Economic and Performance Assessment of Electropositive Filtration as a Pretreatment Process for Reverse Osmosis

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27th Annual WateReuse Symposium
September 9-12, 2012

AND

Study of a Depth Filter (Disruptor™) for the Novel Application of Reducing SWRO Membrane Fouling

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October 8-12 2012

Presentation Outline

- **Project motivation**

– RO performance & membrane fouling

– Electropositive filtration

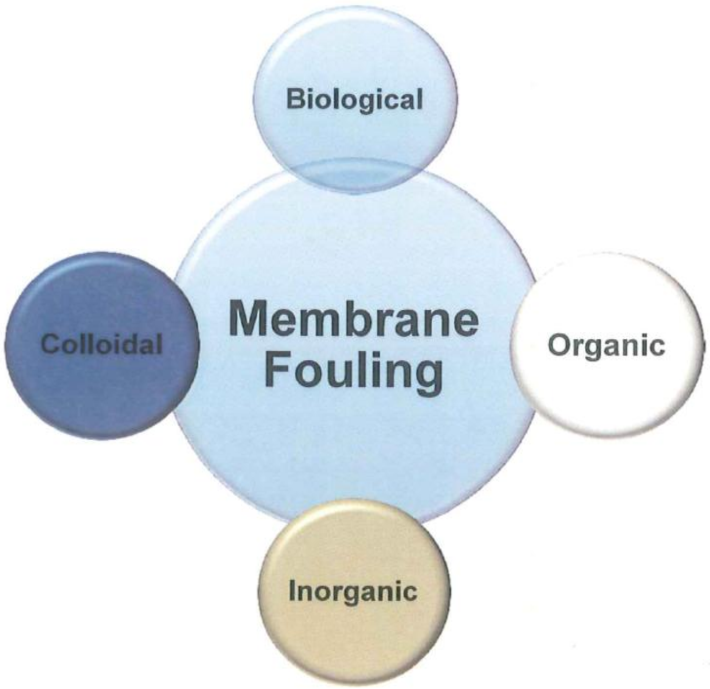
- **Experimental approach**

– Membrane test unit

– Water quality analyses

- **Preliminary results and key findings**
- **Summary and conclusions**

Membrane Fouling



- **Fouling is a significant impediment to membrane process operation**
  - System downtime, cleaning costs
  - Lost productivity (permeability loss)
  - Increased energy needs
- **Array of organics in secondary effluent (EfOM)**
  - Natural organic matter
  - Biopolymers, cellular debris
  - Algogenic organic matter
- **Particulate & dissolved forms**
  - Nano-particulate foulants

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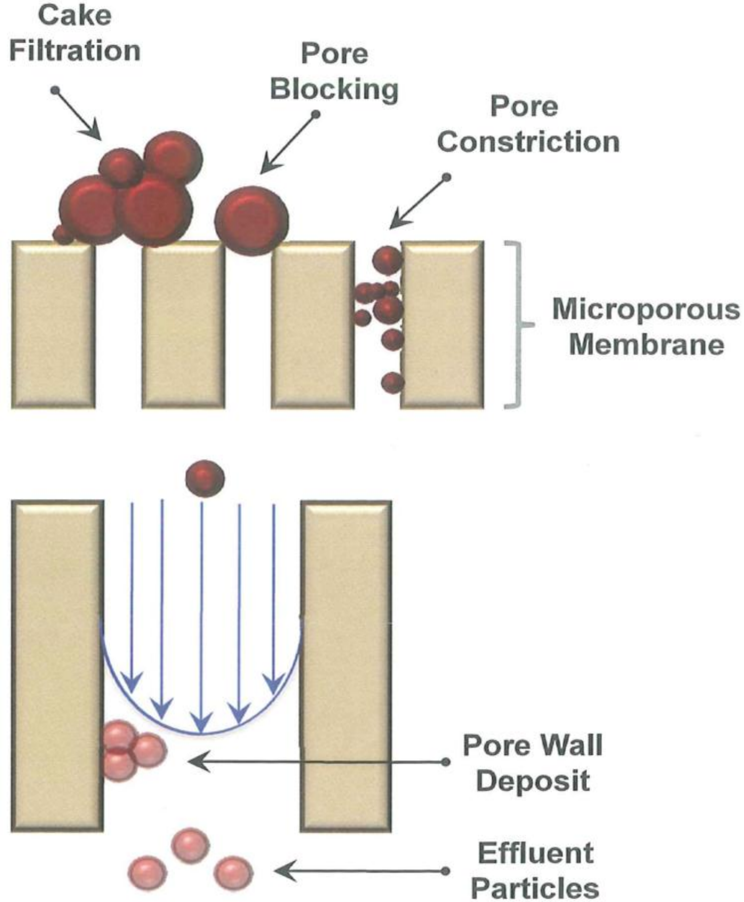
Fouling Mechanisms



- **Fouling mechanisms for MF/UF membranes:**
  - Cake filtration
  - Complete pore blocking
  - Intermediate pore blocking
  - Standard pore blocking
- **Incomplete removal of particulates and organics by MF/UF**
  - Formation of cake and gel layers on RO surfaces

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RO Pretreatment

- **Pretreatment strategies designed to mitigate RO membrane fouling**
  – Organics, microbial, & colloidal substances removed
  – Prefiltration targets particulates

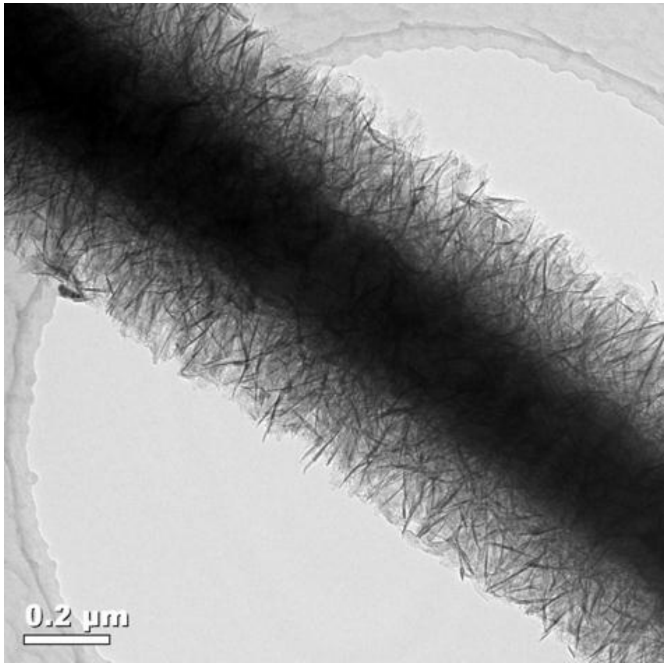
- **MF/UF are successful pretreatment techniques**
  – Tighter microporous membranes + higher pressures + higher energy consumption = increased treatment costs

- **Fouling remains an issue for microporous and salt rejecting membranes**

Electron Microscopic Image

Nanoalumina Fibers

The active ingredient of the filter media is a nano alumina (AlOOH) fiber, only 2 nanometers in diameter.



The nano fibers are dispersed and adhere to glass fibers and appear as a fuzz on the microglass fiber.

The composite fiber is formed into a non-woven media by wet processing. The water filter's pore size is ~ 2 microns.

Since the electropositive nano alumina fibers are dispersed and fixed in place, particles have easy access to their charged surface.

Overview & Summary NanoCeram®/Disruptor™

- Argonide invented the NanoCeram® filter media (2000)
- Ahlstrom, a leading manufacturer of non-woven media is licensed to manufacture and sell the media under name Disruptor™
- The fibers are unique in that they have a very high surface area for contact as compared to granular media where most of the surface area is inside the particle. This high surface area promotes greater effectiveness in very thin 0.8 mm layers.
- This layer has about 400 vertical pores each having >550,000 fibers. Thus, the calculated proton charges of 2×10^{12} thus the ability to capture a variety of negatively charged soluble organics as well as nanoparticles.
- An alternate cartridge includes powdered activated carbon (NC-PAC). It is capable of retaining both small particles and soluble contaminants with high efficiency.
- Both have wide application for purifying process water and for upstream and downstream filtration/purification in industrial and pharmaceutical manufacture.

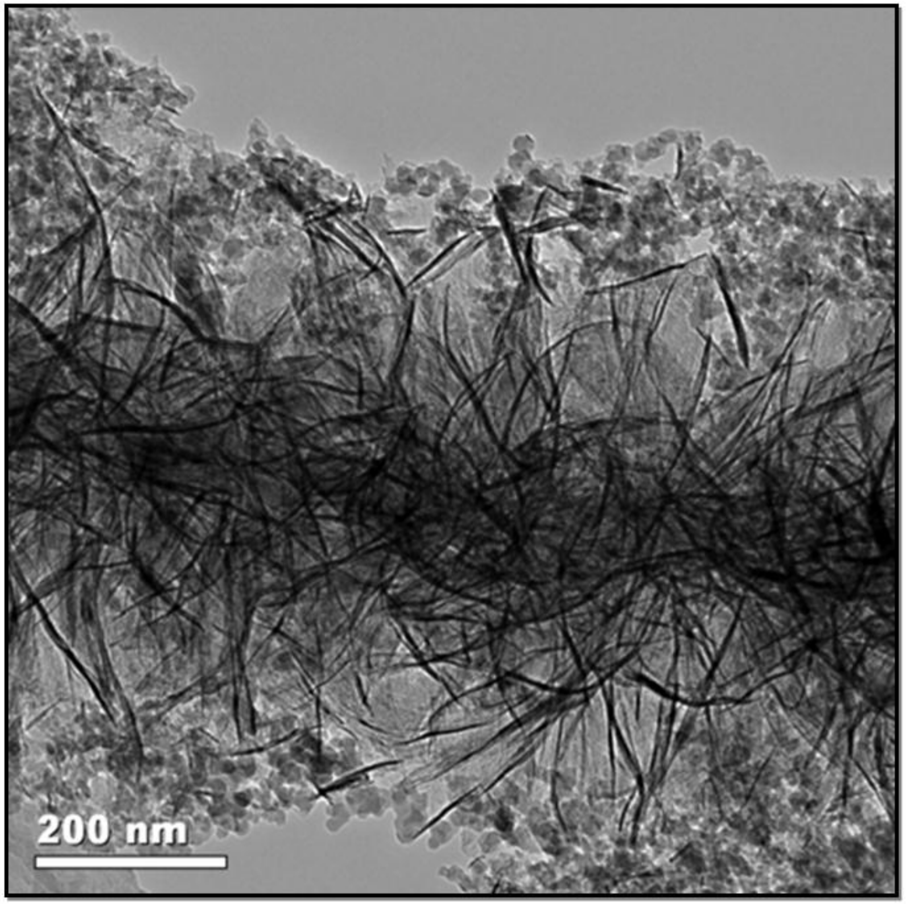
Overview & Summary NanoCeram®/Disruptor™ (continued)

- In the case of nano-alumina/microglass composite's the attraction is the cumulative effect of forces generated by the *assembly of nano alumina fibers on the second fibers in a highly organized structure*.

- This creates a significant electric field in the region far from the surface of the composite that penetrates farther and generate much stronger force than that generated by a single nano alumina fiber at ~ 10-20 nm.

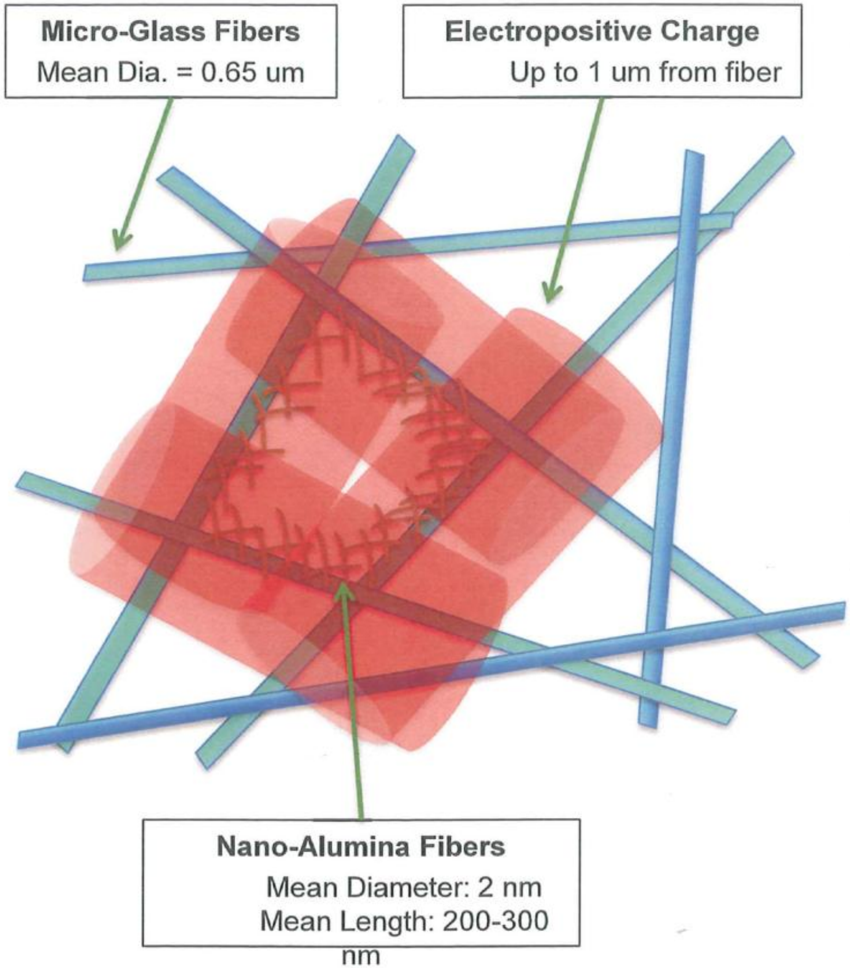
- These forces attract and retain much smaller particles such as fumed silica nanoparticles. (See next slide).

Nanosilica Sorption on NC Media



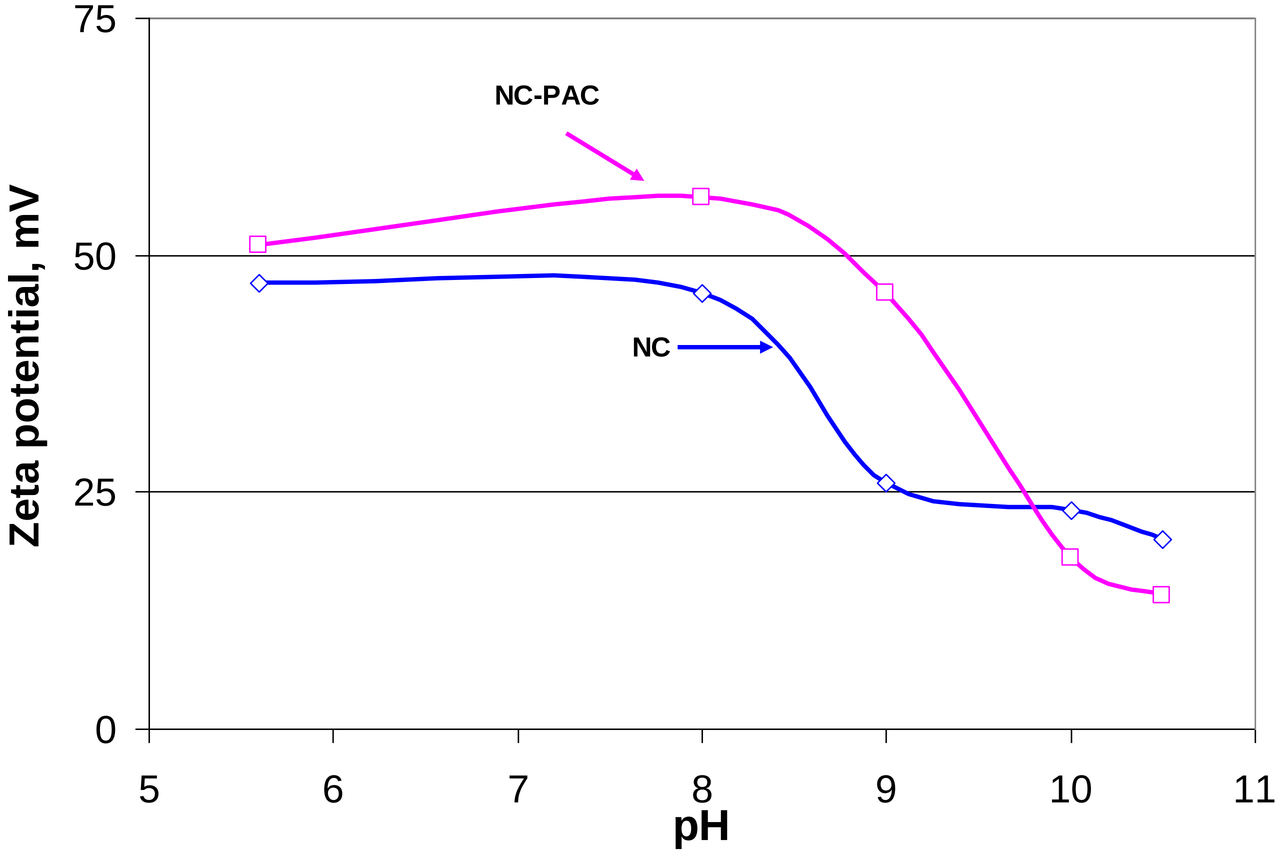
Note accumulation of 10 nm silica spheres on surfaces

Electropositive Filtration



- **Pleated cartridge design**
  - Mean pore size = 2 µm
  - Avg. Headloss = 1 – 3 psi
- **Removal via charge interactions**
  - Most solutes carry net (-) charge
  - Filter media carries net (+) charge
- **Removal of "small" substances not captured by conventional filters**
  - Nano-particulates and
  - Organic/microbial macromolecules
  - Viruses/bacteria

Zeta Potential of Media



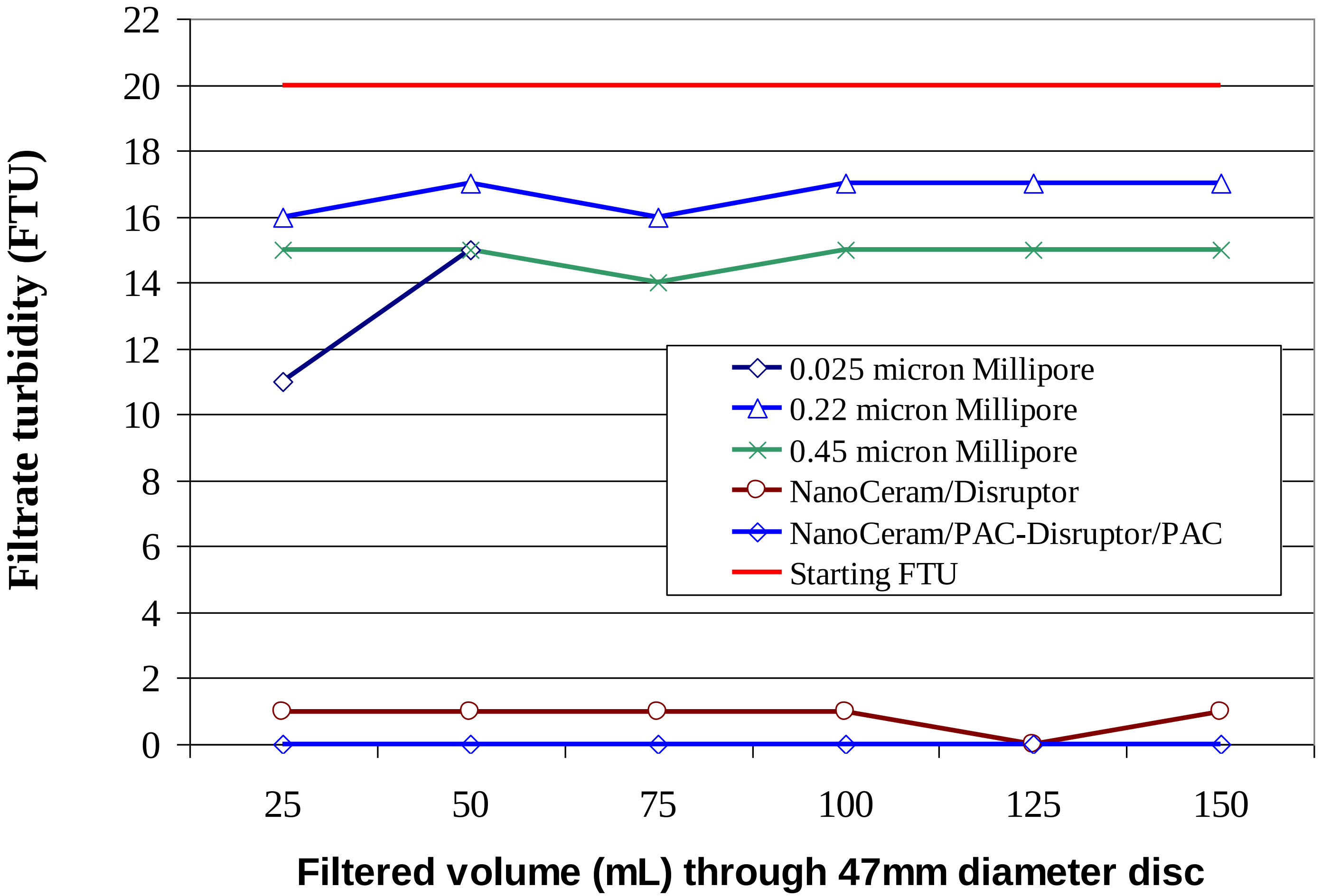
NC and NC-PAC have a high zeta potential in pH range from 5 to 10

Zeta potential and virus removal

Weight % Nano alumina on glass	True zeta potential, mV	MS-2 % removal	PRD-1 % removal
0	-35	8	Not done
5	-10	29	Not done
10	7	94	Not done
15	15	>99.9999	>99.99999
25	35	>99.9999	>99.99999
40	29	>99.9999	99.99991
50	23	>99.9999	>99.99999

- **Pure microglass fiber, which is electronegative, is very ineffective for filtering MS2 virus**
- **As the ratio of nano alumina increases, the charge becomes positive.**
- **At about 15 weight percent (wt %) alumina, virus retention becomes very high.**
- **At about 50 wt % nano alumina, the surface of a 0.6 μm glass fiber is saturated with nano alumina fibers**

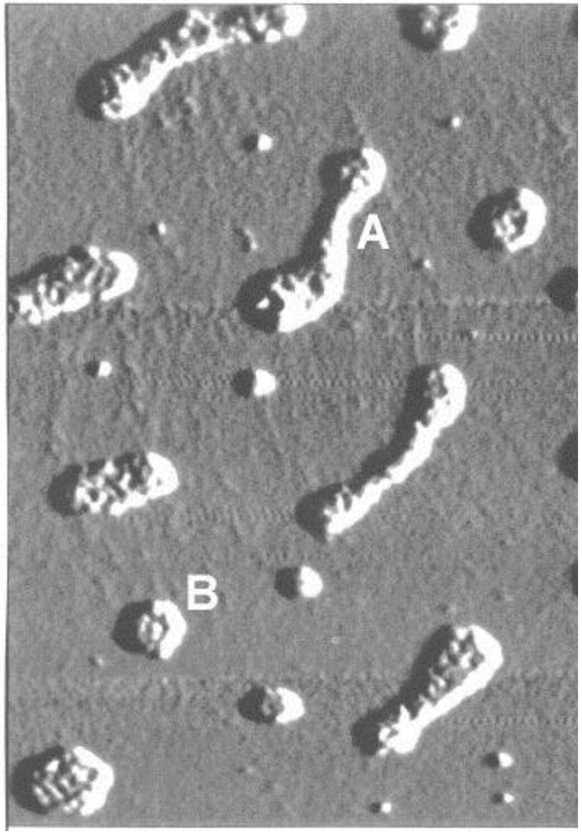
Filtration of Sub-Micron Organic Particles



Data Courtesy of Heather Mowers, Ahlstrom Filtration

Membranes and NC media are challenged with humic acid, a particle smaller than a virus (see next slide). Note that both NC and NC-PAC had far better retention than even a 0.025 μm membrane (which clogged almost immediately)

AFM Image of humic particles



Courtesy of M. Mertig, Dresden Univ.

- A - 250 nm x 60 nm elongated agglomerates
- B - 50 nm diameter disc-like agglomerates
- Both exhibit a thickness of 1.5 to 2 nm
- Agglomerates are monolayer clusters of 'humic acid subunits' believed to be individual humic acid molecules
- The very small particle size explains why humic acid is not efficiently retained by MF or UF

Project Objectives

- **1. Characterize nanoparticle and organic matter removal by electropositive filters as a function of solution chemistry / composition**
- **2. Assess performance impacts for UF and RO membranes associated with treating UF filtrate (RO feed) with electropositive filtration**
  - Membrane performance (transmembrane pressure, permeability / flux decline) that result from the treatment of water using an electropositive filter
- **3. Evaluate practicality of using electropositive filtration in full-scale water reuse treatment systems**
- **4. Evaluate benefits of using electropositive filtration to polish backwash fluid**

Feedwater Composition

Stirred Cell (Dead End)

- **Simple electrolyte solution**
  - pH = 6 to 8
  - Ionic strength = 10 mM NaCl (0.06%)
  - $[NP]_{Tot}$ = 0.5-2.0 mg/L (d_p = 50 nm)
- **RO feed grab samples**
  - pH = 7.77
  - Conductivity = 300 µS/cm
  - Turbidity = 16 to 25 mNTU

Pilot-Scale Tests

- **Tap water dosed with humic acid (HA)**
  - HA = 5 mg/L
  - Conductivity = 300 µS/cm
  - pH = 7.7
  - Turbidity = 3.5 NTU
  - Characterized as "hard" water
- **Tap water pre-filtered to ensure consistent composition**

UF Membranes

- **Hollow fiber UF module**
  - Hydrophilic PVDF
  - Out-In configuration
  - 0.03 µm nominal pore diameter
  - Active area = 355 ft^2 / module
- **Surface properties**
  - θ_{water} = 30°
    - Measured for wet-out membrane (soaked in 70% ethanol solution)
  - $\zeta_{pH\ 3\text{-}8}$ = > -10 mV

Operating Condition	Value
Filtrate Flux, gfd	7
Recovery	63%
Max Operating Pressure	
TMP, psi	30
At Inlet, psi	93
Backwash	
Frequency, min	40
Duration, sec	40
Flush, sec	5

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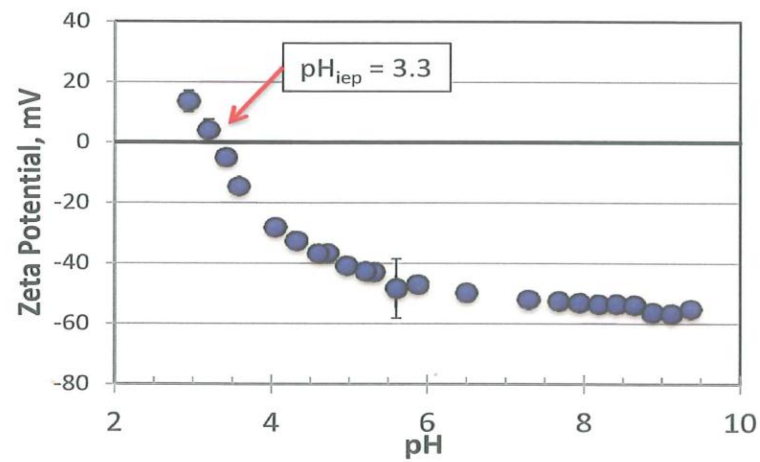
Brackish Water RO Membrane

RO Membranes

- **Low-pressure BWRO membrane**
  - Polyamide TFC
  - Max ΔP = 600 psig
  - Area/Element = 28 ft^2
- **Operating conditions**
  - Recovery = 11%
  - Flux rate = 8.50 gfd



Membrane Surface Chemistry

- Hydrophobic w/ θ_{water} = 86° ± 5°
- Negatively charged ($\zeta_{pH\ 7}$ = -50 mV)

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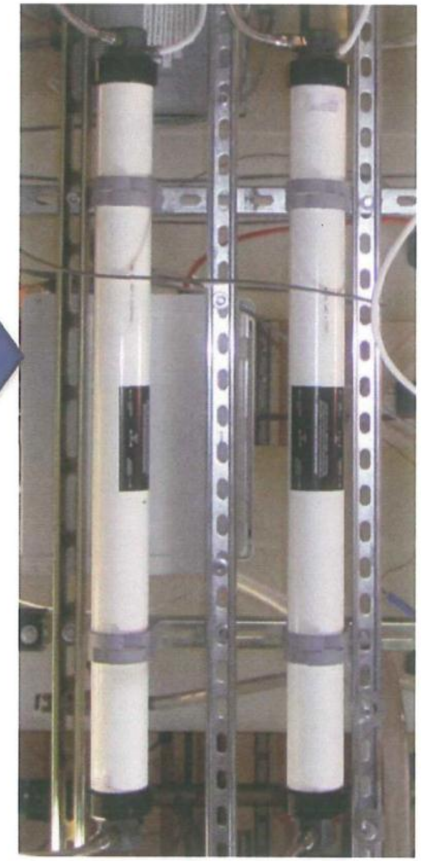
Membrane Test System

UF Modules
Parallel Process Streams

Electropositive Filter
Single UF Filtrate Stream



RO Elements
Parallel Process Streams

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Electropositive Filter

Electropositive Filter (Disruptor)

- Pleated Filter Cartridge
- Non-woven, nano-fibrous
- Micro-glass fiber substrate with nano-alumina fibers
- Inherent positive (+) charge
- PAC available

Part Number	P2.5-5	P2.5-10	P2.5-40	P4.5-10	P4.5-40
Surface Area	1.4 ft^2	3.4 ft^2	14.1 ft^2	8.3 ft^2	35.0 ft^2
Dimensions	2.8 x 4.85 in	2.8 x 9.75 in	2.8 x 40 in	4.5 x 9.75 in	4.5 x 40 in
Suggested Flow Rate	2 gpm	4 gpm	16 gpm	10 gpm	40 gpm
Dirt Holding Capacity	114.4 g	280.3 g	1161.2 g	683.5 g	2882.9 g

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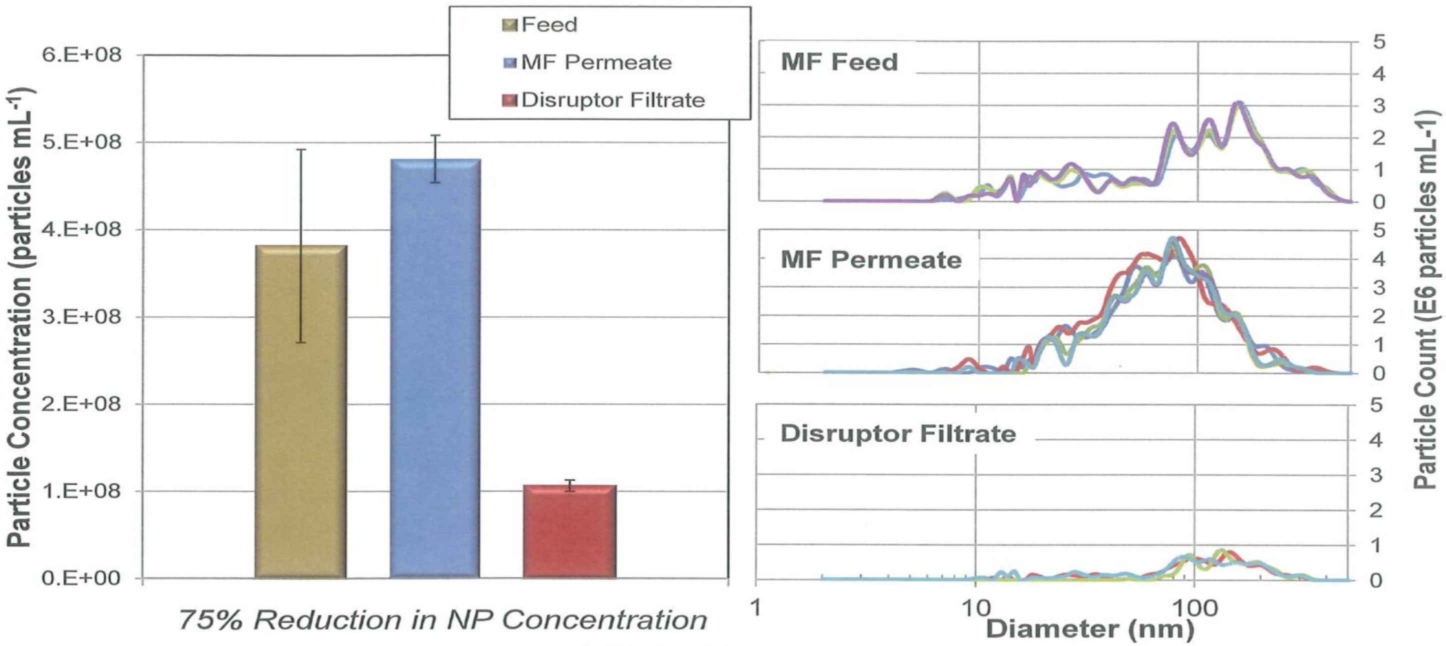
Nanoparticle Removal



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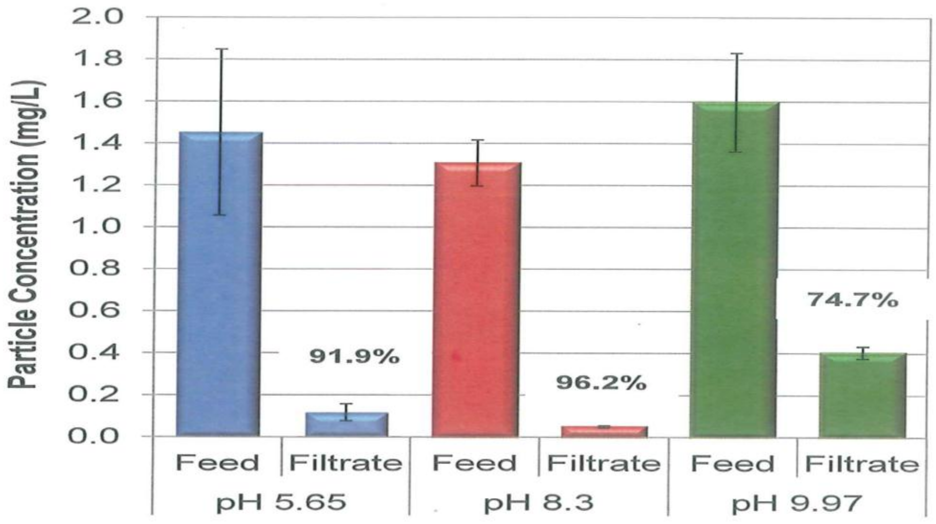
- **Tap water dosed with humic acid**
  pH = 6 to 8
– Ionic strength = 10 mM NaCl (0.06%)
– [NP]Tot = 0.5-2.0 mg/L (dp = 50 nm)

Conclusions

•Hollow Fiber Microporous membrane module removes NP larger 0.1 μm

•NanoCeram® removes >75% of all sizes NP

Nanoparticle Removal



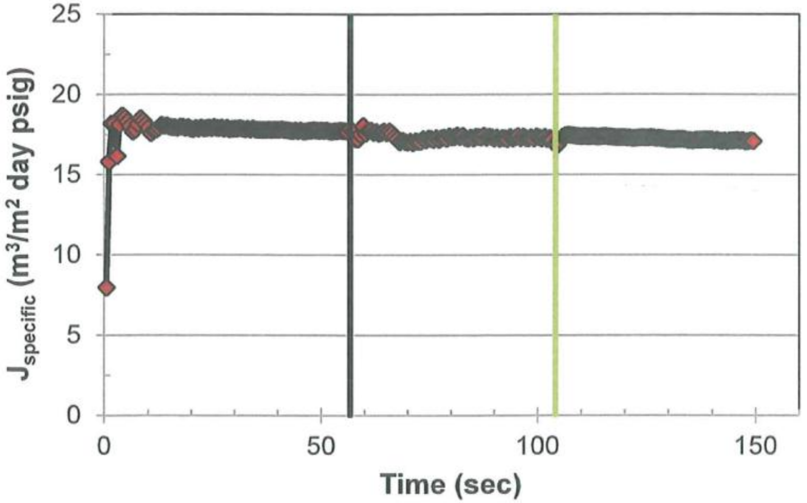
NanoCeram® has isoelectric point at pH ~ 11

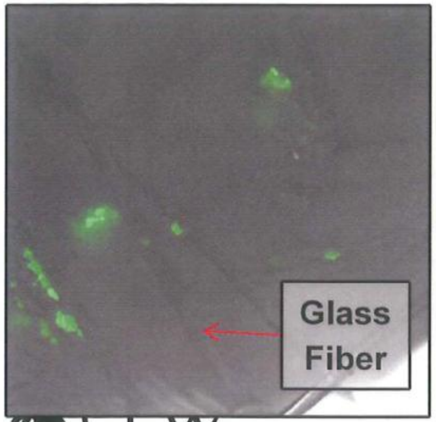
NanoCeram® shows:

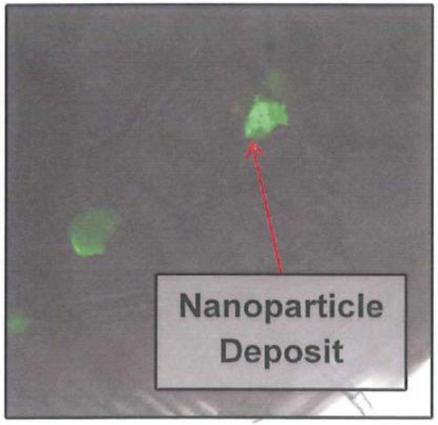
•very high (>92%) removal rate of nanoparticles in the pH range from 5.6 to 8.3

• high (>75%) removal rate of nanoparticles at pH 10.0

Nanoparticle Removal

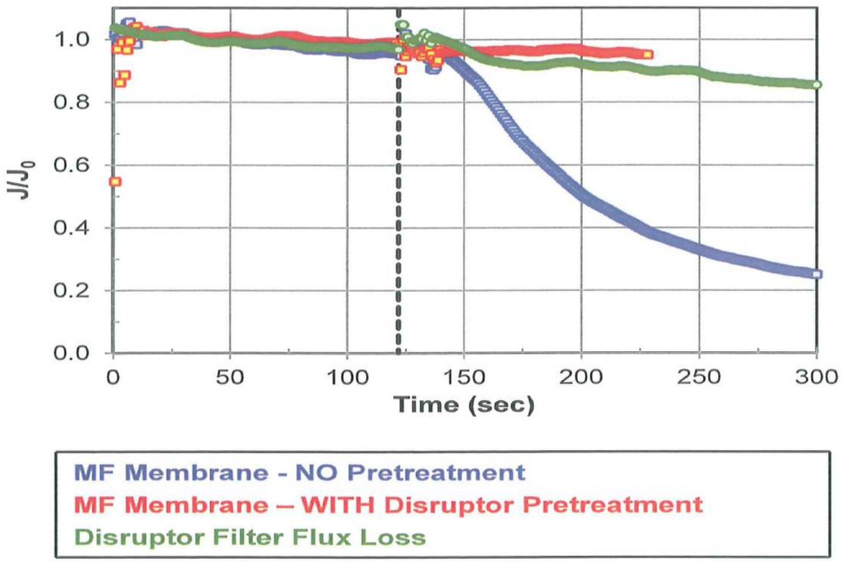






- **Headloss development over time is an important variable**
  - Nano-particulates, organics form deposits with low permeability = rapid flux loss
- **Challenge test with nanoparticle suspension**
  - pH = 7.5
  - $[NP]_{feed}$ = 2 mg/L
  - ζ_{NP} = -42 mV
  - d_p = 57 nm
- **Little change in filter headloss over time**
  - NP clumping suggests aggregation in filter (charge zones)

Nanoparticle Removal



- **Pretreatment with EPF reduced nanoparticle fouling of MF membrane**
  - J_{loss} = 2% (with pretreatment)
  - J_{loss} = 80% (no pretreatment)
- **Headloss development over time evident**
  - Indicative of filter clogging (low)

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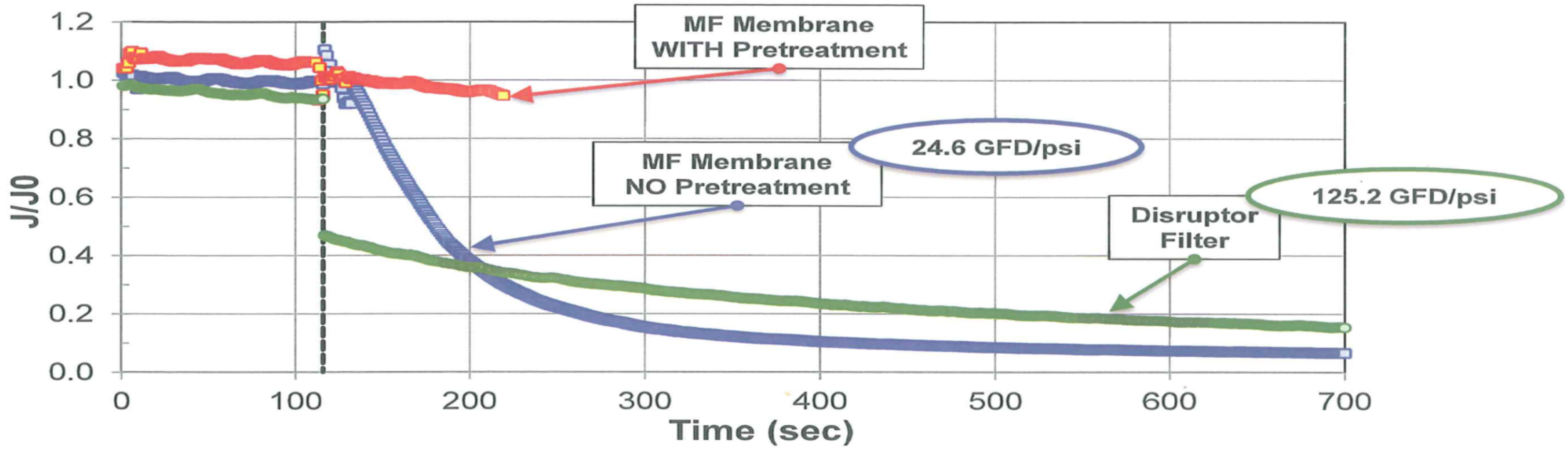
NanoCeram® (ElectroPositive Filtration (EPF)) reduces losses of initial flow J_0 by 2% as compare to 80% losses without the EPF pretreatment

Organics Removal



- **EPF reduces organic fouling of MF membrane**
  - No pretreatment = > 90% flux loss
  - EPF pretreatment = < 5% flux loss
- **High organic concentration (15 mg/L) results in clogging of EPF**

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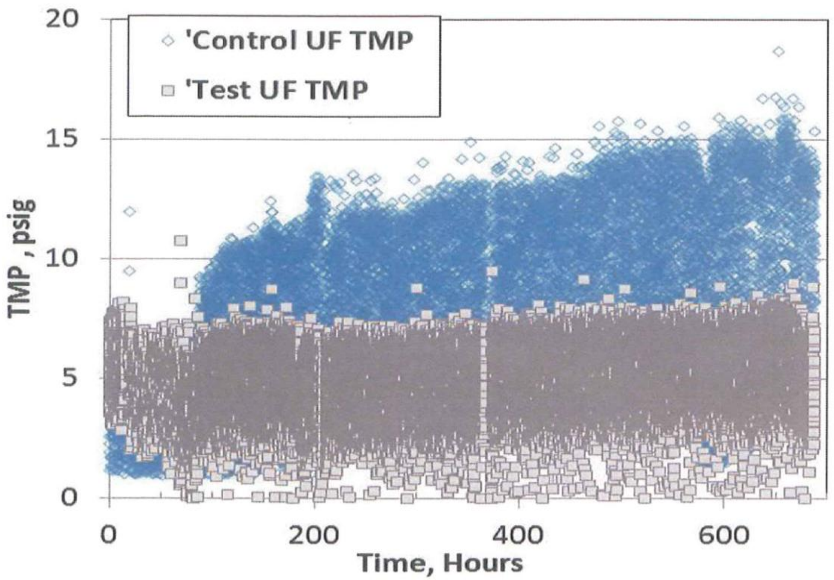
NanoCeram® (ElectroPositive Filtration (EPF)) reduces losses of initial flow J_0 to less than 5% as compare to greater than 90% losses without the EPF pretreatment

UF Fouling



- **Greater increase in TMP over time for UF Membrane backwashed with "unpolished" filtrate**
  - CIP initiated at *t* = 25 days
  - pH = 9 cleaning solution (98% permeability recovery)
- **UF membrane backwashed with "polished" filtrate maintaining constant TMP**
  - Reduced fouling of filtrate side of membrane during backwashing

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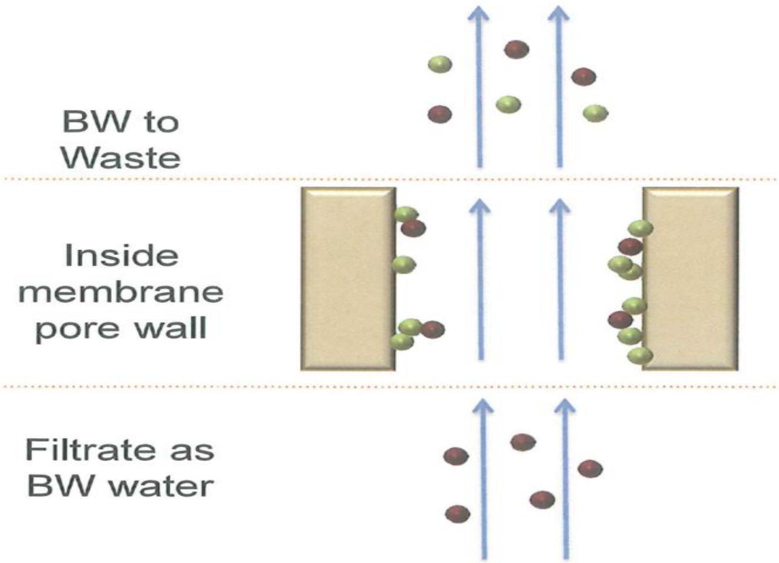
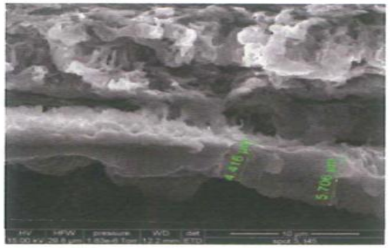
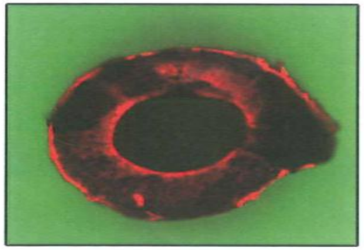
Transmembrane pressure (TMP) increases more rapidly after backwashing the hollow fiber microporous membrane unit with "unpolished" water as compare to the same water treated with NanoCeram® (ElectroPositive Filtration (EPF))

UF Fouling - Backwash



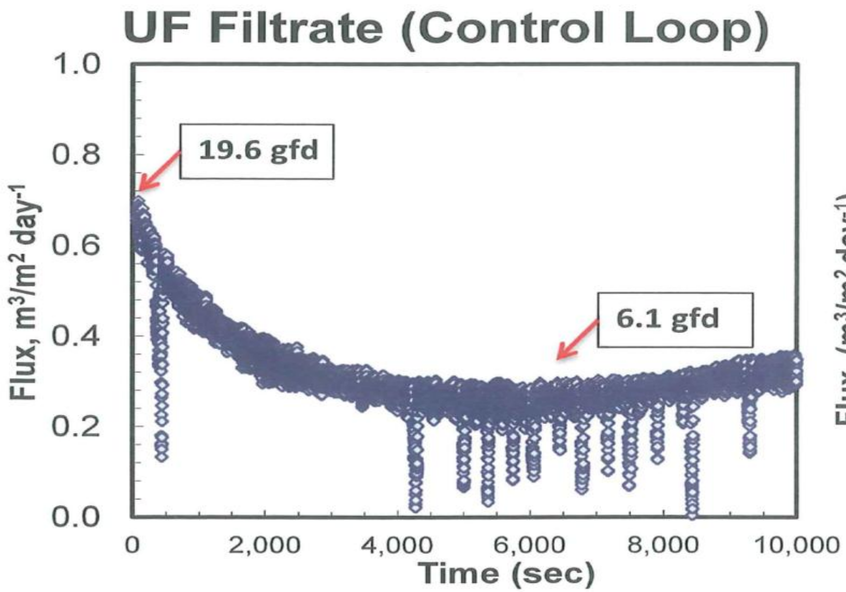
- **Substances not rejected by membrane are present in filtrate**
  - Filtrate used to backwash membrane
- **Substances accumulate on filtrate side of membrane during backwashing**
  - Also present in membrane interior

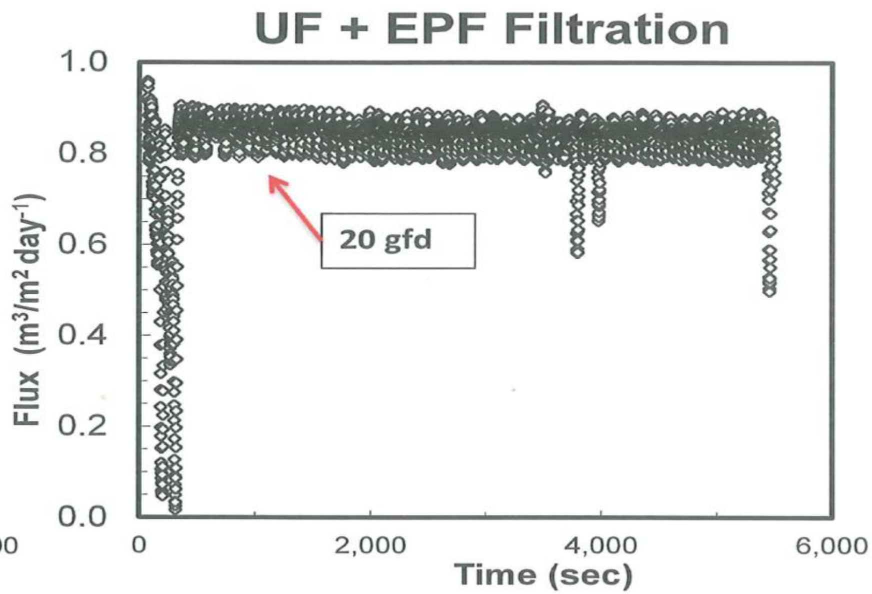




Backwashing (BW) the hollow fiber microporous membrane unit with "unpolished" water shows substances not rejected by membrane

RO Fouling





Flux Loss = 69%

Flux Loss = 4%

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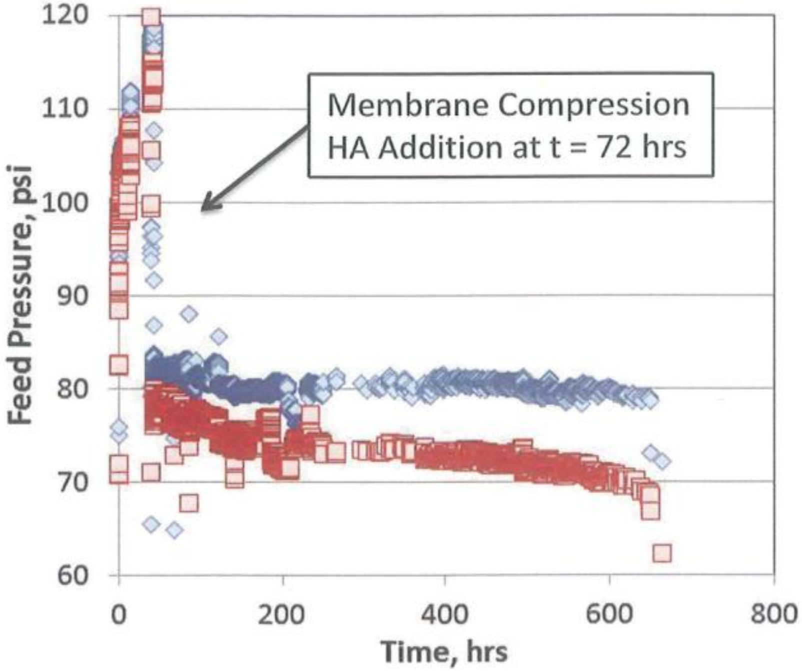
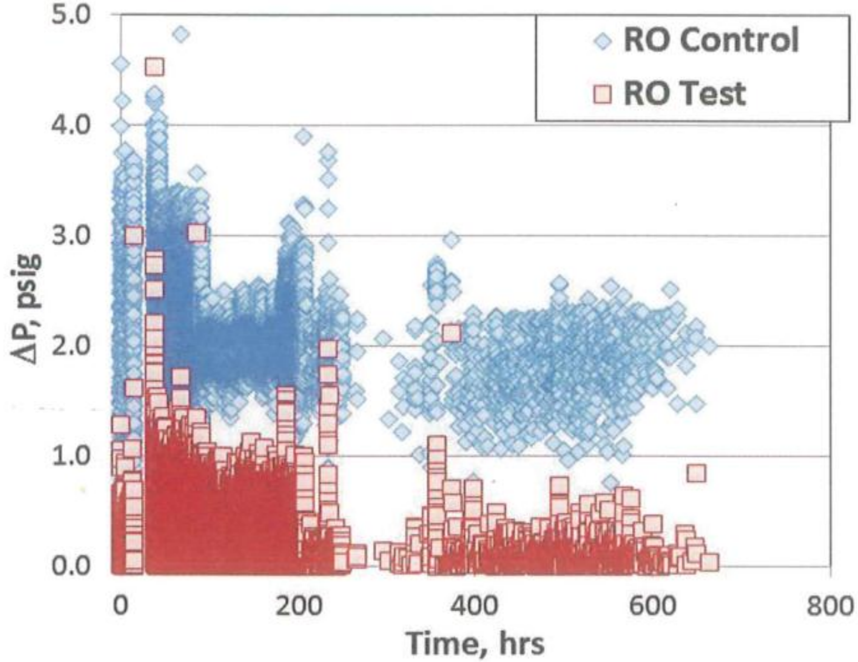
NanoCeram® (ElectroPositive Filtration (EPF)) reduces losses of initial flux J_0 to 4% as compare to 69% losses without the EPF pretreatment

RO Fouling





$\Delta P = P_{feed} - P_{reject}$

- **Pressure increases rapidly following HA addition**
  - Semi-equilibrium state reached at t = 100 hrs
- **Higher salt rejection for test loop (99% vs. 96%)**

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Preliminary Conclusions on Economic and Performance Assessment of Electropositive Filtration as a Pretreatment Process for Reverse Osmosis

- **NanoCeram® Electro-positive filtration effectively removes negatively charged nanoparticulates and organic matter**
  - >75% NP removal (function of solution pH) and >98% organics removal
  - Negatively charged organics deposit / adhere to electro-positive filter surface (surface fouling)
  - New filter designs aim to mitigate surface fouling
- **Treating MF or UF filtrate with NanoCeram® electro-positive filtration benefits both MF/UF and RO process performance**
  - Reduced membrane fouling through removal of nano-particulates and organics
  - Filters can be integrated into existing process configurations

Study of a Depth Filter (Disruptor^{TM}) for the Novel Application of Reducing SWRO Membrane Fouling

by

Ibrahim M. El-Azizi
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American Membrane Technology Association

AMTA Annual Conference & Exposition
Austin, TX – July 13-16, 2009

Session 3d – Pretreatment to Seawater Desalination Plants
Annual Meeting

By Fred Tepper*, Argonide Corporation and Ibrahim El-Azizi, University of Sheffield (U K)

Introduction

- Long -term performance of SWRO plants depends on:
  -Proper design
  -Proper pre-treatment
  -Proper operation and maintenance.

- Why effective Pre-Treatment is required?
  -To prevent membrane fouling
  -To increase the efficiency of RO membrane systems.
  -To reduce the operation and maintenance costs.

Introduction (continued)

Pre-Treatment Technology

Conventional Pre-Treatment

- -Widely used in SWRO desalination plant
- -However, optimization is required

Membrane filtration (MF/UF)

- -Effectively reduce SDI and microorganisms
- -However, costly and can not remove small organic molecules responsible for biofouling development. *(Bonnelye, et al. 2008)*
- -Back flush and Self cleaning filter.
- -Limited removal efficiency of small particles (1-5µm).

Introduction (continued)

➢ Disruptor^{TM} Technology

-Made of nano-alumina fibers composed of mineral *boehmite (AlOOH).*The fibres appears as hair-like strands which is 2nm in diameter and 250 nm in length.

-High surface area 500m^2/g .

-Dense electropositive charge (>52 mV at pH 7.2)

-High flow rate and low differential pressure.

-Reduces fouling by removing viruses, bacteria, colloids, silica and dissolved Fe, Al, Cu and Pb.

➢ The separation mechanism of Disruptor^{TM} based on

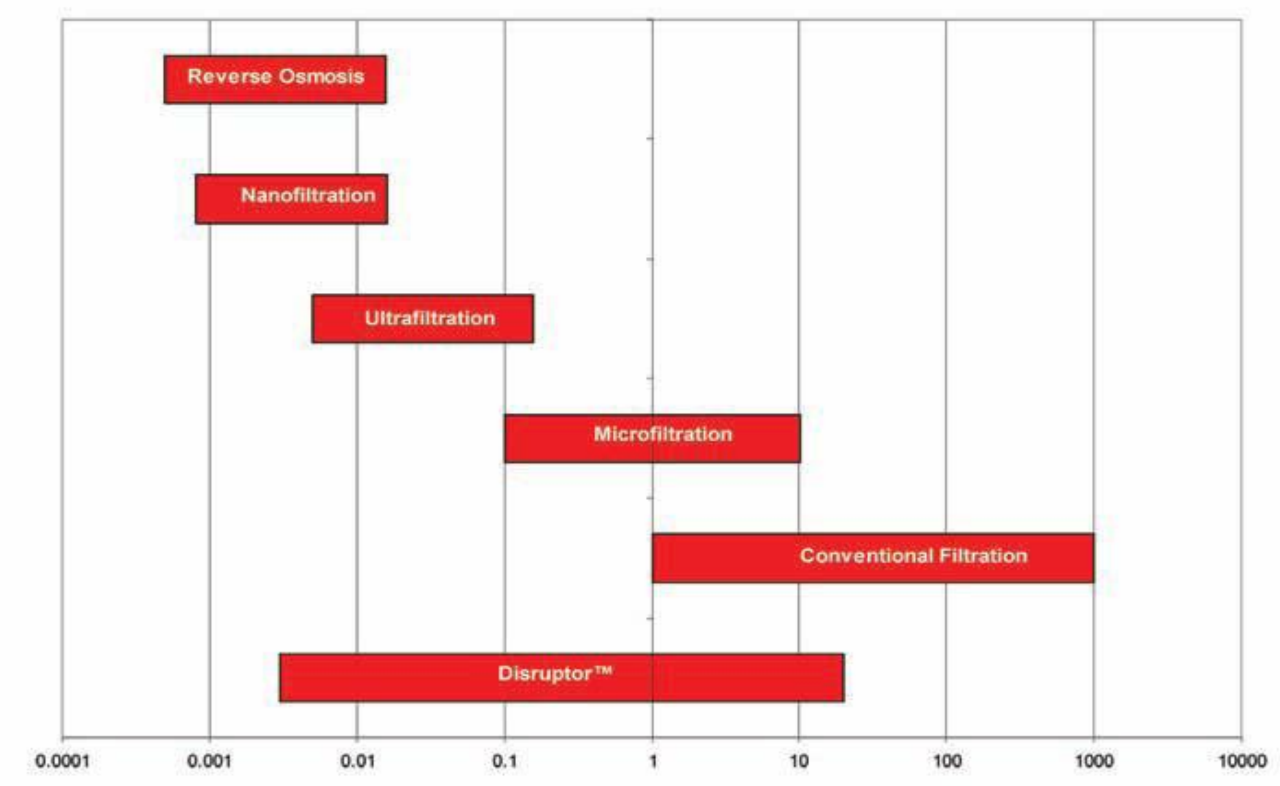
-electrokinetic adsorption and mechanical entrapment

Mechanically retains particles >0.5µm while electropositive charge retains particles <0.5µm).

Introduction (Continued)
Disruptor^{TM} Technology

-Produces filtration efficiency similar to MF/UF with low cost and ***very low*** value of Silt Density Index ($0.5 \leq SDI_{30} \leq 1.0$)

-Disruptor PAC can remove chlorine and organic matter.



Retention efficiency in microns

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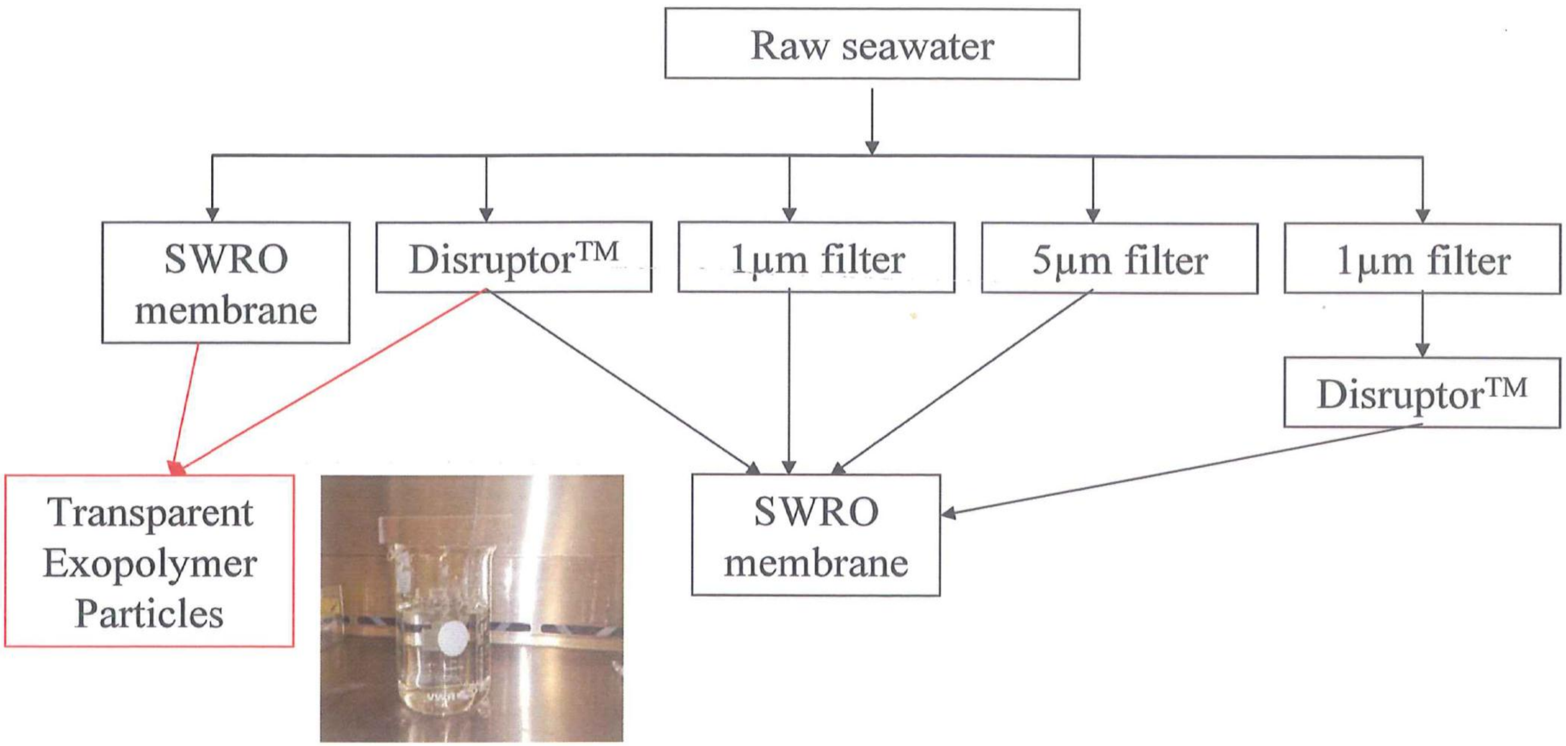
Materials and Methods

- Filtration Scenarios



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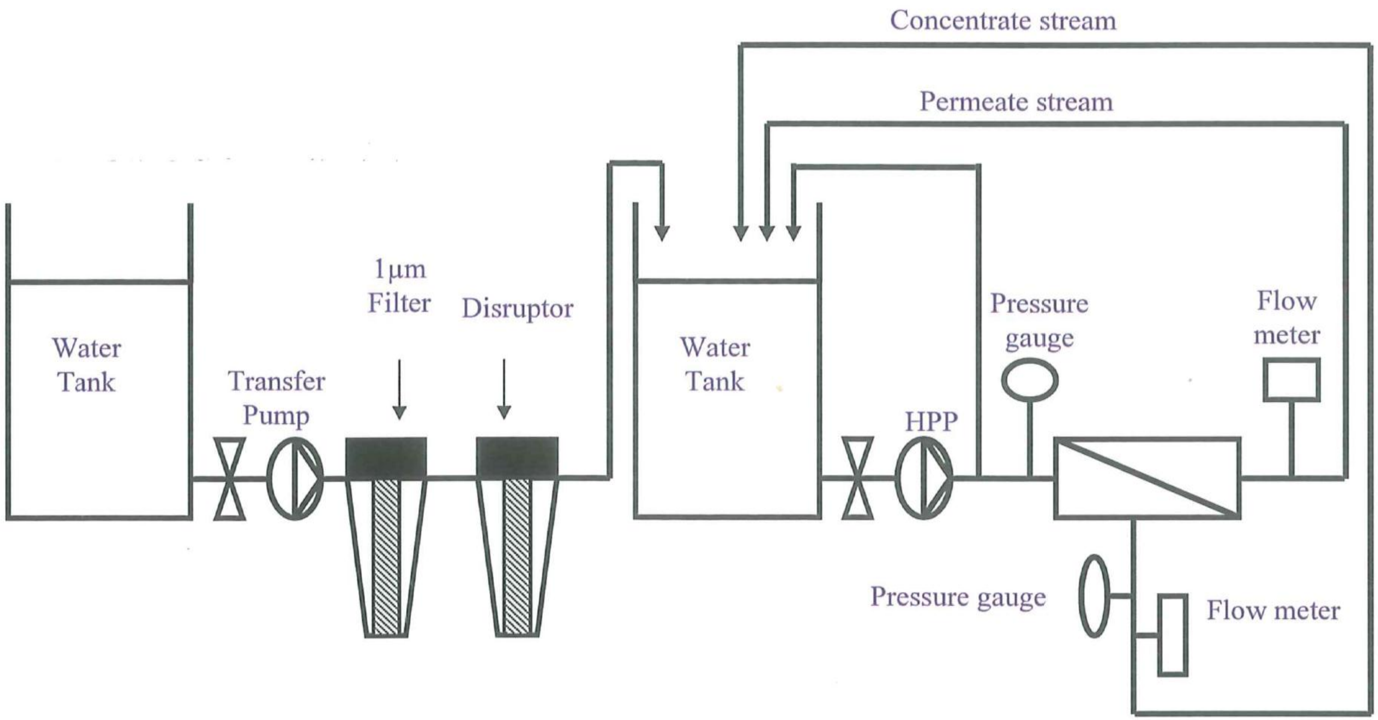
- # Experimental Set-UP



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- Characterisation of SWRO membrane

Characteristic	
Manufacturer	Toray
Membrane material	TFC polyamide
Surface charge at pH 7	Negative
Contact angle	52.5±0.42
Membrane roughness (nm)	49.144
Salt rejection (%)	99.75
Pressure (PSI)	1000
Temperature (°C)	4-45
pH	2-11

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- Contact angle, AFM, SEM, ATR-FTIR, light microscope measurements

Contac angle - sessile drop method

AFM – Tapping Mode

SEM – Inspect F

ATR-FTIR

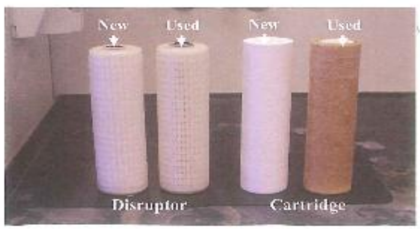
Light Microscope

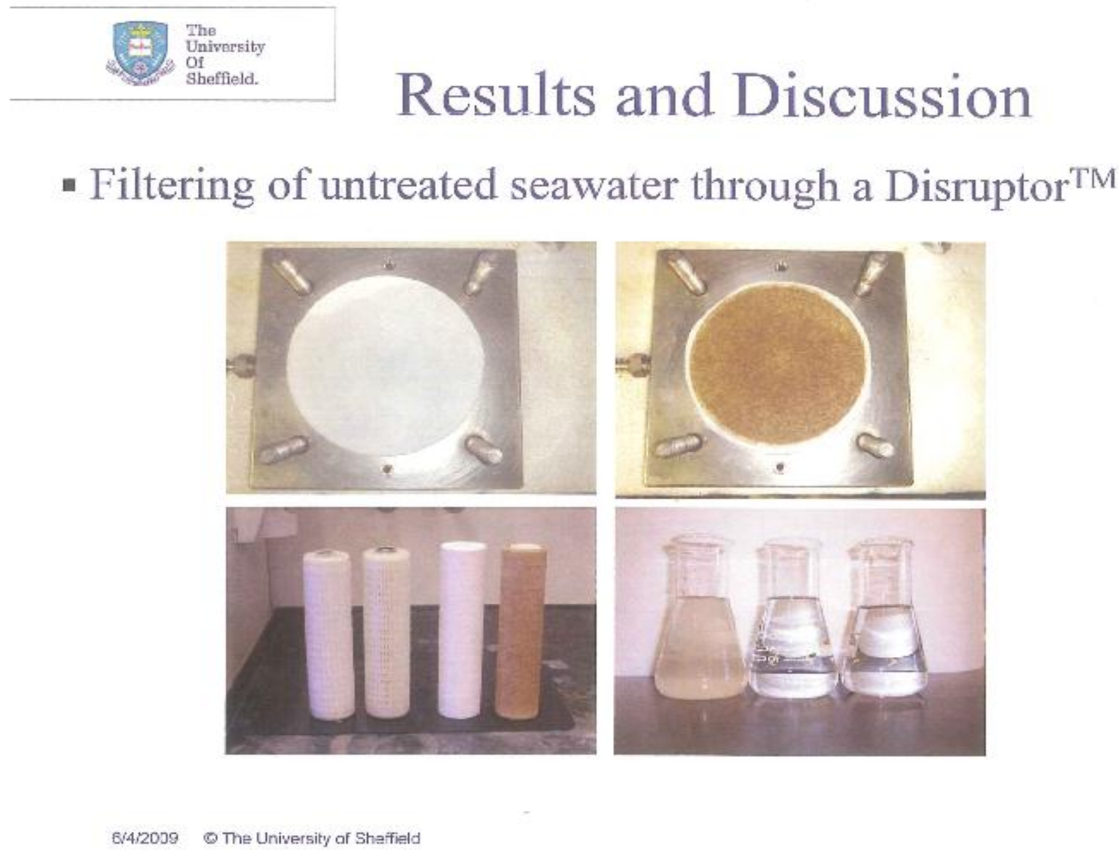
TEP

AFM -Atomic Force Microscopy
SEM- Scanning Electron Microscopy
ATR-FTIR - Attenuated Total Reflectance Fourier transform infrared spectroscopy

Results and Discussion

Photos of new and used Disruptor and 1 μm filters





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- Clean and fouled SWRO membrane

Clean RO membrane

Fouled by raw seawater

Pre-filtered through Disruptor™

Membrane Contact Angle and Roughness

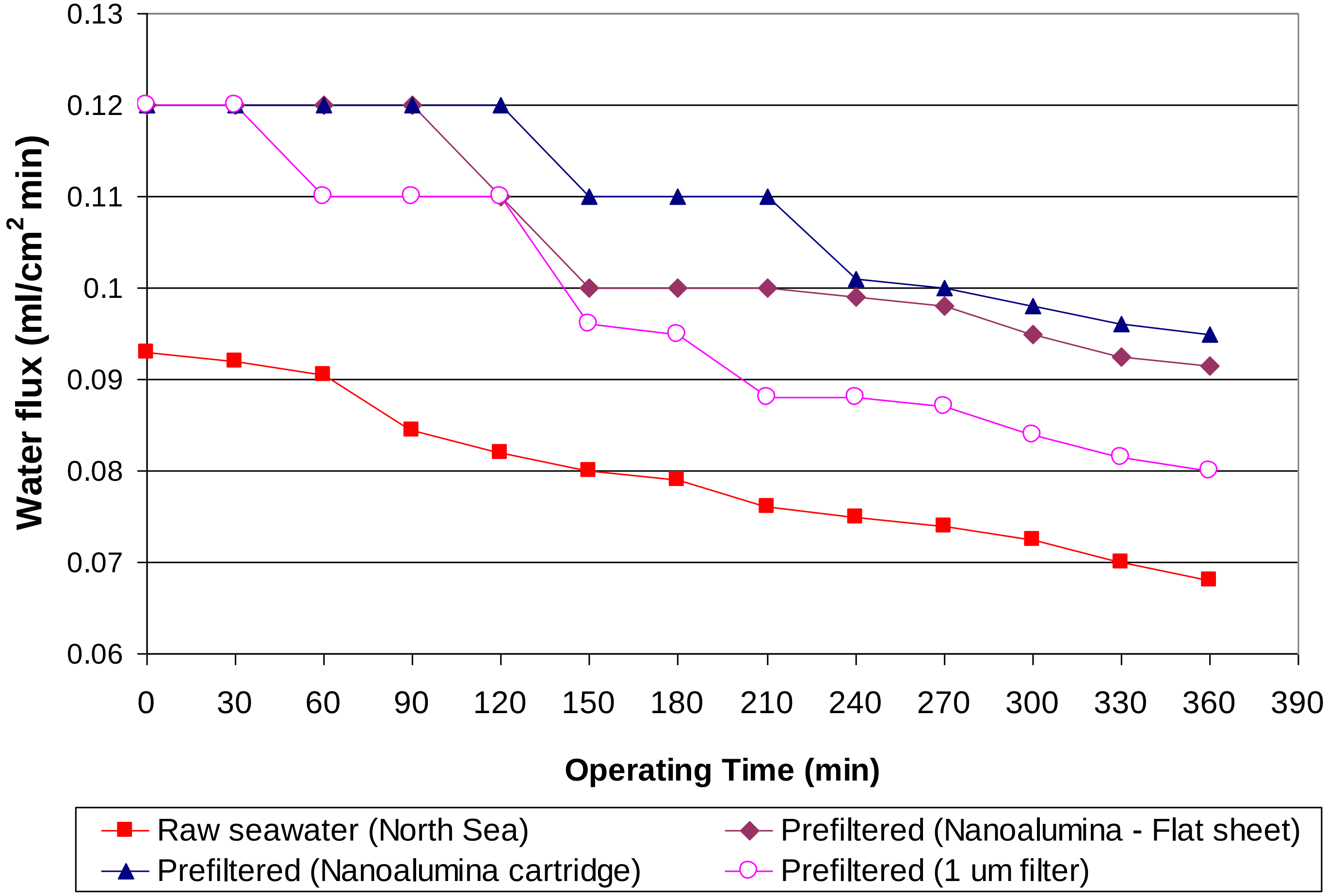
	New Membrane	Fouled membrane Untreated Seawater	Seawater filtered through nano alumina
Membrane Contact Angle	52.5±0.42	41.6±1.19	51.9±4.17
Membrane Roughness (nm)	49.144	78.254	53.988

Conclusion:

Foulant changes contact angle and roughness appreciably

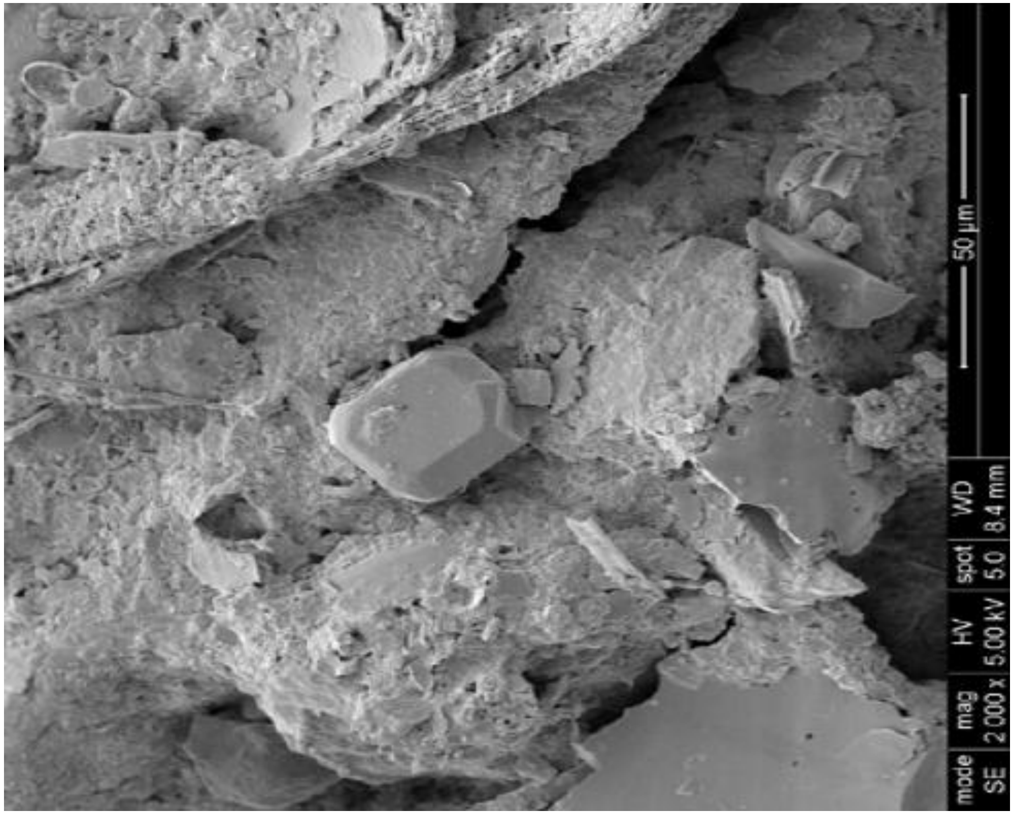
When filtered through nano alumina, no change on contact angle and little change on roughness – When filtered, membrane is protected

RO Flux Rate in North Sea Water



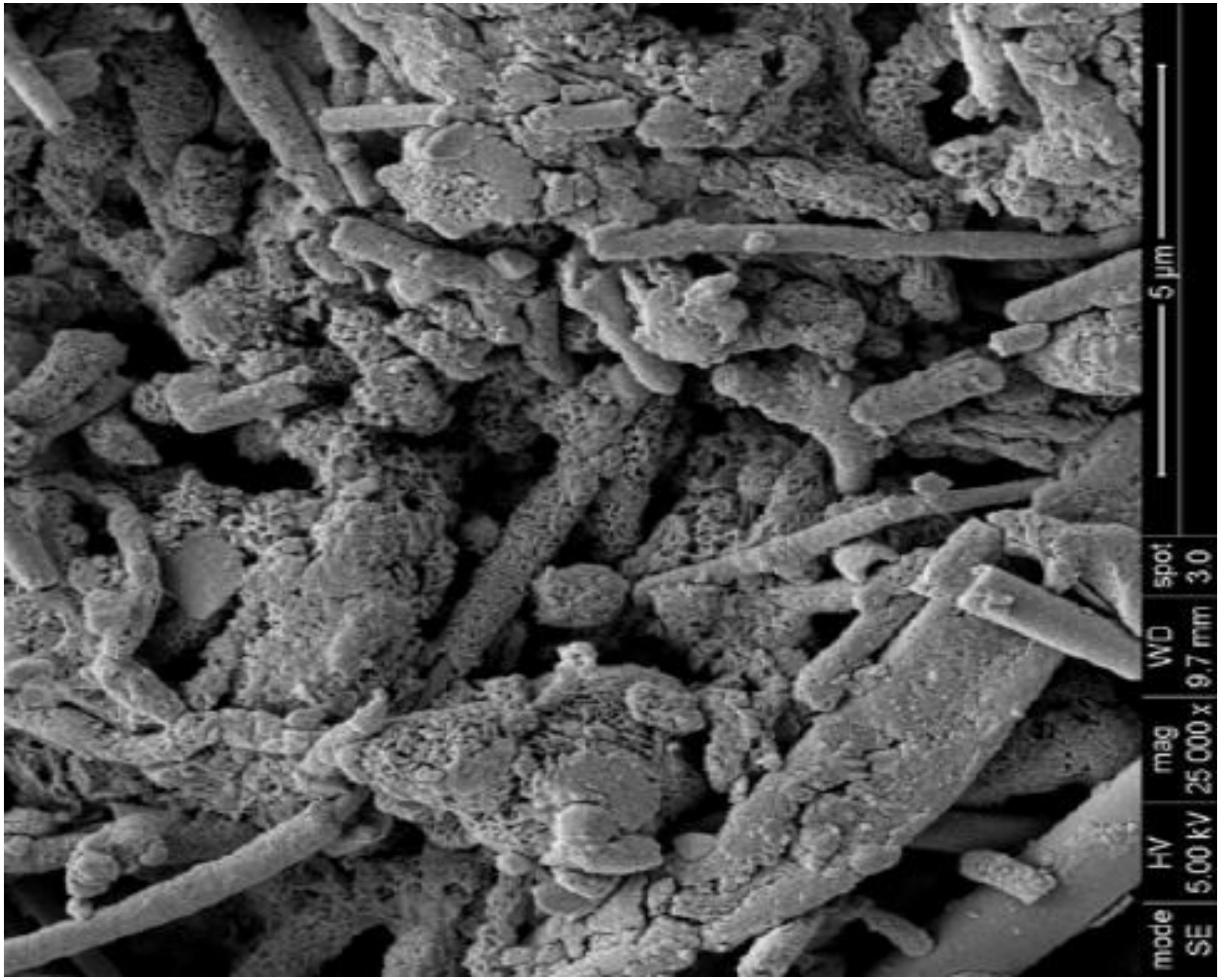
The flux rate of seawater through RO is substantially increased with prefilters of nano alumina and it is superior to protection vs a 1-micron prefilter.

SEM of Seawater Foulants on Membrane



SEM- Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) of Membrane- NanoCeram Filtered Seawater



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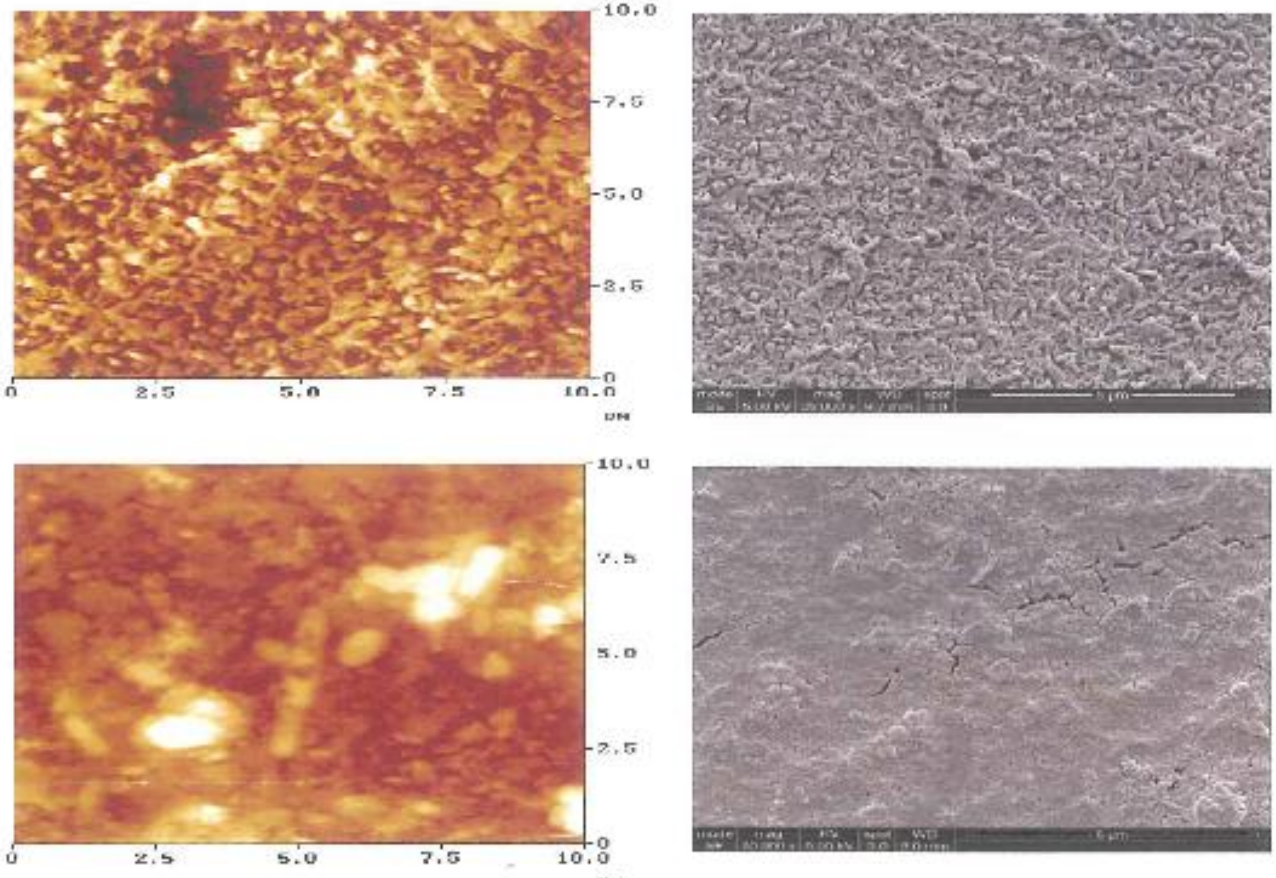
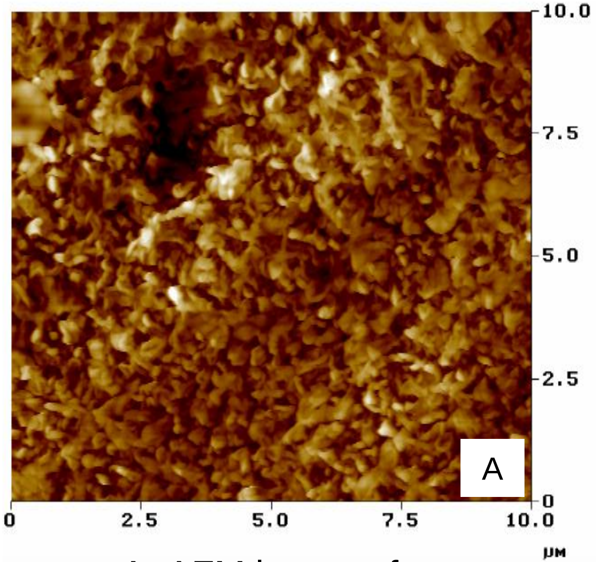
- # AFM and SEM Results.

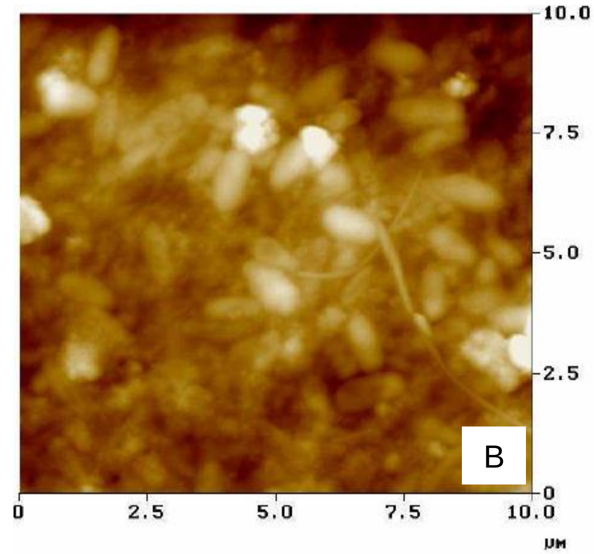
Clean and fouled SWRO membranes by raw seawater.



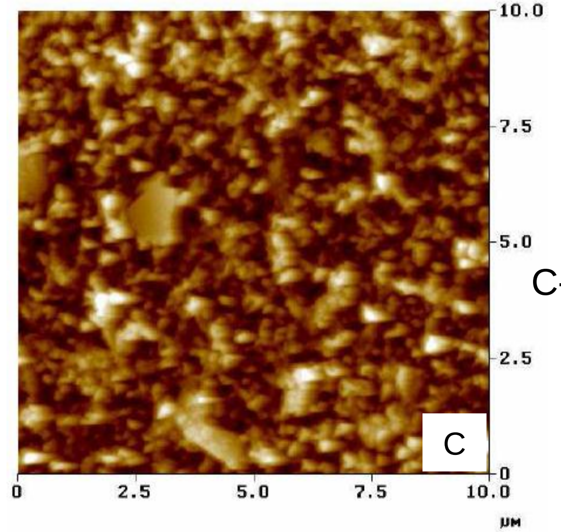
Atomic Force Microscopy (IFM) Images of RO Biofouling



A- AFM image of
new SWRO membrane.



B- AFM image of
fouled SWRO membrane.



C- AFM image of SWRO membrane
after filtration using
Nano alumina prefilter.

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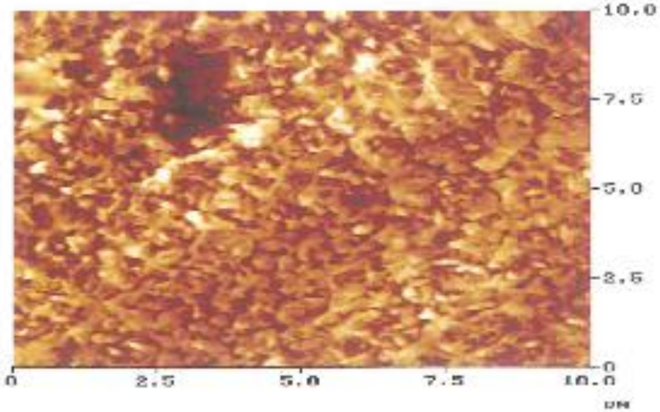
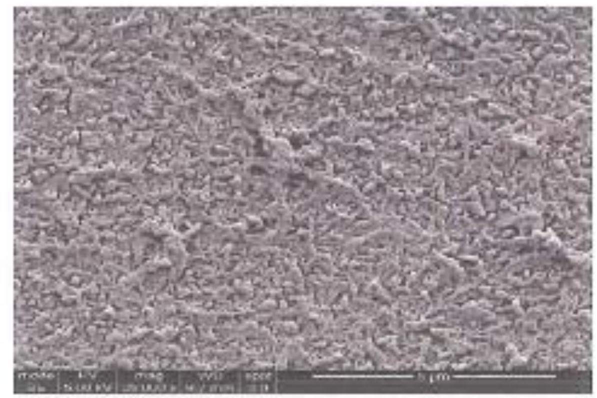
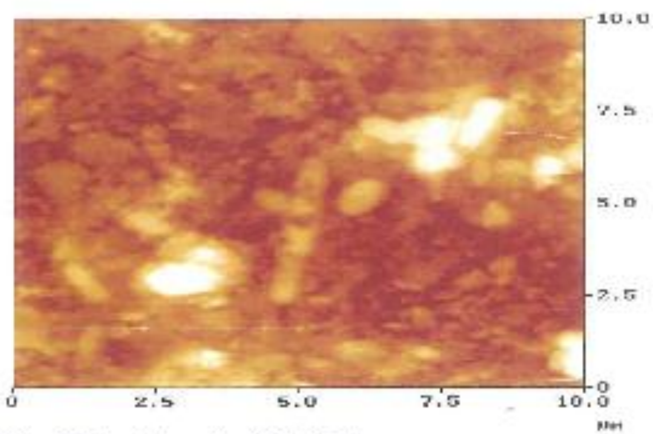
- AFM and SEM Results.

Clean and fouled SWRO membranes by raw seawater.

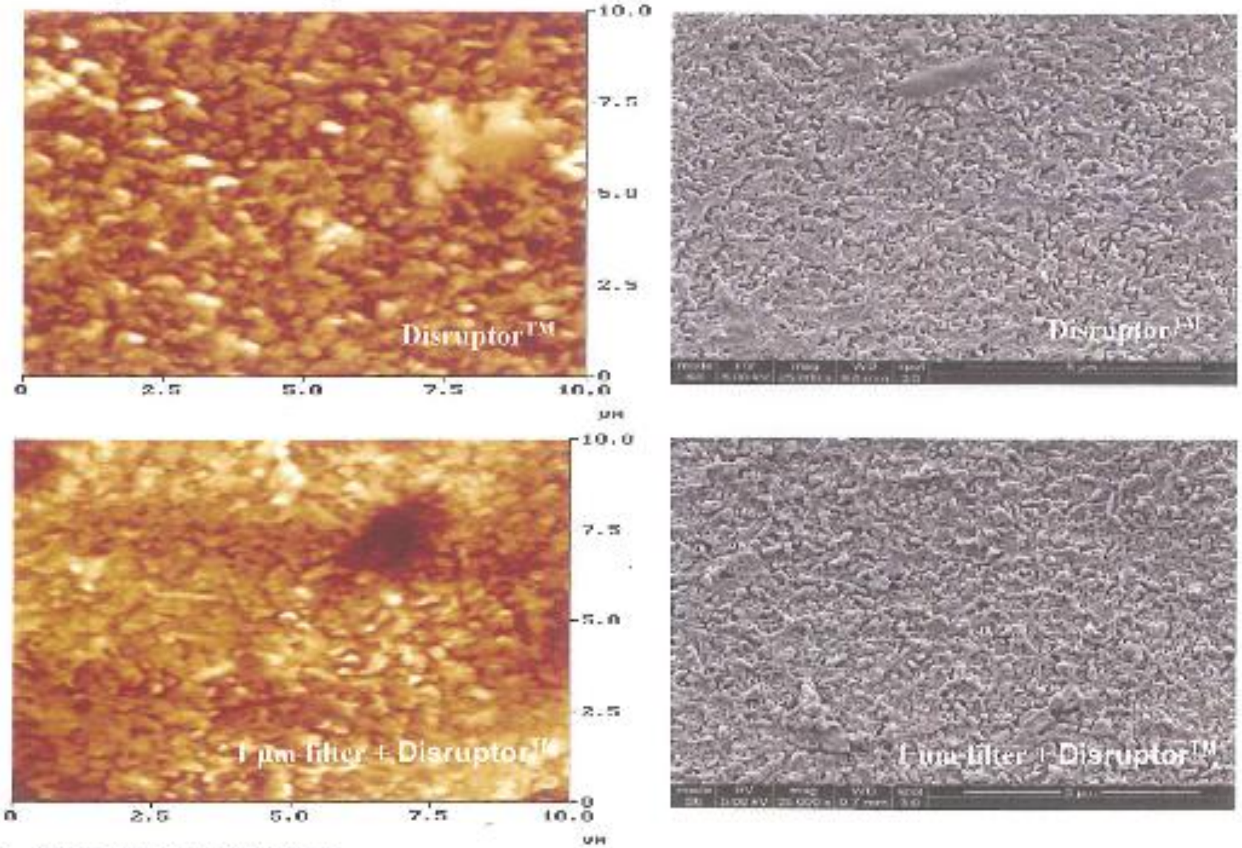






AFM and SEM Results.

Seawater pre-filtered through a Disruptor™ alone and though 1 μm filter followed by the Disruptor™.



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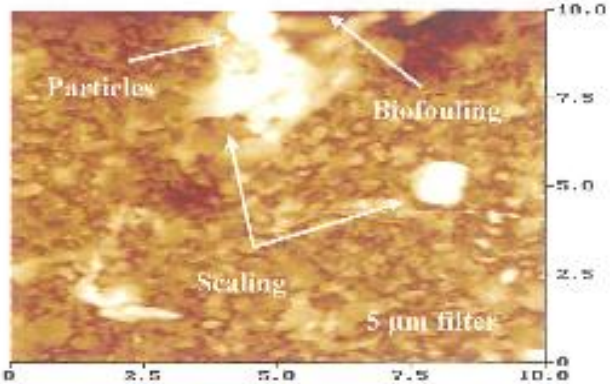
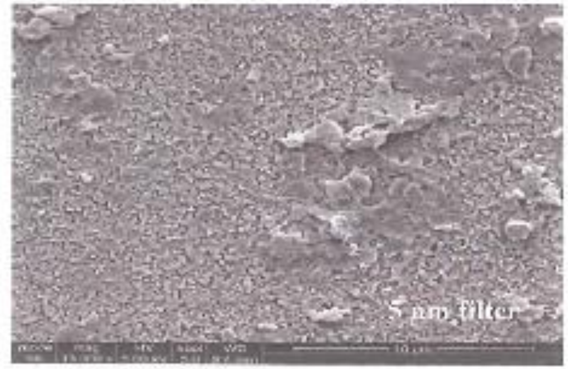
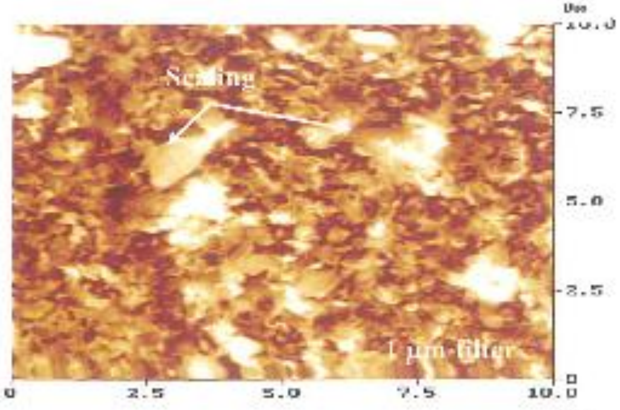
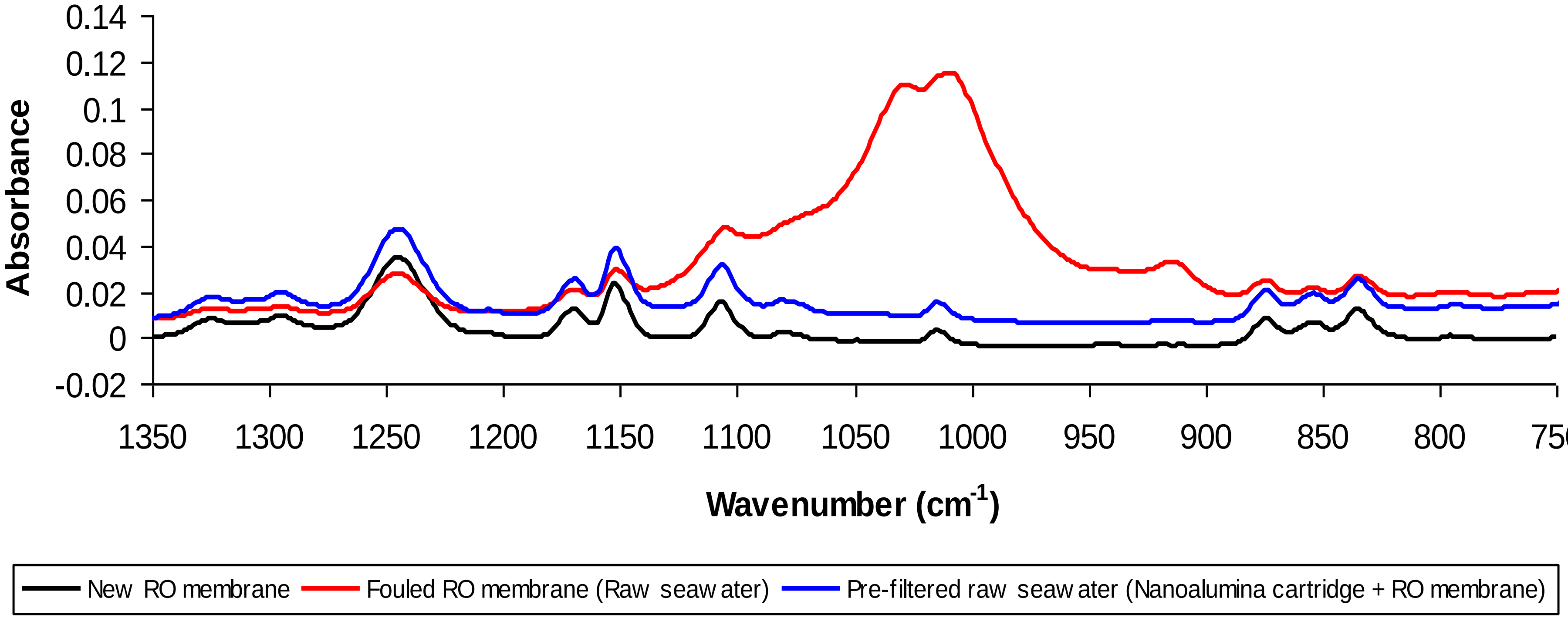
- SEM and AFM Results.
  Seawater pre-filtered through 1 μm and 5 μm filters







ATR-FTIR spectrum of RO

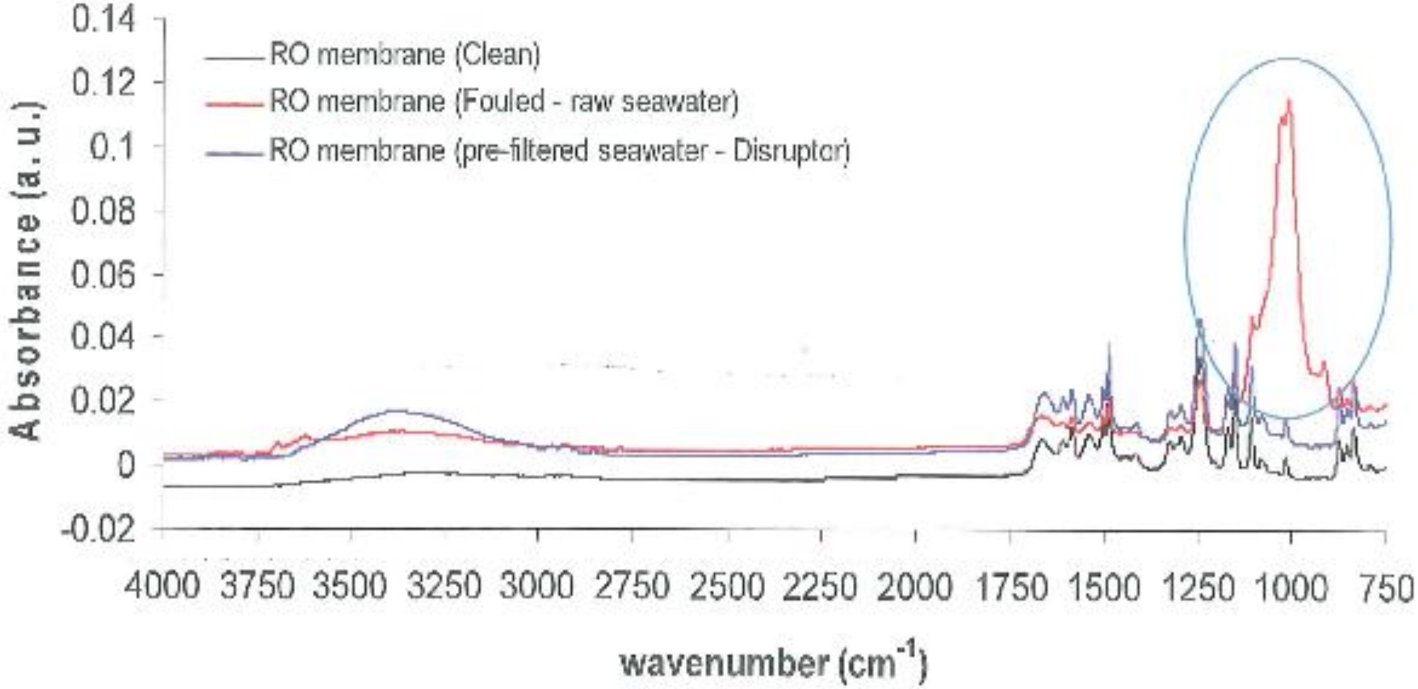


ATR-FTIR spectroscopy is a very useful tool for determining the chemical composition of the RO membrane and fouling material:

Peaks in this spectrum range indicate RO fouling is due to polysaccharides and/or silicates.

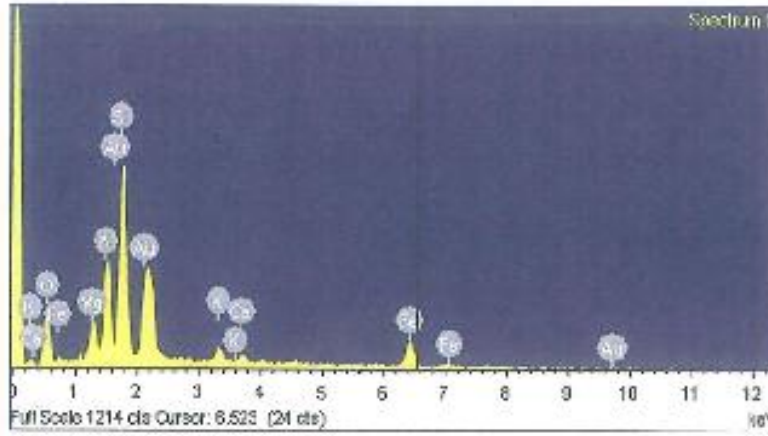
Such foulants are not seen in the spectrum of NanoCeram prefiltered RO.

ATR-FTIR Results



ATR-FTIR Results

Fouled Disruptor™	Fouled RO membrane
910	910
1003	1006
1024	1024
1400	-



- Strong absorption bands at this region (1100 – 900cm^{-1}) indicates that the major components of foulants were polysaccharides and silicates.

(Cho et al., 1998, Schmitt and Flemming, 1998, Howe et al., 2002, Park et al., 2006 and Xu et al., 2006).

- EDX results confirmed presence Si and Al in the fouling material, however these components are not present in the seawater pre-filtered through Disruptor™.

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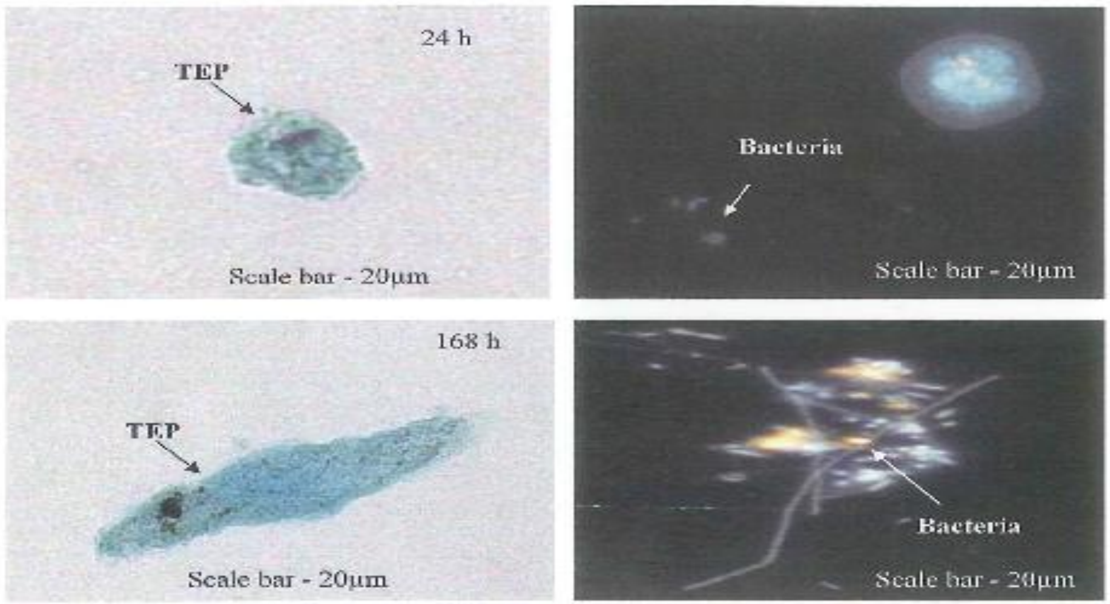
TEP Results - Raw seawater



Similar results (Berman and Holenberge 2005, Bar-Zeer, et al., 2009)

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- Transparent exopolymer particles (TEP), present in high concentrations in most sea and freshwaters, are critical agents for biofilm initiation.

- These gel-like particles ranging in size from ~2 to ~200 µm.

- TEP are mostly polysaccharide, negatively charged, very sticky and are frequently colonized by bacteria ([T. Berman]() et al. Nature Procedings (2007))

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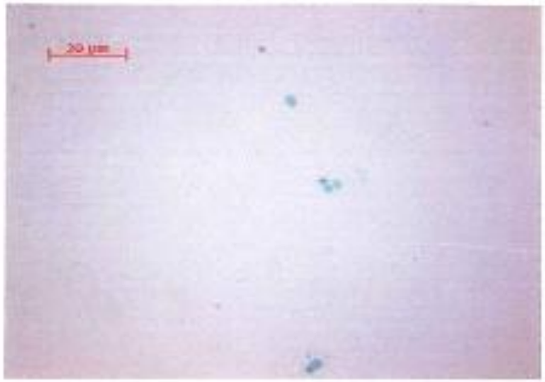
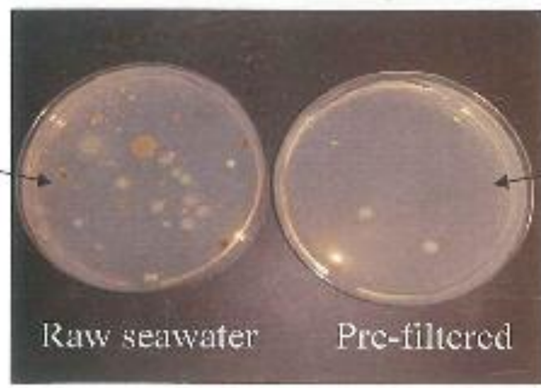
TEP Results - Seawater pre-filtered through Disruptor™



$7.8x10^2$ CFU/ml



30 CFU/ml

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▪ Conclusions

- Disruptor™ media can substantially reduce RO membrane fouling.
- High and stable permeate flux was observed after filtering untreated seawater through Disruptor™ filter media.
- AFM, SEM and ATR-FTIR results demonstrated the high removal efficiency of Disruptor™ filter media.
- The role of TEP in biofouling and biofilm development was investigated. Large sizes of TEP colonized with high number of bacteria were found on the glass slides after 168h of incubation in untreated seawater.
- Disruptor™ media can remove about 80% of TEP.
- Disruptor™ can reduce the severity of fouling in SWRO membrane systems.

ARGONIDE / TOYOTA

Electropositive Filtration Technology in Automobile Manufacturing Applications

- Dr. El-Azizi's work complements data previously reported by Argonide in collaboration with Toyota, where NanoCeram cartridges are being used for protection of RO membranes in recovering and recycling contaminated fresh water in automobile manufacture.
- In one Toyota plant, contaminated fresh water was passed through a five micron prefilter intended to protect an RO unit.
- The RO membranes became so heavily contaminated that they needed to be replaced every second or third month.
- When the five micron prefilters were replaced by a combination of a one micron depth filter, followed by the NanoCeram polishing filter, the RO membranes remained unfouled for at least one year, without requiring any cleaning.
- The payback through six months of operation exceeded 5:1 as compared to costly membrane replacements, exclusive of savings in improved water yield, elimination of cleaning chemicals and their disposal.

Toyota Water Management Group

Erlanger, Kentucky

www.toyota.com