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Membranes to Pretreat Membranes

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Presented at:

AFS Fall Conference 2015

October 6, 2015

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INTRODUCTION

Water Distribution

Although the total quantity of water on this planet is more or less fixed, its quality is deteriorating, because we have been contaminating it for thousands of years, with little concern for the consequences. The issue that confronts us is the availability of water of sufficient quality.

Below is a summary of the world's water resources:

Distribution of World Water Supply (million cubic meters)

	FRESH	SALINE	TOTAL
Rivers and streams	1.3×10^6	–	1.3×10^6
Freshwater lakes	1.3×10^8	–	1.3×10^8
Salt lakes and inland seas	–	1.1×10^8	1.1×10^8
Total surface water	$\mathbf{1.3 \times 10^8}$	$\mathbf{1.1 \times 10^8}$	$\mathbf{2.4 \times 10^8}$
Soil moisture and seepage	6.8×10^7	–	6.8×10^7
Underground water	8.5×10^9	–	8.5×10^9
Total ground water	$\mathbf{8.6 \times 10^9}$	–	$\mathbf{8.6 \times 10^9}$
Glaciers and ice caps	29.8×10^9	–	29.8×10^9
Oceans	–	$1{,}347 \times 10^9$	$1{,}347 \times 10^9$
Total world water supply	$\mathbf{38.5 \times 10^9}$	$\mathbf{1{,}347 \times 10^9}$	$\mathbf{1{,}386 \times 10^9}$

An analogy that may be a bit easier to understand is that if all the world's water were to completely fill a one gallon jug, the fresh water available for use would amount to only about one tablespoon.

Population growth and increased agricultural and industrial activities are contaminating our water supplies, while climate change, more stringent regulations and requirements for higher quality water for processing and potable applications have exacerbated the challenges.

The U.N. estimates that over ten million people a year die from drinking polluted water, mostly children.

They also state that more people die from polluted water than all forms of violence.

The uses of water in industrialized countries can be broken down as follows:

Power production	49%
Agricultural	34%
Municipal/domestic	12%
Industrial	5%

In this part of the world, the climate is arid and the supply of groundwater is limited. Therefore, the primary source of water for the above activities is desalted seawater, either thermally or with reverse osmosis. Whereas these are effective, proven technologies, they do require significant energy utilization and generally must be located close to the seawater source.

This "centralized" treatment requires storage and distribution to the water use areas, with the contaminant problems of the leaking tanks and piping and pumping energy.

Decentralized sources

"Decentralized" treatment involves recovering and treating water at its use location. For industrial plants, the concept of wastewater reuse offers significant potential to access water that would normally be discharged in accordance with possibly stringent regulations and lost forever.

This industrial wastewater may contain high concentrations of contaminants that require significant pretreatment prior to reverse osmosis (RO) processing.

In oil and gas production operations, significant quantities of "produced" water are released with the oil and gas. In the case of the "unconventional oil and gas" operations so prevalent in the U.S., the hydraulic fracturing also generates "flowback" water. Both produced and flowback water represent valuable sources of wastewater that can be treated and reused.

Technologies are now available to process and treat virtually any contaminated water source to meet any quality requirements for reuse.

Traditional Treatment Technologies

Treatment Technologies	Suspended Solids Removal	Dissolved Organic Removal	Dissolved Salts Removal	Microorganism Removal
BIOLOGICAL PROCESSES				
MBR (Membrane Bioreactor)	X	—	—	X
Activated sludge	X	X	—	X
Anaerobic digestion	X	X	—	—
Bio-filters	—	X	—	—
EXTENDED AERATION				
Bio-denitrification	—	L	—	—
Bio-nitrification	X	X	—	—
Pasveer oxidation ditch	X	X	—	X
CHEMICAL PROCESSES				
CHEMICAL OXIDATION				
Catalytic oxidation	X	X	—	X
Chlorination	X	X	—	X
Ozonation	—	L	—	X
Wet air oxidation	X	X	—	X
CHEMICAL PRECIPITATION	—	—	X	—
CHEMICAL REDUCTION	—	—	X	—
Ion exchange	—	—	X	—
Liquid-liquid (solvent)	—	—	X	—
COAGULATION				
Inorganic chemicals	X	X	—	X
Polyelectrolytes	X	X	—	X

L = under certain conditions there will be limited effectiveness

Traditional Treatment Technologies (cont.)

Treatment Technologies	**Suspended Solids Removal**	**Dissolved Organic Removal**	**Dissolved Salts Removal**	**Microorganism Removal**
ELECTOLYTIC PROCESSES				
Electrodialysis	—	—	X	L
Electrodeionization	—	—	X	—
Electrolysis	—	—	X	—
Ultraviolet irradiation	—	—	—	X
EXTRACTIONS				
INCINERATION				
Fluidized-bed	X	X	—	X
PHYSICAL PROCESSES				
CARBON ADSORPTION				
Granular activated	X	X	—	—
Powdered	X	X	—	X
SPECIALTY RESINS	—	L	L	—
FILTRATION				
Diatomaceous-earth filtration	X	—	—	X
Multi-media filtration	X	—	—	X
Micro-screening	X	—	—	X
Sand filtration	X	—	—	X
Flocculation-sedimentation	X	—	—	X
DAF (Dissolved air flotation)	X	X	—	—
Foam separation	X	—	X	—

L = under certain conditions there will be limited effectiveness

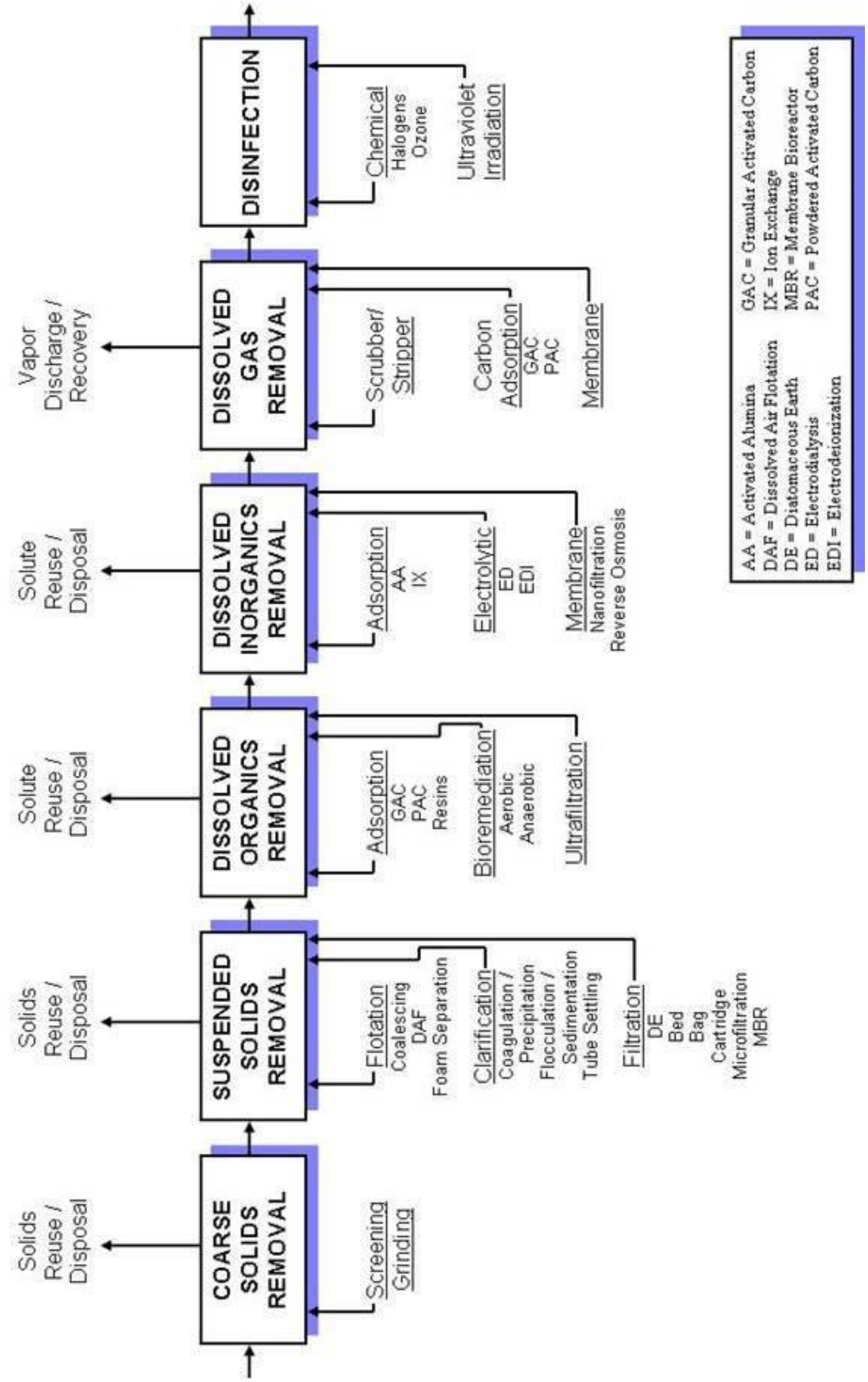
Traditional Treatment Technologies (cont.)

Treatment Technologies	Suspended Solids Removal	Dissolved Organic Removal	Dissolved Salts Removal	Microorganism Removal
MEMBRANE PROCESSES				
Microfiltration	**X**	—	—	**X**
Ultrafiltration	**X**	**X**	—	**X**
Nanofiltation	**X**	**X**	**L**	**X**
Reverse osmosis	**X**	**X**	**X**	**X**
Stripping (air or steam)	**X**	**X**	—	—
THERMAL PROCESSES				
Distillation	**X**	**X**	**X**	**X**
Freezing	—	**X**	**X**	—

L = under certain conditions there will be limited effectiveness

A summary of major industrial treatment technologies follows:

INDUSTRIAL WASTEWATER TREATMENT



As is evident from the previous illustrations, a plethora of treatment technologies is available for removing contaminants from water supplies. For water reuse in most industrial and municipal applications, the most versatile and economical technology platform consists of the four crossflow pressure-driven processes of:

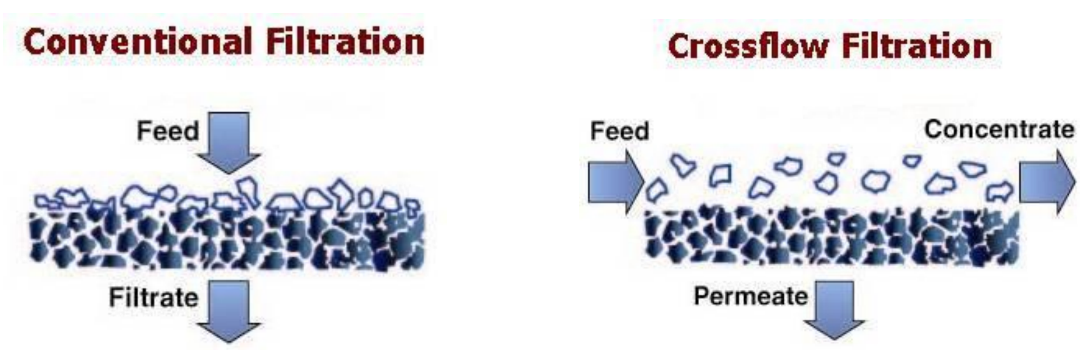
Microfiltration (MF)
Ultrafiltration (UF)
Nanofiltration (NF)
Reverse osmosis (RO)

Membrane Technologies

Membrane technologies are based on a process known as "pressure-driven crossflow" filtration, which allows for continuous treatment of liquid streams. In this process, the bulk solution flows over and parallel to the membrane surface, and because the system is pressurized, water is forced through the membrane and becomes "permeate." The turbulent flow of the bulk solution over the surface minimizes the accumulation of particulate matter.

These technologies behave differently than filters in that (with some exceptions) the feed stream is pumped at a high flow rate across the surface of the filter media (membrane), with a portion of this stream forced through the membrane to effect separation of the contaminants, producing the permeate, and the concentrated contaminants remaining in the other stream (concentrate) exit the membrane element on a continuous basis. The figure below compares conventional with crossflow filtration.

The following figure compares conventional with crossflow filtration.



Conventional vs. Crossflow Filtration

Crossflow filtration offers the following advantages over conventional filtration technologies:

- Continuous and automatic operation.
- Capable of removing contaminants down into the submicron size range
- Usually requires no chemical addition.
- Some have backwashing capabilities.
- Generally can operate in turbulent flow conditions.
- Systems have a very small footprint.
- Low energy – do not involve a phase change.

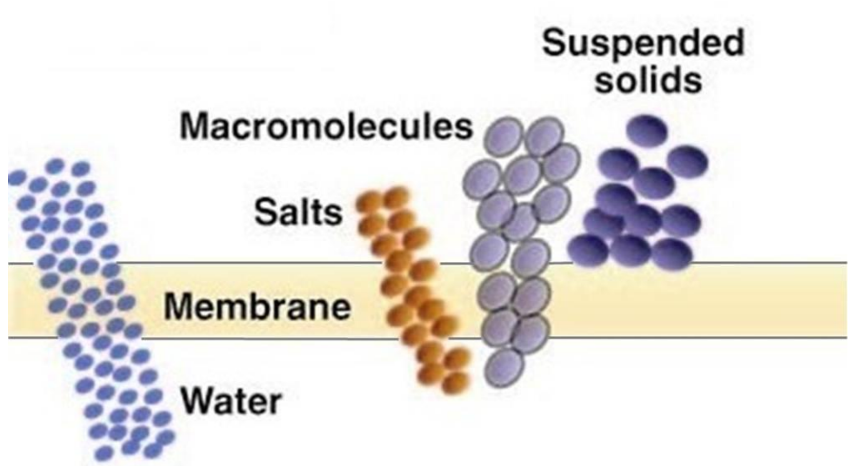
It is important to note that whereas with the media, cartridge and bag filtration technologies, the filtration process must be halted to backwash or replace the medium, crossflow filtration is designed to operate continuously, with the concentrate stream carrying away the contaminants. On the other hand, these membranes eventually do become fouled and usually require backwashing, cleaning, or some other process to remove foulants.

These technologies are described as follows:

<u>Microfiltration (MF)</u> – is typically used to remove particulate material in the submicron range. Most microfiltration devices in use today are designed as cartridge filters in that the entire solution passes through the filter leaving the particulate material behind, either on the filter surface or down inside the filter medium. The microfiltration devices addressed here use the "crossflow" design, which produces two exiting streams: one which has passed through the membrane media and is purified (permeate), and the other which flows across and parallel to the media surface, continuously removing the contaminants (concentrate).

Generally, microfiltration involves the removal of particulate, or suspended materials ranging in size from approximately 0.10 to 1.0 microns (100 to 1,000 nm). MF typically operates within a pressure range of 10 to 30 psi (0.68 to 2.0 bar).

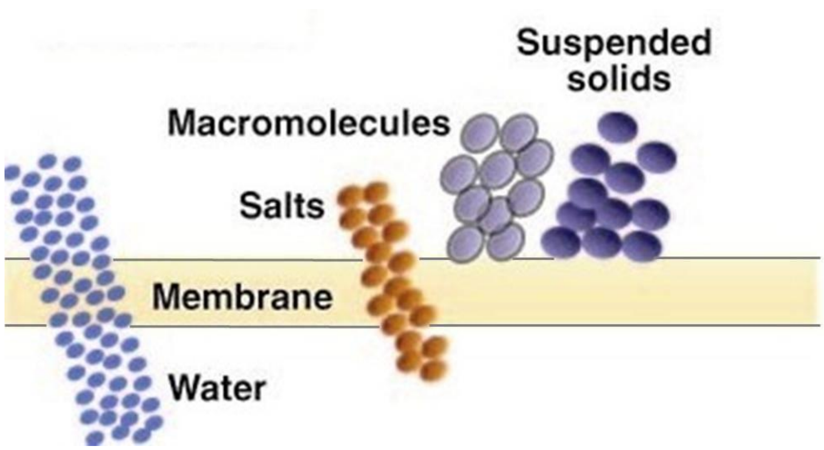
MF is depicted below.



Microfiltration

Ultrafiltration (UF) - is used to separate dissolved, non-ionic materials (macro molecules) typically smaller than 0.10 micron (100 nm). The removal characteristics of UF membranes can be described in terms of "molecular weight cutoff" (MWCO), the maximum molecular weight of dissolved compounds that will pass through the membrane pores. MWCO terminology is expressed in Daltons. Basically, ultrafiltration is used to remove dissolved organic contaminants, while suspended solids are removed by microfiltration. UF normally operates in a pressure range of 10 to 100 psi (0.68 to 6.8 bar). UF membranes are available over a wide range of MWCO removal properties, from about 1,000 to over 100,000 Daltons.

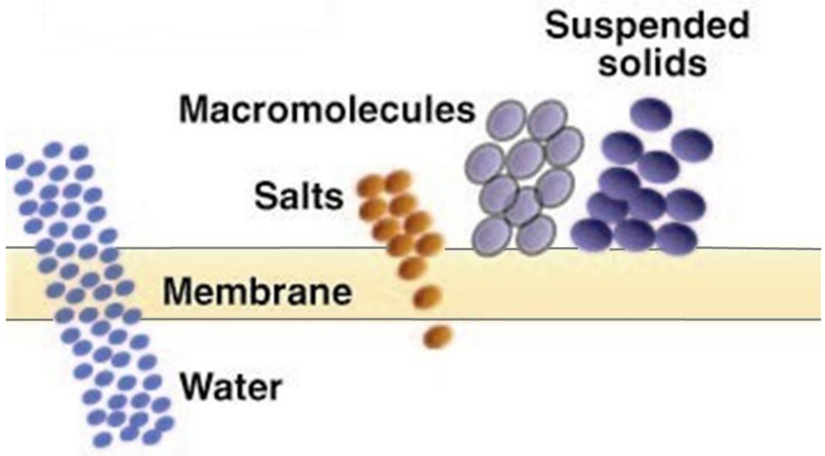
UF technology is illustrated below.



Ultrafiltration

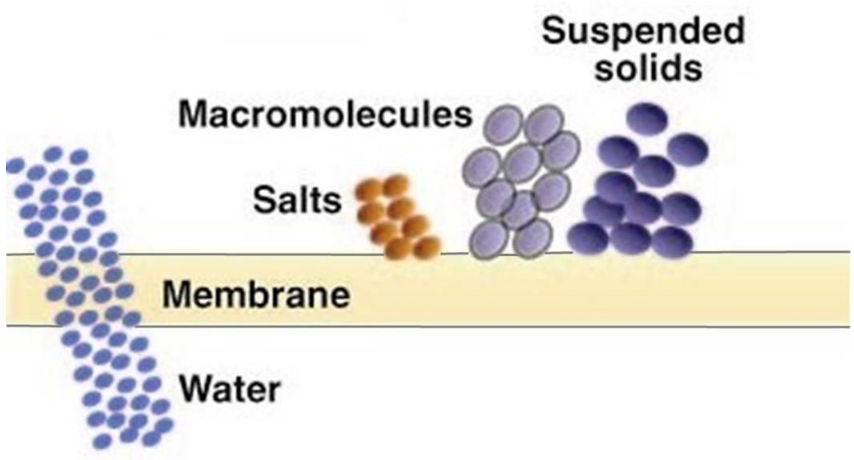
The above processes (MF and UF) separate contaminants based on a "sieving" process; that is, any contaminant too large to pass through the pore is rejected and exits in the concentrate stream.

Nanofiltration (NF) - can be considered "loose" reverse osmosis. It rejects dissolved ionic contaminants but to a lesser degree than RO. NF membranes reject a higher percentage of multivalent salts than monovalent salts (for example, 99% vs. 20%). These membranes have molecular weight cut-offs for non-ionic solids below 1000 Daltons. NF is illustrated below.



Nanofiltration

Reverse osmosis (RO) - produces the highest quality permeate of any pressure driven membrane technology. Certain polymers will reject over 99% of all ionic solids, and have molecular weight cut-offs in the range of 50 to 100 Daltons. RO is illustrated below.



Reverse Osmosis

Both NF and RO membranes reject salts utilizing a mechanism that is not fully understood. Some experts endorse the theory of pure water preferentially passing through the membrane; others attribute it to the effect of surface charges of the membrane polymer on the polarity of the water. Monovalent salts are not as highly rejected from the membrane surface as are multivalent salts; however, the high rejection properties of the newer thin film composite RO membranes exhibit very little differences in salt rejection characteristics as a function of ionic valance. As indicated earlier, this difference is significant with NF membranes.

In all cases, the greater the degree of contaminant removal, the higher the pressure requirement to effect this separation. In other words, reverse osmosis, which separates the widest range of contaminants, requires an operating pressure typically an order of magnitude higher than microfiltration, which removes only suspended solids.

The water passage rate through the membrane to generate treated water (permeate), is know as “flux rate”. It is a function of applied pressure, water temperature, and in the case of NF and RO (and to a limited extent, UF), the osmotic pressure of the solution under treatment. Flux rate is usually measured as GFD (gallons per square foot per day) or LMD (liters per square meter per day).

Increasing the applied pressure will increase the permeate rate; however, a high flow of water through the membrane will promote more rapid fouling. Membrane element manufacturers usually provide limits with regard to maximum applied pressures to be used as a function of feed water quality.

Heating the water will also increase the permeate rate, but this requires significant energy and is generally not considered practical.

The following table summarizes the various properties and other features of these technologies.

Membrane Technologies Compared

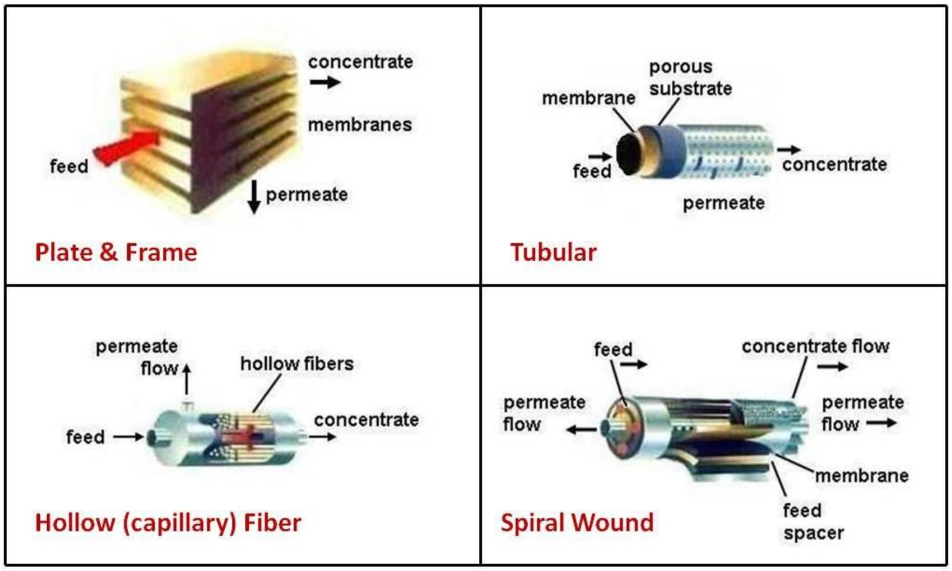
Feature	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
Materials of Construction	Ceramics, Sintered metals, Polypropylene, Polysulfone, Polyethersulfone, Polyvinylidene fluoride, Polytetrafluoroethyliene	Ceramics, Sintered metals, Polypropylene, Polysulfone, Polyethersulfone, Polyvinylidene fluoride	Thin film composites, Cellulosics	Thin film composites, Cellulosics
Pore Size Range (micrometers)	0.1 - 1.0	0.001 - 0.1	0.0001 - 0.001	<0.0001
Molecular Weight Cutoff Range (Daltons)	>100,000	1,000 - 100,000	300 - 1,000	50 - 300
Operating Pressure Range	<30	20 - 100	50 - 300	225 - 1,000
Suspended Solids Removal	Yes	Yes	Yes	Yes
Dissolved Organics Removal	None	Yes	Yes	Yes
Dissolved Inorganics Removal	None	None	20-95%	95-99+%
Microorganism Removal	Protozoan cysts, algae, bacteria*	Protozoan cysts, algae, bacteria*, viruses	All*	All*
Osmotic Pressure Effects	None	Slight	Moderate	High
Concentration Capabilities	High	High	Moderate	Moderate
Permeate Purity (overall)	Low	Moderate	Moderate-high	High
Energy Usage	Low	Low	Low-moderate	Moderate
Membrane Stability	High	High	Moderate	Moderate

** Under certain conditions, bacteria may grow through the membrane.*

Device Configurations

To be effective, membrane polymers must be packaged into a configuration commonly called a "device" or "element". The most common element configurations are: Plate & Frame, Tubular, Hollow (capillary) Fiber, and Spiral Wound.

The element configurations are described and illustrated below.



Membrane Element Configurations

Plate & Frame. Sheet membranes are stretched over a frame to separate the layers and facilitate collection of the permeate, which is directed to a collection tube. This device can be compared in construction to a filter press.

Tubular. Manufactured from ceramics, carbon, stainless steel, or a number of thermoplastics, these tubes have inside diameters ranging from ¼ inch up to approximately 1 inch (6 to 25 mm). The membrane is typically coated on the inside of the tube and the feed solution flows under pressure through the interior (lumen) from one end to the other, with the permeate passing through the wall and collected outside of the tube.

Hollow (Capillary) Fiber. These elements are similar to the tubular element in design, but are smaller in diameter, and are usually unsupported membrane polymers or ceramics. In the case of polymeric capillary fibers, they require rigid support on each end provided by an epoxy "potting" of a bundle of the fibers inside a cylinder. Feed flow is either down the interior of the fiber ("lumen feed") or around the outside of the fiber ("outside-in").

Spiral Wound. This element is constructed from an envelope of two membrane sheets wound around a permeate tube that is perforated to allow collection of the permeate. Water is purified by passing through one layer of the membrane and, following a spiral path, flows into the permeate tube. It is by far the most common configuration in water purification applications, but generally requires extensive pretreatment in wastewater applications.

From the perspective of cost and convenience, it is beneficial to pack as much membrane area into as small a volume as possible. This is known as "packing density". The greater the packing density, the greater the membrane area enclosed in a certain sized device, and generally the lower its cost. The downside of the high packing density membrane elements is their greater propensity for fouling. The following table compares the element configurations with regard to their packing densities.

Membrane Element Configuration Comparison

Element Configuration	Packing Density *	Fouling Resistance **
Plate & Frame	Low	High
Tubular	Low	Very High
Hollow (Capillary) Fiber	High	Medium
Spiral Wound	Medium	Low

** Membrane area per unit volume*
*** Tolerance to suspended solids*

To illustrate the membrane materials used for the various element configurations, the following tables are provided. As new materials are constantly being introduced, these tables are subject to frequent updating.

Microfiltration (MF) & Ultrafiltration (UF)

Materials of Construction	Device Configuration: Hollow Fiber	Tubular	Plate & Frame	Spiral Wound
Polymeric				
PS	X	X	X	X
PES	X	X	X	X
PAN	X	X	X	X
PE	–	X	–	–
PP	X	X	X	–
PVC	–	X	–	–
PVDF	X	X	–	–
PTFE	X	–	X	–
PVP	X	X	–	–
CA	X	–	–	–
Non-Polymeric				
Coated 316LSS	–	X	–	None
a- Alumina	–	X	X	None
Titanium Dioxide	–	X	–	None
Silicon Dioxide	–	X	–	None

PS = Polysulfone
PES = Polyethersulfone
PE = Polyethylene
PP = Polypropylene
PAN = Polyacrylonitrile
PVDF = Polyvinylidene Fluoride
PTFE = Polytetrafluoroethylene
CA = Cellulose Acetate
PVP = Polyvinylpyrrolidone
TF = Thin Film Composite

Nanofiltration (NF) & Reverse Osmosis (RO)

Materials of Construction	Device Configuration: Hollow Fiber	Tubular	Plate & Frame	Spiral Wound
Polymeric				
PS*	–	X	X	X
PES*	–	X	X	X
CA	–	X	X	X
TF	–	X	X	X
Non-Polymeric				
None				

** Base polymer below TF polymer*

PS = Polysulfone
PES = Polyethersulfone
CA = Cellulose Acetate
TF = Thin Film Composite

Note that to date, no commercially available salts rejecting NF or RO hollow fiber device is available.

FOULING

Without a doubt, the greatest operational issue in membrane technology is fouling. Membrane fouling is caused by the accumulation of "rejected" materials on or in the membrane surface. These materials include suspended solids (inorganic and organic), dissolved solute (inorganic salts and organic molecules) and microorganisms. In actuality, microorganisms are suspended solids, but are considered a separate category because they are comprised of living organisms, and bacteria are capable of producing biofilms, considered by many to be the single most significant foulant.

It is important to remember that although these membrane technologies operate in a crossflow mode where the bulk of the fluid moves across and parallel to the membrane surface, the "purification" process involves passage of a portion of the stream through the membrane in a process not unlike filtration. Because of the drag effect of the membrane surface on the parallel flow of the fluid, on a molecular scale, there is no flow at the membrane surface. This produces a stagnant layer on the surface.

The actual thickness of this stagnant layer depends on surface roughness, degree of turbulence, charge on the membrane surface, membrane "wettability," and other factors, but it is in this layer that some of the foulants that are rejected accumulate and build up over time.

The actual mechanisms of fouling are numerous and there is a lack of universal agreement on them, but the consensus appears to be these:

1) Cake formation from suspended solids accumulation.
2) Precipitation of compounds resulting from concentrations beyond solubility limits (e.g. $CaCO_3$, $CaSO_4$, $BaSO_4$, etc.).
3) Organic adsorption on membrane surface.
4) Bacterial biofilm formation on membrane surface.

By accurately identifying those contaminants in a feedwater stream that could foul a membrane and by designing a prefiltration or pretreatment scheme to specifically remove them, it is possible to significantly reduce the fouling potential of a given water supply.

The initial activity here is to obtain a thorough water analysis, which not only identifies all of the chemical components, such as ionic and organic constituents, but also addresses suspended solids, and, if necessary, even the particle-size ranges of these suspended solids.

The downside to these pretreatment technologies is that most are batch operations, in that once the prefiltration technology has reached its capacity for contaminant removal, it must be taken offline, discarded or otherwise treated to restore (or replace) its capabilities.

Because of the extreme value of backwashing/backpulsing to minimize the effects of fouling on membrane surfaces, the following chart categorizes membrane devices with this capability.

Backwashing

Membrane Element Cleaning Capability

Element Configuration	Membrane Technology				Backwashable?
	MF	UF	NF	RO	
Plate & Frame	Yes	Yes	Yes	Yes	No (except for inorganic membrane)
Tubular	Yes	Yes	Yes	Yes	Yes
Hollow Fiber	Yes	Yes	Yes	No	Yes
Spiral Wound	Yes	Yes	Yes	Yes	No (NF, RO) Yes (MF, UF)

Note that no RO or NF spiral membrane can be backwashed.

Spiral Wound Elements

In applications where salts removal are required, NF and RO technologies are leading choices. For these technologies, with almost no exception, the device configuration is spiral wound. The reason is primarily economics; this configuration is significantly less expensive in capital cost than the others. On the other hand, the weakness of this configuration is its susceptibility to fouling. The close spacing and inability to be backwashed exacerbate this problem.

A number of processes have been employed to treat spiral membranes "in situ," without resorting to extensive CIP cleaning. These include "forward flushing," running feedwater across the membrane surface under low recovery operation to utilize high water velocity to remove foulants, and "direct osmosis," which involves feeding a plug of high salinity water into the membrane to use osmosis to force permeate back through the membrane to dislodge fouling materials back up into the feed stream. These processes have their own operational issues, but have experienced some success.

THE SAUDI SITUATION

In this country, the vast majority of water for municipal and industrial applications is desalted seawater. Because reverse osmosis is becoming the major desalination technology, pretreatment of these spiral wound membranes is high priority. In the past, traditional technologies such as coagulation/clarification and media filtration have been employed, but the increased development of MF and UF membrane technologies, coupled with their vastly superior filtration capabilities, have resulted in a paradijm shift towards membranes protecting membranes.

From a capital and operating cost perspective, there is evidence that MF/UF membranes are becoming more competitive, particularly when factoring in the increasing chemical and labor costs associated with frequent cleaning of the spiral membranes.

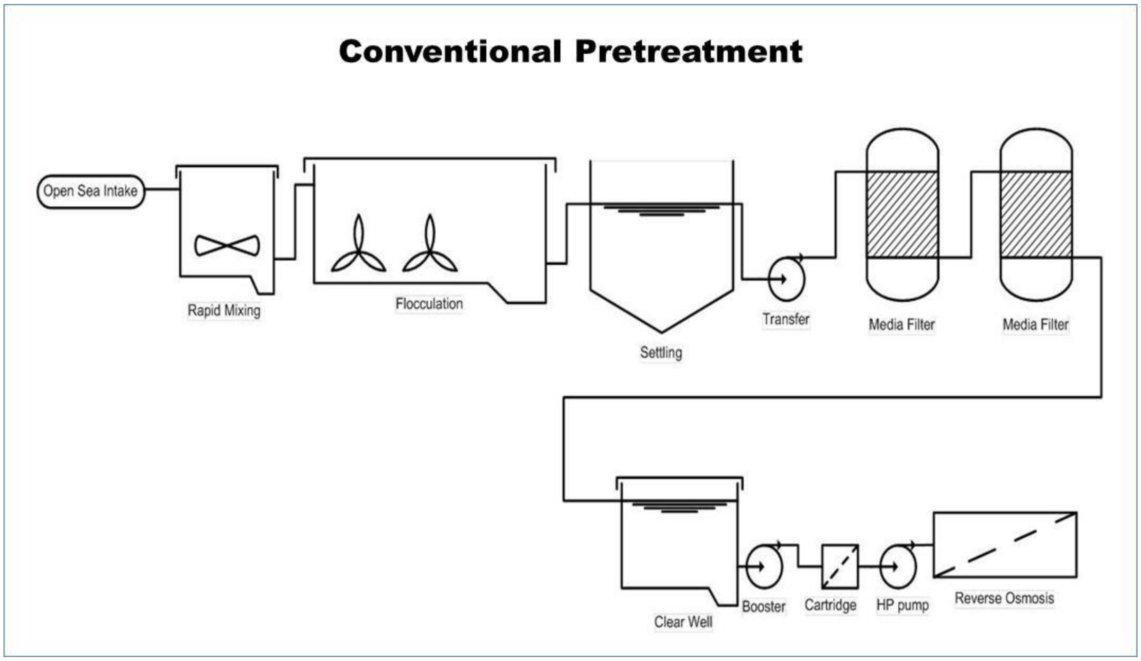
So, now that we have established that membrane elements require significant pretreatment to minimize fouling and make their operation more manageable, are there examples of MF/UF membranes employed for this purpose in the Middle East?

Yes, there are.

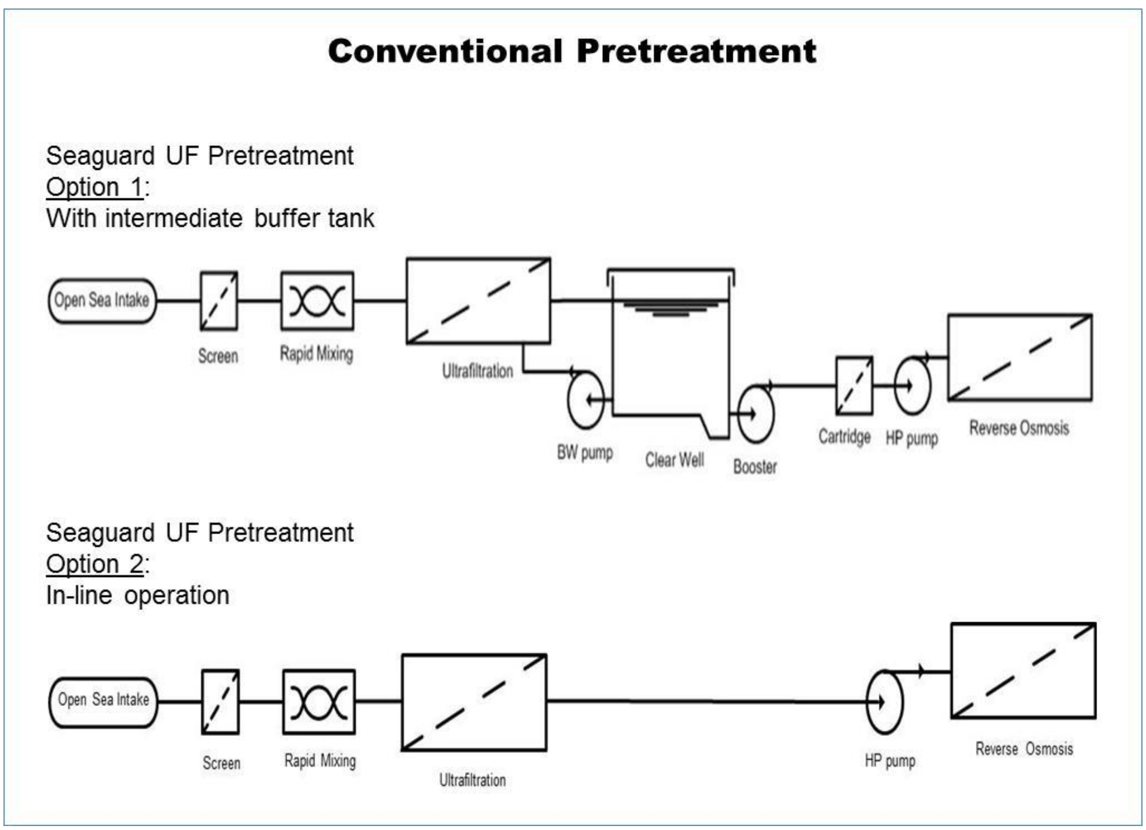
One example is the Al-Jubail SWRO Plant Phase II. This system has been in operation since 2013 and is utilizing multimedia filtration followed by Pentair X-Flow Seaguard UF membranes, prior to the RO membranes. The total permeate rate is 10,000 m^3/hr. (63 MGD).

Another example is the Marafiq SWRO Plant, under construction, also in Al-Jubail. This facility will also use the Pentair X-Flow Seaguard membranes. The pretreatment to this UF system is DAF (dissolved air flotation). The total production rate is 18,750 m^3/hr. (119 MGD), and is expected to be completed this year.

To put MF/UF pretreatment into perspective, the following illustrations show the traditional technologies (coagulation/flocculation followed by media filtration) as compared to the membrane approach.



Conventional Pretreatment
Open Sea Intake
Rapid Mixing
Flocculation
Settling
Transfer
Media Filter
Media Filter
Clear Well
Booster
Cartridge
HP pump
Reverse Osmosis



Conventional Pretreatment
Seaguard UF Pretreatment
Option 1:
With intermediate buffer tank
Open Sea Intake
Screen
Rapid Mixing
Ultrafiltration
BW pump
Clear Well
Booster
Cartridge
HP pump
Reverse Osmosis
Seaguard UF Pretreatment
Option 2:
In-line operation
Open Sea Intake
Screen
Rapid Mixing
Ultrafiltration
HP pump
Reverse Osmosis

The specific membrane in the above examples is the Pentair X-Flow Seaguard 64 module, and an illustration of it is below.

Seaguard 64 Module

Mdule type	Hydraulic membrane diameter	Recovery	Permeate Silt Density index	Permeate turbidity
	[mm/mil]			
Seaguard 64	0.8 [31]	90-98%	< 3	< 0,1 NTU

MATERIALS OF CONSTRUCTION

Housing	: PVC grey
Flow distributor	: PVC/PP
Potting	: PU resin
Membrane	: PES/PVP

CONCLUSIONS

The field of MF/UF membranes is growing rapidly, and as the benefits of this approach are realized, more manufacturers' products will be evaluated and employed as pretreatment technologies.

It is important to emphasize that, depending on the chemistries and concentration of contaminants in the feed water supply, pretreatment to the MF/UF membranes may be required. The key is to ultimately select the total pretreatment combination of technologies that effectively and economically removes feedwater contaminants to ensure optimum operation of the reverse osmosis system.