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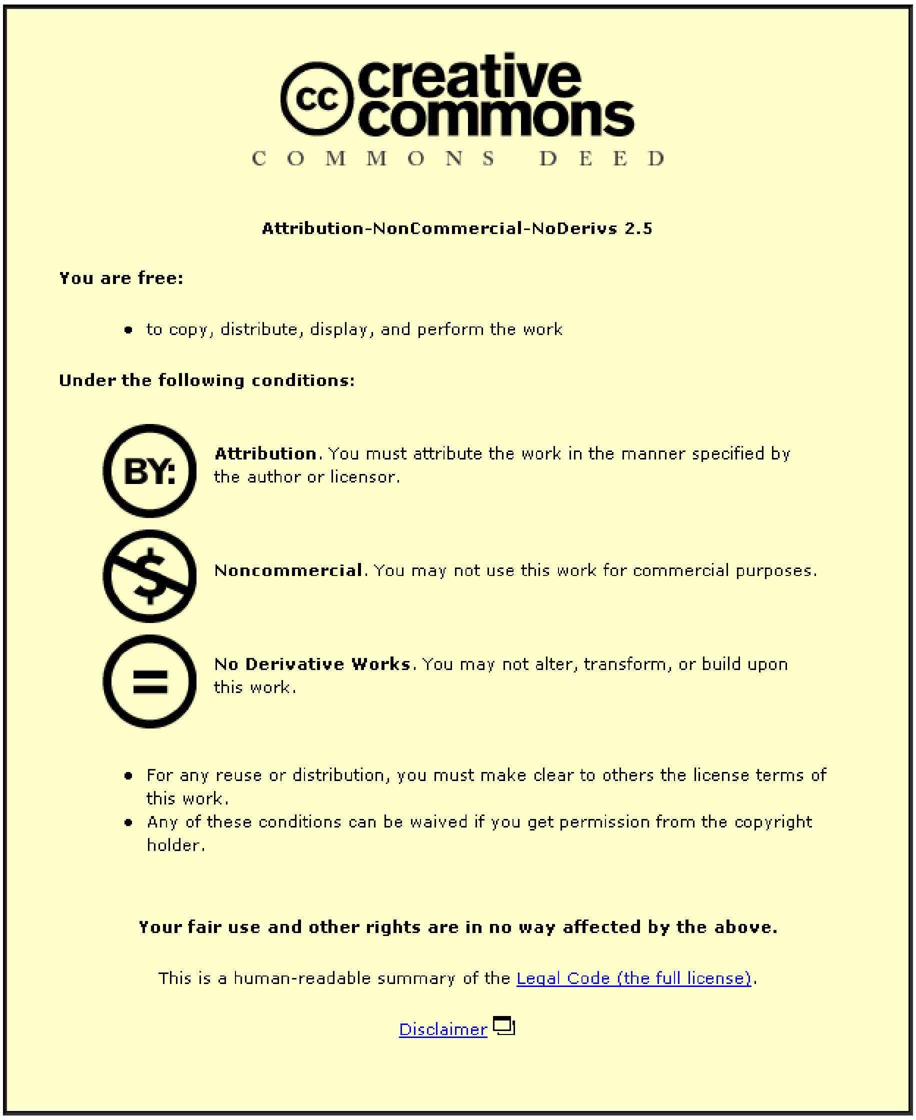

UNDERSTANDING FLUX DECLINE IN CROSSFLOW MICROFILTRATION - PART III: EFFECTS OF MEMBRANE MORPHOLOGY

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ABSTRACT

The influences of membrane type and composition on fouling in crossflow microfiltration are discussed with relation to data obtained from sequences of computer controlled experiments. A number of commercially available polymeric membranes were identified, characterised and challenged with particulate streams of known size, shape and surface charge at a range of well defined, constant process conditions. The flux declines observed during microfiltration are related to the known characteristics of the particle stream and the filtering membrane septum. The fine particles in the feed suspension are shown to control the rate of filtration, and render the rate insensitive to membrane pore size or size distribution. The greatest rate of filtration is obtained with membranes whose pore sizes are smaller than the finest particles in the feed stream. Effects of membrane hydrophilicity/phobicity are short lived, and surface charge effects are secondary.

KEYWORDS

Membranes; Fouling; Morphology; Surface charge; Contact angle

INTRODUCTION

In Part I[1] of this series of papers experimental data were presented which showed the effects of particle size, size distribution and membrane pore size on flux decline. Part II[2] considered the influences of process parameters such as trans-membrane pressure difference, crossflow velocity, suspension concentration and pH and highlighted how their effects were inter-related with the parameters examined in Part I. The current paper examines the influences of membrane type, construction and morphology on the microfiltration of aqueous based mineral suspensions. Examples of the range of polymeric microfiltration membranes commercially available were characterised in terms of pore size and distribution, topography (pore shape), cross-section and contact angle and subsequently challenged with a number of equally well characterised feed streams. The data obtained show how membrane performance indicators such as rate of flux decline and particle rejection are closely related to the known characteristics of the feed over the range of experimental conditions investigated.

CHARACTERISATION PROCEDURES

The particle systems and membrane types used in this work were chosen to encompass the variety of environments commonly found in microfiltration systems. The characterisation of the particles has been described in detail previously[1,2] and employed standard laboratory techniques to evaluate the size, shape and surface charge (interpreted through zeta (ζ-) potential over a range of pH) for a yeast suspension and suspensions made from calcite, anatase, china clay and aragonite powders dispersed in double distilled water. The membranes subsequently used in the microfiltration tests (see Table 1) were examined to determine parameters such as pore size/size distribution and clean water fluxes/permeability. The authors have shown[1,3] that microfiltration membranes will typically exhibit mean pore sizes somewhat different from the quoted ratings with the range of pore sizes present widening for membranes with larger ratings. Whilst these findings

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are confirmed by the data shown in Table 2, a number of other factors must be examined to complete characterisation.

Figures 1-4 show scanning electron micrographs of four of the six polymeric membranes identified for use in the microfiltration experiments: micrographs of the Nuclepore PC and Sartorius CN are shown in Part I of this series of papers[1]. The previously described nuclear track etched Nuclepore PC membrane has a morphology notably different from the other membranes tested where single cylindrical pores have an almost uniform diameter throughout the membrane depth and doublets, triplets and greater coincidences display varying shapes in both their axial and radial directions. The other membranes examined are all produced via casting processes and thus showed similar forms with a variety of pore shapes. The Sartorius CN, Pall Posidyne and Gelman Supor microporous membranes exhibited homogeneous, tortuous structures composed of matrices of interconnected pores. A similar form was observed for the top surface of the Gelman Versapor membrane with the ‘skin’ layer laminated onto a thicker, more permeable substrate. The Domnick Hunter Asypor membrane also showed a tortuous pore structure, however, in this case there was a gradual change in the pore size from one side of the membrane the other to form an asymmetric construction.

The stability of pore size for several of the membranes shown in Table 1 was investigated over the range of ionic conditions to be employed in the microfiltration tests. Figure 5 shows some typical results for a sequence of Coulter porometer tests performed in accordance with ASTM E1294-89[4] using double distilled water as the wetting fluid rather than the more usual fluorinated hydrocarbon Porofil™. Each circular membrane sample was allowed to soak in the wetting fluid for a designated time period then removed and the test performed. Prior to immersion of the sample the pH of the water was adjusted using either Analar grade hydrochloric acid (HCl) or sodium hydroxide (NaOH). The uniformity of pore size with both pH and immersion time suggests that for the ranges and membranes examined there was little or no influence of pH on the measured pore size or pore size distributions. Unfortunately, due to experimental difficulties it was not possible to test all the membrane types. For those that could be tested the experimental procedure was difficult due to a design limitation of the porometer at lower pore sizes which resulted in the values measured being slightly different than those recorded when Porofil was used as the wetting fluid. However, the consistency of the results achieved suggests that they are sufficiently reliable for the present purposes.

Although the surface charge which commonly exists on membranes when in contact with electrolyte solutions has not been directly measured in this project a number of publications describe the phenomenon[5-8]. Surface charge is determined by streaming potential or electroosmotic flow techniques which measure the zeta(ζ-) potential of membranes in contact with solutions of known ionic composition and pH. The ζ-potential of membranes varies with pH to a degree dependent on the properties of the material from which they are made and the type of solution environment in which they are immersed. The available literature describes Pall Posidyne membranes as having ‘a high positive ζ-potential over the pH range 3 to 10’ when contacted with aqueous solutions. Here the membrane is deliberately manufactured via a co-casting process to provide an integral, homogeneously distributed positive charge throughout the membrane microstructure[5]. Sartorius CN membranes, on the other hand, are reported to carry a negative or zero surface charge over the pH range 2-12[6] whilst Nuclepore PC, polysulphone (e.g. Gelman Supor), mixed esters of cellulose (e.g. Domnick Hunter Asypor) are also known to exhibit a negative surface charge over the pH range 2-11[7,8] when immersed in the majority of aqueous based electrolytes.

To complete membrane characterisation an attempt was made to measure the wettability of a range of membranes when in contact with various suspensions. The technique involved the use of a high speed camera and video capable of taking and storing 400 frames per second. A sample strip of fresh membrane was placed in front of the high magnification lens attached to the camera such that only the membrane ‘edge’ was visible. A drop of the suspension to be tested was then positioned on the membrane surface using a micro-syringe and pictures of the moving droplet/membrane interface recorded with the video system. In this way it was possible to later examine the dynamic behaviour of the droplet at any time after contact with the membrane. Still images of the video pictures were taken with a thermal image printer (see Figure 6 for an example) and the contact angle between the droplet and the membrane measured with a protractor. Table 3 shows the contact angle variation with time for several membranes of differing construction and material composition. With all the membranes tested there was a fall in the measured contact angle with time as the water in the droplet progressively penetrated the membrane pores and spreadout over the surfaces. A sharp reduction of the contact angle with time is indicative of lateral migration of fluid through the membrane structure being more rapid than spreading over the surface; Nuclepore PC membranes have no lateral connectivity between pores, and hence an almost constant contact angle is observed. Both the magnitude and rate of change of the contact angle were dependent on the material properties of the membrane used, however all the membranes are considered hydrophilic in nature as the initial contact angles are less than 90º. Further experiments were performed to investigate the influence of droplet pH over the range 2--12 and the presence of particles in the droplet. Results showed that neither changing pH with HCl or NaOH nor the presence of solids over the concentration range 0-2% v/v had a significant effect on the measured contact angle and their effects on membrane wettability are considered negligible in the context of this paper. A number of the membranes characterised are thought to be coated during manufacture to either render them more hydrophilic or to change their surface characteristics[5,7,9]. Whilst a fresh, untouched membrane was used for each contact angle measurement it is noted in passing that such coatings can be removed (albeit at elevated temperatures and/or under vacuum) with a consequent increase in the measured contact angle.

MICROFILTRATION TEST RESULTS

The computer controlled apparatus used to assess membrane fouling has been described previously[1,2] and comprised a recirculation flow circuit wherein a challenge stream of known composition was pumped through an integral crossflow microfilter of planar geometry at constant pressure, crossflow and temperature. In this manner sequences of microfiltration experiments could be performed with different polymeric membranes and aqueous feed streams at otherwise identical, precisely controlled process conditions. Although the results of these tests are discussed in detail below it is worth noting some of the problems which render such an investigation potentially difficult.

The conventional method of comparing membranes is to examine filtration performance for a range of membranes under identical test conditions; the membrane yielding the best flux and/or particle retention characteristics is then judged to be the most suited to the given application. Frequently the membranes tested will be of similar pore size ratings with the rating identified prior to the tests on the basis of a knowledge of the size of particulates in the feed. Whilst such a technique is potentially suitable for a ‘one-off’ application, its use requires careful consideration in a more fundamental study. Unfortunately, membrane manufacturers rate their products according to different criteria. Some quote 98% removal ratings above a certain size (without mentioning the type of feed suspension), some 100% removal ratings, others use bubble point measurements whilst many apparently do not define any criteria. The situation is further complicated by the widely different pore sizes present in membranes of supposedly identical retention ratings. For instance the characterisation experiments identified 0.2 μm Nuclepore PC membranes as having a mean pore size in the region of 0.35 μm whilst 0.2 μm rated Domnick Hunter Asypor membranes exhibited a mean pore size of 0.75 μm (see Table 2). This two fold difference in mean pore sizes together with differing pore densities in the membrane sheets translates into a six fold difference in clean water fluxes and a two orders of magnitude difference in membrane permeabilities calculated through the Darcy equation. It follows that choosing membranes of differing structure but otherwise identical pore size, size distribution and/or permeability is all but impossible. Despite such potential problems, and in the absence of standard membrane rating procedures or better relational criteria, membranes with the same pore size ratings are used as the basis for comparison purposes. The data shown below as flux decline curves are typical examples of the many data groups accumulated for calcite and anatase suspensions. Similar trends were observed for numerous microfiltration experiments with china clay, unground and ground aragonite and yeast suspensions.

Effects of Membrane Type (Structure and Composition)

Figures 7 and 8 respectively show the flux decline curves for unground and ground calcite suspensions with different 0.2 μm rated membranes under otherwise identical filtration conditions; these conditions dictating that the calcite particles exhibited low surface charge in the double distilled water dispersant. When the unground calcite suspensions, with measured 10, 50 and 90% sizes of 11, 24.3 and 45.6 μm and thus significant proportions of constituent particles larger than the membrane pores, were tested there was a notable difference between the performance of the various membranes. Here, the asymmetric construction Domnick Hunter Asypor membrane gave the best flux performance and the homogeneous Pall Posidyne the worst whilst all filtrations maintained a visually clear filtrate throughout. As there was no evidence that the different flux decline rates observed were a consequence of adsorption of molecular foulants, membrane material type or particle/membrane surface charge effects it would appear that the flux declines were caused purely by mechanical interactions between the challenging particles and the membrane pore openings. These interactions leading to the formation of layer(s) of particulate deposits. In previous papers[1,2] the authors have suggested that flux decline is a result of two apparently independent fouling mechanisms. The first refers to a stochastic mechanism whereby an essentially irreversible penetration of particulates into the membrane pore entrances occurs. The second is associated with the largely reversible, shear limited, deposition of particulates at or near the membrane surface. Although it is difficult to determine the extent to which either of these two mechanisms contribute toward fouling in a given microfiltration, sufficient data were collected to suggest that for process conditions comparable to those illustrated on Figure 7 the degree of fouling is primarily dependent on the irreversible penetration of the relatively small fraction of finer feed particulates into the larger membrane pores.

Thus, the ‘tight’ Nuclepore PC and Gelman Versapor membranes gave similar fluxes (mean and distribution of pore sizes similar) whilst the Sartorius CN and Pall Posidyne membranes which exhibited larger mean and maximum pore sizes suffered more pronounced flux declines. The Domnick Hunter Asypor membrane, which has mean and maximum pore sizes significantly larger than the other membranes, produced a better flux performance however. An asymmetric membrane by its very nature has a variation of pore sizes from the ‘tight’ feed side to the ‘open’ downstream side which leads to a relatively high clean water fluxes (see Table 2). Although some of the larger surface pores may be blocked during filtration, the open area of the membrane is still significant as the lateral connectivity between pores inside the Asypor membrane is likely to be better than in the other membranes used. This helps to reduce the pressure drop across the membrane and maintain a higher driving pressure for the filtration.

When the median particle size of the calcite feeds was reduced by an order of magnitude from 24.3 μm to 2.6 μm prior to microfiltration through wet grinding, the flux performance became much less sensitive to the type of membrane used (Figure 8). In this case the flux decline curves measured for all the membranes were essentially identical with the filtrate clarity remaining visually clear in each test. Reducing the 50% size of the suspensions effectively increases the number of finer particles in the feed in relation to the (fixed) number of membrane pore entrances present. The similar flux performance for the different membrane types suggests that with more fines being present there is less penetration of particles into the membrane pores which results in the surface deposits largely determining the flux performance and not the membrane type or construction.

Figure 9 shows the effects of membrane type at a raised suspension concentration for unground calcite suspensions. By increasing the solids concentration the flux levels were reduced, but it is more pertinent to compare Figures 7 and 9 and observe the reduced sensitivity of flux decline to membrane type; a similar non-sensitivity being observed with ground suspensions at raised concentrations. The characterisation experiments showed that the membranes used in the microfiltration tests have widely differing properties in terms of structure, pore size and size distribution, permeability and materials of composition[1]. Thus, in a simplistic sense it would be reasonable to assume that a range of membranes would produce considerably different flux performance over a range of conditions. That this is often not the case is perhaps surprising and again illustrates that the surface deposits on the membrane control flux performance to the largest extent with membrane structure affecting flux levels to a lesser degree at higher relative fines concentrations.

The previous paragraphs have described the effects of membrane type where the majority of the particles in the feed are been larger than the maximum pore size found in the test membranes. Figure 10 shows the effects of membrane type when most particulates are similar in size to the pore sizes in the membranes. Here, anatase suspensions were filtered (10, 50 and 90% sizes of 0.20, 0.54 and 1.49 μm respectively) and the different membrane types produced only small differences in flux performance despite there being some instances were 'bleeding' of solids into the filtrate occurred during the initial stages of filtration. At increased feed solids contents there was again a reduced influence of membrane structure on flux levels. The relative closeness of the membrane pore sizes and particle sizes present in the feed indicates that pore penetration by particulates during filtration would have occurred to an extent dependent on the overlap between the size distributions (see Figure 11). That this overlap did not significantly affect the flux levels recorded (in Figure 10) is important and allows some definition of the term 'particle fines' to be made. In the context of crossflow microfiltration, particle fines may be considered to be those particulates forming the fouling layer(s) which have sizes approaching that of the pores in the filtering septum. The extent to which these particulates influence flux performance and filtrate clarity is dependent on their number relative to the number of pore entrances in the membrane.

Influences of Membrane Wettability

Whilst no microfiltration experiments were performed to directly compare membranes of differing wettability, the tests comparing membrane type gave some insight into its effect on flux decline. The data obtained from the characterisation experiments show that Domnick Hunter Asypor membranes give the highest (initial) contact angles when challenged with a variety of suspension mixtures, indicating their greater hydrophobicity. When microfiltration experiments were performed with these membranes the fluxes recorded frequently rose during the initial period of the tests and typically for up to 60 s. Although the membranes were wetted with double distilled water prior to all the microfiltration tests it seems that in the case of the Asypor membranes such a procedure was not always completely successful. However, once the initial rising flux period ended, and all the membrane surfaces were presumably completely wetted, flux performance would follow the trends observed in experiments with the other, more hydrophillic, membranes. Sufficient data were accumulated to suggest that for particulate suspensions, such as those used here, and longer filtration times, flux levels will not be adversely affected by membrane wettability. These findings have recently been confirmed for the crossflow microfiltration of cationic surfactant suspensions with PTFE membranes[10], the latter exhibiting a contact angle in the region of 120° with aqueous solutions. Fluxes here could be seen to rise for the first ten minutes of a test and thereafter follow the flux decline observed with, for instance, Nylon 66 membranes of greater hydrophillicity.

Effects of Membrane Surface Charge

The data in Figure 12 show the typical influence of membrane surface charge on flux decline for aqueous anatase suspensions. These tests were performed at a pH were it is known that the particles in the feed have a high negative ζ-potential and the Sartorius CN and Pall Posidyne membranes have 'high' negative and positive ζ-potentials respectively[5,6]. Although it is difficult to completely isolate the influence of membrane charge due to differences in membrane structures and permeabilities the results obtained with anatase suspensions (the material with the highest potential surface charge tested) indicate that in the absence of adsorption and chemical interaction the ζ-potential of the membrane plays only a relatively minor role in determining fouling rates during microfiltration. Membrane charge has more influence when higher feed concentrations are used, however, flux differences are only small and could easily be accounted for by factors such as membrane structure.

DISCUSSION

The experimental data presented in this paper have shown that when conditions allow mechanical interactions between the particulates drawn toward, and the pores within, a filtering membrane can alone influence flux decline in crossflow microfiltration. In the absence of adsorption of molecular foulants and chemical effects, the greatest differences in flux levels between membranes of varying morphology are seen at lower feed concentrations when a relatively small number of fines are present in the challenge stream. When this is so, the fines are thought to penetrate the internal structure of the membrane and cause essentially irreversible fouling of the pores. Should the converse be true, and a greater proportion of fines be present in the feed, there are a greater number of particles approaching each membrane pore entrance (on average) and the largely reversible deposition of particulates at the membrane surface adjacent to the feed stream is more prevalent. These arguments suggest that when the number of particles approaching each pore is increased, for instance by raising the solids concentration or crossflow velocity of the feed stream, the arrangement of the particulate deposits near the filtering surface(s) of the membrane will dictate the flux decline rather than the type of membrane used. The experimental data presented in Part's I and II of this series of papers[1,2] have proven the hypothesis[11,12] that any of the effects observed when the process conditions are changed can be directly attributed to the properties of the feed stream rather than the properties of the membrane used to achieve the separation. In these instances, the membrane merely acts as a support and the layer(s) of particles deposited during the initial stages of filtration form a so called ‘secondary membrane’ or ‘cake’ through which the remaining suspension is filtered. Moreover when particulates are excluded from the internal membrane pores, fluxes are often enhanced and operations such as backflushing are easier to perform. This infers that it would be prudent to choose a membrane (for a given separation) whose representative pore size is smaller than the size of all particulates in the feed stream, but not small enough to restrict unduly the filtrate flow.

The amount of realistic experimental data accumulated by the authors during the investigations is considered to cover a sufficiently wide range of operating conditions to support the above findings in a general sense. Furthermore, the data indicate that there is little need to manufacture polymeric membranes for crossflow microfiltration with such a wide range of pore sizes and morphologies. Membranes with larger pore size ratings appear to offer no advantage in terms of flux performance, in fact they are detrimental in many cases! From such a conclusion it would seem tempting to suggest that the range of membranes and pore sizes available has developed simply as a consequence of the extrapolation of ultrafiltration concepts rather than fundamental work into microfiltration. If this is true, the potential for improving crossflow microfiltration technology through the development of more appropriate, process specific, membranes is obvious and should be tackled with some urgency, particularly in the light of the new markets recently identified[13].

Previous ultrafiltration studies have suggested that both membrane charge and wettability, estimated through the contact angle between the solvent phase and the membrane, can be related to filtration performance[14-17]. Whilst the interactions between the often complex feed streams and the membrane surfaces are not completely understood their consequences in UF are readily observed as unacceptable permeate fluxes and/or poor solute rejections. When molecular material is present in the feed, adsorption of fouling species (to a degree dependent on the properties of the feed and the membrane) can occur and the material from which the membrane is constructed must be carefully tailored to the requirements of the feed stream to limit fouling. Similarly, when both the feed stream and membrane carry high surface charges, membrane choice can be critical in order to prevent excessive fouling through the additional particle deposition induced by suspension/membrane attractions. In microfiltration molecular species and significant amounts of larger particulate type material could be present in the same feed. Both of these are potential foulants in their own right or in combination and general statements about their contributions to fouling are difficult. Whilst the complexity of such 'mixed' systems is beyond the scope of the present work, and would alone demand an extensive experimental investigation, the data presented in this paper show that for mineral based feeds in the absence of molecular foulants, neither membrane surface charge nor membrane wettability are likely to significantly affect flux decline. Although the surface coatings fixed to some membranes during manufacture can help to modify their wettability and/or surface charge characteristics, it would seem that after an initial short period of microfiltration it is the properties of the deposited layers which govern further fouling and not the chemical of structural composition of the filtering septum.

CONCLUSIONS

The inherent complexity of the interactions which occur near to the surfaces of membranes dictates that many of the experimental programme behind this work was very extensive, and therefore the conclusions drawn in this paper have relied on the results from a large number of experiments. This 'black box' approach has shown that fouling in crossflow microfiltration can be affected by membrane morphology under some process conditions and these are highlighted in Table 4 (the influence of membrane pore size is duplicated from Part I[1] for completeness). The extensive experimental data presented in this series of papers have not only shown how the characteristics of the feed stream and the filtering membrane can be related to flux decline but also pointed the way to a better fundamental understanding of fouling. Such an understanding, in turn, indicates how membrane filtration processes can be improved.

REFERENCES

1. Tarleton E.S. and Wakeman R.J., 1993, Understanding flux decline in crossflow microfiltration - Part I: Effects of particle and pore size, *Trans IChemE*, **71**(A), 399.

2. Tarleton E.S. and Wakeman R.J., 1994, Understanding flux decline in crossflow microfiltration - Part II: Effects of process parameters, *Trans IChemE*, **72**(A), 431.

3. Wakeman R.J. and Tarleton E.S., 1992, Membrane characterisation: The need for a standard, *Process Industry J.*, **July**, 16.

4. American Standard Test Method E1294, 1989.

5. Technical brochure literature (Pall Process Filtration).

6. Bowen W.R. and Clark R.A., 1984, Electro-osmosis at microporous membranes and the determination of zeta-potential, *J. Colloid Interface Sci.*, **97**(2), 401.

7. Ibanez J.A., Forte J., Hernandez A. and Tejerina F., 1988, Streaming potential and phenomenological coefficients in Nuclepore membranes, *J. Mem. Sci.*, **36**, 45.

8. Lee C.K. and Hong J., 1988, Characterisation of electric charges in microporous membranes, *J. Mem. Sci.*, **39**, 79.

9. Technical brochure literature (Nuclepore Corporation).

Cite paper as: Tarleton E.S. and Wakeman R.J., 1994, Understanding flux decline in crossflow microfiltration: Part 3. Effects of membrane morphology, *Trans IChemE*, **72**(A), 521-529.

10. Akay G. and Wakeman R.J., 1993, Permeate flux decay during crossflow microfiltration of a cationic surfactant dispersion, *Proc. FILTECH Conference*, pp.221-232, The Filtration Society, Karlsruhe, Germany.

11. Fischer E. and Raasch J., 1986, Model tests of the particle deposition at the filter medium in cross-flow filtration, *Proc. 4th World Filtration Congress*, pp.11.11-11.17, KVIV, Ostend, Belgium.

12. Murkes J. and Carlsson C.G., 1988, *Crossflow Filtration*, Wiley, Chicheseter.

13. Strathmann H., 1989, Economical evaluation of the membrane technology, in *Future Industrial Prospects of Membrane Processes*, Cecille L. and Toussaint J.-C. (Eds.), Elsevier, London.

14. Fane A.G., 1986, Ultrafiltration: Factors influencing flux and rejection, in *Progress in Filtration and Separation (Vol. 4)*, Wakeman R.J. (Ed.), pp.101-179, Elsevier, Amsterdam.

15. Gekas V. and Zhang W., 1989, Membrane characterisation using porosimetry and contact angle measurements: A comparison with experimental ultrafiltration results, *Process BioChem.*, **October**, 159.

16. Oldani M. and Schock G., 1989, Characterisation of ultrafiltration membranes by infrared spectroscopy, ESCA, and contact angle measurements, *J. Mem. Sci.*, **43**, 243.

17. Gekas V., Persson K.M., Wahlgren M. and Sivik B., 1992, Contact angles of ultrafiltration membranes and their possible correlation to membrane performance, *J. Mem. Sci.*, **72**, 293.

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FIGURES AND TABLES

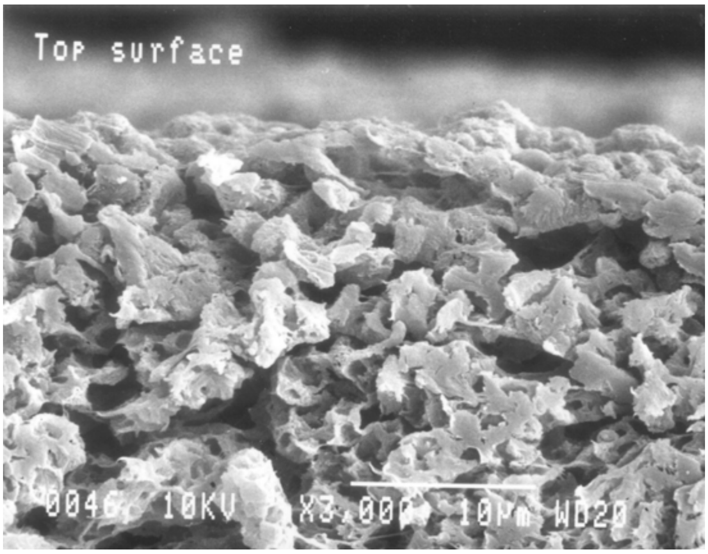

Figure 1: SEM showing the cross-section of a 1.2 µm rated Pall Posidyne membrane.

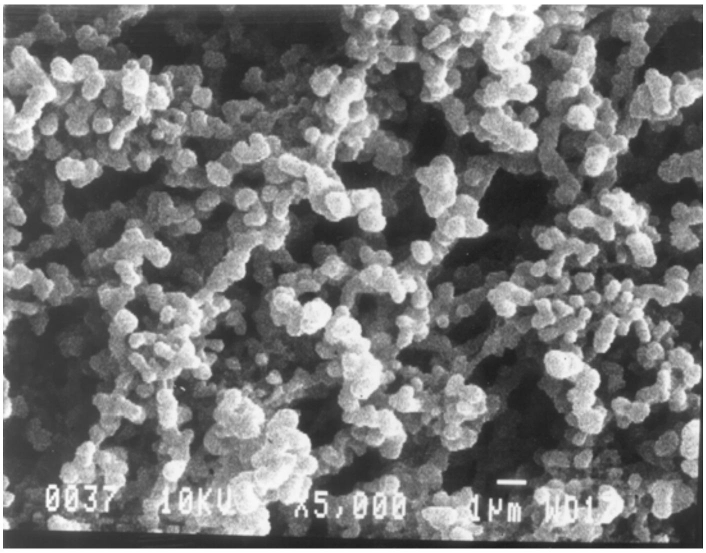

Figure 2: SEM showing the topograhpy of a 0.8 µm rated Gelman Supor membrane.

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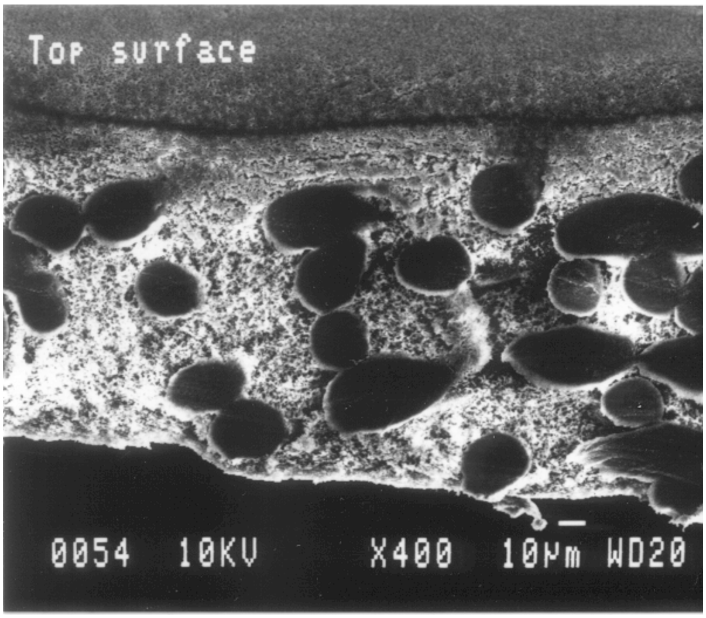

Figure 3: SEM showing the topography and cross-section of a 0.2 µm rated Gelman Versapor membrane.

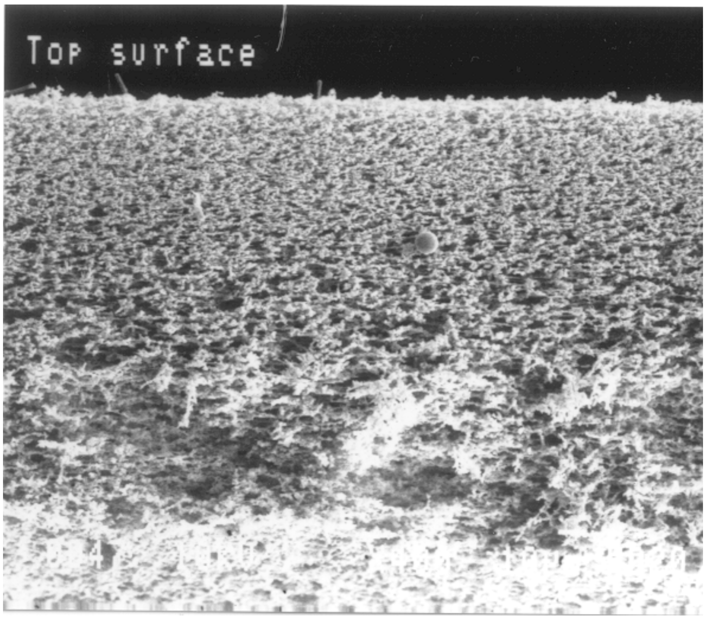

Figure 4: SEM showing the cross-section of a 0.8 µm rated Domnick Hunter Asypor membrane.

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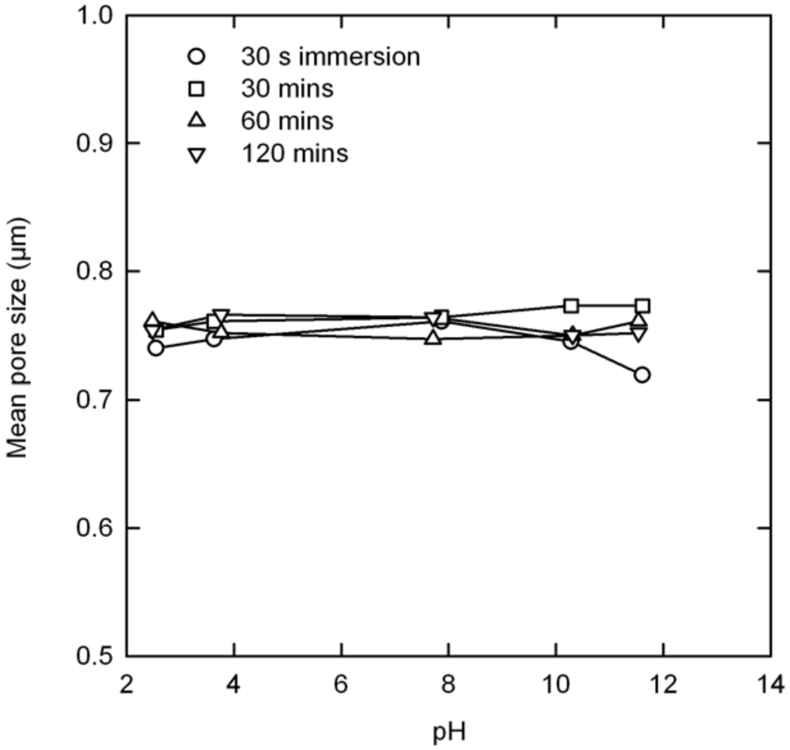

Figure 5: Mean pore size variation with pH for a 0.2 µm rated Pall Posidyne membrane.

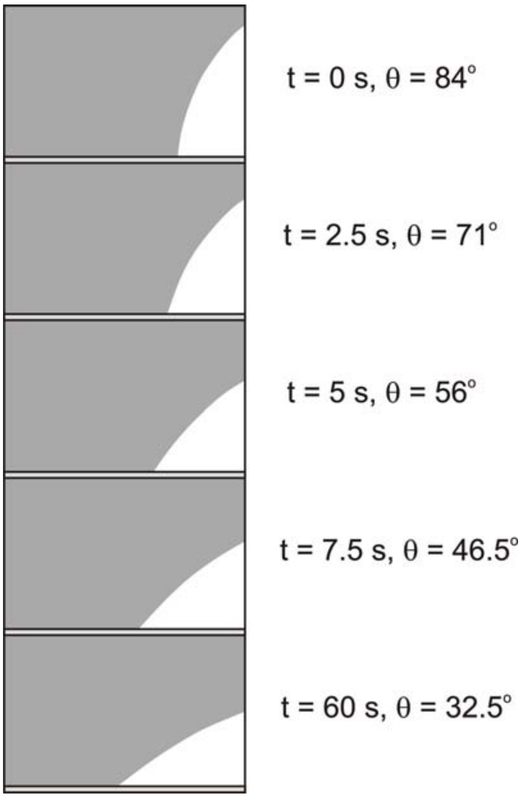

Figure 6: Variation of the contact angle (θ) at the interface between a 0.8 µm Asypor membrane and a droplet of double distilled water with time of contact.

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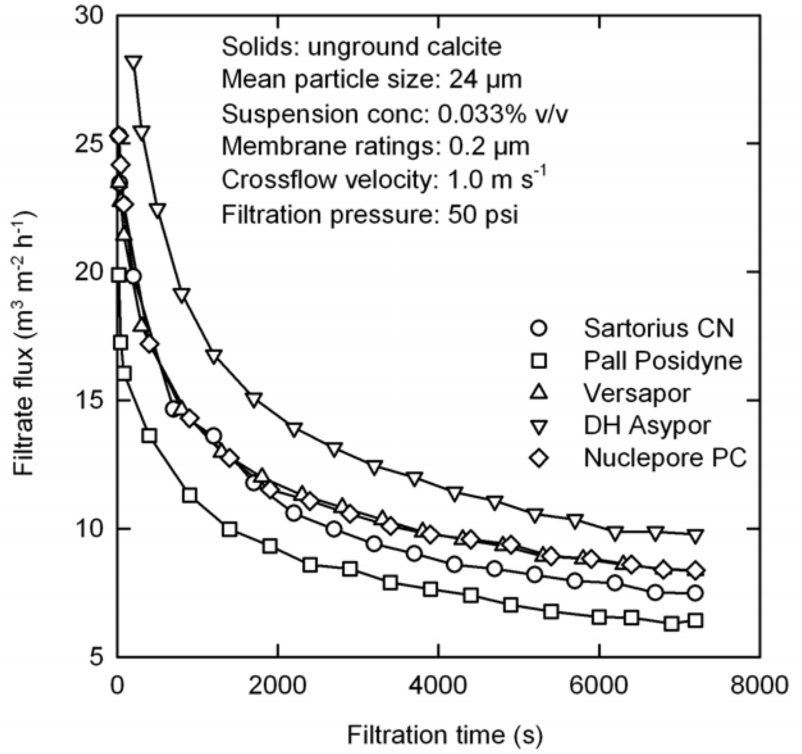

Figure 7: Effect of membrane type on flux decline for unground calcite suspensions at low concentration.

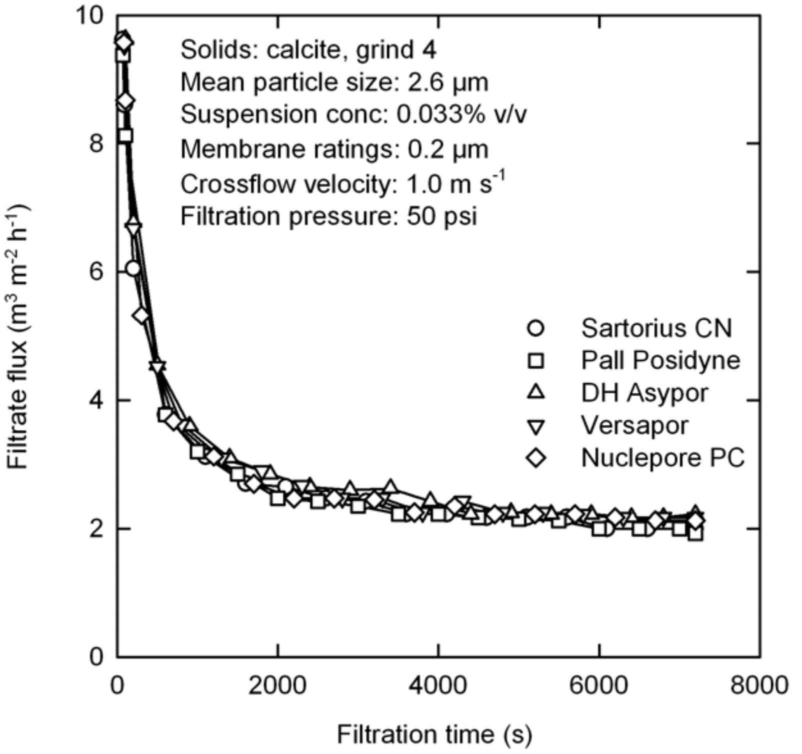

Figure 8: Effect of membrane type on flux decline for ground calcite suspensions at low concentration.

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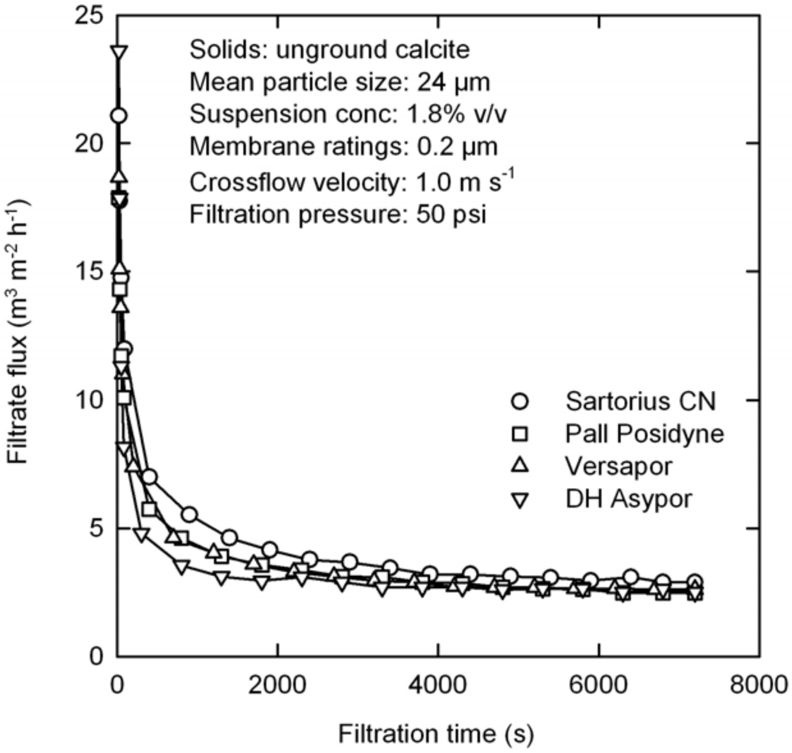

Figure 9: Effect of membrane type on flux decline for unground calcite suspensions at raised concentration.

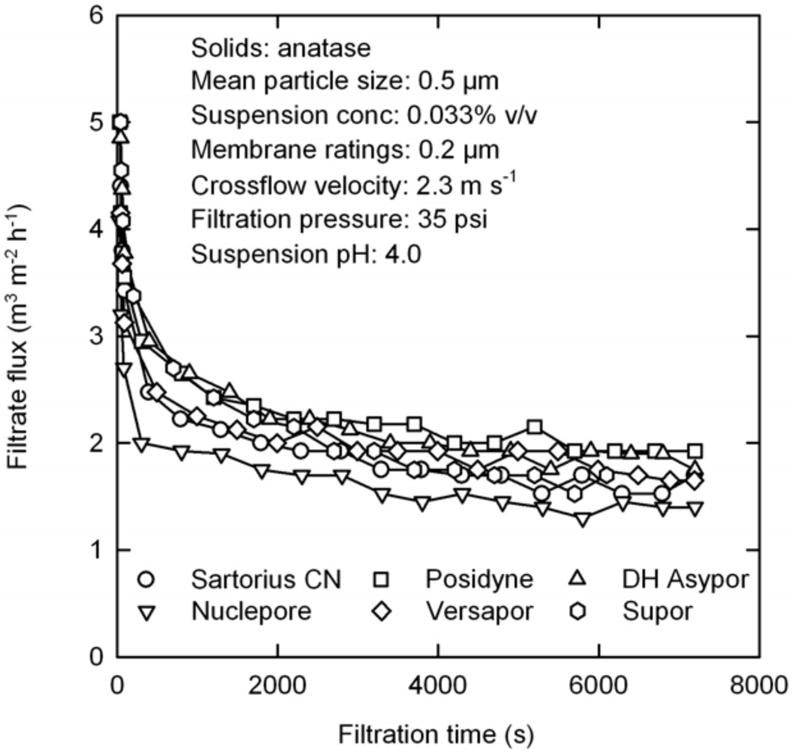

Figure 10: Effect of membrane type on flux decline for anatase suspensions.

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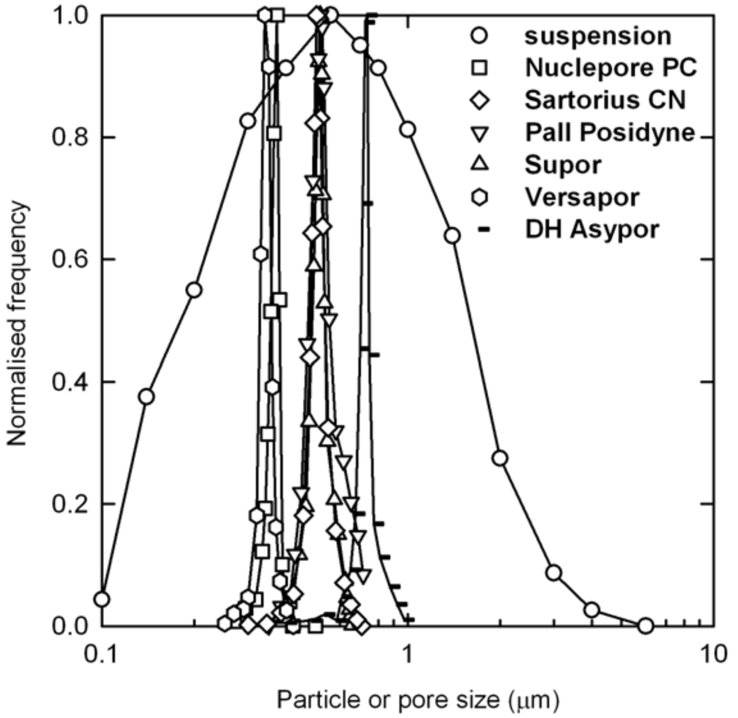

Figure 11: The overlap between the size distributions of an anatase suspension and 0.2 μm rated membranes.

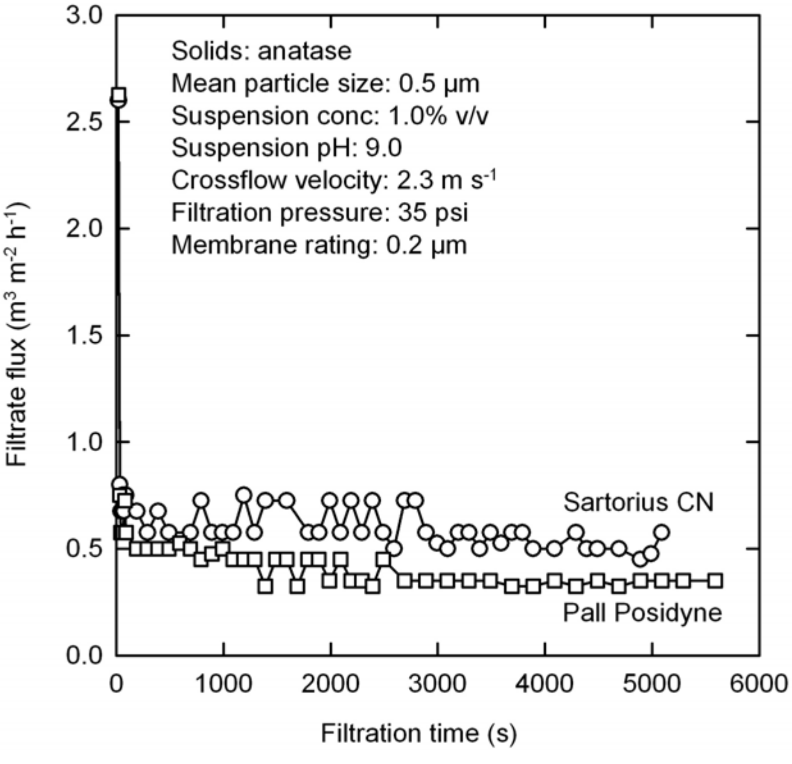

Figure 12: Effect of membrane surface charge on flux decline for anatase suspensions.

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Membrane designation	Polymer type	Membrane morphology†
Nuclepore PC	polycarbonate	nuclear track etched
Sartorius CN	cellulose nitrate	cast, homogeneous membrane of microporous construction
Pall Posidyne	nylon 66	homogeneous membrane cast on a non-woven polyester support
Gelman Supor	polysulphone	homogeneous microporous membrane
Gelman Versapor	acrylic copolymer	homogeneous microporous membrane cast on a non-woven nylon substrate
Domnick Hunter Asypor	mixed cellulose ester	asymmetric microporous membrane

†as described by the manufacturer

Table 1: Range of membranes used in microfiltration tests.

Membrane	Rating (μm)†	Thickness (μm)†	Mean pore size (μm)	Pore size variance (μm^2)‡	Water flux** (ml cm^{-2} min^{-1})
Nuclepore PC	10	10	10.26*	3.18	456
	5	10	5.56*	0.15	390
	1	11	1.26*	0.0047	56.4
	0.2	10	0.35*	0.00029	11.2
Sartorius CN	8	140	3.63	0.195	355
	5	140	3.15	0.108	198
	1.2	140	1.45*	0.026	136
	0.2	130	0.51*	0.0019	15.9
Pall Posidyne	5	135	3.90	0.215	223
	1.2	135	1.94*	0.095	91
	0.2	150	0.54*	0.0052	9.7
Gelman Supor	0.8	150	1.22	0.035	71.6
	0.45	150	0.70	0.0039	23.5
	0.2	150	0.52	0.0028	18.5
Gelman Versapor	0.2	185	0.35	0.00037	16.5
DH Asypor	0.8	165	1.75*	0.024	190
	0.2	175	0.75*	0.0061	66

*average value; †manufacturers quoted value; ‡in one sample disk
**double distilled water @20ºC and 10 psi permeation pressure

Table 2: Measured membrane properties.

Membrane	Rating (μm)	Contact angle at *t* = 0 s (º)	Angle at *t* = 10 s (º)	Angle at *t* = 30 s (º)
Nuclepore PC	0.2	53	51	49
Sartorius CN	0.2	31	<5	< 5
Pall Posidyne	0.2	42	-	-
DH Asypor	0.2	53	45	34
DH Asypor	0.8	84	45	36

Table 3: Contact angles for a range of membranes and double distilled water droplets.

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Property	Comment
Membrane morphology	When a small fraction of fines are present in a low concentration suspension exhibiting a majority of particulates larger than the representative pore size, a significant difference in flux can be observed with different membranes. At higher crossflows and concentrations and smaller particle sizes there was a reduced influence of membrane type on flux. When the majority of particulates in the feed have sizes close to the pore sizes in the membrane, little influence of morphology on flux levels is observed.
Membrane wettability	Membranes exhibiting a higher contact angle and thus greater hydrophobicity produce rising fluxes during the initial periods of microfiltration. At longer filtration times fluxes are similar to those recorded for more hydrophillic membranes.
Membrane surface charge	Only minor differences in flux performance over the range of membranes and experimental conditions used.
Membrane pore size	Little influence on flux or rejection when the majority of the particles in the feed were significantly larger than the pores in membrane. Filtrate quality and flux levels often worse when a significant proportion of the particles in the feed were close to or smaller than the membrane pores. If the pore sizes in the membrane were much larger than the particles in the feed stream, flux rates improved to higher levels although solids rejection was very poor. In a minority of tests poor rejection was observed when comparisons of pore/particle size suggested that filtrate clarity should be good.

Table 4: Summary of the effects of membrane type and construction on flux decline in crossflow microfiltration.