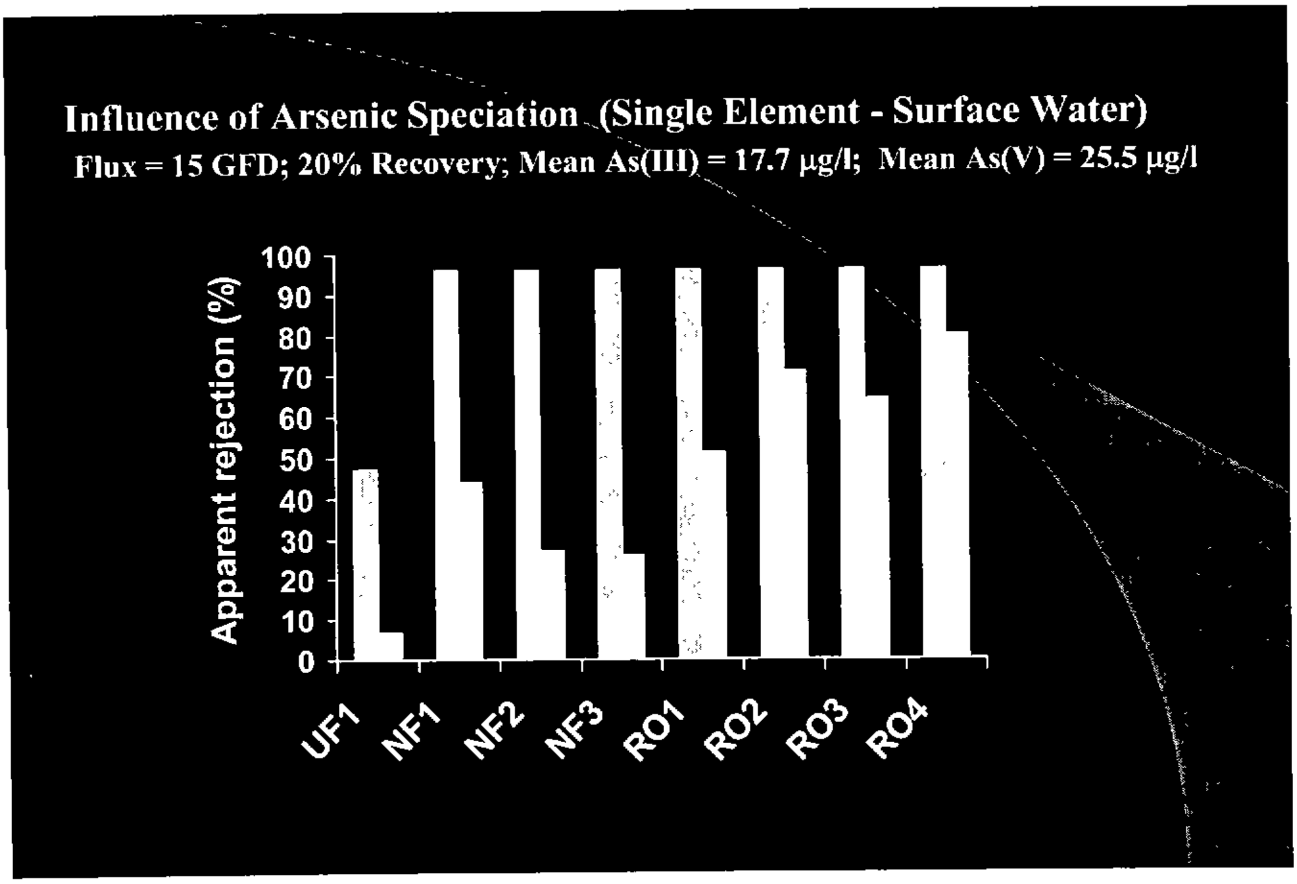
Class	# Tested	As(V) Removal	As(III) Removal
RO	1	86 - > 94 %	NA
NF	1	62 – 89 %	NA
UF	1	34 – 72 %	NA

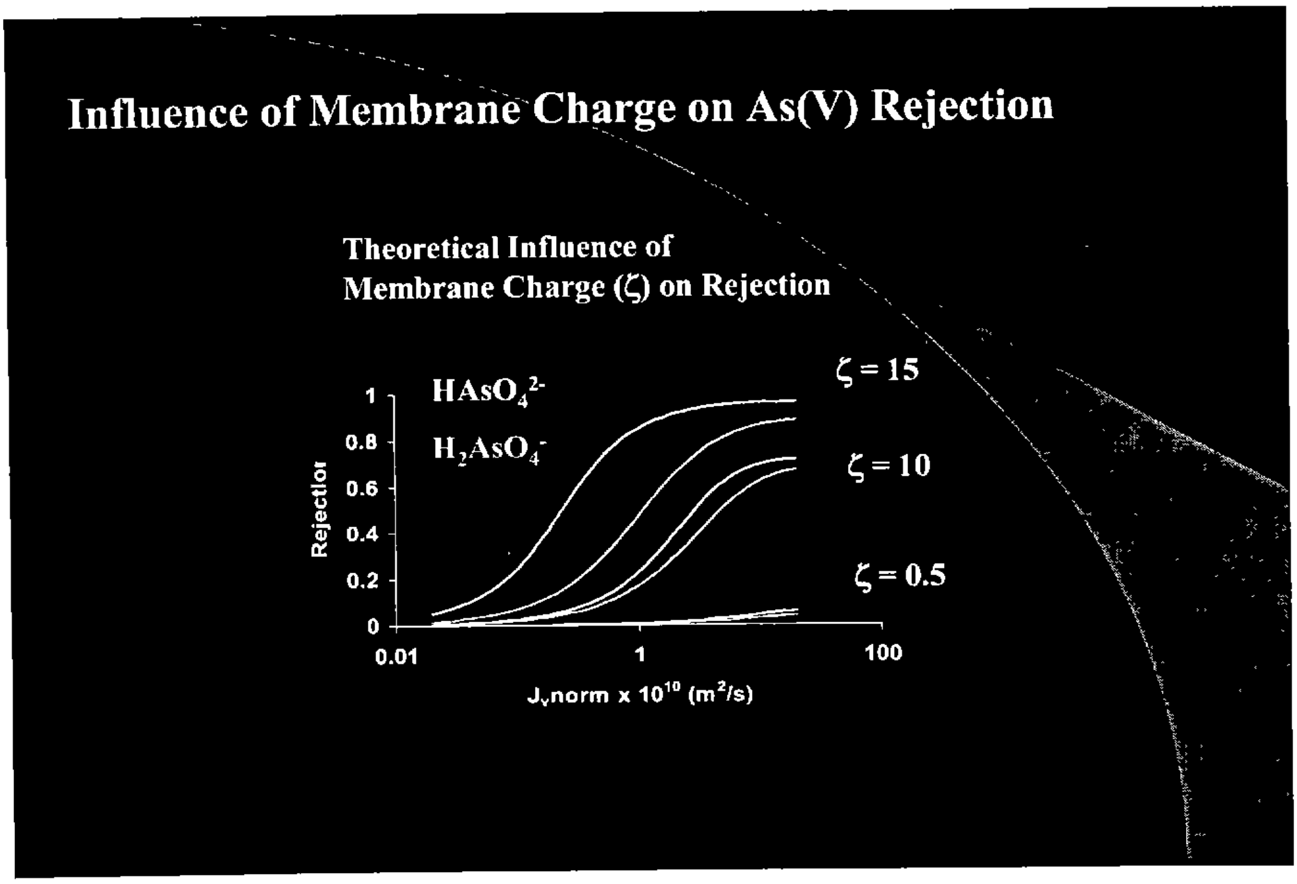
Surface Water

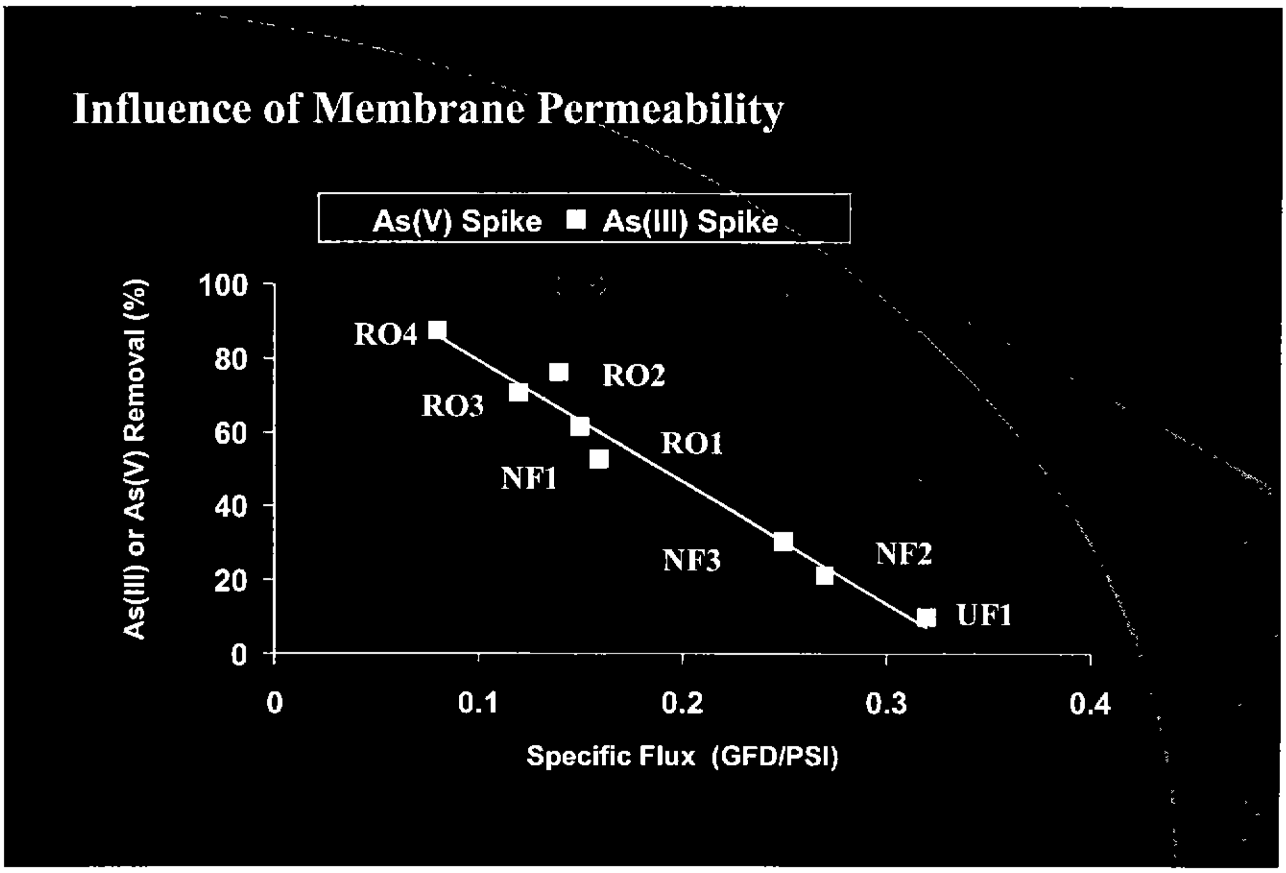
Class	# Tested	As(V) Removal	As(III) Removal
RO	4	> 96 %	51 – 80 %
NF	3	> 96 %	20 – 44 %
UF	1	47 %	7 %

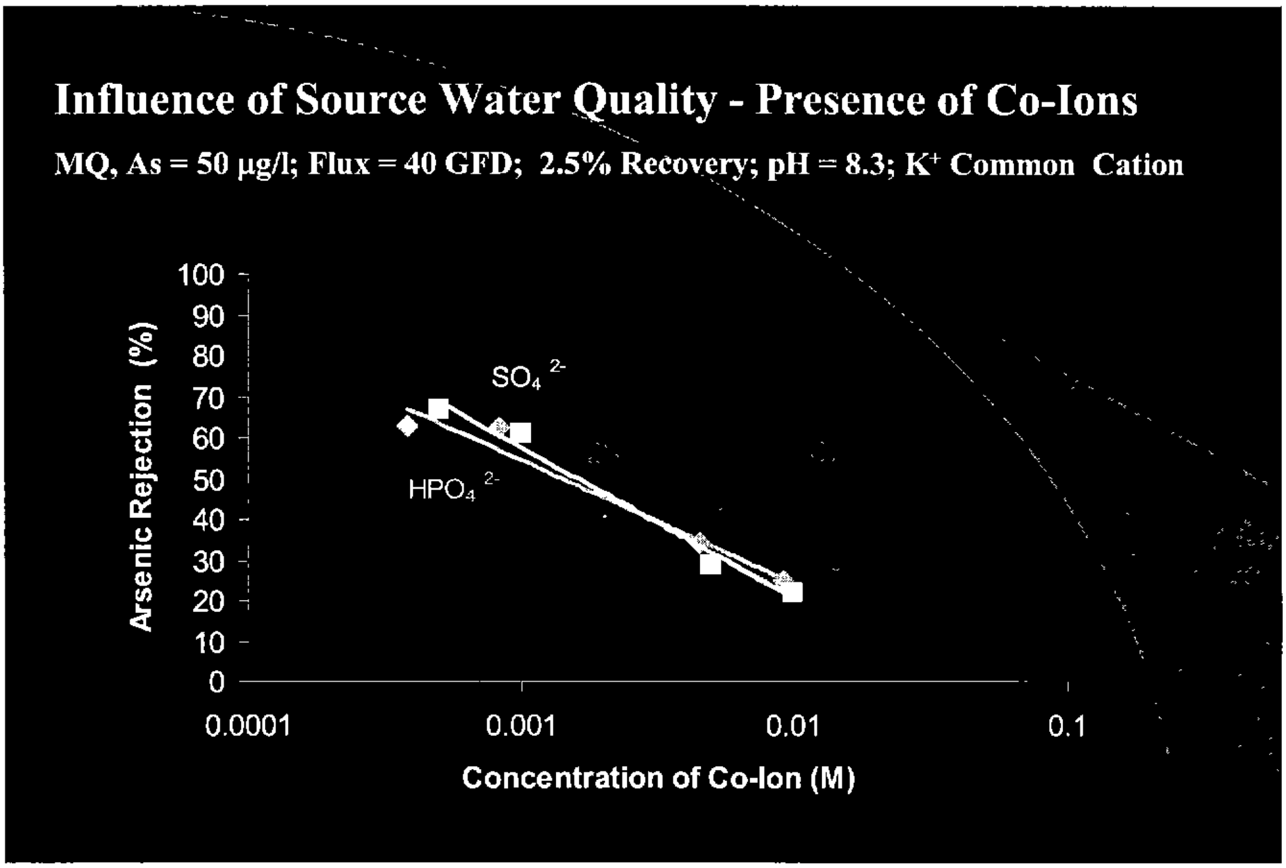
Factors Influencing As Rejection by RO/NF/UF Membranes

- Arsenic Speciation
- Membrane Charge/Permeability
- Source Water Composition
- Hydraulic Operation of Membrane
- Treatment pH


Influence of Arsenic Speciation (Single Element - Surface Water)
Flux = 15 GFD; 20% Recovery; Mean As(III) = 17.7 µg/l; Mean As(V) = 25.5 µg/l
Apparent rejection (%)
100
90
80
70
60
50
40
30
20
10
0
UF1
NF1
NF2
NF3
RO1
RO2
RO3
RO4

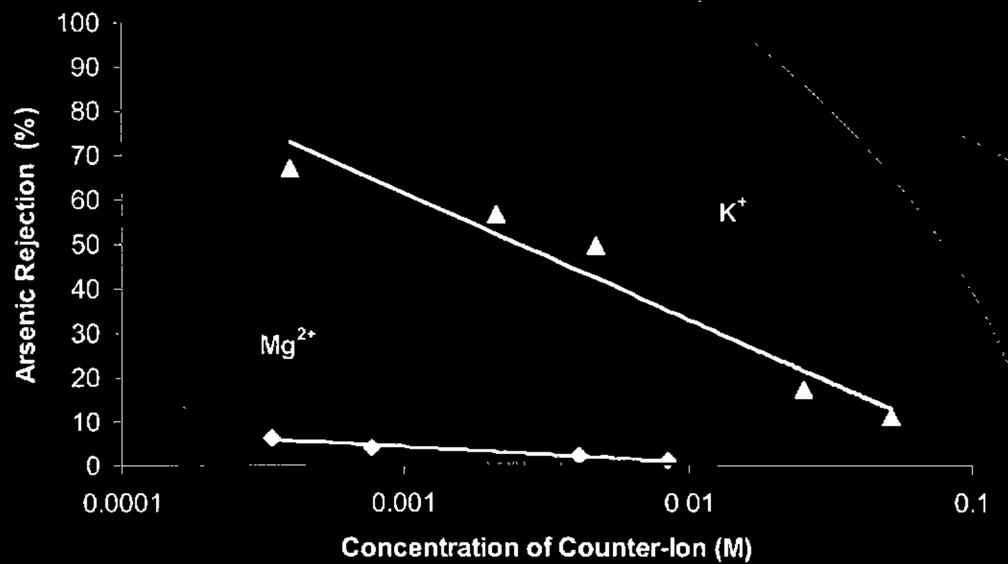

Influence of Membrane Charge on As(V) Rejection
Theoretical Influence of
Membrane Charge (ζ) on Rejection
$HAsO_4^{2-}$
$H_2AsO_4^-$
ζ = 15
ζ = 10
ζ = 0.5
Rejection
1
0.8
0.6
0.4
0.2
0
0.01
1
100
$J_v$norm x 10^{10} (m^2/s)


Influence of Membrane Permeability
As(V) Spike ■ As(III) Spike
As(III) or As(V) Removal (%)
100
80
60
40
20
0
RO4
RO2
RO3
RO1
NF1
NF3
NF2
UF1
0
0.1
0.2
0.3
0.4
Specific Flux (GFD/PSI)


Influence of Source Water Quality - Presence of Co-Ions
MQ, As = 50 μg/l; Flux = 40 GFD; 2.5% Recovery; pH = 8.3; K+ Common Cation
Arsenic Rejection (%)
100
90
80
70
60
50
40
30
20
10
0
SO4 2-
HPO4 2-
0.0001
0.001
0.01
0.1
Concentration of Co-Ion (M)

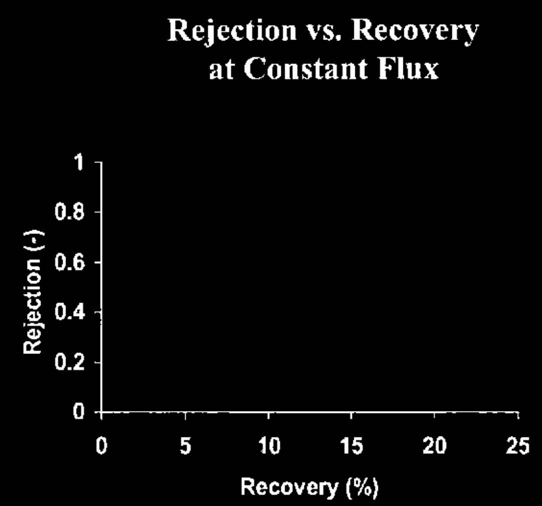
Influence of Source Water Quality - Presence of Counter Ions

MQ, As = 50 μg/l; Flux = 40 GFD; 2.5% Recovery; pH = 8.3; Cl^- Common Anion



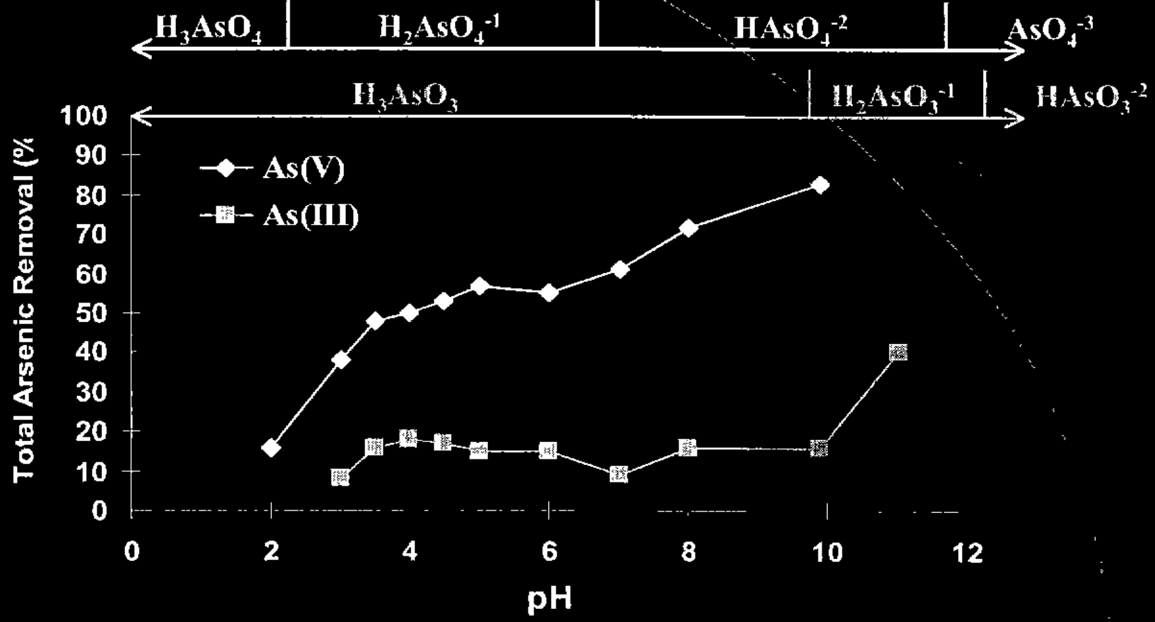
Influence of Hydraulic Operation of Membrane

As = 50 μg/l; I= 0.001M; pH = 8.2; Constant Flux = 40 GFD



Influence of pH on Rejection

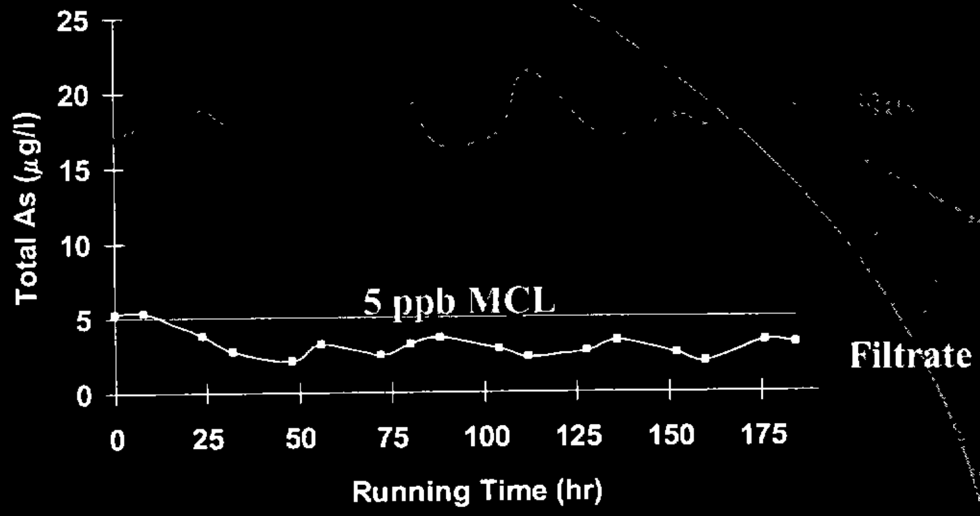
I= 0.01M; As = 50 μg/l; DI; Flux = 15 GFD; 5% Recovery



Summary of Factors Influencing As Rejection by RO/NF/UF Membranes

- Arsenic Speciation
  - As(V) Rejection > As(III) in RO
  - As(V) Rejection >> As(III) in NF and UF
- Membrane Charge/permeability
  - Presence of Membrane Charge vs. Magnitude
  - Low Specific Flux for High As(III) Rejection
- Source Water Composition
  - Influence of Co- and Counter Ions on As(V) Rejection
  - Indirect Influence of NOM?
- Hydraulic Operation of Membrane
  - Possibility of Concentration Polarization
- Treatment pH
  - Treat as $HAsO_4^{2-}$

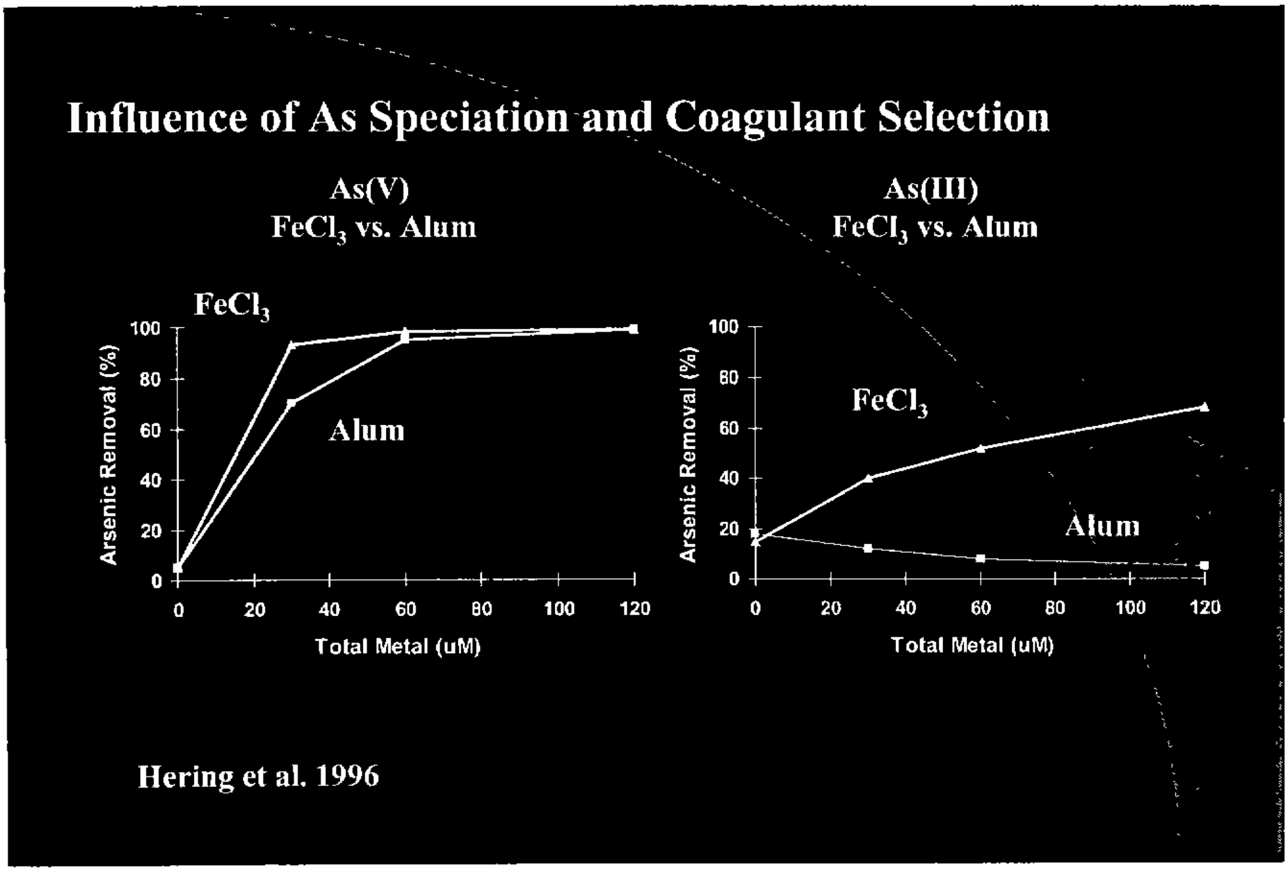
Coagulation-Microfiltration (C-MF): Arsenic Removal for 5 ug/L Pilot Test

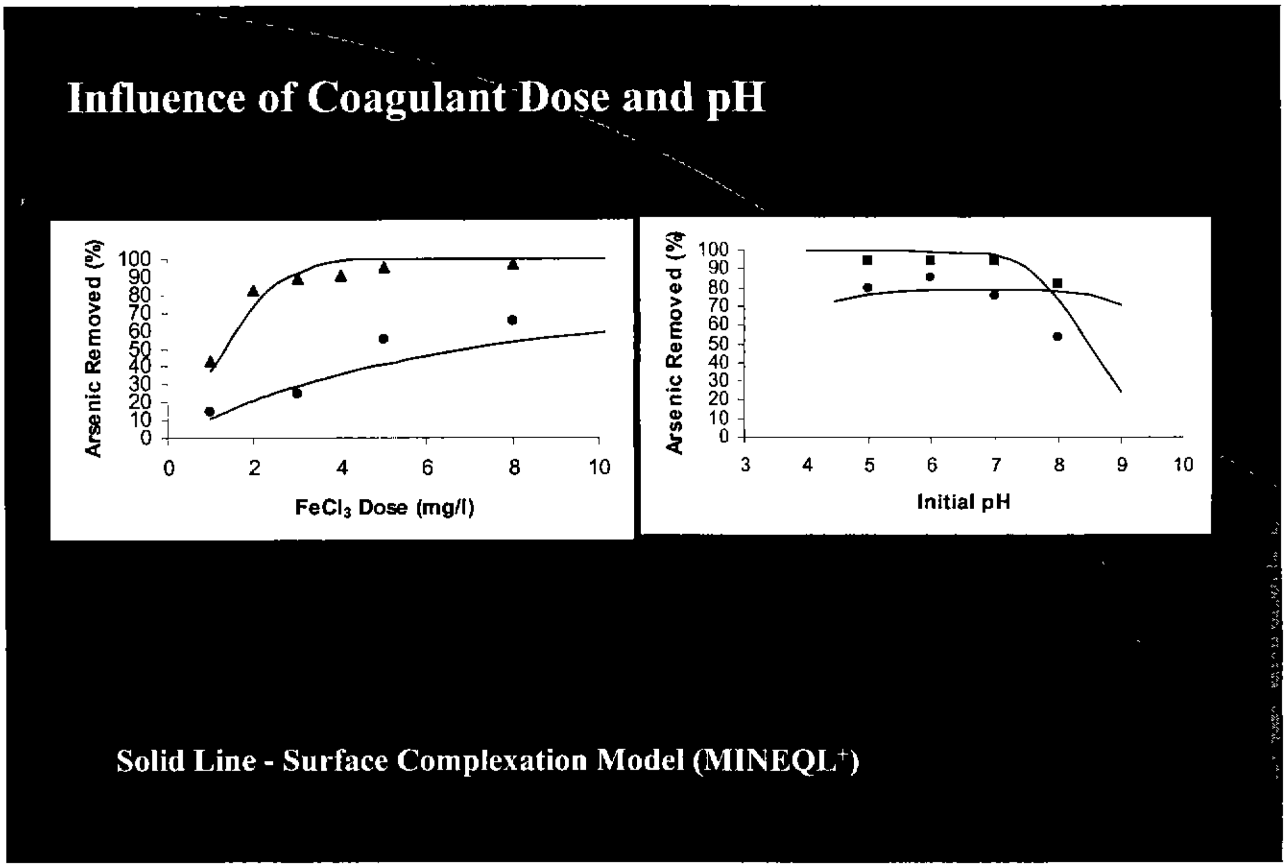


$FeCl_3$ Dose = 6.99 mg/l, Flux = 68 GFD (2 GPM) or 101 GFD (2.97 GPM), Recovery = 92%, As Removal 83%

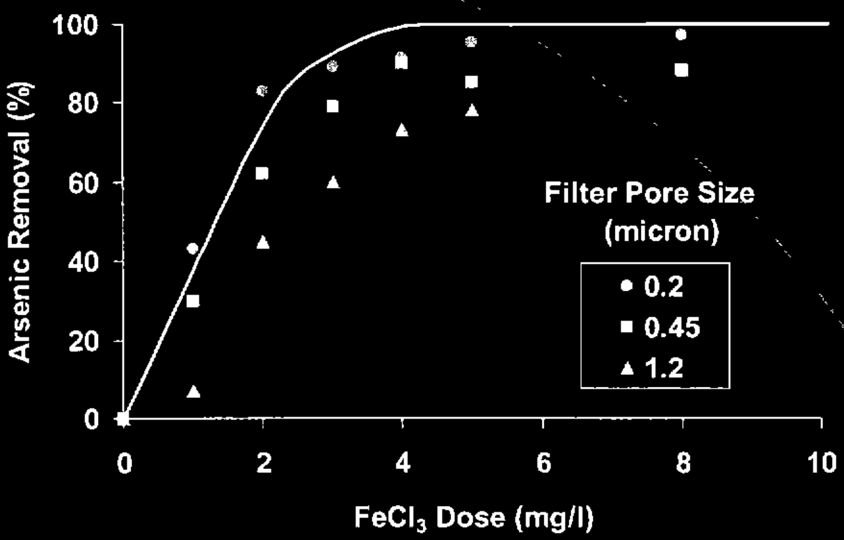
Factors Influencing As Rejection by MF Membranes

- Arsenic Speciation/Coagulant Selection
- Coagulation pH
- Coagulation Kinetics/Floc Size


Influence of As Speciation and Coagulant Selection
As(V)
FeCl3 vs. Alum
As(III)
FeCl3 vs. Alum
FeCl3
Alum
FeCl3
Alum
Arsenic Removal (%)
Total Metal (uM)
Arsenic Removal (%)
Total Metal (uM)
Hering et al. 1996


Influence of Coagulant Dose and pH
Arsenic Removed (%)
FeCl3 Dose (mg/l)
Arsenic Removed (%)
Initial pH
Solid Line - Surface Complexation Model (MINEQL+)

Coagulation/MF Performance - Floc Size



Solid Line - Surface Complexation Model (MINEQL+)

Summary of Factors Influencing As Rejection

Coagulation/Microfiltration

- Arsenic Speciation/Coagulant Selection
  - At pH < 7, Alum and Ferric Coagulation Equally Effective on Molar Basis, Ferric More Efficient on Weight Basis
  - Ferric As(III) Removal < As (V)
  - Alum As(III) Removal << As(V)

- Coagulation pH
  - < pH 7.5 for As(V) with Ferric

- Coagulation Kinetics/Floc Size
  - Sorption Faster than Aggregation
  - Floc Size Optimization for Fouling Control vs. As Removal

Part 2
Perchlorate Rejection: Effect of Zeta Potential of Negatively Charged Nanofiltration Membranes

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Outline

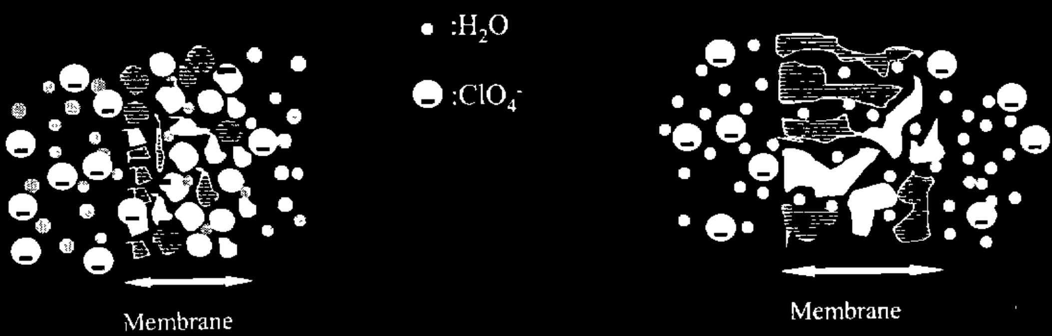
- Objectives
- Hypotheses
- Membrane Unit
- Membrane Characterizations
- Results
  - Perchlorate rejection
  - Zeta potential (ZP)
  - Effect of ZP on ClO_4^- and arsenite (As (III)) rejection
- Summary

Hypotheses

Factors promoting perchlorate rejection

- Membrane: lower MWCO (steric rejection) and higher negative charge (electrostatic rejection; surface charge based on functional groups)
- Water quality: higher pH and lower conductivity (ionic strength), ionic composition based on mono- and divalent co- and counter- ion concentration

Dominant mechanisms for porous and negatively charged NF membranes



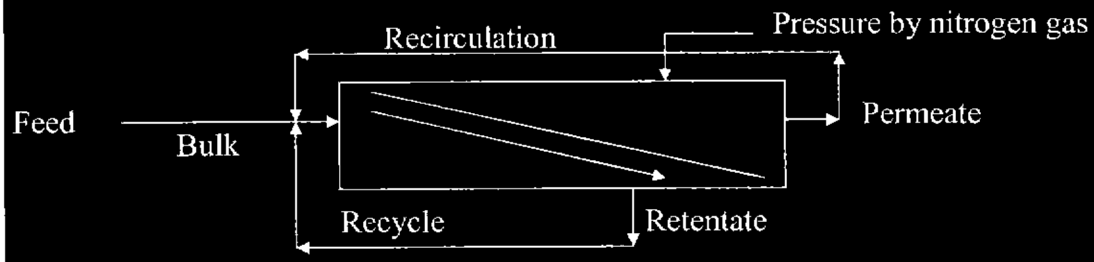
Tight Nanofiltration (negatively charged):

steric/size exclusion and electrostatic exclusion

Loose Nanofiltration (negatively charged):

electrostatic exclusion

- Bench-scale cross-flow flat-sheet unit



* Membrane effective area: 154.8 cm^2

Membrane characterizations

Physical-chemical properties

Membrane	Material	MMCO/ MWCO	ZP at pH 8 and 30 mS/m with conductivity (KCl)
ESNA (NF)	Composite aromatic polyamide	200	-41.2 mV
MX07 (NF)	Composite aromatic polyamide	400	-39.7 mV

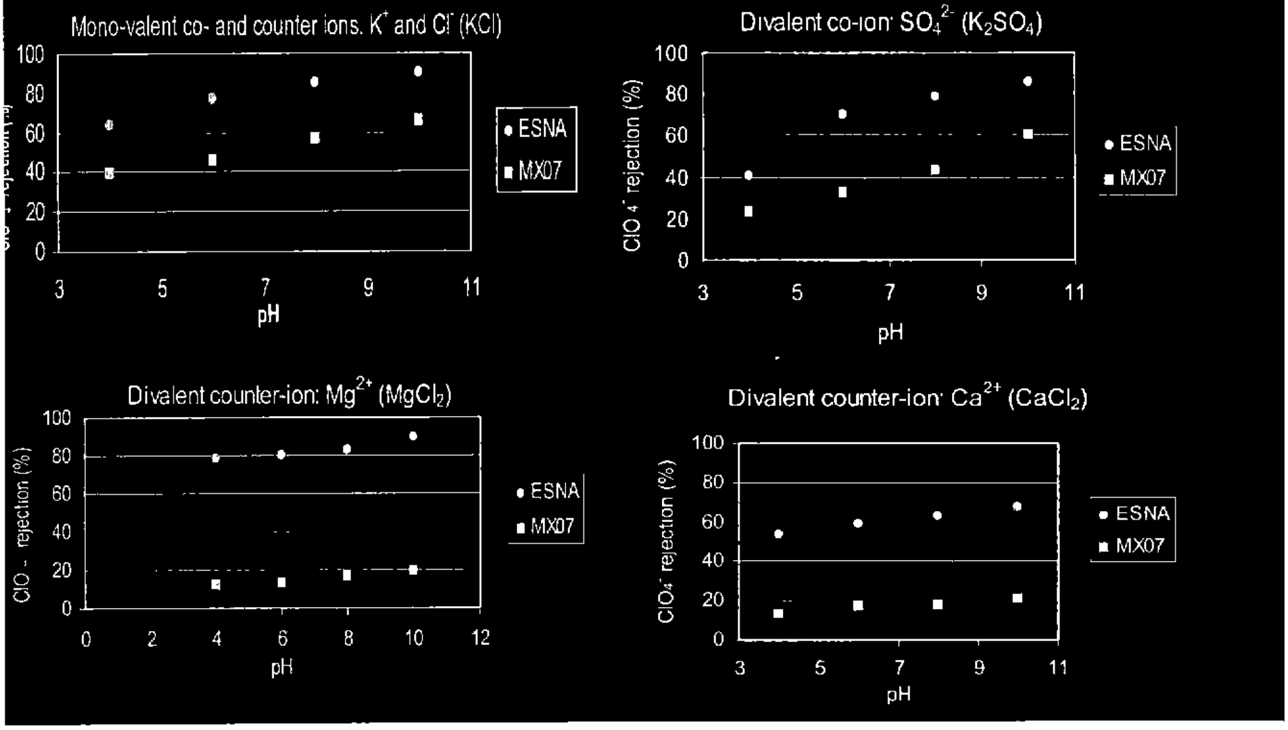
Pure water permeability

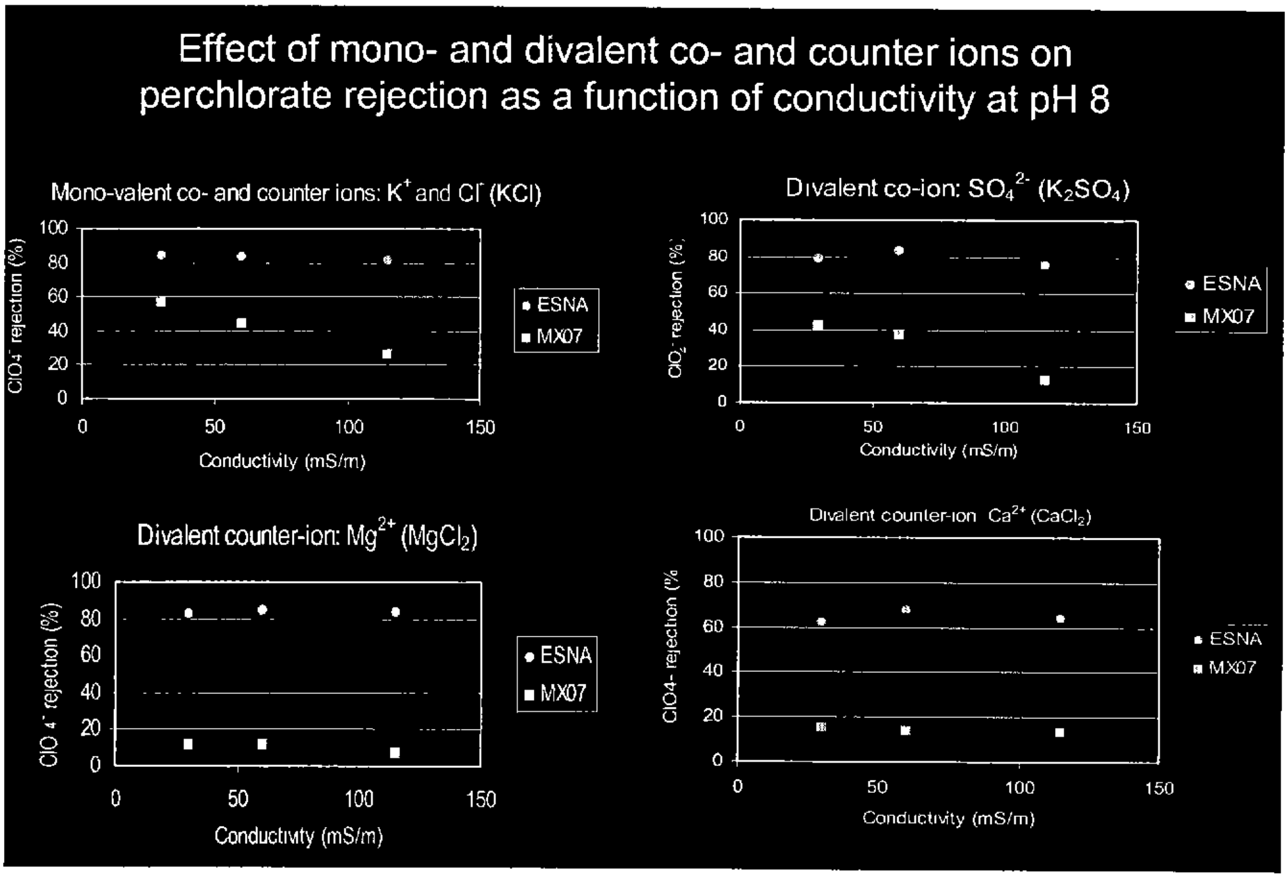
Membrane	Manufacturer	L/day-m^2-kPa
ESNA	Hydranautics	1.05
MX07	Osmonics	0.47

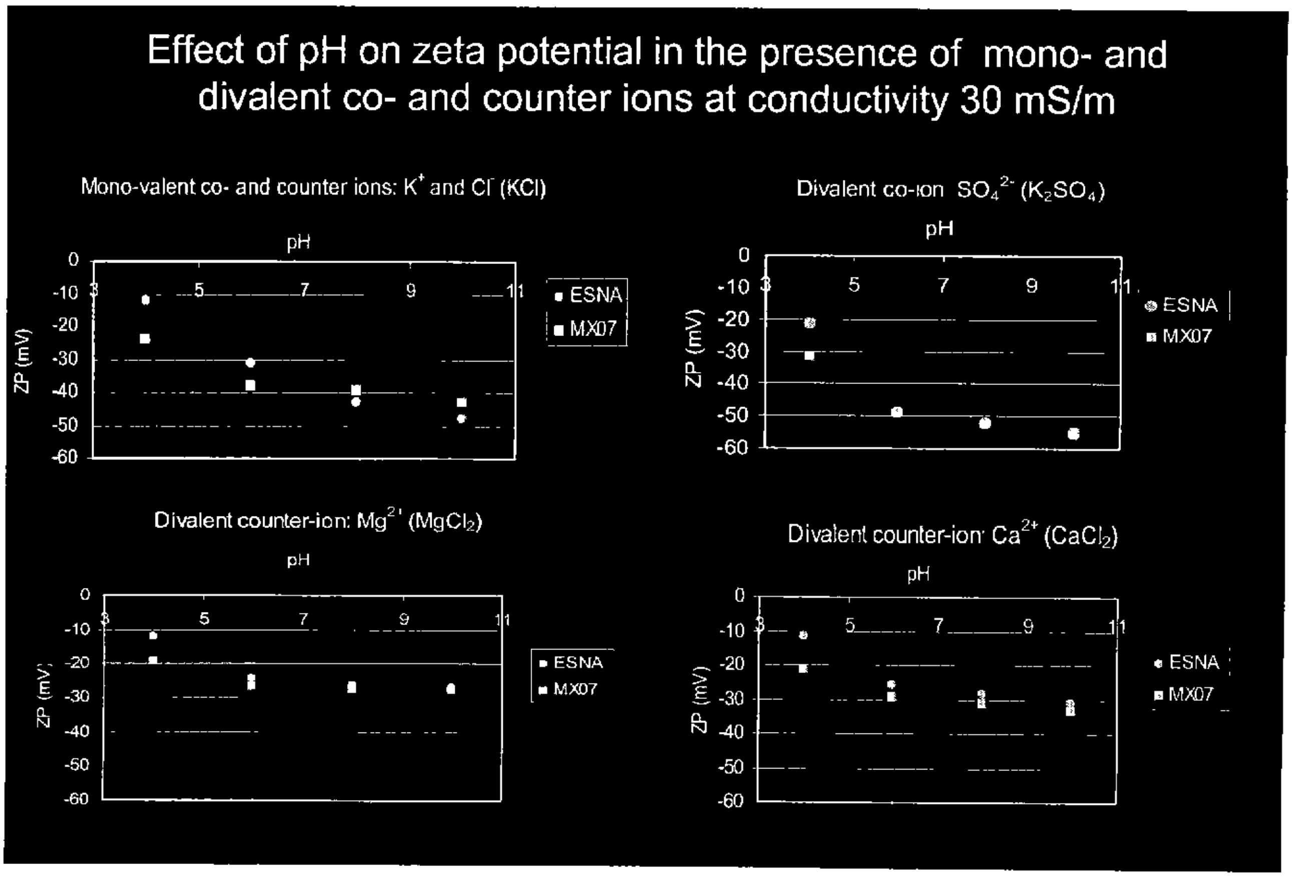
Results

- ClO_4^- rejection with cross-flow flat-sheet test unit as a function of pH and conductivity
- Zeta potential based on measured streaming potential as a function of pH and conductivity
- Effect of ZP on ClO_4^- and arsenite (As (III)) rejection

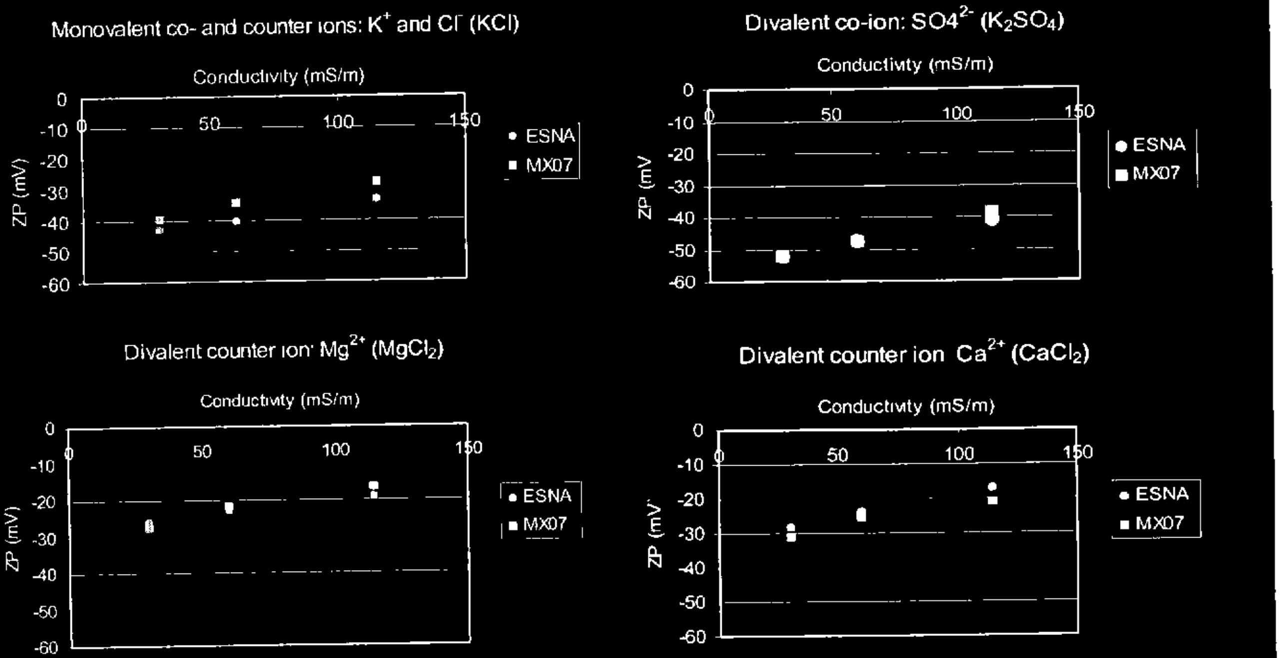
Effect of mono- and divalent co- and counter ions on perchlorate rejection as a function of pH at conductivity 30 mS/m




Effect of mono- and divalent co- and counter ions on perchlorate rejection as a function of conductivity at pH 8
Mono-valent co- and counter ions: K+ and Cl- (KCl)
Divalent co-ion: SO4 2- (K2SO4)
Divalent counter-ion: Mg2+ (MgCl2)
Divalent counter-ion Ca2+ (CaCl2)
ClO4- rejection (%)
Conductivity (mS/m)
ESNA
MX07

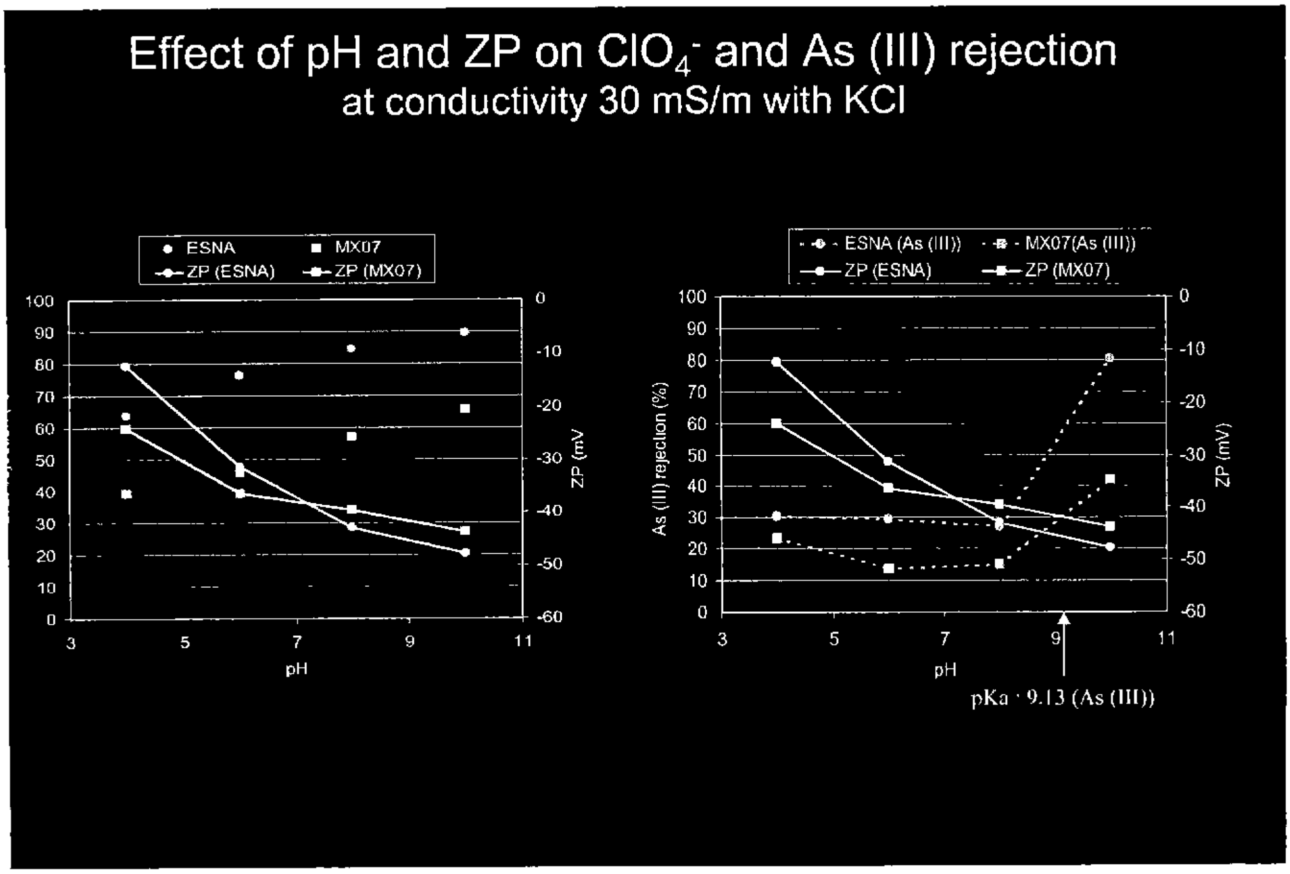

Effect of pH on zeta potential in the presence of mono- and divalent co- and counter ions at conductivity 30 mS/m
Mono-valent co- and counter ions: K+ and Cl- (KCl)
Divalent co-ion SO4 2- (K2SO4)
Divalent counter-ion: Mg2+ (MgCl2)
Divalent counter-ion Ca2+ (CaCl2)
pH
ZP (mV)
ESNA
MX07

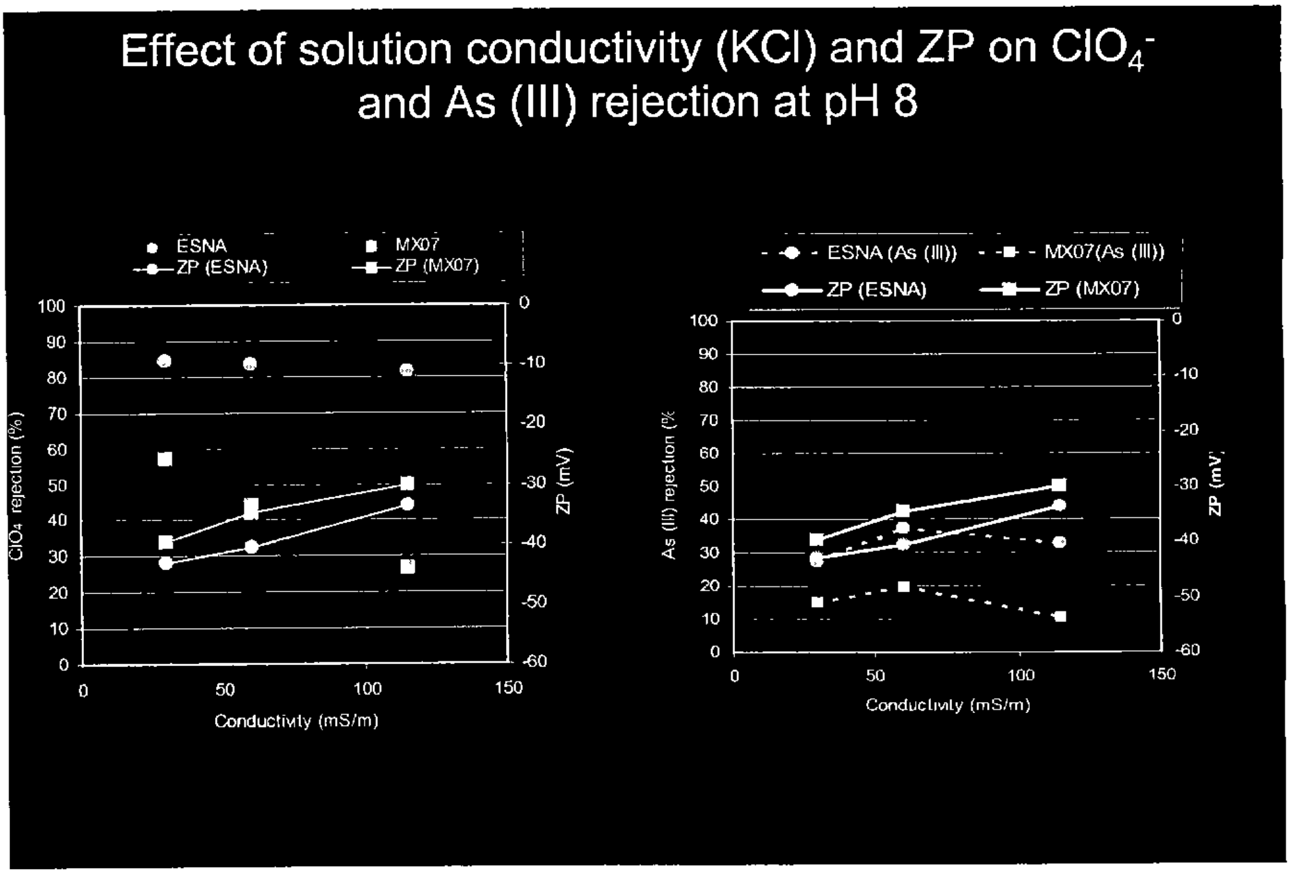
Effect of mono- and divalent co- and counter ions on zeta potential at pH 8



Comparison of estimated ionic radius of anions and As (III) based on mobility (Adkins (1990), Adamson (1979), Brandhuber (1999))

Ionic radius/ hydrated radius:					
	OH^-	Cl^-	As (III)	ClO_4^-	SO_4^{2-}
Molecular mass:	17	35.5	126	99.5	96
Mobility * 10^{13} (mol m^2 J^{-1} s^{-1}):	21.3	8.2	N/A	N/A	4.3


Effect of pH and ZP on ClO4- and As (III) rejection
at conductivity 30 mS/m with KCl
ESNA
MX07
ZP (ESNA)
ZP (MX07)
pH
ZP (mV)
ESNA (As (III))
MX07(As (III))
As (III) rejection (%)
pKa : 9.13 (As (III))


Effect of solution conductivity (KCl) and ZP on ClO4-
and As (III) rejection at pH 8
ESNA
MX07
ZP (ESNA)
ZP (MX07)
ClO4 rejection (%)
ZP (mV)
Conductivity (mS/m)
ESNA (As (III))
MX07(As (III))
As (III) rejection (%

Summary

- Perchlorate rejection
  - ClO_4^- significantly rejected by a negatively charged and relatively small pore NF (ESNA) membrane regardless of presence of co-/counter-ions.
  - ClO_4^- rejection greatly reduced by the presence of co-/counter-ions for a negatively charged and relatively large pore NF (MX07) membrane.
- Zeta potential
  - Zeta potential of both ESNA and MX07 membranes significantly increased with increasing pH in presence of co- and counter ions
  - Zeta potential of both ESNA and MX07 membranes slightly decreased with increasing co- and counter ions
- Effect of ZP on ClO_4^- and As (III) rejection
  - ClO_4^- rejection significantly influenced by size (steric) exclusion for ESNA membrane regardless of membrane charge
  - ClO_4^- rejection significantly influenced by electrostatic exclusion for MXO7 membrane
  - As (III) used as a non-charged model solute to verify electrostatic interaction between ClO_4^- and negatively charged membrane

Part 3

Interactions Between Natural Organic Matter (NOM) and Membranes: Rejection and Fouling

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Outline

- Hypotheses
- Hydrodynamic Conditions: f/k Ratio
- Membrane Unit
- Membrane Properties and NOM Characteristics
- Flux-Decline and Fouling Results
- NOM Rejection Results
- NOM Rejection Equations & Flux-Decline Models
- J_0/k Ratio: Effects on Flux-Decline & NOM Rejection
- Fouled Membrane Characterization

Hypotheses

- Factors Promoting Flux-Decline (& Fouling)
  - NOM: Greater Hydrophobicity, Lower Charge Density
  - Membrane: Greater Hydrophobicity, Lower Negative Charge
  - Water Quality: Lower pH, Higher I, Higher Ca
- Factors Promoting NOM Rejection
  - NOM: Higher MW, Higher Charge Density
  - Membrane: Lower MWCO, Greater Surface Charge
- Rejection (and Fouling) Mechanisms
  - Steric Rejection
  - Electrostatic Exclusion
  - (Adsorption)

Hydrodynamic Conditions: J_0/k Ratio

- k (cm/s)
  - Mass Transfer Coefficient; Back-Diffusional Transport away from the Membrane Surface
- J_o (cm/s)
  - Permeate Flux
- J_0/k Ratio Related to Concentration Polarization
- Implications of f/k Ratio:

Optimum Operating Conditions for Minimizing Flux-Decline and Maximizing NOM Rejection

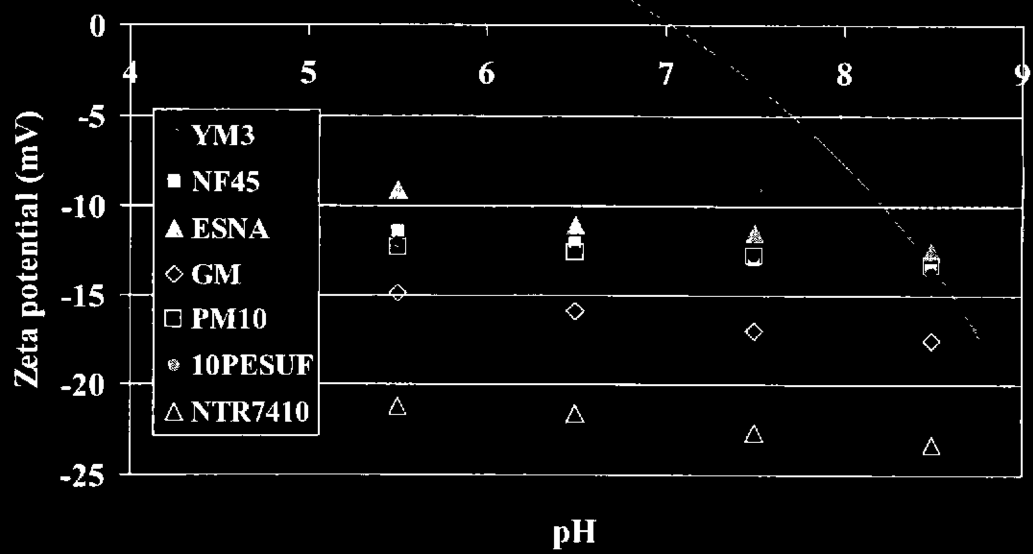
Hypotheses for the J_0/k Ratio

- As the J_0/k Ratio Increases, C.P. Increases,
  - Flux Decline Increases
  - NOM Rejection Decreases
- As the J_0/k Ratio Decreases, C.P. Decreases,
  - Flux Decline Decreases
  - NOM Rejection Increases
- At the Same J_0/k Ratio,
  - Flux Decline and NOM Rejection Trends are Similar for Different Membranes

Membrane Properties:
Type (Polyamide, Polyethersulfone, Cellulose), MWCO, & Contact Angle

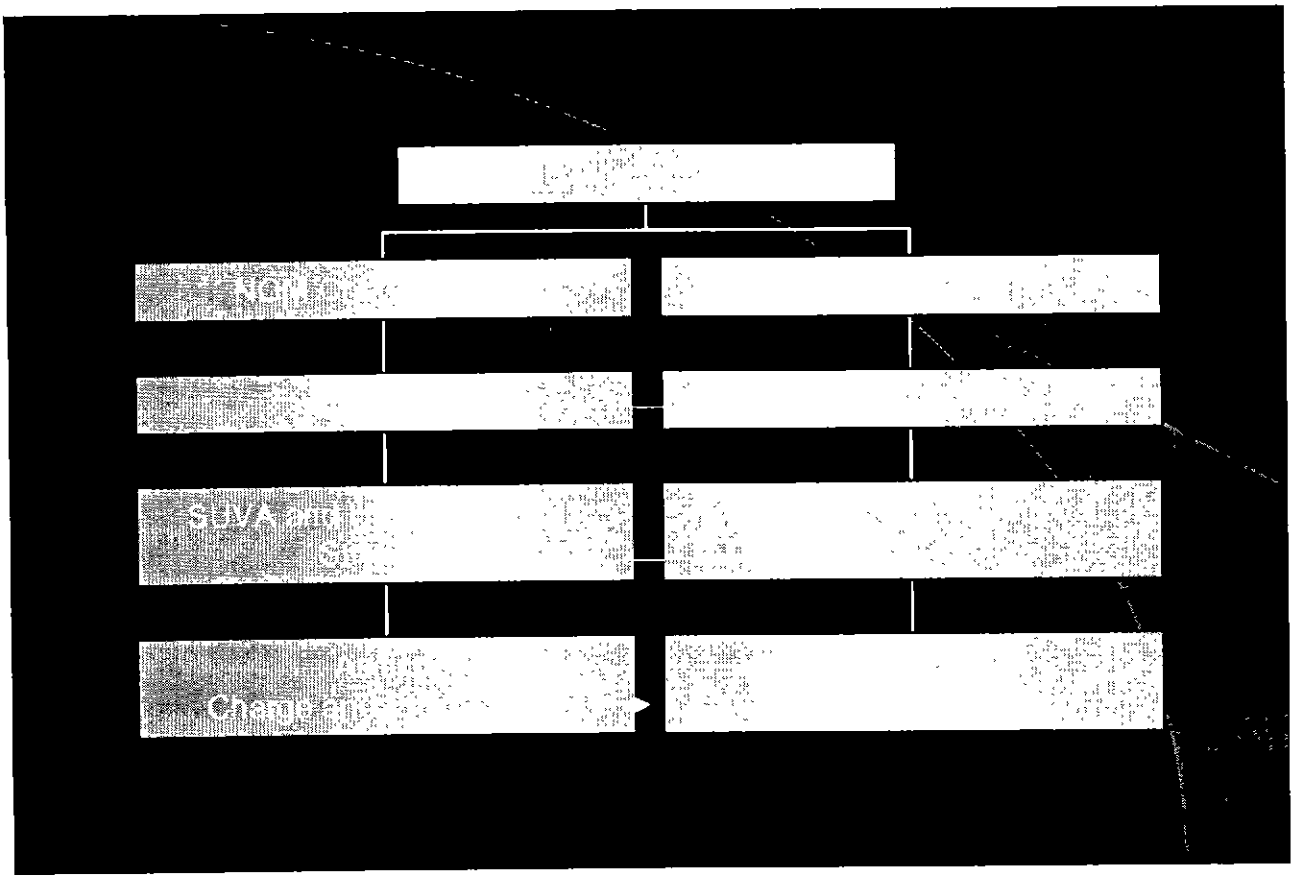
Type	*Code*	*MWCO*	*Contact Angle*
PA	NF45	400	45
PA	ESNA	200	60
PA	GM	8,000	55
PES	NTR7410	20,000	61
PES	PM10	20,000	62
PES	10PESUF	10,000	51
CL	YM3	3,000	13

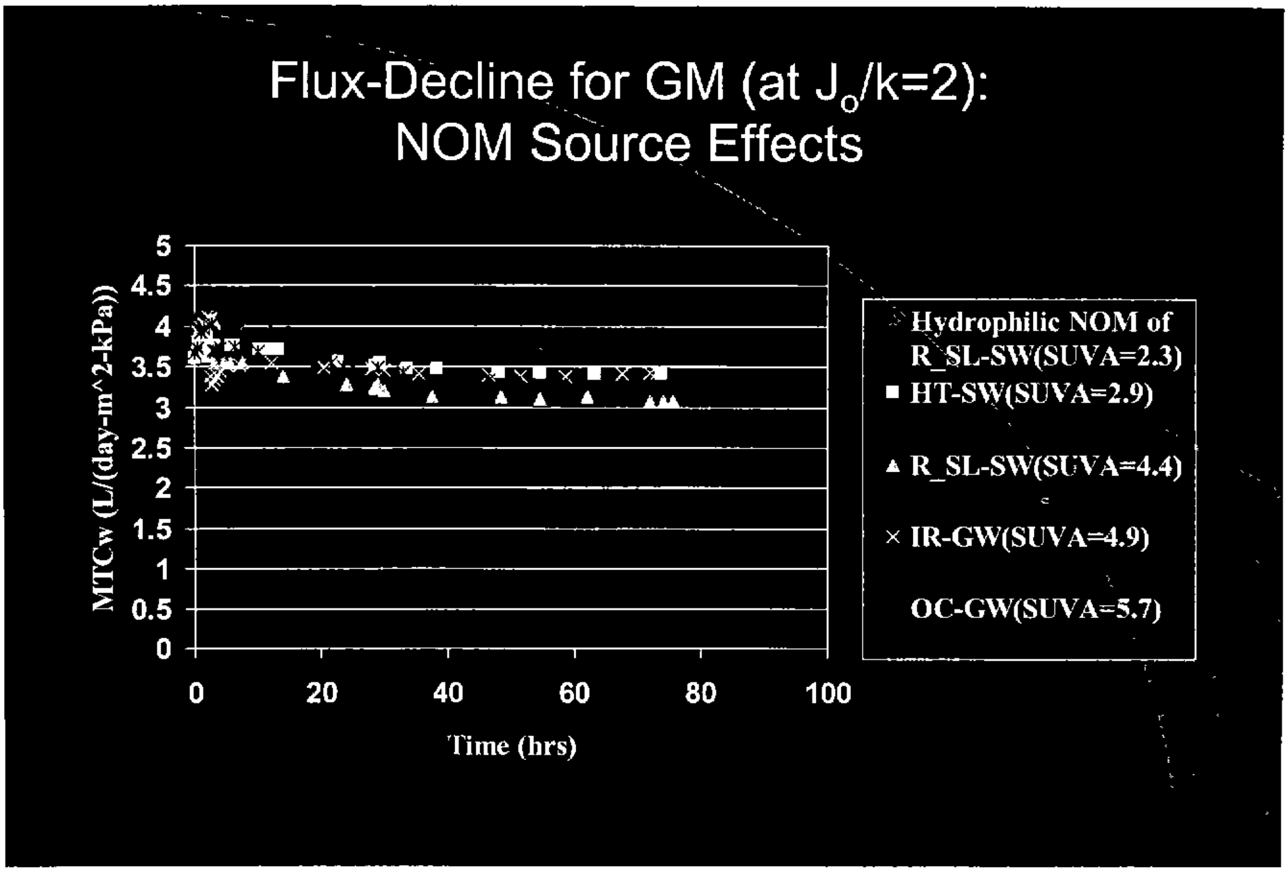
Membrane Properties:
Zeta Potentials

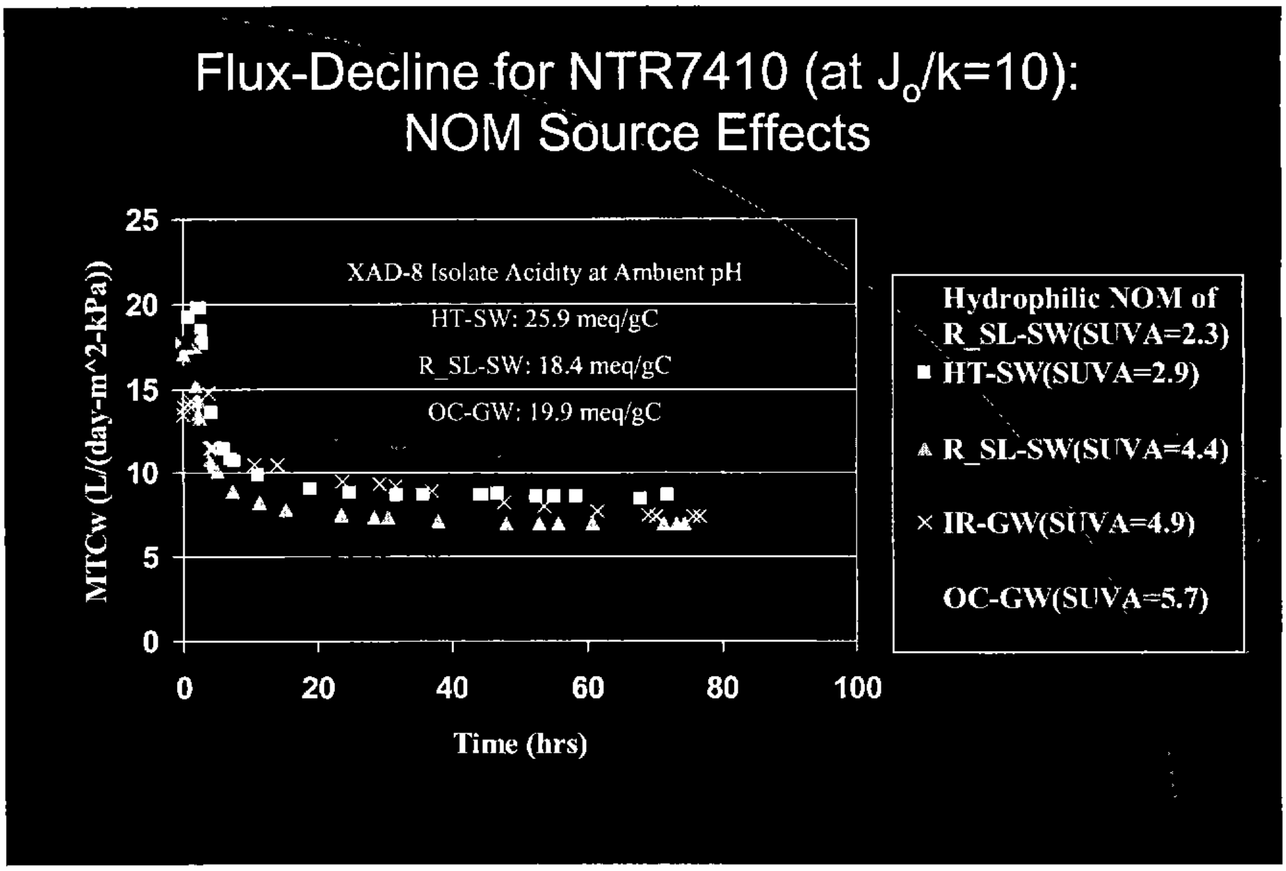


NOM Characteristics:
SUVA and Humic Content, and MW

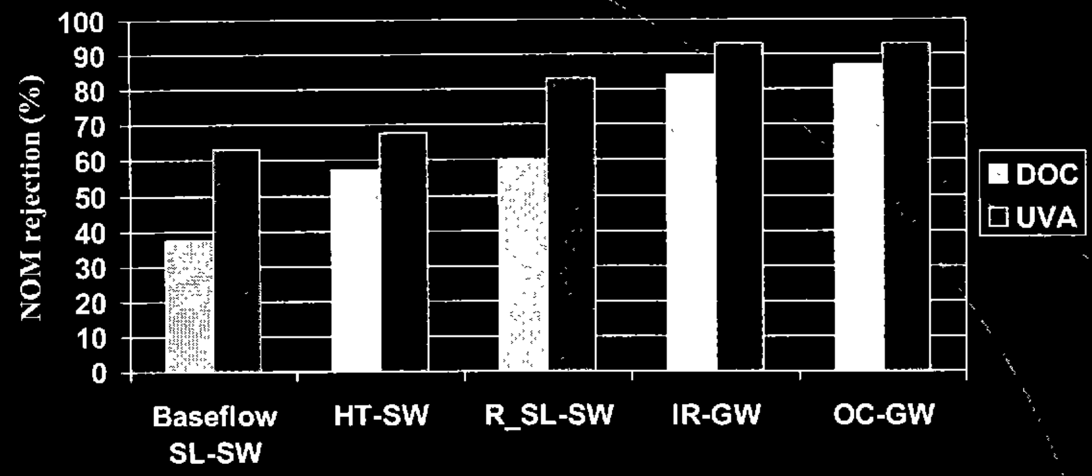
NOM Source	SUVA ($m^{-1}mg^{-1}L$)	Humic Content (%)	Molecular Weight
Baseflow SL-SW	2.4	43	1,200
HT-SW	2.9	59	1,100
Twitchell	3.7	61	
Runoff SL-SW	4.4	57	1,650
IR-GW	4.9	80	1,540
OC-GW	5.7	90	1,550




Flux-Decline for GM (at J_o/k=2): NOM Source Effects
MTCw (L/(day-m^2-kPa))
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
20
40
60
80
100
Time (hrs)
Hydrophilic NOM of R_SL-SW(SUVA=2.3)
HT-SW(SUVA=2.9)
R_SL-SW(SUVA=4.4)
IR-GW(SUVA=4.9)
OC-GW(SUVA=5.7)

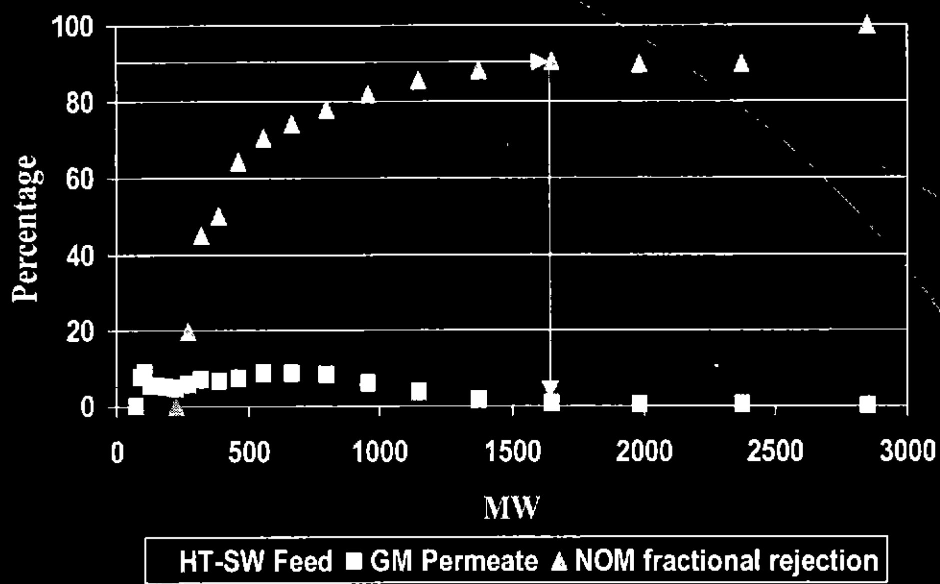

Flux-Decline for NTR7410 (at J_o/k=10): NOM Source Effects
MTCw (L/(day-m^2-kPa))
25
20
15
10
5
0
0
20
40
60
80
100
Time (hrs)
XAD-8 Isolate Acidity at Ambient pH
HT-SW: 25.9 meq/gC
R_SL-SW: 18.4 meq/gC
OC-GW: 19.9 meq/gC
Hydrophilic NOM of R_SL-SW(SUVA=2.3)
HT-SW(SUVA=2.9)
R_SL-SW(SUVA=4.4)
IR-GW(SUVA=4.9)
OC-GW(SUVA=5.7)

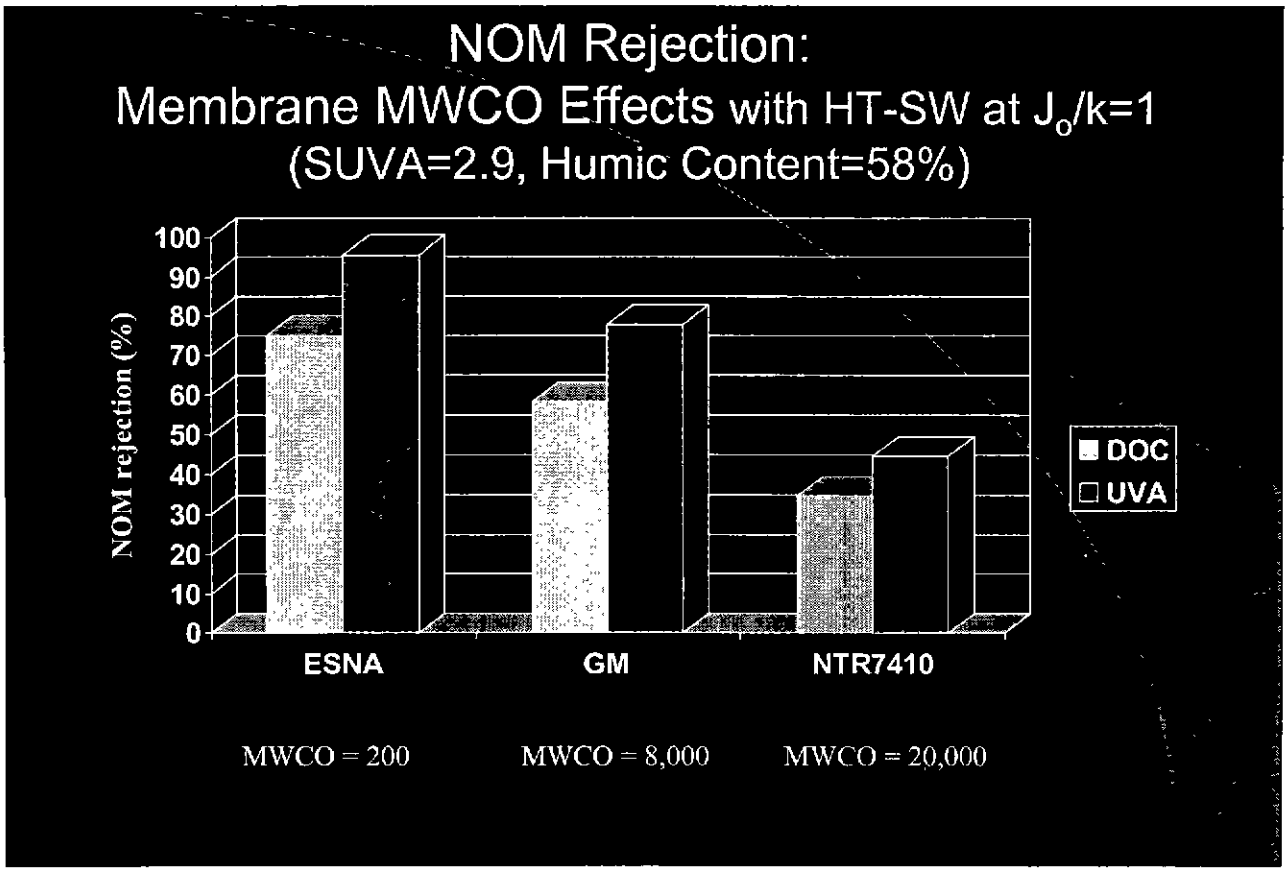
NOM Rejection for GM Membrane at $J_0/k=2$: MW Size and Humic Content Effects

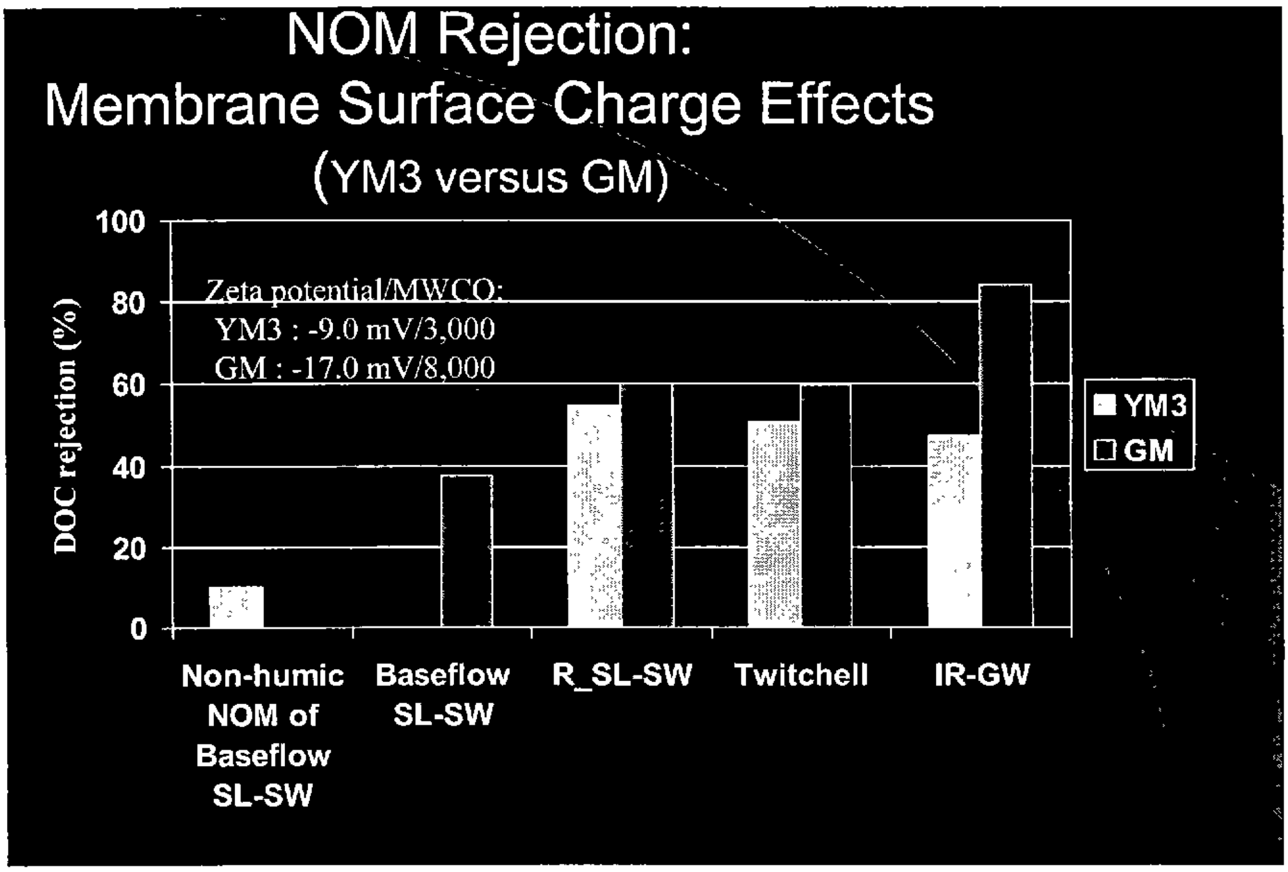


Mw =	1200	1097	1650	1538	1546
SUVA =	2.4	2.9	4.4	4.9	5.7
Humic Content =	43	58	57	80	90

NOM Rejection: Effective MWCO Determination




NOM Rejection:
Membrane MWCO Effects with HT-SW at J_o/k=1
(SUVA=2.9, Humic Content=58%)
NOM rejection (%)
100
90
80
70
60
50
40
30
20
10
0
ESNA
GM
NTR7410
DOC
UVA
MWCO = 200
MWCO = 8,000
MWCO = 20,000


NOM Rejection:
Membrane Surface Charge Effects
(YM3 versus GM)
DOC rejection (%)
100
80
60
40
20
0
Zeta potential/MWCO:
YM3 : -9.0 mV/3,000
GM : -17.0 mV/8,000
YM3
GM
Non-humic NOM of Baseflow SL-SW
Baseflow SL-SW
R_SL-SW
Twitchell
IR-GW

NOM Rejection: Predictive Equations

- $R_{DOC} = 0.251 + 0.134(SUVA) - 0.073(J_0/k)$ for GM

  for NOM with $2.4 < SUVA < 5.7$, $1 < J_0/k < 2$

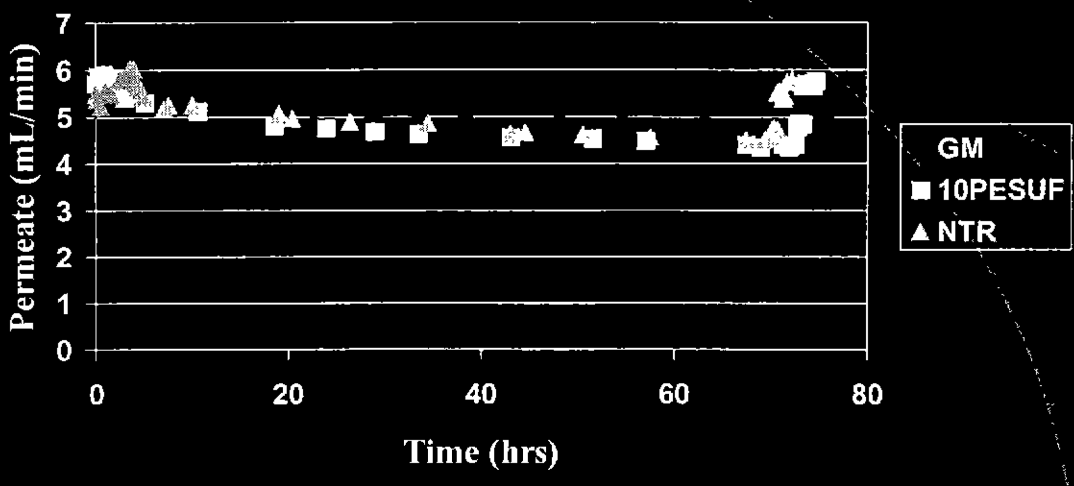
  $R^2 = 87\ \%$

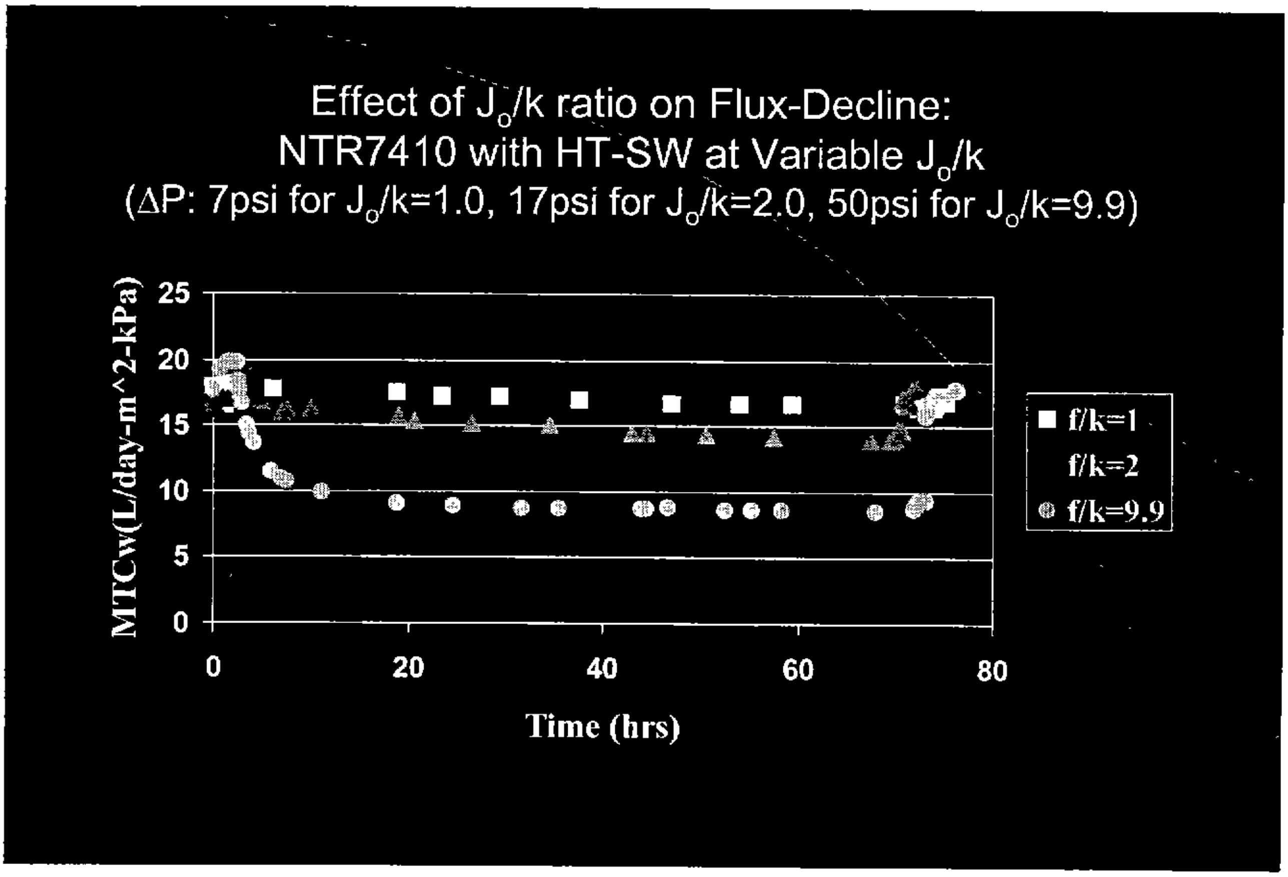
- $R_{DOC} = -0.369 + 0.204(SUVA) - 0.065(J_0/k)$ for NTR7410

  for NOM with $2.4 < SUVA < 5.7$, $1 < J_0/k < 10$

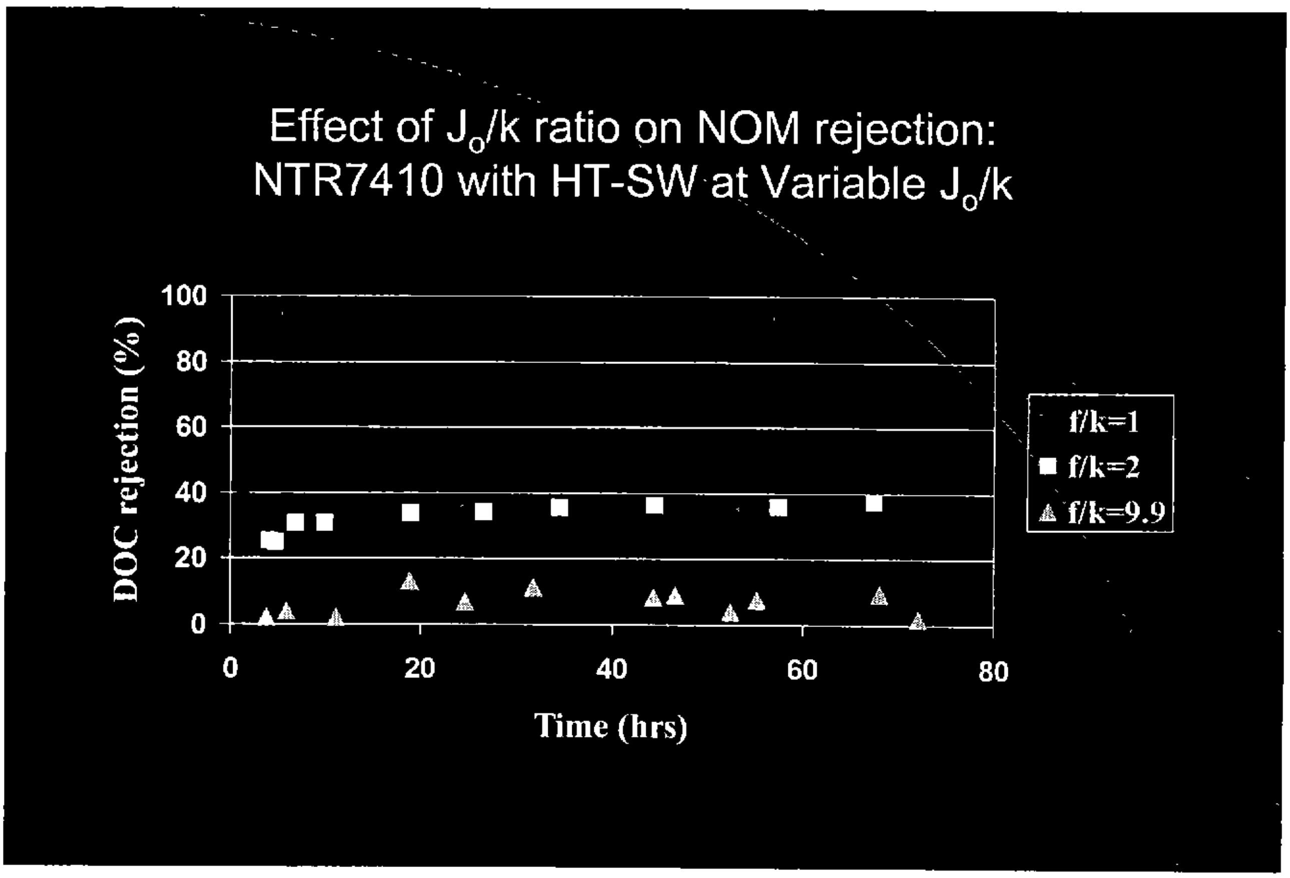
  $R^2 = 86\ \%$

Effects of J_0/k Ratio on Flux Decline: Comparison of GM, 10PESUF, and NTR7410 with HT-SW at Same J_0/k=2 (ΔP= 50psi (GM), 10psi (10PESUF), 17psi (NTR7410))



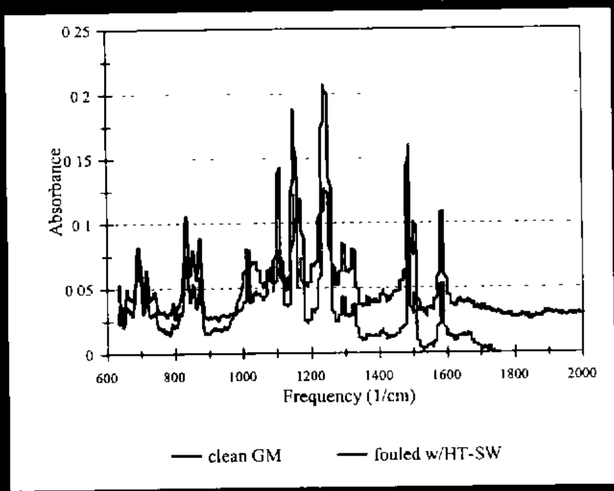


Effect of J_o/k ratio on Flux-Decline:
NTR7410 with HT-SW at Variable J_o/k
(ΔP: 7psi for J_o/k=1.0, 17psi for J_o/k=2.0, 50psi for J_o/k=9.9)
MTCw(L/day-m^2-kPa)
25
20
15
10
5
0
0
20
40
60
80
Time (hrs)
f/k=1
f/k=2
f/k=9.9



Effect of J_o/k ratio on NOM rejection:
NTR7410 with HT-SW at Variable J_o/k
DOC rejection (%)
100
80
60
40
20
0
0
20
40
60
80
Time (hrs)
f/k=1
f/k=2
f/k=9.9

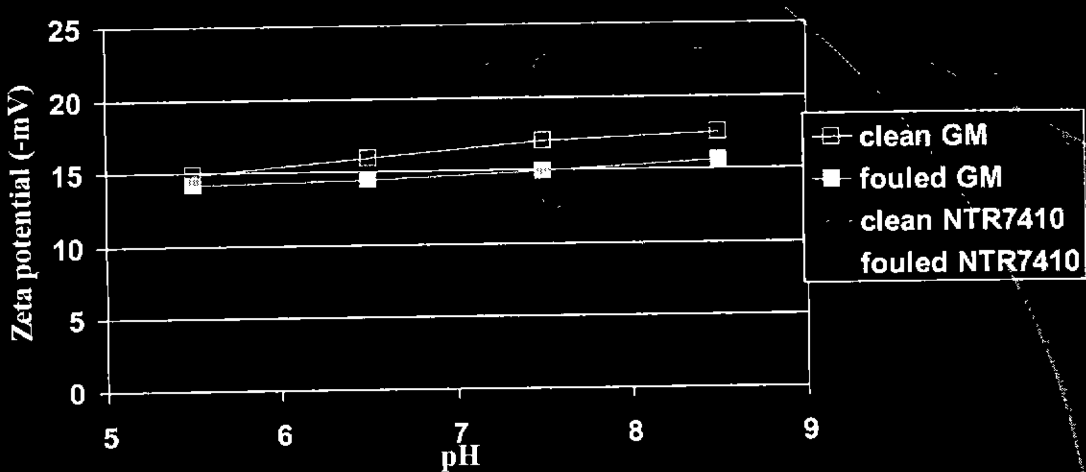
Fouled Membrane Characterization:
IR Spectra for NOM-Fouled Membrane



Leenheer/Bruchet:

Cell Fragments/Polysaccharides

Fouled Membrane Characterization:
Zeta Potentials for Clean and NOM-Fouled Membranes



Summary

- Flux-Decline :
  - NOM Characteristics and Membrane Properties have Little Effect at equal J_0/k ratio
  - Hydrophilic NOM was a Major Membrane Foulant
- NOM Rejection :
  - Negative Charge-Density of Hydrophobic Acids Promoted NOM Rejection by Electrostatic Repulsion
  - Membrane Surface Charge Influenced NOM Rejection
  - NF Rejected More NOM than UF for typical NOM-Source Waters; More Similar Rejections by NF and UF Observed for High Humic NOM-Source Waters

Part 4

Membrane Filtration of Wastewater Effluents for Reuse : Effluent Organic Matter (EfOM) Rejection and Fouling

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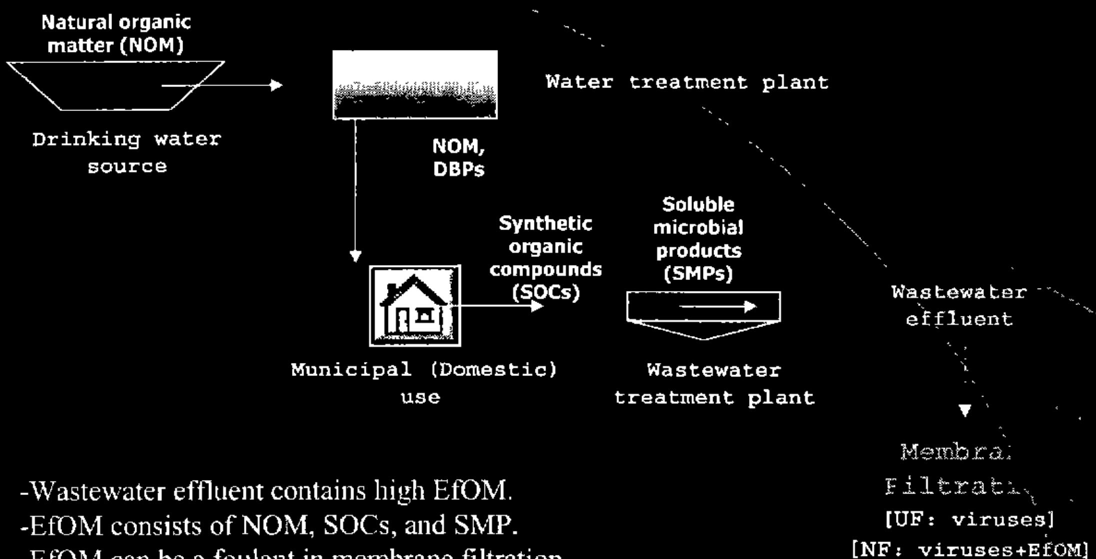
Outline

Introduction
Objectives
Experimental methods
Results
Summary

Effluent organic matter (EfOM)



-Wastewater effluent contains high EfOM.
-EfOM consists of NOM, SOCs, and SMP.
-EfOM can be a foulant in membrane filtration.
-EfOM-fouling leads to a decrease in flux and productivity.
-EfOM as a DBP precursor.

Objectives:

-To investigate the effects of EfOM-fouling on permeate flux and EfOM-rejection by nanofiltration (NF) and ultrafiltration (UF) membranes

-To study the characteristics of EfOM affecting EfOM-fouling and EfOM-rejection

Experimental methods

Source waters:

-Boulder (Colorado, USA) secondary effluent → BO-SE
-Mesa (Arizona, USA) secondary effluent → ME-SE
-Mesa (Arizona, USA) tertiary effluent → ME-TE

Characteristics of source waters:

Source water	pH	Conductivity μS/cm	DOC $mg.L^{-1}$	UVA cm^{-1}	SUVA $L.mg^{-1}.m^{-1}$	[illegible] fract. % DOC
BO-SE	7.04	697	7.1	0.135	1.9	41
ME-SE*	7.58	1812	5.6	0.108	1.9	38
ME-TE*	6.61	1565	7.0	0.123	1.7	36

* different sampling time

Membranes

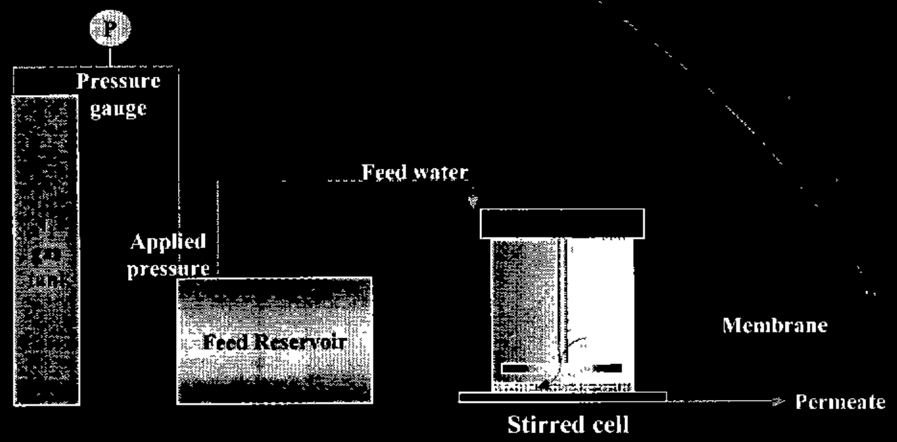
- Nanofiltration (NF) membrane
  - o ESNA membrane
- Ultrafiltration (UF) membranes
  - o GM membrane
  - o PM10 membrane
  - o NTR7410 membrane

Characteristics of Membranes

Membrane	Type	Material	MWCO	Contact angle(°)	Zeta potential (mV) at pH 7	PWP L.day^{-1}.m^{2}.kPa
ESNA	NF	PA	200	60.3	-11.5	1.35
GM	UF	PA	8,000	45.5	-17.0	2.96
PM10	UF	Sulfonated PES	10,000	55.1	-12.8	25.32
NTR7410	UF	PES	20,000	49.5	-22.6	4.86

PA = Polyamide
PES = Polyethersulfone

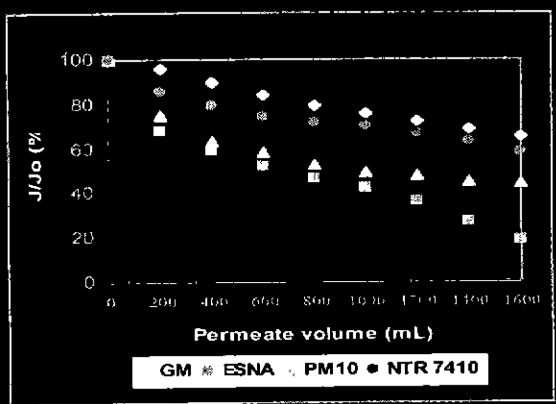
Dead-end stirred cell membrane filtration

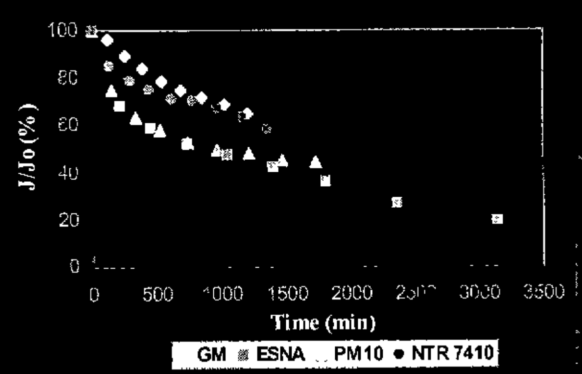


Results:

1. Flux-decline test

Flux decline tests with BO-SE and different membranes



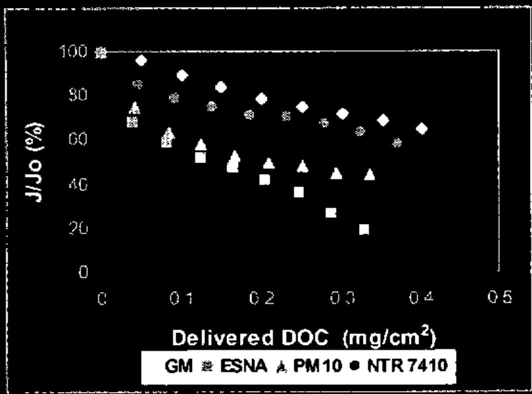


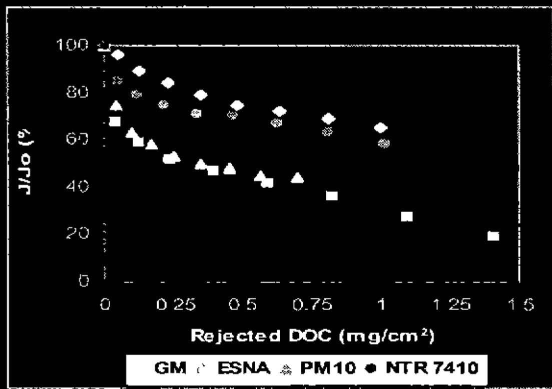
Transmembrane pressure

- ESNA : 73 psi - GM : 42 psi

- PM10 : 5 psi - NTR7410 : 25 psi

Flux decline test with BO-SE based on delivered and rejected DOC *





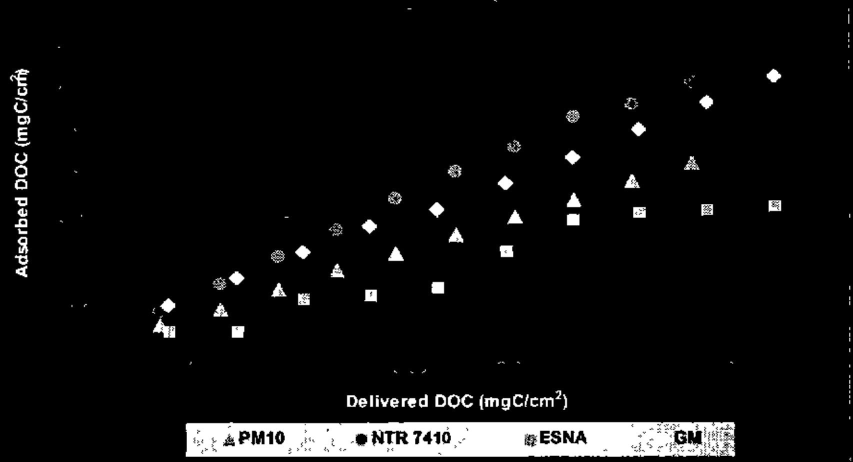
* Delivered DOC = summation of feed DOC mass per unit area of membrane
Rejected DOC = summation of rejected DOC mass per unit area of membrane

Characteristics of membranes vs. flux decline trends

Membrane	MWCO	Contact angle (°) (Hydrophobicity)	Zeta potential (mV) at pH 7	% flux decline for 1.6 L permeate	Volume (mL) For 20% flux decline
ESNA	200	60.3	-11.5	80	125
GM	8,000	45.5	-17.0	35	760
PM10	10,000	55.1	-12.8	58	160
NTR7410	20,000	49.5	-22.6	42	367

Fouling ✪ Hydrophobicity, 1/Surface charge, and 1/MWCO

2. EfOM dynamic adsorption test



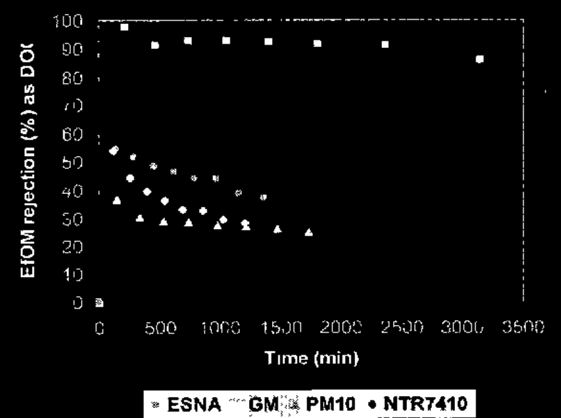
Adsorbed DOC : NTR7410 > GM > PM10 > ESNA

Flux decline : ESNA > PM10 > NTR7410 > GM

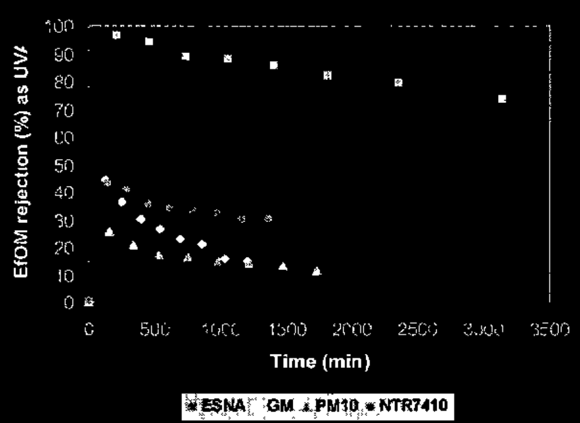
Pore size : NTR7410 > PM10 > GM > ESNA

3. EfOM rejection

Based on DOC

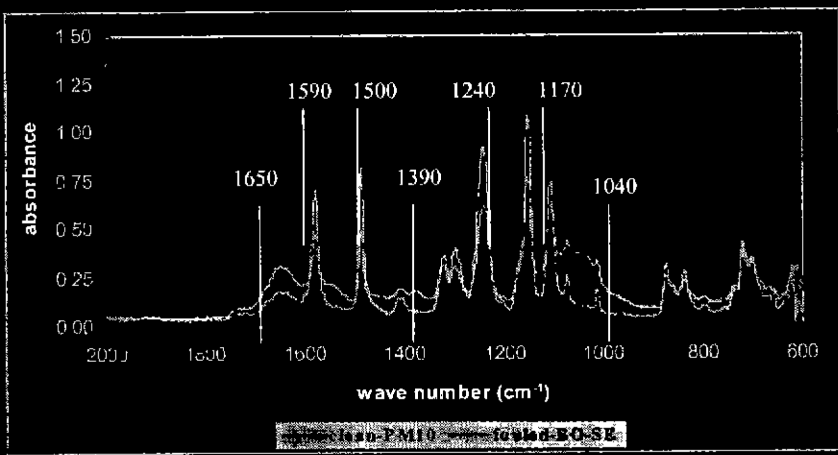


Based on UVA



4. Fouling analysis using FTIR:

FTIR spectra of clean and fouled PM10



Foulants : polysaccharides (1170-950), aromatic acids (1240), aromatic C=C (1620-1600), OH deformation and C-O stretching of phenolic OH (1400-1390), COO-, N-H, and C=N (1590-1517)

Conclusions

1. Flux decline by EfOM , EfOM-rejection, and EfOM-fouling mechanisms are dependent on MWCO, surface charge, and hydrophobicity of membrane; likewise, they are dependent on the characteristics of the source water EfOM as well.

2. Besides the hydrophobic fraction, the hydrophilic fraction of EfOM, e.g. polysaccharides, may act as a major foulant in membrane filtration of wastewater effluent.