Introduction to membranes: Filtration for water and wastewater treatment

In the first of a series of articles, Graeme Pearce looks at the various uses and applications of membranes in water and wastewater.

This article is the first in a series focussing on the use of membrane filtration for water and wastewater treatment. It is intended to provide an introduction to the field and examine the basics of membrane technology in these applications, including the types of membrane used and how they work. Future articles will consider the way in which commercial products have developed including the various membrane polymers used and the different module formats, and will aim to provide an understanding of the factors which influence membrane selection. Other articles will also discuss process design and application issues; look at the reasons for the different approaches taken by different suppliers and will also include a review of commercial products, indicating the applications for which they are best employed.

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Membrane filtration is a term used to describe the removal of particulates from a feed stream. There are two embodiments of the membrane filtration process, namely ultrafiltration UF) and microfiltration (MF), and these two processes are the main subject matter of this series of articles. Two other important membrane processes are used in water and wastewater treatment, namely reverse osmosis (RO) and nanofiltration (NF). RO and NF processes are designed to remove dissolved species from the feed stream, and are not intended to be filtration processes. Indeed, membrane filtration is often used to provide pre-treatment for RO and NF [1].

Water and wastewater treatment encompasses a broad range of applications in both municipal and industrial sectors. These articles cover the field of general purpose treatment including for example municipal water treatment to provide purified drinking water, free of pathogens and fine particulates. It also includes general industrial water treatment applications to provide a process feedstock, or pre-treatment to RO/NF in for example a boiler feedwater system. In the field of wastewater, membrane filtration processes may provide an effluent for discharge, or feedstock for a reuse process. The articles do not cover specialized areas, such as the use of UF for Ultrapure water production (UPW) [2] (which requires a tight UF pore size and particle free construction and process design), or the use of Membrane Bioreactors (MBRs) for wastewater treatment.

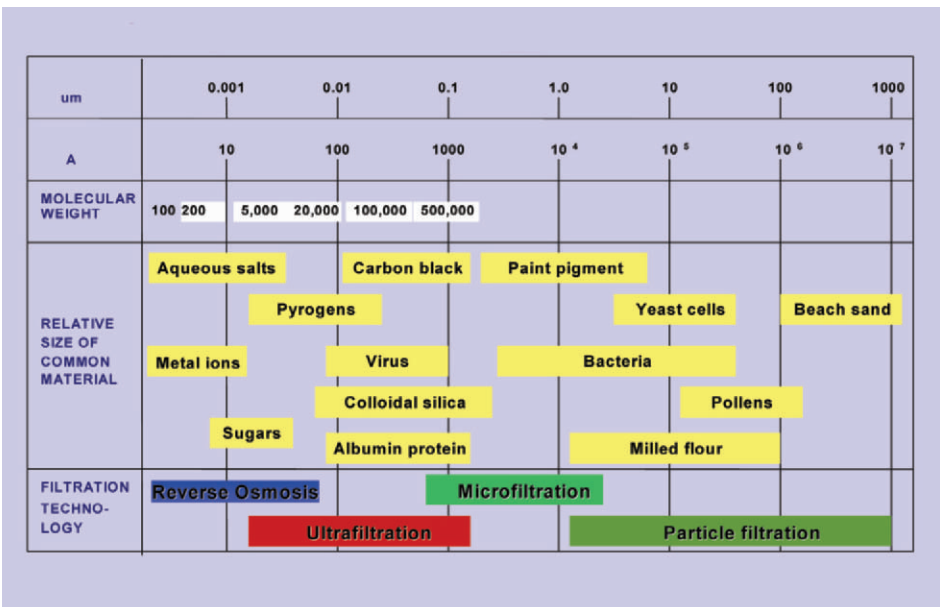

Figure 1. The filtration spectrum.

The Basics of UF and MF Membranes

The separation spectrum for membranes, illustrated in Figure 1 [based on 3, 4], ranges from reverse osmosis (RO) and nanofiltration (NF) for the removal of solutes, to ultrafiltration (UF) and microfiltration (MF) for the removal of fine particulates. UF can remove the finest particles found in water supply, with the removal rating dependent upon the pore size of the active layer of the membrane. The complete pore size range for UF is approximately 0.001 - 0.02 µm, with a typical removal capability of UF for water and wastewater treatment of 0.01 - 0.02 µm. MF typically operates at a particle size that is up to an order of magnitude coarser than this. In water treatment, the modern trend is to use a relatively tight MF with a pore size of approximately 0.04 – 0.1 micron, whereas wastewater normally uses a slightly more open MF with a pore size of 0.1 – 0.4 µm (though wastewater can be treated with UF membranes, or MF membranes used for water applications).

Koch Membranes ROGA® Cellulose Acetate Membranes for high organic fouling environments

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Figure 1 relates the size of some typical particles both to the pore size and the molecular weight cut off (MWCO) of the membranes required to remove them. Historically, it has been customary to refer to MF membranes in terms of their pore size in µm, whilst UF has been defined in terms of the molecular weight of molecules that the membrane pores could reject (typically at 90% efficiency) [4]. Figure 1 attempts to provide an approximate correlation between pore size and MWCO, though in reality, the correlation is highly dependent upon the method of measurement. For the coarser UF membranes used for water and wastewater treatment, the convention of defining UF in terms of MWCO has gradually declined, and it is now just as likely that the UF membrane for these applications will be defined in terms of pore size, as for MF.

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For municipal water applications, a 0.01-0.02 µm cut-off UF membrane provides an essentially complete barrier to the smallest viruses found in water sources. MF removes viruses to some extent, due to its ability to act as a depth filter, but it does not provide a complete virus barrier (defined for practical purposes as 4 log removal (LRV) or 99.99% removal). It does however provide a barrier to bacteria, and protozoan parasites such as cryptosporidium and giardia, and is therefore also applied in municipal water treatment applications.

The separation mechanism for UF and MF membranes differs from conventional treatment devices, such as granular or fibrous media filters. Media filters rely on a gravity removal mechanism [5]. They have a nominal pore size considerably greater than the particles they are capturing. For a granular media filter, the grain size may be >100 micron, creating pores of a similar size. The absolute rating of such a filter will be of the same magnitude.

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However, due to the depth of the media and the tortuous path created for the feed as it moves through the media bed, relatively high removal rates can be achieved, even for particles significantly below the nominal pore size. Media beds of 150 micron sand particles can routinely achieve removal efficiencies of 90-99% for particles down to 10-20 micron [6]. With the use of flocculants, a further significant improvement can be achieved. However, the nominal rating of the depth filter means that the removal efficiency is variable, and is dependent on a host of environmental and operating parameters.

In contrast, UF and MF membranes operate by a surface removal mechanism, and resemble a fine screen or sieve [7]. The pore size at the surface of most membranes used for water and wastewater treatment is highly uniform, with a narrow pore size distribution. Particles larger than the size of the largest pore are rejected by the membrane surface, and remain on the feed or concentrate side. The bulk carrier fluid, and any particles finer than the largest pore, can pass through the membrane to the filtrate side.

This feature of size selection makes membranes ideal for meeting absolute filtration quality requirements, whether in ultrapure applications, or in meeting the exacting legislative standards of the Municipal Regulation Authorities. Provided that the initial integrity of the membrane surface remains intact, the removal efficiency can be guaranteed.

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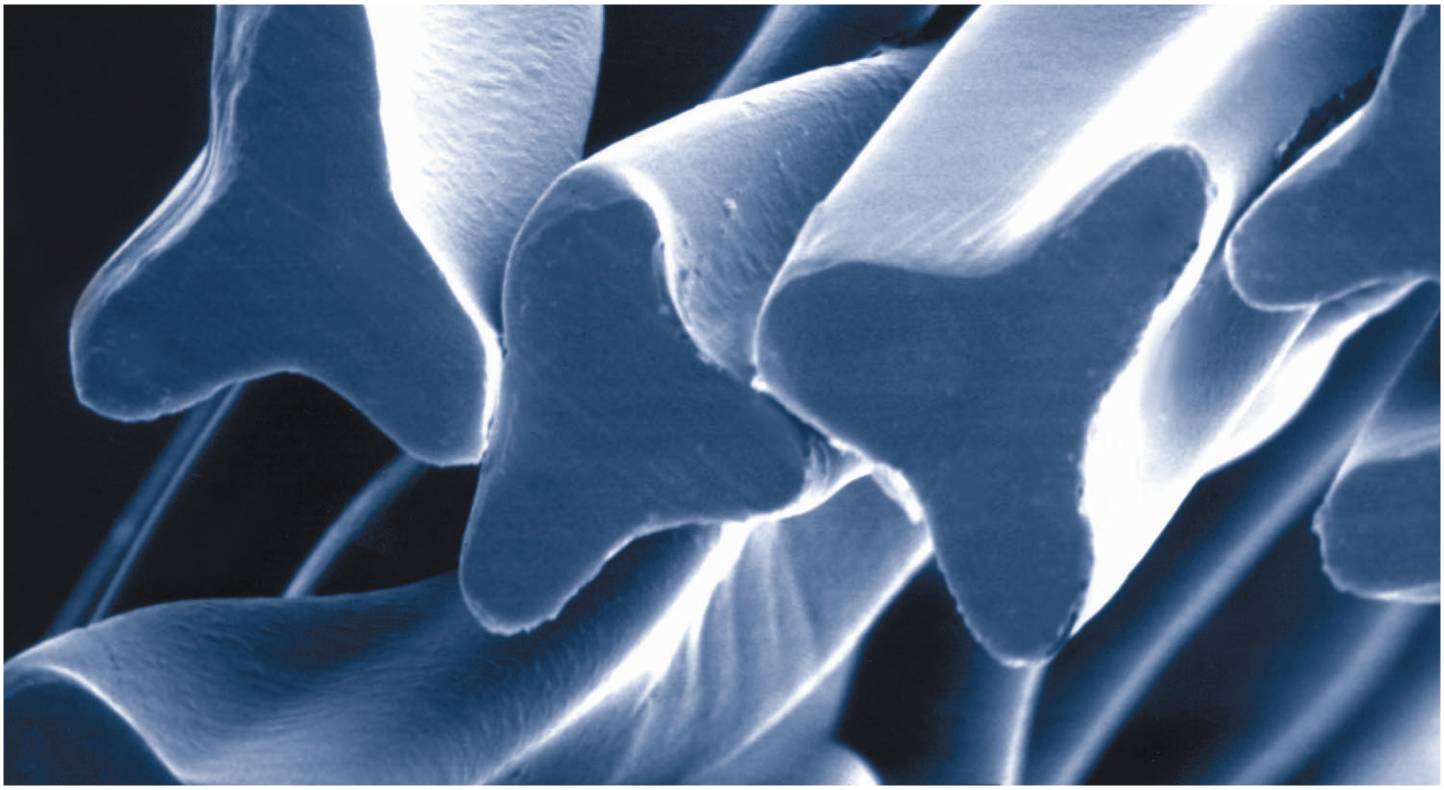

Trilobal filaments in a non-woven media. Picture courtesy of Fiberweb.

treatment; membrane systems tend to be more compact (typically occupying 33% less space), lend themselves to automation (normally with unattended operation), and have lower chemical usage (less chemical cost, and reduced waste generation).

History of UF/MF Development

Ultrafiltration was first developed for process applications such as protein separation in the emerging biotechnology industries of 30 years ago [7]. There was an initial interest in utilizing the substrates that were being developed for Thin Film Composite RO spirals. However, although these could function as UF membranes, process performance suffered from particle fouling problems, inherent to the spiral configurations if they are used in a filtration application. UF development switched instead to tubular and capillary formats, which could cope with particle challenges without becoming fouled [8].

The membranes in these early developments had molecular weight cut offs (MWCO) in the 3-50 kilodalton (KD) range, i.e. considerably tighter than the current range used for water and wastewater applications, which would typically be 80-150 KD for a 0.01-0.02 µm membrane. Although UF membranes with a cut-off in the range of 3-50 KD were suitable for ultrapure water applications, they were too tight for general water treatment applications. These tight UF membranes had permeabilities that were too low, and hence operating pressures that were too high for municipal water treatment.

MF was developed even earlier than UF. The target for MF was the 0.22 micron sterilising filter cartridge, to provide guaranteed bacterial removal in medical and biotechnology applications. Crossflow MF then developed for a wide range of process and waste treatment applications, but it was not until the mid 1980's that a suitable MF format was introduced for general water treatment.

The box opposite shows the key milestones in the development of UF/MF membranes for water treatment applications. The forerunners for today's water treatment applications were the Polysulfone (PS) membranes invented in the 1970's. Initial application was mainly in the ultrapure field, and for miscellaneous process applications. Then, a series of important developments occurred during the 1980's, with the introduction of CA and PES UF membranes, which opened up the potential for municipal water treatment. The key invention in the case of UF was the extension of membrane morphology to larger pore size membranes with higher permeability, whilst maintaining the high strength of the earlier process membranes. These water treatment membranes contained pores of about 0.01 micron, almost an order of magnitude greater than the early protein separation UF membranes. In the case of MF, the key was to control the pore size of polypropylene (PP), the most important early MF membrane polymer, to get a reliable 0.2 micron cut off with an acceptable permeability.

UF vs MF

MF has pore sizes one or two orders of magnitude greater than UF. Simplistic logic would suggest that if MF meets the treated water quality criteria of a particular application, it should be the automatic membrane technology of choice for general water treatment applications. However, although MF is widely applied in water treatment, UF and MF have similar market share, even in those applications for which either technology would be suitable. In this section, the reasons for this apparent anomaly are explored.

UF membranes are made with a pronounced asymmetry, normally having a thin active layer of finer pores, supported by a sub structure of pores which could be similar to those found in an MF membrane

MF membranes are made either with a homogeneous pore structure through the membrane cross section (due to the manufacturing method used), or with a limited asymmetry, with the pores of the active or separating layer not much smaller than those of the supporting sub structure [9, ch 3]. In order to ensure that the MF membrane has satisfactory strength, the pore density may be relatively low, or a homogeneous structure may be used.

Key Milestones in UF/MF Membrane Development

1950s

- MF membranes commercialized for sterilization applications

1960s

- RO CA membranes commercialized

1970s

- PS UF flat sheet support used for RO Thin Film Composites
- PS UF capillary invented with finger pore structure

1980s

- Foam or spongey structures developed for PS/PES CA capillary introduced
- First large scale municipal UF installed in 1988
- PP MF fibre developed
- PES/PVP UF developed

1990s

- PVDF and PAN membranes developed
- Submerged membrane concept developed

2000s

- Hydrophilic PES and PVDF membranes introduced by several companies

In contrast, UF membranes are made with a pronounced asymmetry, normally having a thin active layer of finer pores, supported by a sub structure of pores which could be similar to those found in an MF membrane. A UF membrane gains considerable strength from the fine pore size of the thin active layer, and therefore it is possible to make the supporting layer much more open than the active layer, and still meet strength targets for the membrane. To enhance permeability, the active layer of the UF membrane can be made with a high porosity and high pore density.

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The resistance to flow in the UF membrane is dictated by the thin active layer, rather than by the open supporting sub structure. Most UF membranes have a skin, or active layer only on the side of the membrane contacting the feed. Some membranes have active layers on both sides of the membrane fibre, the so called double skin phenomenon. This improves strength, but at the expense of permeability.

For a 'real' water feed, including a City Water supply which contains a multitude of fine particles, the initial permeability difference between UF and MF is quickly removed. The reason for this is the phenomenon of pore plugging.

As a consequence of the structural differences, the permeability difference between UF and MF is not as great as the pore size difference would indicate. UF membranes may have fluxes in the range 500-1000 lmh.bar for a new clean membrane with RO feed; MF fluxes may be 3000-10,000 lmh.bar, i.e. lower than the pore size ratio would have indicated based on the inverse exponential relationship between resistance and pore size [9, ch 6].

For a 'real' water feed, including a City Water supply which contains a multitude of fine particles, the initial permeability difference between UF and MF is quickly removed. The reason for this is the phenomenon of pore plugging. Typical water feeds contain large numbers of fine particles, with many below 0.1 micron. These particles enter the pores of the MF membrane, partially plugging the pores, and quickly reducing permeability to levels typically seen for UF membranes. The particles are only partially removed by backwashing and cleaning, resulting in a loss of advantage of MF over UF. Indeed, MF permeabilities may fall below those of UF.

UF can achieve a more stable performance than MF in water applications, since the pores of UF are tend to be too small for the pore plugging mechanism. Particles below 0.01 micron are less independent than larger particles in the feed water since surface charge effects dominate the behaviour of the particle. The mass of these fine particles is too low for gravity forces to control the particle in comparison with electrical forces, and particles tend to agglomerate, flocculate, or stick to surfaces.

MF tends to do better than UF in applications where there are larger solids present in significant concentrations, especially if the solids can form a pre-coat on the membrane surface. Robust flocculated solids are particularly suitable. Under these conditions, stable performance may be possible at higher pressures. For example wastewater applications operate well with MF, and can give stable performance at low transmembrane pressure.

Conclusion

Membrane filtration is suitable for a wide range of water and wastewater applications. Coarse UF or tight MF membranes have been developed for general purpose water treatment; both perform well, though UF may have an advantage in resisting the effects of pore plugging in some applications, and in achieving virus removal in drinking water applications.

For wastewater, UF or MF can be used, though MF pore sizes may be larger than in water treatment applications; MF may have an advantage over UF where feed particles create a pre-coat on the membrane surface. ●

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References

[1] *The Guidebook to Membrane Desalination Technology*, M Wilf et al, Balaban Desalination Publications, 2007

[2] *Ultrapure Water System Design Considerations*, P S Cartwright, Desalination 67 91987), 171-184

[3] *Osmonics Filtration and Separation Spectrum*, www.osmonics.com/library/filspc.htm

[4] *Handbook of Industrial Membranes*, K Scott, published by Elsevier, 1995

[5] *The Scientific Basis of Filtration*, K J Ives, Noordhoff, Leyden, 1975

[6] *Water Treatment Processes and Practice*, T Hall and R A Hyde (ed), Ch 13, WRc 1992

[7] *Microfiltration and Ultrafiltration: Principles and Applications*, L J Zeman and A L Zydney, publ Marcel Dekker, 1996

[8] *Membrane Processes: A Technology Guide*, P T Cardew and M S Le, Royal Society of Chemistry, 1998

[9] *Basic Principles of Membrane Technology*, M Mulder, Enschede, The Netherlands, 1990