Comparative characterisation of different commercial UF membranes for drinking water production

Bernhard Schlichter, Valko Mavrov and Horst Chmiel

ABSTRACT

In this study, nine commercially available ultrafiltration membranes used in drinking water production were characterised. The aim of the study was to compare the molecular weight cut-off (MWCO) and the membrane permeability of a selection of currently available ultrafiltration membranes. Permeability and MWCO are important criteria for the selection of ultrafiltration membranes with regard to efficiency and rejection of dissolved and particulate substances. This study provides an overview of the differences in cut-off and permeability between commercial UF membranes with similar specifications.

To this end, tests were conducted using eight hollow fibre membranes with effective membrane surface areas of between 0.04 and 0.26 m^2 and one type of flat sheet membrane with an effective filtration area of 0.0044 m^2. Cross-flow filtration experiments using a mixture of dextrane as a feed solution were performed to determine MWCO. The molecular weight of the dextrane used in the feed solution ranged from 8–2,000 kD. The concentration distribution of the dextrane in the feed and the permeate was determined by gel permeation chromatography (GPC) in the range of 10–1,000 kD.

These tests showed that, from the nine UF membranes tested, four of them displayed a MWCO of below 1,000 kD with pure water permeabilities of 180–400 $l/(m^2 \cdot h \cdot bar)$. A further four displayed no MWCO in the range examined (10–1,000 kD) with pure water permeabilities of 130–880 $l/(m^2 \cdot h \cdot bar)$ and therefore their cut-offs must be in the range above 1,000 kD. One membrane, which showed no rejection for any dextrane fraction with a pure water permeability of 2,700 $l/(m^2 \cdot h \cdot bar)$, could be classed as a microfiltration membrane.

Key words | characterisation, dextrane, drinking water, molecular weight cut-off (MWCO), ultrafiltration

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INTRODUCTION

To produce drinking water from surface water effectively, various impurities have to be removed from the raw feed water, depending on its quality. A combination of processes including an ultrafiltration stage is considered to be adequate for the removal of particles, turbid matter, microorganisms (cysts, bacteria, viruses) and, to a certain extent, natural organic matter (NOM) (Hagmeyer 1996). However, nanofiltration or reverse osmosis have to be applied if further natural organic matter, water hardness or salinity are to be reduced in addition to these components.

In contrast to nanofiltration or reverse osmosis membranes, microfiltration and ultrafiltration membranes are purely pore membranes whose rejection capacity is similar to a sieving effect. Therefore, rejection of the above-mentioned components by these membranes is determined by their pore size. Whereas microfiltration membranes are defined as having a pore size of
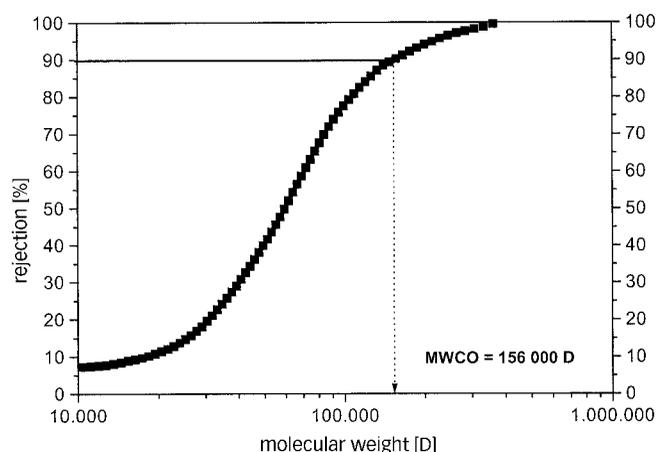
Figure 1 | Rejection as a function of molecular weight for an ultrafiltration membrane.

10–0.05 μm (Ripperger 1992), ultrafiltration membranes are generally determined by the 90% rejection of dissolved substances of a defined molecular weight (Figure 1). This rejection characteristic of an ultrafiltration membrane, is defined as the molecular weight cut-off (MWCO) and is specified in Dalton (D) or Kilodalton (kD) (1 Dalton = 1 g/mol). As opposed to microfiltration membranes, bubble-point measurement is not suitable and to some extent electron microscopy is not sufficient to determine the pore size of ultrafiltration membranes.

As a rule, filtration experiments using various test substances with a specific molecular weight, such as proteins (e.g. BSA), polysaccharides or other synthetic polymers, are performed to define the cut-off for ultrafiltration membranes (Ripperger 1992). However, it is necessary to conduct a series of individual tests with selected substances of different molecular weight so as to assess the rejection capacity of UF membranes over a wide molecular range (Scharnagl 1997).

In contrast, filtration experiments with mixtures of one kind of polymer with a defined composition and wide molecular distribution are less complicated because, in this case, one single filtration test is sufficient to determine cut-off. When combined with a suitable analytical process, these experiments allow rapid and non-destructive membrane characterisation.

MATERIALS AND METHODS

In this study, membrane cut-off was determined using a test mixture of dextrane. This characterisation process was chosen to determine MWCO because it has proven to be a reliable and easily reproducible method. The filtration tests were performed according to both the ASTM (American Society for Testing and Materials) Designation: E 1343-90 (1990) and the French AFNOR (Association Francaise de Normalisation) Standard NF X 45-103 (1997). These standards define the operating conditions for the filtration tests and the principles for the analytical determination of dextrane concentration by GPC.

A cross-flow laboratory-scale plant, as shown in the following diagram (Figure 2), was used to determine membrane permeabilities and to conduct the filtration tests.

To minimise concentration polarisation and cover layer formation on the membrane surface, the filtration tests were conducted in cross-flow mode–in accordance with standard practice.

The pure water permeability (PWP, l/(m² · h · bar)) for these membranes was determined using de-ionised water (electrical conductivity below 0.1 μS at 20°C) at trans-membrane pressures of 0.50 and 0.70 bar with a retentate flow of 200 l/h. The permeate volume was determined by measuring the permeate mass for a time interval of 90 seconds after a filtration time of 48 hours. The measuring of permeate mass was repeated ten times within the following hour. The PWP was calculated by the following equation (1):

$$PWP = \left(\frac{V}{A \cdot \Delta t \cdot \Delta p} \right),\qquad(1)$$

PWP, pure water permeability [l/(m² · h · bar)];
V, Δ*t*, Volume of permeate [l] for a filtration time Δ*t* [h] calculated from the permeate mass determined by a balance for a pure water density at 20°C of 0.9982 g/l;
A, membrane area [m²];
Δ*p*, trans-membrane pressure [bar].

The PWP was determined both before and immediately after the dextrane tests so as to assess any changes in the membranes. A 0.7% dextrane solution with molecular
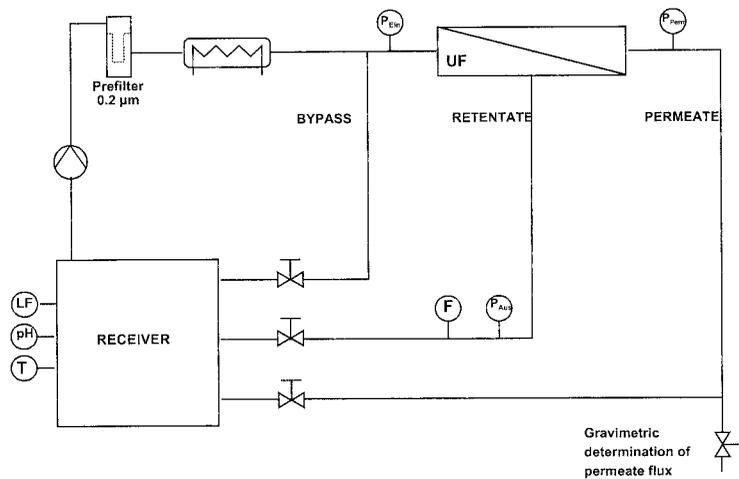
Figure 2 | Flow sheet of the laboratory-scale test set-up.

weights ranging from 8 kD to 2,000 kD was selected for these tests, because no adsorption effects could be observed for the dextrane polymer on the membrane materials under investigation. Sodium azide (0.01% by mass) was added as a biocide to ensure the durability of the solution. Table 1 gives an overview of the dextrane fractions used for the dextrane solution preparation in filtration tests.

The laboratory-scale set-up, used for these tests, is similar to the plant illustrated in Figure 2, the only differ-

ence being that a prefilter was not installed in order to avoid any interaction with the polymer solution used. The filtration tests using dextrane were conducted under the same conditions as the tests to determine the PWP, i.e. at a temperature of 20°C, at a trans-membrane pressure of 0.50 bar and a retentate flow of 200 l/h.

Cross-flow velocities were between 0.8 and 2.2 m/s. Owing to the different module structures and the construction of the laboratory plant, it was not possible, at constant trans-membrane pressure, to maintain one constant cross-flow velocity for all the modules under study. However, according to Gerner's investigations (Gergen *et al.* 1989), maintaining a constant flow velocity is only of minor significance. It is more important to set the trans-membrane pressure accurately, a fact that is verified by tests with a UF membrane, characterised for two different trans-membrane pressures of 0.50 and 0.70 bar (Figure 3).

As Figure 3 illustrates for the membrane under study, even a minor pressure increase of 0.20 bar can result in the MWCO being doubled. After a filtration period of 30 minutes, 5 ml samples were taken from the feed and permeate solutions to determine the dextrane concentrations.

The concentrations of the different dextrane fractions in the feed and permeate solutions were determined in the range of 10–1,000 kD by gel permeation chromatography. These measurements were conducted using the analytical

Table 1 | Overview of the composition of the dextrane solution for filtration tests

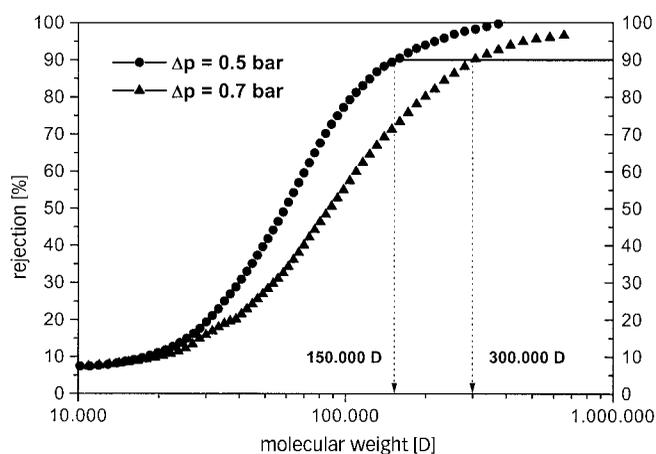| Product	Manufacturer	Range of molecular weight [kD]
Dextrane 8	Serva/Boehringer	8–12
Dextrane 15	Serva/Boehringer	15–20
Dextrane 35	Serva/Boehringer	35–50
Dextrane 60	Serva/Boehringer	60–90
Dextrane 100	Serva/Boehringer	100–200
Dextrane 200	Serva/Boehringer	200–300
Dextrane T 500	Pharmacia	60–2000

Figure 3 │ Rejection as a function of molecular weight for a ultrafiltration membrane, characterised at 0.50 bar and 0.70 bar.

column BIOSEP SEC S-4000 supplied by the Phenomenex company. A refractory index detector was used to detect the dextrane concentrations. In the range between 10 and 1,000 kD, the detector can measure up to 850 different fractions.

The dextrane quantity of a specific molecular weight fraction i, rejected by the membrane, was calculated according to equation (2) for each fraction i (De Balmann & Nobrega 1989; Schock *et al.* 1989).

$$R_i = \left(1 - \frac{C_{i,P}}{C_{i,F}} \right) \cdot 100 , \tag{2}$$

i, Fraction number ($i = 0$–850);
R_i, Rejection of the molecular weight fraction i [%];
$C_{i,P}$, Concentration of dextrane fraction i in the permeate [mg/l];
$C_{i,F}$, Concentration of the dextrane fraction i in the feed [mg/l].

The MWCO of the membrane was determined (Figure 1) by plotting the rejection R_i calculated for 850 different molecular weight fractions of dextrane against the respective molecular weight. The MWCO is obtained at 90% rejection.

In this study, nine commercially available UF membranes, used to produce drinking water from surface water, were tested and compared. Table 2 summarises the membranes characterised and the respective manufacturing specifications. The new membranes underwent operation according to manufacturers' specifications and

Table 2 │ Overview of the membranes tested (manufacturing specifications, as far as declared)

Membrane	Type of membrane	Material	MWCO [kD]	PWP [l/(m² · h · bar)]	Filtration area [m²]
UF1	Flat sheet	Polyaramide	50	500	0.0044
UF2	Hollow fibre	Polyacrylonitrile	13	200	0.10
UF3	Hollow fibre	Cellulose acetate	150	—	0.26
UF4	Hollow fibre	Cellulose acetate	100	250	0.08
UF5	Hollow fibre	Polysulfone	100	700–800	0.09
UF6	Hollow fibre	Polyacrylonitrile	100–200	—	0.10
UF7	Hollow fibre	Polyether sulfone	150–200	—	0.04
UF8	Hollow fibre	Polyether sulfone	50	—	0.08
UF9	Hollow fibre	Polysulfone	50	—	0.11

Table 3 | MWCO and PWPs of membranes in Group I

Membrane	MWCO Results [kD]	PWP [l/(m² · h · bar)]
UF 1	150	180–360
UF 2	300	280–320
UF 4	150	200–210
UF 9	400	380–400

Figure 4 | Rejection as a function of molecular weight for UF membranes in Group I.

were in operation with de-ionised water for 48 hours before characterisation took place.
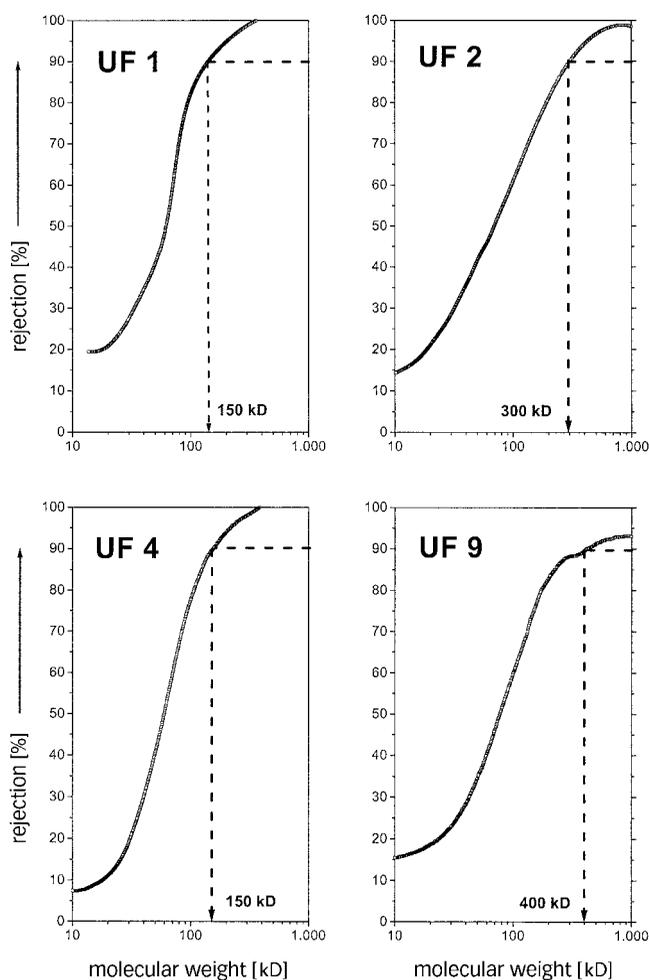
RESULTS AND DISCUSSION

The aim of the tests was to characterise commercially available UF membranes used for drinking water production according to a uniform process, so as compare the MWCOs of the membranes.

In this case, the absolute values for the MWCO are of secondary importance because changes in test conditions can lead to different results as experiments on the pressure dependence of the process showed.

In accordance with the characterisation results, the membranes can be divided basically into two groups as follows: Group I containing membranes which achieved 90% rejection for dextrane and Group II comprising membranes which did not achieve a MWCO in the range from 10 to 1,000 kD, but showed some rejection for dextrane with a molecular weight of 1,000 kD. Therefore the MWCO for the membranes in Group II could be defined as MWCO>1,000 kD.

Group I comprises the membranes that showed 90% rejection of dextrane in the molecular range of between 10–1,000 kD and includes the ultrafiltration membranes UF1, UF2, UF4 and UF9 (Table 3). The cut-offs determined for these membranes are in the range of 150–400 kD with PWPs of between 180 and 400 l/(m² · h · bar).

The rejection behaviour for Group I membranes is illustrated in Figure 4.

Group II comprises the remaining ultrafiltration membranes, which clearly showed rejection values of under 90% in the molecular range tested (Table 4). This group includes the ultrafiltration membranes UF3, UF5, UF6, UF7 and UF8 with PWPs ranging from 130 to 880 or in one exceptional case 2700 l/(m² · h · bar). These membranes showed rejection values of between 50% and 70% for a dextrane solution of 1,000 kD, the only exception being the membrane UF6, which showed high pure water permeability but no rejection for any dextrane fraction.

Table 4 | MWCO, rejection for Dextrane 1000 kD and PWPs of membranes in Group II

Membrane	MWCO Results [kD]	Rejection for Dextrane 1000 kD	PWP [l/(m² · h · bar)]
UF 3	> 1000	65%	130–160
UF 5	> 1000	70%	740–770
UF 6	> 1000	0%	2600–2700
UF 7	> 1000	50%	810–880
UF 8	> 1000	50%	500–520

Figure 5 | Rejection as a function of molecular weight for UF membranes in Group II.

Membrane defects could be ruled out for this membrane by integrity tests with a particle counter.

By comparing the pure water permeability rates determined for the membranes in both Groups I and II, it can be seen that, with the exception of the membrane UF3, PWP increases when MWCO is higher. As PWP does not solely depend on pore size, but also on other parameters such as surface porosity, pore size distribution or membrane material hydrophilicity, a direct relation between MWCO and membrane permeability cannot be expected.
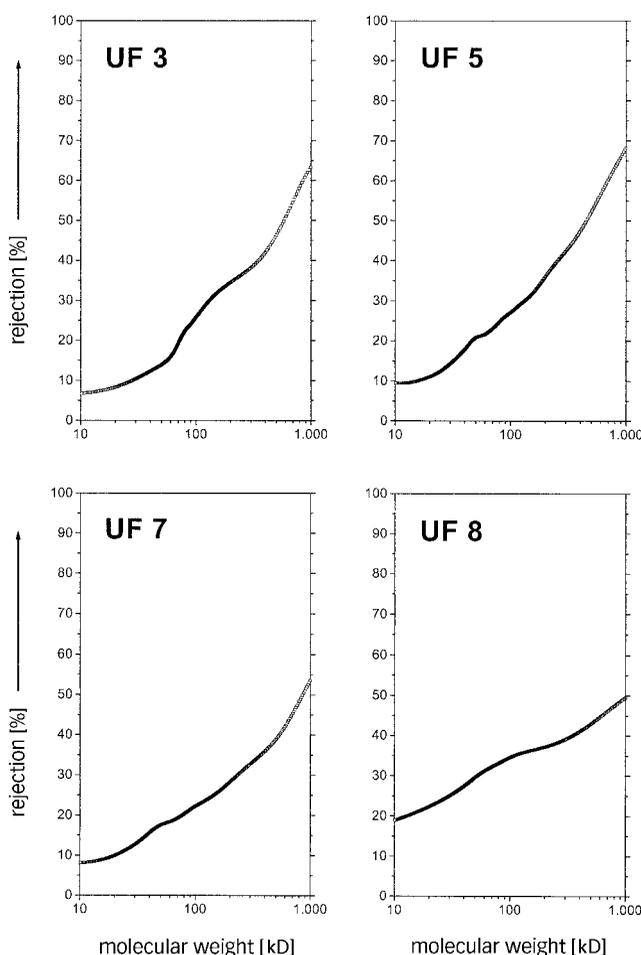
The rejection behaviour for Group II membranes is illustrated in Figure 5. In this case, it is evident that the pore size distribution of these membranes is much broader than that of Group I membranes.

According to studies by Granath and Kvist (1967) focusing on the molecular size of dextrane in neutral aqueous solutions, dextrane diameter can be calculated from the molecular weight by using the following equation (3).

$$d_{\mathrm{DEX}} = 2 \cdot 10^{(0,47 \cdot \lg MW - 1,513)}, \qquad (3)$$

d_{DEX}, diameter of a dextrane molecule [nm];
MW, molecular weight of dextrane [D].

The size of the membrane pores can be deduced by determining the molecule diameter of the dextrane which permeates or is rejected (Zeman & Wales 1981). To calculate the average pore size of the membranes, the molecule diameter of the dextrane fraction *i*, with a rejection of 90%, was used for equation (3). For Group I, pore sizes in the range of 17–26 nm (Table 5) were determined.

Pore sizes for Group II membranes were in the range of over 40 nm. This result was confirmed by an electron micrograph for the membrane UF7 (Doyen 1997). This micrograph can detect pores in the range of 40–80 nm on the membrane surface. For the membrane UF6 under study, which exhibited no rejection for dextrane with a molecular weight of 8–2,000 kD at all, a minimum pore width of 56 nm can be calculated. Owing to this large pore width and the high permeability of 2700 l/(m² · h · bar), this membrane is classed as a microfiltration membrane.

Table 5 | Pore sizes of the UF membranes estimated from the molecular weight of the dextrane fraction at 90% rejection

Membrane	Classification	MWCO Results [kD]	Pore Size [nm]
UF 1	Group I	150	17
UF 2	Group I	300	23
UF 4	Group I	150	17
UF 9	Group I	400	26
UF 3	Group II	> 1000	> 40
UF 5	Group II	> 1000	> 40
UF 7	Group II	> 1000	> 40
UF 8	Group II	> 1000	> 40

The membrane cut-off values, which were determined in the tests described here, tended to be above manufacturers' specifications. However, deviation from manufacturers' specifications are not surprising when considering the fact that in-house characterisation standards vary and that essential details for the manufacturers' test procedure are normally not published and therefore unknown. The cut-off for UF membranes is partly determined in tests with flat sheet membranes in stirring cells (dead-end filtration) by applying different trans-membrane pressures and by using various test substances whose permeation behaviour cannot be compared to that of dextrane because of their molecular structure (Zeman & Wales 1981). For this reason, a direct comparison of our results with manufacturers' MWCO specifications is not feasible. However, some of the MWCOs, which were determined, deviated so greatly from manufacturers' specifications that the reason for this could not be due only to different characterisation methods.

CONCLUSIONS

The test methods described in this work showed, that cross-flow filtration with aqueous dextrane solutions is a suitable method for the comparative characterisation of UF membranes.

The commercial ultrafiltration membranes, which were characterised, showed cut-offs ranging from 150 to over 1,000 kD with PWP of 130 up to 880 l/(m² · h · bar). In view of this, the membranes could be divided into two groups:

Group I: MWCO of 150–400 kD and PWP of 180–400 l/(m² · h · bar);
Group II: MWCO of >1000 kD and PWP of 130–800 l/(m² · h · bar).

Only the UF6 membrane showed no rejection of any dextrane fraction and the PWP at 2700 l/(m² · h · bar) was surprisingly high. As no defects were detected for this membrane, it can therefore be classified as a microfiltration membrane.

Estimation of the size of the membrane pores was possible by correlating the molecular weight of the permeated dextrane with the respective molecular radii. Pore sizes ranged between 17 and 26 nm for the membranes examined from Group I and over 40 nm for the Group II membranes. By comparing these results with manufacturers' specifications, it can be seen that the cut-offs, determined in the tests, are several times higher than those specified, with the exception of the UF4 membrane. For example, cut-offs for the membranes UF4 and UF5 were stated as being the same by the manufacturers, whereas a distinct difference in cut-off and pore-size distribution was determined.

Normally, the variations in MWCO can be explained by different characterisation conditions. In many cases, manufacturers define membrane cut-off not at 90% rejection but lower than this value. Manufacturers do not usually perform characterisation with a dextrane mixture at 0.5 bar in a cross-flow process but rather with various individual substances with a specific molecular weight at trans-membrane pressures around 1 to 3 bar, (dead-end filtration). In these cases, concentration polarisation and a covering layer are unavoidable.

These effects have a considerable influence on membrane separation behaviour and frequently lead to varying results.

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