Nanofiltration: New Developments Show Promise

Dr Graeme K Pearce, Membrane Consultancy Associates
www.membraneconsultancy.com

Introduction

There has been a dramatic evolution in the application of membranes in water and wastewater treatment during the last 30 years. The early 1980's saw the introduction of the thin film composite (TFC) membrane for reverse osmosis (RO). This was followed a few years later by developments in ultrafiltration (UF) and microfiltration (MF) that enable these membranes to be applied for large scale drinking water treatment.

The membrane research community expected nanofiltration (NF) to undergo similar radical change. The need for this technology appeared to be as compelling as for the other membranes. However, the very success of first RO, then of UF/MF drew attention away from the potential opportunity for NF.

Pore Size, µm	0.001	0.01	0.1	1	10	100
Approx equiv MWCO, kDa	2-5	100	500-1000			
Relative Size of Common Material	Salts Metal ions DOC	Pyrogens Sugars	Virus Colloidal silica	Bacteria	Yeast cells	Sand
Membrane Technology	RO NF	Process UF UF	MBR MF MF ww	Nominal Cartridge Sterilizing Cartridge		

Figure 1: The Filtration Spectrum for Membranes in Water Treatment

Figure 1 shows the filtration spectrum for filtration technologies in the water industry. RO removes dissolved salts, while UF and MF remove fine particles. However, the critical application of the removal of dissolved organic carbon (DOC) is not well addressed. UF/MF does not remove dissolved organics unless combined with coagulation. Even then, removal efficiency is not that high and any specific target molecules are likely to require further treatment to meet water quality targets.

RO membranes are fine enough to retain organics. However, the energy cost of RO is high due to the simultaneous retention of salt. This gives RO high operating costs since water transport across the membrane has to overcome the osmotic pressure as salinity increases on the concentrate side. Unless salt removal is the primary goal, for example for a seawater feed or a brackish water source, RO is likely to be too energy intensive for general water treatment purposes. In addition, the removal of low levels of dissolved salts may be undesirable necessitating the re-mineralisation of the permeate after RO treatment by adding calcium to stabilize the water. This has a cost and is inefficient if the removal of salts is not required. NF offers the promise of removing organics without a significant reduction of ionic species, thereby meeting important water quality targets that are developing in the water industry.

Drivers

In broad terms, the driver for RO has been the need to develop alternative water supplies by removing a wide range of contaminants from impaired water sources. In contrast, the primary driver for UF/MF has been to meet newly introduced drinking water quality legislation.

There has been a need for additional water resources in arid areas such as the Middle East for some decades. More recently, this pressure has increased due to a gradual coastal migration, with populations tending to move towards warmer drier climates often near the coast. Seawater desalination using RO has been a primary solution to this requirement and the market has been growing at a compound growth rate of 17% pa for more than a decade [1].

Drivers for UF/MF have been developed to provide a disinfection barrier. The targets have focused on the removal of small particles including viruses, bacteria and protozoan parasites such as cryptosporidium and giardia [2].

However, for several years there has been an increasing concern with dissolved organics such as pesticides, agricultural residuals and pharmaceuticals. So far legislation has not been systematically introduced to address these contaminants but the Environmental Protection Agency (EPA) in the USA and the European Union have undertaken comprehensive reviews of the problem and potential solutions.

Currently, ozone is used in an Advanced Oxidation Process (AOP), potentially in combination with granular activated Carbon (GAC), to reduce pesticides. Also, UV can be used. However, the target molecules are now smaller and more stable than the original compounds of interest making the challenge for destruction and/or removal even greater.

Historical Review and Current Status of NF in the Water Industry

In the early days of RO development, Quality Control (QC) failures were sold at reduced prices and in some cases these elements were referred to as NF. This did a great disservice to NF from which it has taken years to recover. These QC rejects from RO did not perform at all like NF is supposed to, since monovalent salt rejection was far too high.

Specific products were developed for NF in the 1990’s based on an open TCF membrane in a spiral wound element like RO. These products have been very successfully employed in the oil and gas sector. The application here is for the rejection of divalent ions, particularly barium and sulphate, from injection water for offshore oil wells. The fact that monovalent ion rejection with these membranes was also quite high did not matter in this application. The important targets of divalent ion removal needed to be achieved with high efficiency.

By 2000, NF spiral development received a boost with the introduction of products designed to remove organics without reducing the inorganic ion concentration too much. Some of these products utilized the original TFC chemistry while others use different polymers such as cellulose acetate and polyethersulfone. They have been quite widely applied in the North American municipal water industry in Florida, the Pacific coast and Canada for the removal of compounds responsible for colour. They have also been used outside America in Scotland and Scandinavia.

In Europe, there is some use of NF spirals for pesticide removal. The best known example is one of the largest municipal water plants in France at Mery sur Oise [3]. This plant targets pesticides but legislation threatens to exceed the ability of the plant as smaller pesticide molecules are targeted.

Energy Requirements in Water Treatment

A critical issue for water treatment is energy cost and this is becoming more important with the development of alternative sources. Figure 2 shows the relative energy use of treating energy from various sources and compares that energy with the cost of transfer and distribution [4,5]. The diagram shows that the energy cost of traditional fresh water sources is generally very low. At the opposite end of the spectrum, the energy cost of desalination is up to tem times as high and can only be justified on energy terms where the alternative is to transfer the water from far away, as for the State Water Project in California. Wastewater offers promise as a lower cost resource but this too is fairly energy intensive due to aeration requirements.

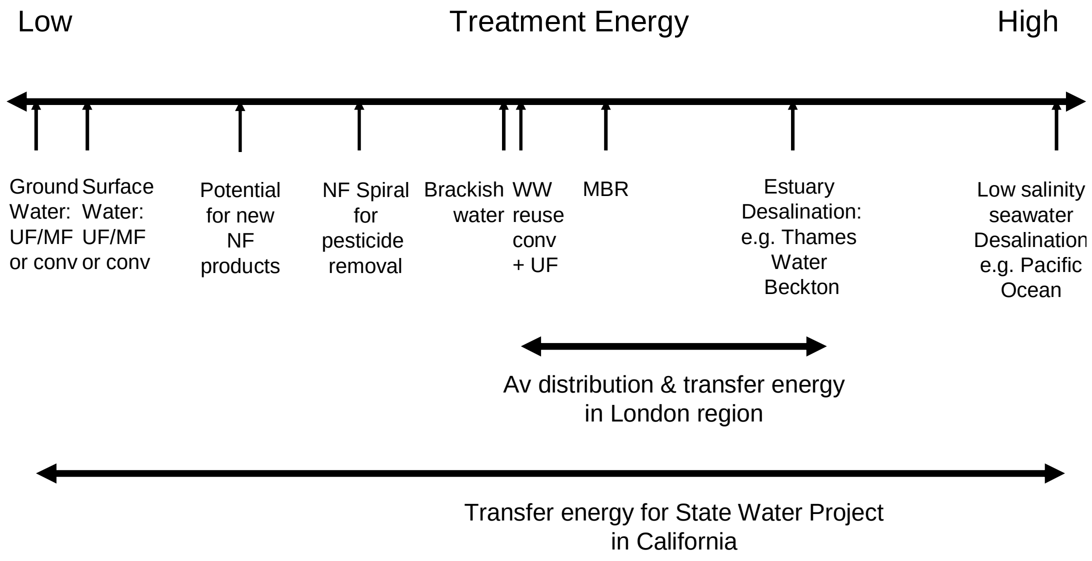

Figure 2: Energy Requirements for Treatment, Distribution and Transfer

Current NF spirals use less energy than wastewater reuse schemes but are significantly more energy intensive than freshwater due to the rejection of salts. New NF products offer the potential to reduce energy by being more selective and offering a simpler treatment flowscheme.

New NF Product Developments

The problem with spirals is that they require excellent feed quality to avoid fouling. Thus the NF stage is effectively added on to existing treatment. This article will now consider a new range of NF products which target the removal of organic molecules but minimize the rejection of inorganics. By doing so, they offer the promise of lower pressure operation. However, high organic rejection means that it is important that the membrane is low fouling since at high recovery, the concentration of organics in the feed stream will rise sharply.

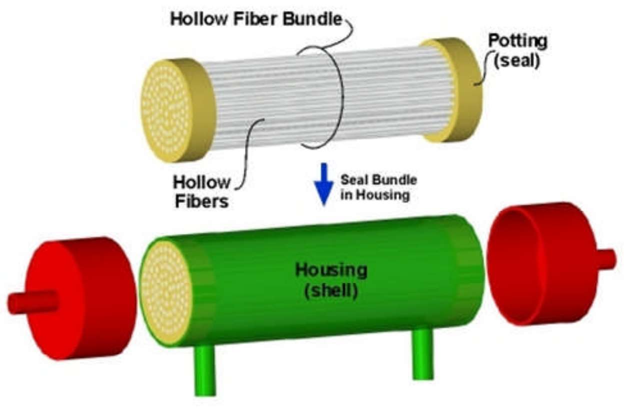

Figure 3: Hollow Fibre NF

Another feature of these new product developments is that they do not utilize a spiral format thereby reducing the need for pre-treatment. The first NF product reviewed here has been launched recently from Pentair-Xflow (formerly Norit) and is based on a hollow fibre format. This product is based on the same PES fibre used for UF but with a molecular weight cut-off < 1.8 kDa, providing a rejection of 75% UV 254 organic compounds. The product is commercially available and is being used on demonstration scale. The great advantage of hollow fibre compared to spiral wound is the elimination of any significant pre-treatment since solids introduced into the feed channel during the filtration cycle are efficiently displaced during backwash or flushing.

A different approach has been taken by DXV, a new start up in the US. Their product is based on a low fouling flat sheet format as shown in Figure 4. The module does not use a spacer between the sheets and relies on cross flow circulation to keep the channels clean. DXV has reached the stage of pilot operation and has focused on wastewater polishing using a single membrane treatment stage, with infrequent chemical cleaning. Pilots have shown that the chemical cleaning requirement for the RO stage can potentially be eliminated or at least significantly reduced.

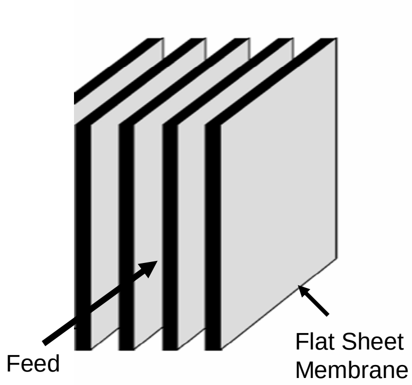

Figure 4: Flat Sheet NF Module Schematic

Another US start up with an interesting NF membrane technology is Clean Membranes Inc. This early stage start up is commercializing technology developed at MIT. The grafted co-polymer membrane is a modified highly hydrophilic polyacrylonitrile (PAN) membrane which can be produced at pore sizes from NF to fine UF. The membrane has shown exceptionally high permeability and high resistance to organic fouling, without the need for air scour. The company secured development funding earlier this year.

Figure 5: ItN Ceramic Membranes

The final company in this brief review is the German company ItN, which is commercializing a range of ceramic membranes, as shown in Figure 5. The products vary from singe hollow fibres to multi-bore monoliths. A wide range of pore size cut-offs is claimed extending down to the NF part of the spectrum, which is unusual amongst commercial ceramic products. ItN recently announced a commercial installation in Saudi Arabia pre-treating a highly brackish well water in place of conventional or UF/MF pre-treatment. The NF pre-treatment is claimed to allow 20% higher RO throughput.

Conclusions

Nanofiltration (NF) has been an overlooked technology in the membrane separations spectrum. NF spirals have been introduced into water and wastewater applications for some time but they are dependent on extensive pre-treatment. Existing NF products targeting organic molecule removal also tend to remove salts making energy use high.

Drivers are now emerging, particularly in drinking water treatment, which will reinvigorate the application of NF membranes and a new generation of products are being developed to address the market needs. These products promise improved energy efficiency since they all feature low fouling membranes with limited salt rejection. Equally important, they utilize module formats that do not require pre-treatment.

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