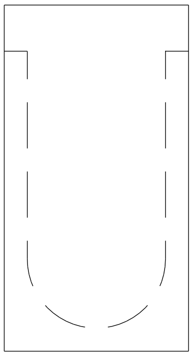

Introduction to PRETREATMENT of Feed Streams Prior to Membrane Filtration

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Introduction

Pretreatment prior to membrane filtration is extremely important and the nature and thoroughness of the pretreatment is, in many cases, determining the overall plant performance.

Two facts should be kept firmly in mind when deciding pretreatment strategies:

a. "Membranes do not lie." This means that membranes do exactly what they are able to do under the given circumstances. If the membrane and the raw feed stream are not compatible and the membrane does not perform to expectations, then it is not a fault or deficiency of the membrane.

b. "Membranes are designed to reject dissolved solids." *This was true until membranes started to be used in MBRs.*. Most membrane systems work very poorly if the feed contains a substantial amount of suspended solids or if solids precipitate during the process of membrane filtration. A main objective of the pretreatment is therefore to ensure that the feed does not contain disturbing amounts of suspended solids or species which may precipitate, for instance due to an increase in concentration during the process.

This paper does by no means claim to give more than an introduction to pretreatment. You will not find engineering details. The objective of this paper is to point out a number of things which may be troublesome and it is not intended to be a "cookbook" for pretreatment. It is the plant producer or plant operator which must make sure that pretreatment is done thoroughly, correctly and according to the guidelines of this book.

All good principles for pretreatment of the feed to membrane filtration equipment can be condensed into three rules of which rule number 3 applies to pretreatment as well as operation of the plant. If these rules are followed the chances for good plant performance improve dramatically.

- **Remove harmful suspended solids.**
- **Remove oxidizers (prior to thin fim membranes).**
- **Prevent precipitation in the plant.**

Pretreatment Methods and Strategies

Pretreatment strategies may have widely varying purposes, and sometimes they are aimed toward completely opposing goals. See table 1.

Table 1. Pretreatment	
Increasing solubility	pH, temperature, complexing
Decreasing solubility (cause crystallization)	Controlled crystallization to produce micro crystals, e.g. by heat-and-hold.
Retard crystallization	Using an anti-scaling agent
Removing solutes with low solubility	Using ion exchange media, e.g. Ca - Na exchange.
Removing suspended solids	Applying filters, centrifuges/decanters, precipitation, sedimentation, flotation
Removing organic solvents	Distillation
Reduction of heavy metals oxidizing of heavy metals	$Cr^{+6} \rightarrow Cr^{+3}$ $Fe^{+2} \rightarrow Fe^{+3}$ followed by precipitation as hydroxide
Killing microorganisms	Pasteurization, sterilization and chemical treatment. Whenever possible remove the dead micro-organisms.
Secure high concentration of one strain of microorganisms	Fermentation of egg white
Removing dissolved organic solids prior to reverse osmosis	Use nanofiltration or ultrafiltration, e.g. to remove humic acid or dissolved mineral oil

Suspended solids in the feed is a very difficult problem to handle. Conventional filtration is by far the most common pretreatment method. Centrifugation is used to some extent, foremost in the dairy industry.

Microorganisms present a special problem. No matter if they are dead or alive they can foul membranes. Alive, the fouling can be caused by the microorganism itself, by its metabolic products or by its interaction with material in the feed solution. Dead, the cell debris, mainly the cellular membrane, can cause fouling. Removing cell debris and metabolites from a feed stream can be surprisingly difficult, and the various materials from the cell are often very resistant to oxidizing and high-pH environments.

Table 2 present an overview of the most common materials found on the surface of membranes.

Table 3 and 4 present an overview of the most common methods used in pretreatment. Although the array of pretreatment methods is quite impressive the number of methods commonly used is small. A consequence of this is, that if you need to pretreat a product not mentioned here, there is a good chance that you can find a similar product and use the same pretreatment. So although the subjects in this paper is mentioned after industry they could just as well have been listed according to product type.

Examples

Protein	cheese whey, milk (cow, goat, horse, buffalo), soy protein, pea protein, enzymes, egg white, blood plasma, fish stick water and gelatin
Polysaccharide	carrageenan, pectin, agar, guar gum, xantan
Fruit juice	apple juice, pear juice, pineapple juice

Table 2. Materials interfering with membranes				
Interfering Materials	In-organic	Organic	Biomass	Fibers
Acid	X			
Algae			X	
Aluminum hydroxide ($Al(OH)_3$)	X			
Aluminum oxide (Al_2O_3)	X			
Bacteria			X	
Barium sulphate ($BaSO_4$)	X			
Calcium carbonate ($CaCO_3$)	X			
Calcium phosphate ($CaHPO_4$)	X			
Cations		X		
Chalaza		X		
Chromium+3 ($Cr(OH)_3$)	X			
Dyeing, polyamide, polyester, cotton		X		X
Fat		X		
Fibers (textile)		X		X
Filter aid	X			
Fines (fruit, cheese, casein, etc)		X		X
Flies			X	
Flocculating agents		X		
Grass			X	X
Grease		X		
Hair			X	X
Humic acid		X		
Husks			X	
Iron hydroxide ($Fe(OH)_3$)	X			
Latex		X		
Magnesium carbonate ($MgCO_3$)	X			
Manganese ($Mn(OH)_2$)	X			
Medium density fiberboard		X		X
Metal filings	X			
Oil		X		
Paint		X		
Paper machine effluent	X	X		X
Protein		X		
Pulping effluents	X	X		X
Sand	X			
Silica (SiO_2)	X			
Silicon oil	X			
Silt	X			
Solvents		X		
Strontium sulphate ($SrSO_4$)	X			
Yeast			X	
Zinc	X			

Table 3. Pretreatment Methods - 1				
	Physical	Chemical	Thermal	Electrochemical
Centrifuge / decanter	X			
Complexing		X		
Dissolved air flotation	X			
Electro flocculation		X		X
Filter	X			
Flocculation		X		
Heat-and-Hold	X		X	
Membranes (UF, NF, MF)	X			
Ozone, Cl_2		X		
Pasteurization			X	
pH		X		
Sedimention	X			
Distillation	X			
Temperature change			X	
UV				X

The term FILTER mans several different types of filters. Traditionally they are dead end filters but cross flow filters exists. The most common types of filters used in connection with membrane filtration systems are cartridge filter, bag filter, sand filter, moving band filter and precoat filter.

Table 4. Pretreatment Methods - 2					
	Dairy	Food	Waste water	Drinking water	Process water
Centrifuge / decanter	X	X			X
Complexing				X	
Dissolved air flotation			X		X
Electro flocculation			X		
Filter	X	X	X	X	X
Flocculation			X		
Heat-and-Hold	X				
Membranes (UF, NF, MF)				X	X
Ozone, Cl_2				X	
Pasteurization					
pH	X	X			
Sedimention			X		
Distillation		X			X
Temperature change	X	X	X		X
UV				X	
UV + H_2O_2			X		

Simple pre-filtration rules

Spiral Wound elements

Spacer thickness (nominally)		Max. prefilter pore size	
mil	mm	Micron	mm
30	0,76	10	0,01
50	1,20	100	0,10
80	2,03	200	0,20

In other words: Filter pore size shall/can be 10% of the spacer height.
Valid for a process element.
Info Dan Combstock. Fax of 19900605

Other elements

Other element types have different rules.

- **Fiber systems** (1 - 2 mm fibers) with *dirty product inside the fibers* are quite tolerant to small size suspended solids since they can be back-flushed. Pressure is driving force. Can also be cleaned chemically. Ceramic membranes belong to this group of membrane systems.
- **Fiber systems** (1 - 2 mm fibers) with *dirty product outside the fibers* are extraordinarily tolerant to suspended solids. Vacuum is driving force. Cleaned by back-flush (maybe with chemicals) and by constant scouring with air.
- **Tubular systems** (21 - 25 mm ID) can take huge loads of suspended solids and can even take fibers without plugging. Pressure is driving force. They rely on chemical and/or mechanical cleaning. Can not be back-flushed. Sintered stainless steel belong to this group of membrane systems.
- **Plate and frame systems** is a mixed bag of equipment. Tolerance is better than spirals and worse than fibers. They can most often not be back-flushed. Pressure is driving force. Must be cleaned chemically.

Algae, Bacteria, Yeast, Vira

As a general rule, the count should be less than 100 per ml. Sometimes as little as 10 per ml can be problematic and sometimes 10^8 per ml does not represent a problem. An experienced application engineer should be consulted. Experience and experiments are the only methods to decide on adequate pretreatment.

Heat treatment or chlorination followed by conventional filtration are methods that are used with some success.

Biofouling

Biofouling is a term used to describe deposits of microbes, bacteria, yeast, cell debris or metabolic products. Biofouling is far from well defined and, however it is defined, general experience bears out that it is usually difficult to remove. The only pretreatment that really helps is to ensure that the feed product has a very low cell count, and that the membrane filtration equipment is operated at a bacteriologically safe temperature.

Several pretreatment strategies will achieve the goal of inhibiting or arresting microbial growth for as long as the treatment is ongoing but leaves the liquid open to continued bacterial growth once the treatment stops. However, there are two exceptions to this rule.

1. Addition of harsh chemicals, e.g hypochlorite in concentrations which leaves an excess of the chemical in the feed to ensure continued growth prevention.
2. Heat to and operate at 75°C or higher. This strategy is not generally used at this time, except for a few systems producing high purity water, treating pulp and paper effluent and for evaporator condensate.

Blood plasma

Blood is a by-product from every slaughterhouse. In some cases it is simply discharged to the sewage system, in others is collected, mixed with other waste and dried at very high temperature. There is a small market for good quality blood products.

Blood does not coagulate if there is little or no calcium available, and coagulation of blood can be prevented by addition of a complexing agent for calcium. It is most common to add **sodium citrate**, but **sodium phosphate** is also used. Addition of citrate and phosphate is essential pretreatment if membranes shall be used to treat blood. The blood should be drawn in a way which secures that there is no contamination. Citrate or phosphate must be added immediately during drawing blood. The blood should be processed immediately.

Whole blood is difficult to treat with membranes. It is common to remove the **red blood cells** from whole blood by centrifugation. It is essential that the centrifugation process is relatively gentle in order to prevent rupturing the cells, which will release hemoglobin into the plasma and complicate the membrane filtration process and subsequent cleaning of the equipment difficult. The quality of blood plasma is considered to be low if there is too much color from hemoglobin.

Carrageenan

This product is extracted from seaweed at very high pH and contains a high level of suspended solids.

It is common and mandatory to perform a prefiltration, most often with precoat filters prior to ultrafiltration. The prefiltration step removes a certain amount of protein and color together with suspended solids. The use of filter aid make a security filter before the UF system mandatory. If a breakthrough of filter aid occurs, the security filter will be blocked which is better than blocking the membrane filtration equipment.

The filters normally used have a nominal pore size of 200µ. In reality the resulting filtration is better because the filter rapidly blocks up. This result is still a far cry from the 5 or 10µ demanded in water treatment, but for several reasons it is not realistic or necessary to demand a better prefiltration:

- It is technically almost impossible to perform a better filtration.
- It has been used for years in the industry.
- The flow channel provided by a 90 mil parallel feed spacer corresponds to 2,200µ, which is 10 times the particle size.

The pre-filtered liquor is close to 14 pH, which is normally adjusted to 8 pH with acetic acid. Without pH adjustment prior to ultrafiltration the membrane life is shortened since membranes tend to get brittle at very high pH. This is aggravated by the fact that the operating temperature is higher than 80°C.

The viscosity of carrageenan is so high that it may be necessary to heat the product to an even higher temperature as a kind of pretreatment.

Cations

This group of materials (e.g. cationic detergents) are in many cases detrimental to the membrane flux which can drop significantly, sometimes to zero.

The only pretreatment possible is to add enough anionic chemicals to neutralize the cationic materials. That can often be done by adding simple detergents, e.g. lauryl sulfonic acid, which is a common and relatively inexpensive product.

CIP Liquids

CIP liquids represent a special problem in connection with membrane filtration, because their composition is not well defined. CIP stands for cleaning-in-place which is a common procedure for cleaning of processing equipment in food and dairy plants.

The only pretreatment possible is to clarify the liquid, which can be done by many types of filters. Cartridge filters are most commonly used. They are effective but also rather expensive since the cartridges cannot be reused. Another relatively efficient method is to clarify in a centrifuge. This type of equipment is normally used for fat removal from milk, but it will clarify

CIP liquids efficiently. Since centrifuges are being used in most food and dairy plants, the availability of this type of equipment does not represent a problem.

Color Substances

Many naturally occurring or artificial dye stuffs in food products may present problems in connection with membrane filtration, with the naturally occurring colored substances being the most troublesome. The more water soluble a dye stuff is, the less likely is it to cause problems.

It is rarely possible to perform a pretreatment which removes the color since color in most cases form an important characteristic of the product, for instance the red color of red wine. In the case of waste water treatment from food processing, flocculation has achieved some success in cases where color can be removed without detriment to the product quality, but it is very tricky because the flocculation agent in itself may foul the membrane. The best strategy for flocculation is to ascertain a slight deficit of flocculation agent, leaving a slight amount of color in the product. This will, in most cases, ensure that the product contains no unused flocculation agent, that the permeate has sufficient quality, and that dye precipitation causes only minimal problems.

Color substances are found in numerous foods and food related products, e.g. waste water from processing peas and carrots, thin juice from sugar production, coffee, fruit juice, beer and wine. Some other troublesome color substances are naturally occurring humic and fulvic acid. All of these colors substances have low solubility in water and a pronounced tendency to precipitate on membranes. They have one chemical feature in common, namely one or more benzene rings in their molecular structure, making polysulphone membranes extremely susceptible to fouling because polysulphone contains numerous aromatic rings, which tend form chemical bonds leading to severe and sometimes often irreversible fouling. Cellulosic, PVDF and other non-aromatic polymers are preferred as membrane materials for these applications.

There is no such thing as a good generally accepted pretreatment for removal of color substances. It is a problem one has to learn to live with.

Textile Dyeing Effluent.

Reactive dyeing, dyeing of polyamide and polyester.

Dyeing of cotton is the largest dyeing operation int the world. Close to 50% of all dyeing is made with reactive dyes on cotton. Adding dyeing of polyamide and polyester materials to cotton dyeing cover most dyeing operations in the world.

Pretreatment is simple: filtration to remove fibers. Most often a conventional 10 to 20µ filter cloth is sufficient. It seems that enzymatic treatment, e.g. so called stone washing done with enzymes, results in fibers and fiber fragment considerably smaller than usually experienced, and even 1µ filters seem to leak small fibers through. In that case either an extraordinary effort with conventional filters is needed or the use of inexpensive tubular ultrafiltration membranes is required.

It is a good ideas to keep the effluent from the various dyeing baths and other process streams in a textile dyeing operation separate to avoid causing problems in the treatment of an aggregate stream.

No other pretreatment than filtration is required before the normally used nanofiltration and reverse osmosis membranes.

Washing water.
The same comments as above. The main difference is that the membrane process is ultrafiltration, since the waste water can contain oil. A surplus of detergent is needed to emulsify the oil.

Egg Products

Chalaza is the two white strings extending from the egg yolk to the opposite ends of the lining membrane of the egg. Membrane filtration is used to de-water egg white, and the chalaza needs to be removed before entering the membrane system. It can be accomplished by conventional filtration but it is not easy. Chalaza has a spring like character, which means that it may pass through a filter only to curl up again immediately. Therefore filtration must be performed at a low pressure differential in order not to force the chalaza through.

It is impossible to prevent all chalaza from entering a membrane system, and it is extremely difficult to remove by the daily cleaning. Besides the daily alkaline cleaning it is common to soak the system during the weekend in a detergent solution with a large dose of a proteolytic enzyme, which can digest the chalaza and thus clean the systems thoroughly.

Egg shells are common and can easily be removed by filtration.

Protein denaturation by heat or shear force is a real danger when treating egg white. Shear forces in pumps or valves can quickly denature soluble egg and turn it into insoluble protein which will foul any membrane system. Use slow action homogenizer type pumps and positive displacement pumps to solve the shear problem. This point does not qualify as pretreatment but is included for the sake of completeness.

Viscosity of egg white is known to be problematic in connection with membrane filtration. The viscosity can be reduced (and glucose removed at the same time) by fermentation. The removal of glucose is desirable to avoid Maillard reaction (browning) in subsequent spray drying. The fermentation typically takes 10-20 hours and may, in fact, be performed while a batch reverse osmosis system is running.

Fermented egg contains a lot of microorganisms, and it may seem problematic to use reverse osmosis for de-watering, However, experience tells that the reverse osmosis process works fine. The idea of simultaneous fermentation and reverse osmosis is unique, from the standpoint that microbial growth in membrane filtration equipment normally should be avoided, but in this case the fermentation does not disturb the function of the membranes. On the contrary, it helps to reduce the viscosity of the product, and since the process operates at ambient temperature, the high count of one microbial species helps subdue the growth of all other species.

Fibrous Material

All fibrous materials must be removed before most membrane filtration processes, which can usually be done using one of the many conventional filter types available.

Short fibers can be a nuisance and they are difficult to remove. Very short fibers are found in the textile industry and in the pulp and paper industry. The only totally effective method to produce fibre free liquids is ultrafiltration. This is often the last option to be investigated due to price, but the possibility should not be ruled all together because the price for ultrafiltration have decreased. Ultrafiltration completely eliminates passage of fibrous material without the use of any filter aid.

Fruit Juice

Color as a general problem is mentioned in another section. Fruit juice represents a special challenge, because juice is always colored. Since color is an essential part of the product there is little or nothing to do about it, except to design membrane filtration equipment with low flux and to use a membrane and membrane material that can be made to work and be cleaned.

Fines is a less complicated problem. Fines can be removed by conventional filtration or by centrifugation. Prefiltration is only problematic from the point of view that it must be consistent and effective.

Pectin and cellulose are always present in the juice in varying amounts. It is common practice to add an enzyme, mostly pectinase, to clarify the juice, and pectinase also effectively prevents precipitation during the membrane filtration process.

Pretreatment by adding enzyme is not absolutely necessary to make a membrane system work, but in many cases it will literally double the membrane flux and thereby make the membrane filtration process more economical. Is has been attempted to use membrane filtration to replace de-pectination with enzymes, but the idea never succeeded.

Latex Containing Feeds

Pretreatment is in principle very simple. Remove all latex prior to membrane filtration, but in reality it is exceedingly difficult. Centrifuges are used in some cases, but they have to be dismantled totally every few hours(!)

Latex will plug up a spiral wound element and consequently the use of spirals wound elements is not possible on latex containing feeds. ½" or 1" tubular membrane filtration systems will, to some extent, tolerate latex.

Laundry Waste Water

Fibers is the real problem when membrane filtrating laundry waste water, because fibers, dirt and detergent forms large, loose flocks. Conventional filtration with all kind of filter types is being used. Experience shows that 20-40 micron filters provide a sufficiently good prefiltration, but tighter filters will certainly result in longer membrane life time.

Detergents rarely present a problem for membrane filtration, because the detergents used in washing usually are anionic. The only real problem is the products used for fabric softening because they are cationic. The only possible pretreatment is to ensure that this particular water is mixed well with all the other materials used in a laundry operation, because they contain a big surplus of anions, which can effectively neutralize the cations.

Oil, grease and solvent can be present in astonishing amounts in industrial laundry waste water. The best pretreatment method is to strip solvents prior to washing. The only pretreatment possible is to make sure that there is a surplus of detergent, thus securing that fat and grease are emulsified. Addition of detergent is not just a loss, because they will make ultrafiltration work better and the surplus detergent can be reused since it passes freely into the permeate.

The Metal Working Industry

Oil emulsions are used in machining, e.g in cutting and milling. Sedimentation followed by conventional filtration are the only possible pretreatment and that will provide adequate pretreatment, since the metal particles are heavy and precipitate quickly.

Mineral acid is used extensively in mining and surface treatment of many types of metals. Some examples are

- H_3PO_4 for surface treatment of Aluminum
- H_2SO_4 for etching of copper rods and foil
- H_2SO_4 for heap leaching
- HCl/HF/HNO3 for surface treatment of stainless steel
- HCl for cleaning or iron.

Conventional filtration is the only pretreatment possible and necessary.

Dairy industry

Hair, grass and flies sounds like ridiculous things to mention but in the dairy industry they can present a very real problem. The flies are easy to remove. Hair is a lot more difficult to see and to remove. When treating dilute raw milk, hair from the cows as well as hairs from brushes are found in a surprising quantity, and grass often is brought in with the milk. Bag filters, which can be washed and sterilized, are commonly used and present probably the best solution to removal of this type of impurities.

Casein fines are present in large quantities in cheese whey. It is common to remove the larger particles with a self-cleaning screen. The remainder of casein fines are usually removed by centrifugation. If the centrifuge is run at a relatively low capacity, the fines content is reduced sufficiently for the whey to be treated in a membrane system. Experience has shown that an RO system with 47 mil spacer can handle the amount of suspended solid passing a casein sieve and that a centrifuge is not compulsory.

Milk fat and phospholipids. Milk has a natural fat content in the 3.0% to 4.5% range. Membrane systems can handle milk fat but operate much better when the fat content is below 0,05%. Milk fat can be skimmed off in a centrifuge, which is a very common piece of equipment in dairy plants. Phospholipids stem from the envelope of the fat globules and are liberated when the envelope is disturbed, for instance by homogenization, pumping or churning. They are trouble-some, because they stick to the surface of membranes and they require high pH and temperature to be washed off. There is no known method to remove phospholipids from milk and whey.

Pasteurizing prior to membrane filtration is literally an industry standard. Pasteurizing means heating to 72°C and holding for 15-20 seconds, followed by cooling to the operating temperature. There are very few exceptions to this rule. The objective is to reduce bacteriological activity. At the same time calcium phosphate crystals are made (see section about calcium phosphate). If pasteurizing is not made the capacity tend to be lower and pH in the product will drop after a few hours of operation due to formation of lactic acid. The drop of pH can very quickly render the product useless. In spite of 25 years of tradition for pasteurizing there is now a trend to avoid it in order to reduce investment and running costs. Very careful analysis of the job to be done is needed if membrane filtration of non-pasteurized products shall be a success.

Calcium phosphate or rather calcium orthophosphate ($CaHPO_4$) is present in all dairy products. The solubility of calcium phosphate decreases with increasing temperature. This is troublesome, since many dairy processes take place at elevated temperature, and since it is next to impossible to remove the calcium phosphate from milk and cheese whey prior to membrane filtration. Pretreatment can help to make the amount of precipitation acceptable but it will not prevent the phenomenon.

It is common practice to pasteurize dairy products prior to membrane filtration, which means heating to 72°C and holding for 15-20 seconds, followed by cooling to the operating temperature. If cooling of the product is not done immediately but according to the so called "heat-and-hold" method, whereby the temperature of the product (most often sweet cheese whey) is maintained at 55-60°C for an hour, a surprising amount of micro crystals of calcium phosphate will form and precipitate. Some of the crystals formed can be removed as a sludge. They do not interfere with the membrane process but may even help to prevent further precipitation on the membranes, due to the affinity of the solute to an already formed crystal rather than material alien to the solute. When concentration takes place in a membrane system and the concentration of calcium phosphate exceeds the solubility, the already formed crystals will continue to grow, thus stripping excess calcium phosphate from bulk of the liquid.

This procedure may be compared with crystal seeding techniques known from many other industries. Although it is not totally effective it does allow 20 hours of operation between cleaning cycles.

Denaturated protein is problematic in feeds to membrane systems. A slight damage will usually reduce the solubility, and total damage will result in a material with the consistency of a hard boiled egg. Slightly damaged proteins which are still soluble can not be removed by any pretreatment and they will lead to reduced flux and increased fouling. Precipitated proteins are removed fairly easily by conventional filtration.

Oxidizing Environments

The tolerance of membranes to oxidizing agents vary widely. Thin-film membranes do not tolerate any oxidizing environment, with the notable exception of ClO_2. Integral membranes of polysulphone (Desal E-, F- and P-series), PVDF (Desal J-series), PTFE (Desal K-series) and polyacrylo-nitrile (Desal Q-series) are very resistant to all kind of oxidizers.

The general rule for thin film membranes is, that all oxidizing substances should be removed before a feed enters the membrane system. In the following only oxidizing agents as they pertain to thin-film membranes will be discussed.

Chlorine (Cl_2), sodium hypochlorite (NaOCl). If one of these are present de-chlorination is a necessary pretreatment step. The following methods can be used:

- Addition of a reducing agent, e.g. sodium bisulfite ($NaHSO_3$), is commonly used method. The method has the drawback that sulfate will be formed in the system.
- An activated carbon filter is often used. It should be born in mind that it may be a source of microbial growth and a potentially severe source of biofouling. Another worry is the disposal of the spent carbon.
- Ultraviolet (UV) light is perhaps the best but also an expensive method.

Chlorodioxide (ClO_2) has been reported to be harmless to thin-film membranes, but real life experience is lacking. Chlorodioxide is difficult to handle and difficult to get free of Chlorine. It is rarely in membrane filtration plants.

Hydrogen peroxide (H_2O_2), peracetic acid (CH_3CO_2OH). Both are relatively weak oxidizing agents which can be used with care for disinfection of thin-film membranes once a week. It they are present in a feed stream, they must be removed by addition of a reducing agent.

Bromine (Br_2) is similar to chlorine and demand an identical pretreatment.

Iodine (I_2) is similar to chlorine and demand an identical pretreatment.

Nitric acid (HNO_3) can be used for cleaning once a day in moderate concentration (<<½%) at room temperature. Higher concentration and/or high temperature is not acceptable. It is highly recommended *not to use nitric acid*, if it can be replace by an acid which is not oxidizing. Good alternatives are phosphoric acid, hydrochloric acid and citric acid.

Chromate (CrO_4^{2-}), Chromium as Cr^{+6} in a feed stream can be a problem since chromate is a quite strong oxidizing agent. The aggressiveness of chromate is pH dependent and at its most severe at neutral pH. The life of a thin-film membrane at 7 pH and high chromate concentration can be measured in weeks rather than months. If pH can be lowered to less than 2, most membranes will operate satisfactorily. Another pretreatment method is to reduce Cr^{+6} to Cr^{+3} which is harmless to a thin-film membrane. This strategy, however, renders reuse of the chromate impossible.

Paint

Paint contains inorganic pigments whereas the paint itself is always organic in nature. It commonly contains high molecular weight substances of a very sticky nature. Pigments in paint are not considered to be a problem because they literally look and act like small pebbles which roll over the membrane without sticking to it.

Water based traditional paint generate waste water from washing of tanks and pipes. The only possible pretreatment is conventional filtration, which can be difficult due to soft and sticky precipitates.

In the opinion of the writer, a tubular system is by far the best suited for membrane filtration of water based paint, since it has very little demand to prefiltration. A sieve will be adequate and foam ball cleaning is possible. All other systems will need prefiltration which is expensive in order to be efficient.

Water based paint precipitated by electricity (electrophoretic paint, ED paint) is used in the automotive industry for the first coat of paint. In the context of membrane filtration, the only pretreatment possible is self cleaning sieves for the removal of lumps of paint and that has proven to be adequate for spirals. Filtration is done anyway in order to secure a smooth surface. The paint and its pigments can pass through almost any membrane module.

An-ionic paint is fairly easy to treat.

Kat-ionic can be very difficult to treat.

Pulping Effluent

There are a number of quite different effluents from the pulping industry. A few are:

SSL	Spent Sulphite Liquor
KBL	Kraft Black Liquor
KBE	Kraft Bleach Effluent
CTMP	Chemical Thermo Mechanical Pulping
NSSC	Neutral Sulphite Semi Chemical
VBL	Vanillin Black Liquor

Cellulose fibers. All type of effluents from the pulp and paper industry contains cellulose fibers. Traditional self cleaning filters can most often give adequate fiber removal. Drum filters with stainless steel mesh is commonly used. The trend to recycle more and more cellulose fibers has the effect, that the amount of very short fibers increases. This will eventually mean that more sophisticated pre-filters are needed, e.g. low cost ultrafiltration systems.

Calcium salts can be a real problem by sulphite pulping. The precipitation of calcium sulfite and sulphate is likely in the liquid and - what is worse - in the membrane structure. There is not sufficient knowledge to evaluate the problem. In a major ultrafiltration system it was necessary after some time to install a Ca-Na ion exchanger to solve the problem of calcium salt precipitation.

Pitch/Rosin is a severe problem in sulphite effluents. The products are very sticky and they come in quite big quantity. The writer does not know any effective pretreatment, but possibly flotation can be used.

Ultrafiltration has been used for rosin removal, but it is not a common process.

Silicon Oil

Distinguish between silicon oil and siloxanes.

Silicon oil is poison for membranes. The only effective pretreatment is not to use silicon oil at all. In most cases, silicone oil can be substituted by products which does not harm membranes, e.g. siloxane. The only way to minimize the problems with silicon oil was discovered by chance, namely adding enough organic material to emulsify and thereby cover the silicone oil droplets.

Solvents and Hydrocarbons

Table 5. Water soluble organic solvents	
Alcohols	Harmless
Ketones	Keep concentration well below 1000 ppm
Esters Tetra hydro furan di-methyl-sulfoxide di-methyl-acetamide N-methyl pyrrolidone	Keep concentration well below 10000 ppm

Table 6. Water insoluble organic solvents / Hydrocarbons	
Aromatic Hydrocarbons	Detrimental to polysulphone membranes Detrimental to polysulphone parts Keep out of RO systems. <50 ppm in NF systems. Good resistance of Desal-J, Q and Y
Aliphatic Hydrocarbons	Keep out of RO systems. <50 ppm in NF systems. Good resistance of most UF systems.

Organic solvents is a very broad category of organic chemicals may or may not cause damage to membranes, and it is difficult to provide good guide lines. Of one safeguard is to remove as much as possible, leaving only a few parts per million in the liquid to be treated. It is necessary to distinguish between water soluble and water insoluble solvents. The water insoluble solvents can be treated as hydrocarbons.

NOTE: Only a few membranes, and prominently among them the Desal Y-series membranes, are resistant to organic solvents. A very special element construction is necessary to match the resistance of membrane and support.

Starch

Membranes are used in some very big systems for waste water treatment from manufacturing of starch. Pretreatment consists of conventional filtration to remove suspended solids.
Sapponins present a problem in waste water from potato processing which is difficult or impossible to solve with pretreatment. The solution is to clean the membranes frequently.

Potato waste water can start fermenting very quickly. The only pretreatment, if it can be called pretreatment, is to process the effluent **immediately** and to design and operate the equipment as if treating a high grade food product. If this rule is not observed, acidification and subsequent protein precipitation is the result.

Suspended Solids, Sludge

The general rule is to reduce the amount of suspended solids to a few parts per million before membrane filtration. That can be achieved by conventional filtration, sedimentation, flocculation or a combination of these processes

If the suspended material occurs in the form of small, hard particles they will usually not present problems.

If the suspended material is fibrous, slimy or in any way bulky, it will usually pose problems for membrane filtration equipment and must be removed. Unfortunately such products are difficult to remove by pretreatment.

Water Treatment

Hardness is observed as precipitation of calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$) and magnesium sulfate ($MgSO_4$). It is the most common problem in water treatment and not only in connection with membranes. It is usual to calculate the Langelier index or Stiff & Davis index to evaluate the risk of precipitation and to decide on a possible pretreatment method. If the Langelier index is positive the water is considered to be scaling.

Three methods are generally used to prevent precipitation.

- Acidification
- Softening
- Addition of anti-scaling agents

Acidification is an old and proven process.

Sulphuric acid is inexpensive and effective and it is the acid of choice for most large scale systems. However, sulphuric acid may cause $CaSO_4$ precipitation, if the calcium content is high. -Handling of sulphuric acid requires great care. Using sulphuric acid is a much cheaper than dosing anti-scaling agents.

Hydrochloric acid is comparatively expensive, It is corrosive and it is rarely used to prevent precipitation in connection with water treatment.

Organic acids, e.g. citric acid, are effective but rarely used.

Carbon dioxide (CO_2) injection is strangely enough an effective possibility. But it is rarely used since it is difficult to handle.

Addition of acid may cause release of CO_2 which makes the permeate very aggressive. It can be necessary to remove CO_2 prior to the reverse osmosis plant, and it is certainly necessary to adjust pH with alkali after the reverse osmosis plant to avoid corrosion in the distribution net.

Softening is a more novel process.

An ion exchange medium swaps calcium with sodium. The result is soft water with an increased content of sodium, which will result in an increased sodium content in the permeate. The process requires large amounts of sodium chloride of good quality, and it may be a problem to dispose of the volume of very saline water produced in the regeneration of an ion exchanger.

Anti-scalants used to control precipitation in water is a fairly new process.

The product is added in very small amounts, typically a few parts per million. It interferes with the crystallization process and allow a high degree of supersaturation. It is a striking fact that, for instance, barium sulfate at 30 times of saturation still does not precipitate. Anti-scaling agents are expensive and must be dosed very correctly. Too little means that precipitation can take place. Too much means waste of money and a potential danger for flux decline.

Iron, aluminum and manganese hydroxide must be removed from the feed stream since the hydroxides of these metals have very low solubility, typically 0,05 mg/l. In water saturated with oxygen and with a pH-value close to neutral, most types of filtration will remove sufficient amounts of iron, manganese and aluminum. Sand filtration is very commonly used, because sand filters can be back washed. Dead end filtration (bag filter, candle filter) is mostly used for small systems.

Rust scales are easily removed by almost any type of filter. If rust scales are present in the prefilter, it is always a good idea to find the origin, because it indicates a source of dissolved iron, which can cause serious problems.

Humic acid fouling may cause problems for all types of membranes, but given the right working conditions membranes can be used for removal of humic acid. It is very hard to remove or destroy humic acid, except by liberal dosing of hypochlorite or energy intensive photo chemical processes. The latter uses UV light and hydrogen peroxide to generate OH-radicals, which attack literally all organic material and oxidize them to water and carbon dioxide. The most common solution to limiting humic acid fouling of membranes is to keep the flux low (<20 lmh) and clean frequently in order to avoid or limit pretreatment requirements.

Silica (SiO_2) is always present in natural water. The solubility is very temperature dependent. If silica precipitation is a problem, it is common and very effective to increase the temperature slightly. Addition of anti scaling agents has an effect and suppliers of such products claiming good result up to 300 mg/l SiO_2 in the concentrate.

Calcium, Barium and Strontium has very low solubility as sulphate. Calcium sulphate (gypsum) is a common problem, specially in the middle east. Barium and Strontium sulphate are more commonly experienced in surface water. It is fairly easy to prevent precipitation using small amounts of an anti-scaling agent, which delays or inhibits crystallization even at concentrations above saturation point and ensures that precipitation does not take place in the membrane system.

Sand is easily removed by precipitation or filtration. Since sand is very abrasive it must be effectively removed before the feed enters any membrane filtration system.

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