

A rapid small scale evaluation of ultrafiltration performance for surface water treatment at Alcantarilha's WTW (Algarve, Portugal) *

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Abstract A rapid small scale evaluation of ultrafiltration (UF) performance with and without physical-chemical pre-treatment was performed to up-grade the conventional treatment used for drinking water production in Alcantarilha's WTW, Algarve, Portugal. Direct UF and pre-ozonation/ coagulation/ flocculation/ sedimentation/ UF (O/C/F/S/UF) were evaluated using polysulphone membranes of different apparent molecular weight cut-off (MWCO) (15–47 kDa). The results indicated that (i) UF is an effective barrier against microorganisms, including virus larger than 80 nm; (ii) for surface waters with low to moderate SUVA values, direct UF performance is equivalent or better than the conventional treatment in terms of residual turbidity, while UV_{254nm} and TOC residuals require the use of O/C/F/S/UF; (iii) the permeate quality improves with the membrane apparent MWCO decrease, especially for the direct UF, although the conventional treatment performance is never reached using UF; (iv) membrane fouling and adsorption phenomena are more severe in direct UF than in O/C/F/S/UF sequence (pre-ozonation decreases the membrane foulants by decreasing their hydrophobicity) and these phenomena increase with the membrane hydraulic permeability and, particularly, with the membrane apparent MWCO.

Keywords Drinking water; NOM; turbidity; ultrafiltration

INTRODUCTION

The importance of membrane technology in the treatment of surface and ground waters for drinking water production has been increasing in the last years. On one side, the increase in number and stringency of water quality regulations that cannot be effectively met by conventional treatment processes and, on the other hand, the deterioration of surface and ground waters quality, the better membrane performance, the lower costs due to technological advances and the development of new applications for membrane processes have been indicated as responsible for the increasing importance of membrane technology (Doyen (1997); Jacangelo *et al.* (1997)). The most popular membrane processes for drinking water production from surface water are the membrane pressure-driven processes, particularly ultrafiltration (UF). UF is a low pressure ($0.5\text{--}5 \times 10^5$ Pa) process using membranes of 1–500 kDa molecular weight cut-off (MWCO). It is adequate for water clarification and disinfection because it acts as an absolute physical barrier to particles, including suspended solids, turbidity, large colloids, algae, and bacteria, parasite and virus (viable and resistant forms). It also removes macromolecules, thus reducing the natural organic matter (NOM) content in water. Therefore, UF reduces the use of chemicals (coagulant, flocculant and chlorine), the toxic residuals (aluminium, acrylamide, trihalomethanes and other disinfection by-products) and the sludge production, with positive health, environmental and economical impacts. Despite these advantages, UF water treatment is limited by membrane fouling and adsorption phenomena, responsible for the flux decline with operation time, which decreases the water production and increases the consumption of energy and membrane cleaning chemicals. Most studies relate the flux decline with the membrane composition and the dimension of the membrane pores, as well as with the raw water physical/chemical parameters, *e.g.* suspended inorganic particles and organic molecules (*e.g.* humic substances) (Jucker and Clark (1994); Ericsson and Tragardh (1996); Hong and Elimelech (1997); Ribau Teixeira and Rosa (2002)).

Many UF studies have been done, most of them facing the removal of turbidity, NOM, humic substances, the membrane fouling reduction and UF performance increase. Glucina *et al.* (1998) obtained permeate turbidity values lower than 0.1 NTU (rejections above 99%), using feed pre-filtration and hollow-fibre UF modules with 100 kDa MWCO polymeric membranes. Similar results were obtained by Panglisch *et al.* (1998b), using capillary 50 kDa MWCO membranes. Oe *et al.* (1996) and Mavrov *et al.* (1998) obtained total organic carbon (TOC) rejections lower than 27% with UF modules. Other authors, using UF membranes, obtained NOM rejections ranging from 47% to 85%, namely Nakatsuka *et al.* (1996) using hydrophilic cellulose acetate hollow-fibre membranes of 150 kDa MWCO, and Botes *et al.* (1998) with 50 kDa MWCO capillary membranes.

UF disinfection efficiency has been often studied. Hillis (1997) and Hong *et al.* (2000) demonstrated that microfiltration (MF) could remove microorganisms as *Cryptosporidium* for the levels claimed in the legislation in adverse conditions of operation. Botes *et al.* (1998) and Panglisch *et al.* (1998a) showed the inexistence, or existence below the legislated standards, of *E. coli* and total coliforms in ultrafiltered surface water. For MS2 coliphage (dimensions of virus), the MF rejection was 1.5 to 3 logs and the UF rejection higher than 4.5 logs (Panglisch *et al.* (1998a)).

UF was also evaluated as an alternative the conventional treatment or to integrate the drinking water production sequence. Results of Lipp *et al.* (1998) demonstrated that UF was effective for particle removal, obtaining rejections of 99% and concentrations below 1 particle/ml in the treated water. In comparison treated water resulting from microtamination/ ozonation/ rapid filtration/ chlorination exhibited residual concentrations of 800 to 2000 particles/ml depending on seasonal variations. In Vigneux-sur-Seine WTW, south-east of Paris (55000 m³/d capacity), Baudin *et al.* (2000) demonstrated the enhanced disinfection and NOM removal achieved by the PAC (powdered activated carbon)/ UF process installed before the secondary ozonation (CRISTAL[®] process), which increased the distributed water quality and decreased the disinfection by-products formation.

This literature review shows that the UF performance depends on the feed water quality, and type of membrane and module. Therefore, each application requires a previous evaluation of the UF performance, particularly when the raw water quality and the drinking water demand have both important seasonal variations as in Alcantarilha's WTW (Algarve, Portugal) (Ribau Teixeira, 2001). Therefore, the objective of the present study was to perform a rapid small scale evaluation of the UF performance at Alcantarilha's WTW, using membranes of different MWCO (10 to 100 kDa range) and treatment sequences with or without physic-chemical pre-treatment, *i.e.* UF after conventional clarification of pre-ozonation/ coagulation/ flocculation/ sedimentation (UF used for final polishing and disinfection) and direct UF (UF used for both clarification and disinfection).

The role of pH on UF performance is very important due to the well known pH effect on both membrane surface charge, and configuration and solubility of humic matter, major responsible for membrane fouling and adsorption phenomena (Jucker and Clark (1994); Hong and Elimelech (1997); Ribau Teixeira and Rosa (2002)), and it was studied elsewhere (Ribau Teixeira (2001), Ribau Teixeira and Rosa (2002), Ribau Teixeira *et al.* (2002)).

METHODS

Water characterisation

The water supply system defined for the western part of Algarve is based on Alcantarilha's WTW, run by Águas do Algarve, SA, a holding of Águas de Portugal, SGPE, SA. It was designed to treat up to 3 m³/s (*c.a.* 1 million people, year 2020), of surface water by conventional treatment of pre-ozonation, coagulation/flocculation/sedimentation (O/C/F/S), rapid sand filtration, pH adjustment and chlorination, using three treatment lines in parallel (1 m³/s each) to face the seasonal drinking water demand.

Six samples were collected before ozonation (raw water), after coagulation/ flocculation/ sedimentation (decanted water) and after filtration (filtered water). All samples were analysed for pH (at 20°C, using a Crison GLP22 pH meter), turbidity (HACH 2100N turbidity meter of high resolution (0.001 NTU)), TOC (Shimadzu TOC 5000A analyser (50 ppb – 4000 ppm)) and UV_{254nm} absorbance (HITACHI 2000 UV/VIS spectrophotometer) using standard methods of analysis (Table 1.1). During this study it was not possible to filter the water samples before UV_{254nm} measurements, so UV_{254nm} values cannot be directly related to the humic substances. In fact, the large difference in UV_{254nm} readings between the raw and decanted water (Table 1.1) must be in part due to the scattering caused by the turbidity particles.

Table 1.1 Characteristics of the water samples collected at Alcantarilha's WTW (confidence interval for the mean value with $\alpha = 95\%$, n° of samples = 6).

Type of water	pH (at 20°C)	Turbidity	UV _{254nm} ⁽¹⁾	TOC
		(NTU)	(1/cm)	(mg C/l)
Raw	7.60±0.23	32.50±3.61	0.25±0.047	4.19±1.53
Decanted	7.40±0.08	4.04±0.70	0.05±0.004	2.60±0.61
Filtered	7.54±0.23	0.22±0.06	0.03±0.008	1.94±0.30

⁽¹⁾ Samples not filtered.

Earlier experiments (Ribau Teixeira (2001)) showed that seasonal variations correspond to two major types of raw water quality: clear waters (0.94 – 5.63 NTU, 0.05 – 0.08 1/cm and 2.98 – 3.66 mg C/l) and turbid waters (23.4 – 40.1 NTU, 0.19 – 0.32 1/cm and 2.78 – 8.02 mg C/l TOC), after intense rainfall periods. Unfortunately, it was not possible to sample clear raw waters during this study. Although these decanted water samples are quantitatively equivalent to clear raw waters in terms of turbidity, UV_{254nm} and TOC, they may differ significantly in terms of the type of NOM they contain. The SUVA values measured in related studies were 2.6 - 3.8 l/(m.mgC) for raw water and 0.95 - 2.40 l/(m.mgC) for decanted water (Ribau Teixeira (2001)). As expected (particularly due to pre-ozonation effects) based on Edzwald and Van Benschoten (1990) classification, raw water DOC is richer in humic substances, hydrophobic and aromatic and of higher molecular weight than decanted water DOC.

UF experiments

A series of UF polysulphone membranes were chosen to cover the range 10 – 100 kDa of apparent molecular weight cut-off (MWCO): GR40PP, GR61PP and GR81PP membranes from Danish Separation System (DSS). The UF experiments were performed at 25°C, 2×10^5 Pa and 1.3 m/s circulating velocity using a small-scale plate-and-frame Lab-unit M10 from DSS (336 cm² of membrane surface area).

Membrane characterisation

The membranes were characterised in a previous work (Ribau Teixeira (2001)): the pure water (< 1 µS/cm) permeability, L_p , was 3.30×10^{-13} m (i.e. 132.4 kg/(h.m².bar)), 1.97×10^{-13} m (i.e. 79.2 kg/(h.m².bar)) and 0.82×10^{-13} m (i.e. 32.9 kg/(h.m².bar)), respectively for GR40PP, GR61PP and GR81PP membranes, and the apparent MWCO was 47 kDa, 41 kDa and 15 kDa, respectively. These results correspond to a MWCO range smaller than it was expected (10 – 100 kDa).

Permeation of WTW Water Samples

These experiments consisted of concentration runs, simulating the industrial UF operation at different water recovery rates (WRR), defined as (equation_1.1):

$$WRR (\%) = 100 \times \left(\frac{V_p}{V_b} \right) \quad \text{1.1}$$

where V_p and V_b represent the permeate and the initial feed volumes (m³), respectively.

In these runs, permeate was not recycled to the feed reservoir until a stipulated permeate volume was obtained. At this time, permeate was recycled to the feed reservoir during a 10 minutes stabilisation period, after which the flux (J) was measured and feed and permeate samples were collected and the run followed to the next WRR. Samples were analysed for turbidity, UV_{254nm} absorbance and TOC. Between each run, membranes were washed until pure water flux (J_w) reached 90% of the initial value measured after compaction.

Two types of water recovery runs were performed to evaluate the UF disinfection efficiency, one was the determination of microbiological contents of raw and permeate water and another to evaluate the membrane virus removal ability, using raw water spiked with H40 bacteriophages (Rossi (1994)). This H40 bacteriophage (82 – 85 nm in head and 39 – 43 nm in tail) is easy to manipulate in laboratory since it is a parasite virus of bacteria and is not human pathogenic.

Two treatment sequences were studied: UF of raw water to simulate direct UF (without pre-treatment) and UF of decanted water (produced in Alcantarilha's WTW) to simulate the conventional UF pre-treatment.

The adsorption occurring during the water recovery runs (0-78% WRR) was computed by mass balance (equation_1.2), where $Mass_0$ is the initial mass in the feed solution (before the trials started), $Mass_B$ is the mass in the feed for 78% WRR (the last WRR) and $Mass_i$ is the mass in the permeate solution at a given WRR.

$$\text{Adsorption (\%)} = \left(Mass_0 - Mass_B - \sum_{i=WRR 0\%}^{WRR 78\%} Mass_i \right) / Mass_0 * 100 \quad \text{_1.2}$$

RESULTS AND DISCUSSION

Results from the disinfection trials are displayed in Table 1.2. As expected, GR40PP membrane completely removes the microorganisms present in the water as well as the bacteriophages (82-85 nm diameter) added to the raw water. The other two membranes were not tested since GR40PP membrane has the largest apparent MWCO of this membrane series.

Table 1.2. UF disinfection efficiency (GR40PP, 25°C, 2×10^5 Pa, 1.3 m/s).

	Raw water	Permeate
Total coliform (CFU/100 ml)	46	0
Fecal coliform (CFU/100 ml)	1	0
Fecal streptococci (CFU/100 ml)	4	0
Sulphite-reducing clostridium (n°/20 ml)	8	0
Total germs (n°/ml) at 37 °C / at 22°C	83 / 298	0 / 0
Bacteriophages (PFU/l)	10^9	0

Figure 1.1 presents the flux increase with the membrane hydraulic permeability, with raw and decanted water. The most permeable membrane (GR40PP) has indeed the highest flux, but the lowest relative flux (J/J_w) (Figure 1.2). Flux also varies with the water quality, raw water (richer in NOM and turbidity particles, Table 1.1) presenting lower fluxes than decanted water. The differences between raw and decanted water fluxes with WRR are more significant for larger membranes (GR40PP and GR61PP), which also show the highest flux decrease with WRR (Table 1.3).

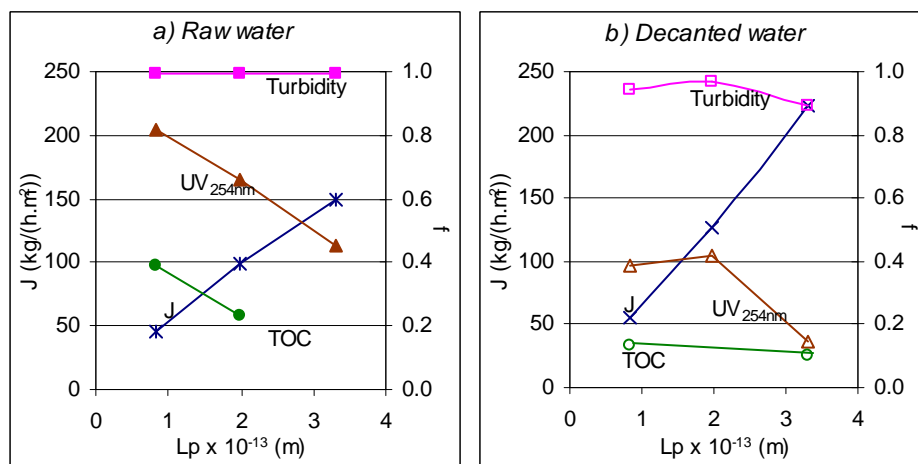


Figure 1.1 Variation of fluxes and rejections with membrane hydraulic permeability for a) raw and b) decanted water (25°C, 2×10^5 Pa, 1.3 m/s, 78% WRR).

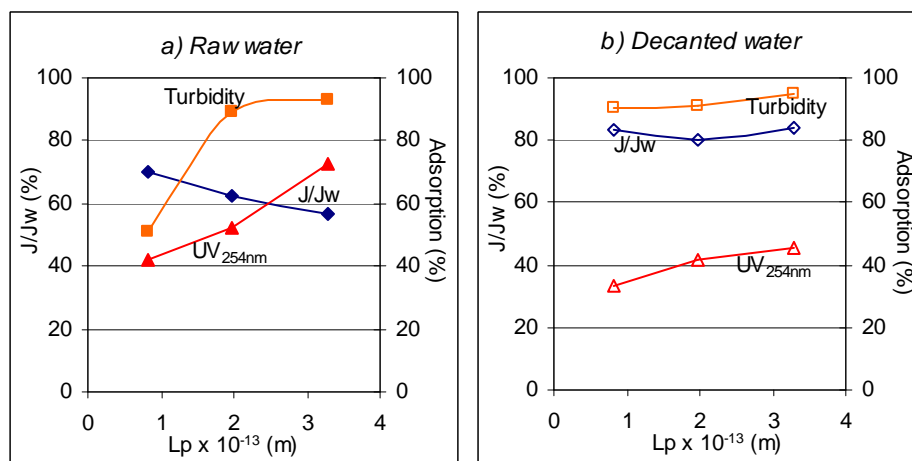


Figure 1.2. Variation of relative flux, turbidity adsorption and UV_{254nm} adsorption with membrane hydraulic permeability for a) raw and b) decanted water (25°C, 2x10⁵ Pa, 1.3 m/s, 78% WRR).

These results demonstrate that the fouling phenomena increase with the membrane hydraulic permeability and, particularly, with the apparent MWCO, i.e. with the membrane pore size. Larger pores, besides increasing membrane surface rugosity, allow the solutes to penetrate into the membrane while smaller pores exclude the material improving the surface filtration and therefore the membrane performance. From GR61PP to GR40PP, although the hydraulic permeability has increased (from 1.97 x 10⁻¹³ m to 3.30 x 10⁻¹³ m), the apparent MWCO does not significantly increase (41 kDa to 47 kDa) and the fouling phenomena (expressed by the J/Jw decrease) does not intensify (Figure 1.2). As expected, the same applies for adsorption GR40PP membrane has the highest adsorption and GR81PP membrane the lowest (Figure 1.2). UV_{254nm} absorbing substances and turbidity particles adsorb onto membrane surfaces, so the adsorption is higher with raw turbid water than with decanted clear water (Figure 1.2), which has more hydrophilic and less foulant matter (lower SUVA values). As explained elsewhere (Ribau Teixeira and Rosa (2002)), these membrane fouling and adsorption phenomena are enhanced by the moderate hardness of the water.

Table 1.3 UF performance with raw (direct UF) and decanted water (O/C/F/S/UF) (25°C, 2x10⁵ Pa, 1.3 m/s).

Membrane		GR40PP	GR61PP	GR81PP
WRR (%)		31 – 78	31 – 78	31 – 78
J (kg/(h·m ²))	Raw water	191.4 – 149.4	120.0 – 98.5	47.7 – 46.2
	Decanted water	226.5 – 222.6	137.6 – 127.4	55.3 – 54.7
Turbidity rejection	Raw water	0.99 – 0.99	0.99 – 0.99	0.99 – 1.00
	Decanted water	0.95 – 0.89	0.97 – 0.97	0.96 – 0.95
UV _{254nm} rejection	Raw water	0.64 – 0.45	0.73 – 0.66	0.78 – 0.82
	Decanted water	0.28 – 0.14	0.55 – 0.42	0.52 – 0.39
TOC rejection	Raw water	0.29 – 0.22*	0.23 – 0.23	0.36 – 0.39
	Decanted water	0.12 – 0.10	0.14 – 0.18**	0.31 – 0.13
Permeate quality				
Turbidity (NTU)	Raw water	0.246 – 0.070	0.119 – 0.134	0.226 – 0.102
	Decanted water	0.098 – 0.082	0.085 – 0.057	0.072 – 0.058
UV _{254nm} (1/cm)	Raw water	0.074 – 0.074	0.054 – 0.068	0.051 – 0.068
	Decanted water	0.026 – 0.024	0.016 – 0.021	0.025 – 0.035
TOC (mg C/l)	Raw water	3.70 – 3.81*	3.39 – 4.35	3.08 – 3.78
	Decanted water	2.02 – 2.93	2.12 – 2.29	1.67 – 3.22

* for WRR = 84%; ** for WRR = 64%

Turbidity, UV_{254nm} and TOC rejections decrease with the membrane hydraulic permeability (and apparent MWCO) and are higher for raw water than for decanted water (Figure 1.1). This must be especially due to the pre-ozonation, which may slightly decrease the contaminants concentration (their concentration is mostly removed by C/F/S), but especially decreases their size and molecular weight,

with major effect on NOM constituents (UV_{254nm} and TOC). The turbidity rejections are high (0.89 – 0.99) with all membranes and types of water. The rejections of UV_{254nm} are intermediate, whereas TOC rejections are low (0.06 – 0.38), the highest values being obtained for raw water and GR81PP membrane. These results indicate the low apparent molecular weight of the TOC constituents, particularly in the decanted water, also expressed by the variation in SUVA values in raw and decanted water, 2.6 - 3.8 l/(m.mgC) and 0.95 - 2.40 l/(m.mgC), respectively (Ribau Teixeira (2001)).

Comparing the permeate quality (Table 1.3) with the quality of the water filtered in Alcantarilha's WTW (Table 1.1) different behaviour is found for turbidity and for UV_{254nm} and TOC constituents. In terms of residual turbidity (0.22 ± 0.06 NTU in the filtered water, Table 1.1), the direct UF of these surface waters with relatively low SUVA values is equivalent or better than the conventional treatment, but the WTW filtered water quality for UV_{254nm} and TOC (0.03 ± 0.008 l/cm and 1.94 ± 0.30 mgC/L, Table 1.1) is achieved only by O/C/F/S/UF. In addition, the permeate quality improves with the membrane apparent MWCO decrease (GR81PP membrane presents higher permeate turbidity because the raw water presented a higher turbidity higher than raw waters used with the other membranes), being this improvement more pronounced with raw water than with decanted water (which contains NOM of much lower molecular weight). This means that the membrane apparent MWCO decrease is particularly advantageous for direct UF. Nevertheless, the conventional treatment performance for UV_{254nm} and TOC removal is never reached by UF. Although there are no national standards for UV_{254nm} and TOC in drinking water, these are very important parameters because of their connection to the trihalomethane (and other disinfection by-products (DBPs)) formation potential (THMFP) in the finished water. Enhanced NOM removal, and THMFP and DBPs control will require the use of nanofiltration or powdered activated carbon and UF.

Clear waters contain NOM of high molecular weight and present low content of fouling matter, so good results of direct UF could be expected.

CONCLUSIONS

The results obtained with a series of polysulphone membranes of MWCO in the range of 15–47 kDa demonstrated that:

- UF is an effective barrier to against microorganisms, including virus larger than 80 nm;
- membrane fouling and adsorption phenomena are more severe in direct UF than in O/C/F/S/UF sequence; these phenomena increase with the membrane hydraulic permeability and, particularly, with the apparent MWCO (larger pores allow the fouling matter to accumulate inside the membrane matrix);
- O/C/F/S pre-treatment decreases the membrane foulants but also decreases the NOM removal (ozonation decreases NOM molecular weight);
- comparing final water qualities, direct UF is equivalent or better than the conventional treatment in terms of residual turbidity, while UV_{254nm} and TOC residuals require the use of O/C/F/S/UF; the permeate quality improves with the membrane apparent MWCO decrease, especially for the direct UF, although the conventional treatment performance is never reached. Enhanced NOM removal and DBPs control by nanofiltration and powdered activated carbon/UF is under investigation.

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