# Cost Factors and Chemical Pretreatment Effects in the Membrane Filtration of Waters containing Natural Organic Matter

A.I. Schäfer<sup>1,2,\*</sup>, A.G. Fane<sup>2</sup>, T.D. Waite<sup>1</sup>

Centre for Water and Waste Technology, Civil and Environmental Engineering, University of New South Wales, Sydney, NSW 2052, Australia (\*corresponding author) A.Schaefer@unsw.edu.au, ph++61 2 9385 4470, fax ++61 2 9385 6139 D.Waite@unsw.edu.au, ph ++61 2 9385 5060, fax ++61 2 9385 6139

<sup>2</sup> UNESCO Centre for Membrane Science and Technology, Chemical Engineering, University of New South Wales, Sydney, NSW 2052, Australia T.Fane@unsw.edu.au, ph ++61 2 9385 4315, fax ++61 2 9385 5966

# ABSTRACT

This paper compares the membrane processes available for water treatment. Membranes have the advantage of currently decreasing capital cost, a relatively small footprint compared to conventional treatment, generally a reduction in chemicals usage and comparably low maintenance requirements.

Three membrane processes applicable to water treatment, micro- (MF), ultra- (UF), and nanofiltration (NF), are compared in terms of intrinsic rejection, variation of rejection due to membrane fouling and increase in rejection by ferric chloride pretreatment. Twelve different membranes are compared on the basis of their membrane pore size which was calculated from their molecular weight cut-off.

A pore size of <6 nm is required to achieve substantial (>50%) organics removal. For a fouled membrane this pore size is about 11 nm. UV rejection is higher than DOC rejection. Coagulation pretreatment allows a higher rejection of organics by MF and UF and the cut-off criterion due to initial membrane pore size is no longer valid.

A water quality parameter (WQP) is introduced which describes the product water quality achieved as a function of colloid, DOC and cation rejection. The relationship between log (pore size) and WQP is linear.

Estimation of membrane costs as a function of WQP suggests that open UF is superior to MF (similar cost at higher WQP) and NF is superior to tight UF. Chemical pretreatment could compensate for the difference between MF and UF. However, when considering chemicals and energy costs, it appears that a process operated at a higher energy is cheaper at a guaranteed product quality (less dependent on organic type). This argument is further supported by environmental issues of chemicals usage, as energy may be provided from renewable sources.

# **KEYWORDS**

Coagulation, microfiltration (MF), nanofiltration (NF), natural organic matter (NOM), ultrafiltration (UF), water quality parameter (WQP).

# **INTRODUCTION**

Membrane processes for surface water treatment are microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF), depending on the target material to be removed and the limiting process economics.

MF will remove turbidity (particulates and bacteria), but no dissolved compounds, unless associated with colloids. UF will, depending on the molecular weight cut off (MWCO), remove natural organic matter (NOM) partially and viruses. NF will remove NOM and hardness almost completely, but for a price often considered as uneconomic due to capital and energy costs.

Chemical addition prior to MF or UF enhances the NOM removal capacity of these processes to a level comparable to that achieved with NF.

In this paper a process comparison is carried out. Key issues are the organics rejection as a function of estimated pore diameter, the variation of rejection with fouling and coagulation pretreatment and membrane cost as a function of a water quality parameter (WQP). The WQP was defined in terms of colloid, organics and cation rejection.

# MATERIALS AND METHODS

# 2.1 Membrane Filtration

Experiments were carried out in a stirred cell apparatus which has previously been described and characterised in detail (Schäfer *et al.* (1998)).

Membranes used were commercially available hydrophilic flat sheet MF (GVWP, Millipore, Australia), UF (MWCO 1, 3, 5, 10, 30, 100 kDa; regenerated cellulose, Millipore, Australia) and NF (TFC-SR, TFC-S, TFC-ULP, CA-UF, Fluid Systems (now Koch Membrane Systems), San Diego, U.S.) membranes which show minimal adsorption of NOM. Information for membrane costs were received from the Water Factory 21, Orange County, US and not adapted from the cost of membranes purchased for this study.

# 2.2 Chemicals and Natural Organics

Chemicals were purchased from Ajax Chemicals (Australia) and were all of analytical grade. MilliQ water with a quality of  $>18M\Omega/cm$  was used for all experiments.

Organics were purchased from the International Humic Substances Society (IHSS) as Suwannee River fulvic (FA) and humic (HA) acids. Further, NOM was concentrated from a local source using MF and reverse osmosis (RO). This NOM was further fractionated into humic, fulvic and hydrophilic fractions using ion exchange resins (Schäfer (1999)).

## 2.3 Solution Composition

If not indicated otherwise, a background solution of 20 mM NaCl, 1 mM NaHCO<sub>3</sub> and 0.5 mM CaCl<sub>2</sub> was used. For MF the calcium concentration was 2.5 mM. Organic concentration ranged from 5 to 12.5 mgL<sup>-1</sup> as DOC. The pH was normally between 7 and 8 determined by the carbonate buffer of the background solution.

If colloids were present, their concentration was  $10 \text{ mgL}^{-1}$  as hematite ( $\oint$ -Fe<sub>2</sub>O<sub>3</sub>). Hematite colloids were monodispersed and spherical and sizes of 40, 75, 250 and 500 nm were produced for this study.

Solution composition is tabulated in Table 1.

# 2.4 Ferric Chloride

Ferric chloride was used as the coagulant. Concentrations were adapted from enhanced coagulation as 25 and 100 mgL<sup>-1</sup> (Crozes (1995)). Solutions were coagulated in jar testing equipment and filtered without settling of the flocs. pH was not adjusted at 25mgL<sup>-1</sup>, while at 100 mgL<sup>-1</sup> the final pH was 3 and experiments were conducted with both, solutions at pH 3 and solutions readjusted to pH 7-8.

The ferric chloride cost range was provided by Orica Watercare, Australia. The large range of costs was explained with variations in purity and delivery costs depending on the location of the facility. The effect of coagulant purity on membrane performance is unknown.

#### 2.5 Analytical

Dissolved organic carbon (DOC) was analysed using a Skalar 12 (Skalar, The Netherlands) instrument.

Ultraviolet/visible absorption was analysed with a Varian Cary 1E spectrophotometer. While samples were scanned from 190 to 500 nm, the results at 254 nm were used for calculations. Cation concentration was determined with a Perkin Elmer Optima 3000 spectrometer. Sample vials were cleaned with 1M NaOH and 1M H<sub>2</sub>SO<sub>4</sub> solutions to remove organic and inorganic contamination, respectively.

### **RESULTS AND DISCUSSION**

#### Membrane Characteristics

Twelve membranes were used in this study. The membranes were characterised by pure water flux and permeability, membrane resistance, molecular weight cut-off (as supplied by the manufacturers) and a calculated pore diameter (Table 2). The pore size calculations are based on an equation determined by Worch (1993) and the Stokes Einstein equation (see Schäfer (1999) for calculations and characterisation of surface roughness, contact angle and charge of the membranes used).

#### **Rejection Characteristics of Clean Membranes**

Rejection characteristics of all membranes were studied in detail and published elsewhere (Schäfer *et al.* (1999), Aoustin *et al.* (2000), Schäfer *et al.* (2000)). In this section the results obtained with the individual processes are summarised and illustrated as a function of calculated membrane pore size.

Figure 1 shows the rejection of DOC as a function of membrane pore size for various organic fractions. A clear cut-off can be seen where rejection drops from about 80% to 10%. This cut-off is around a pore size of 6 nm. The various organics are retained to a different extent depending on their size. The organics were characterised in detail elsewhere (Schäfer (1999)). Sizes were determined to be 1.6 to 2.7 nm as equivalent sphere diameters.

Comparing DOC to UV rejection, a higher rejection of UV absorbing compounds is observed (see Figure 2). This indicates a preferential removal of larger and more aromatic compounds over the entire range of membrane pore sizes.

Cation rejection is shown in Table 3. Only the NF membranes remove sodium. Calcium rejection increases gradually with decrease in pore size. Substantial removal is only achieved with the TFC membranes.

The rejection and membrane characterisation results indicate that for each application (and desired product quality) there will be an optimal membrane, which can be selected yielding highest flux and acceptable rejection for the contaminant of concern.

#### **Rejection Characteristics of Fouled Membranes**

Fouling changes the surface characteristics and pore size of membranes and these changes have an impact on the rejection behaviour. Figure 3 compares the organics rejection by fouled membranes with that of clean membranes as shown in Figure 1.

The cut-off where rejection of natural organics drops is shifted from about 6 to 11 nm due to fouling. The fouling layer consists of a deposit formed with calcium and IHSS HA as previously described (Schäfer *et al.* (1998)). Childress and Elimelech (1996) have reported a more negative membrane surface charge due to the deposition or adsorption of organics in the presence of calcium. This more negative surface charge may increase the rejection of the generally negatively charged natural organics.

Further, calcium causes the aggregation of organics and subsequent pore size reduction due to the deposition of aggregates. Both of these effects would also enhance organics rejection.

#### Rejection Characteristics with Coagulation (FeCl<sub>3</sub>) Pretreatment

In MF and UF, where the pore sizes are larger than the cut-off required to remove a substantial amount of organics (6 nm), rejection can be increased by coagulant addition.

The coagulant, in this case ferric chloride (FeCl<sub>3</sub>), precipitates and adsorbs natural organics on the precipitate surface. The particulates are subsequently retained which leads to an increased rejection of organics. The extent of increased removal is shown in Figure 4 for three types of organics and two ferric chloride dosages. The coagulant dosages are typical of those used in enhanced coagulation applications (Crozes (1995)).

The natural organics removal is higher for the higher coagulant dose and can reach levels similar to those of the small pore size membranes. However, the low rejection at low ferric chloride concentrations and the large scatter in data with organic type indicate that the removal is dependent on the water characteristics and thus potentially subject to considerable variation during water treatment.

#### Membrane Fouling Behaviour and Influence of Coagulation

In MF and UF, coagulation is used as a means of increasing natural organics rejection. The organics are adsorbed on a ferric oxyhydroxide precipitate which is retained by the membrane. This precipitated colloid can cause membrane fouling by pore blocking or cake deposition, a mechanism which depends on the membrane pore size and the conditions under which the precipitates are formed.

Flux ratios  $(J/J_0)$  is the ratio of flux to initial flux) over permeate volume are shown in Figure 5 and Figure 6 for MF and UF, respectively. Flux decreases with increasing ferric chloride dosage and the more open the membrane the larger is the effect. This is because the more open membrane with higher  $J_0$  appears to be more sensitive to cake formation.

In NF, natural organics rejection is high and no coagulation pretreatment is required. However, since coagulation targets large, hydrophobic organics which foul NF membranes by precipitation and gel layer formation, coagulation pretreatment can control fouling.

This effect is shown in Figure 7, where  $J/J_0$  is the ratio of permeate flux to flux at the beginning of the experiment. The flux declines rapidly and irreversibly without coagulation. If ferric chloride is added flux decline ceases.

This pretreatment effects the fouling and with the alteration of the deposit, also the rejection of the membrane. The foulant is bound to precipitates which are too large to foul the NF membranes. This pretreatment also modifies the rejection of solutes by a variation of the surface charge of the organic. Organic rejection decreases from 93% to 79% at pH 3 where a very positively charged precipitate is formed. The rejection of calcium generally increases from 55% to almost 99% at pH 3, while sodium rejection increases from 24 to 43% at these conditions (for details on these results see Schäfer (1999)).

## Water Quality Parameter (WQP)

Fane (1996) proposed an overall water quality index for treatment based on pathogen, turbidity, colour and salt removal. This criterion was modified to suit the study in this project and is presented in Table 4.

Pathogens were not included in this study as 100% removal is assumed. However, for MF this may not be achieved under all operating conditions as reported by Jacangelo *et al.* (1995). Log removals of the virus *MS2 bacteriophages* (0.025  $\mu$ m) reported were as low as 0.4 (60%) for MF (0.2  $\mu$ m), while a UF membrane (100 kDa) removed >6 log. *Cryptosporidium parvum* (4 to 6  $\mu$ m in diameter) and *Giardia muris* (7 to 14  $\mu$ m) cysts removal was complete (>6 log, below detection limit) by both MF and UF. The removal of viruses is thus a criterion which needs to be considered in the process choice. Log removal describes the number of orders of magnitude by which the feed concentration is removed and is defined as log<sub>10</sub>(feed concenmtration / permeate concentration) (Ho and Sirkar (1992)).

As a sum criterion, the water quality parameter (WQP) is introduced. The maximum score for WQP is 300. The total score for each parameter suite (colloids, DOC, and ions) is 100. The columns are subdivided into equal fractions, resulting in total points of 25 for the individual colloid fraction, 33.3 for each organic fraction, and 50 for the major cations (Na<sup>+</sup>, Ca<sup>2+</sup>).

For colloids, stable primary colloids (in our other work described as "organic-particle-salt (OPS) systems"- colloids which are stabilised by organics) are assumed as these appear most abundant in natural waters. These colloidal systems are described in detail elsewhere (Schäfer *et al.* (1999)).

Ion rejection is represented by sodium and calcium rejection in the absence of organics. In the case of DOC rejection, solutions contain  $0.5 \text{ mM CaCl}_2$  (except for MF where calcium concentration is 2.5 mM).

The WQP values increase with membrane tightness as expected. The relationship between log (pore size) and WQP is linear (Figure 8). The CA-UF membrane performs overall as a UF membrane in the 5 kDa cut-off range.

MF and UF membranes with a MWCO above 10 kDa achieve a WQP below 150 (i.e. only 50% of the maximum score) while the NF membranes achieve values in the range 230 to 280.

Under fouling conditions, the WQP is only slightly modified. Values are presented in

Table 5. For the UF membranes with a pore size close to the cut-off a clear increase in WQP due to fouling is observed. This can be explained by an effective pore closure by the foulants.

With ferric chloride addition, the WQP changes significantly for the more open membranes due to a higher rejection of colloids and organics. These results are presented in Table 6.

## Membrane and Energy Cost Estimation

The membrane materials selected for cost estimates are the MF PVDF (62.5 US\$/m<sup>2</sup>), the UF CA (16.7 US\$/m<sup>2</sup>), and the NF PA (20.8 US\$/m<sup>2</sup>). Costs were provided by Leslie (1999) and originate from comparative studies at Water Factory 21 in Orange County (USA). Values are tabulated in Table 7. The selection was based on the comparability to membrane materials used in this study. The cost for MF is high, but PVDF is chosen as this appears to be the best membrane material despite other materials being installed currently. For polypropylene the cost will be about one third of the estimate and possibly lower for a submerged membrane system (Johnson (1999)). Membrane life can be estimated in the order of five years, thus the membrane cost will be a maintenance cost as well as an investment cost.

Membrane cost was estimated from fluxes obtained in experiments and the membrane area required to produce 1000  $m^3/d$  product water. Figure 9 shows the membrane cost as a function of WQP (values were shown in Table 4) based on pure water fluxes.

Costs for the MF and open UF membranes are comparable. For tight UF membranes MWCO 1-5 kDa) the costs increase to unacceptable levels and are in fact lower for the TFC-SR and –S membranes. The CA-UF membrane lies well in the UF range and is cost wise extremely competitive given the high WQP. It should be noted that for applications requiring turbidity removal only (WQP of 50 to 100) MF or loose UF have a major cost advantage.

When fluxes of fouled membranes are considered (Figure 10 and Table 5), the cost increases, but the overall trend is similar. Membrane costs for the TFC-S and –ULP membranes increase significantly compared to pure water due to the high salt rejection which causes a flux reduction due to an osmotic effect. The high salt rejections of these membranes are not usually required for surface water applications.

Cost values for membranes fouled with ferric chloride coagulant are shown in Table 6. With ferric chloride pretreatment the cost becomes prohibitive for MF operated at low flux and high ferric chloride dosage (see also no 3 in Figure 11). This is due to the larger membrane area required at low flux.

Ferric chloride increases the WQP for MF and UF and MF moves into the area of UF (see nos 1,2,3 and 4; the areas were defined previously based on rejection without pretreatment).

At the low dosage cost is lowest at the highest initial fluxes. For the higher dosage (see no 4) the cost is not determined by initial flux, but fouling becomes the crucial criterion. At identical WQP, the 30 kDa UF membrane is lowest in cost, followed by low flux MF, then the 100 kDa and 10 kDa membranes.

The membrane cost for NF (TFC-SR) is comparable at a much higher WQP. Membrane costs are reduced with ferric chloride addition as fouling is reduced as was shown in Figure 7. However, the ferric chloride would add to the overall treatment costs.

## If one further considers the cost of ferric chloride (see

Table 8) and the energy cost (see Table 9) the advantage of a process which does not require chemical pretreatment becomes even more important. Recovery is defined as the product to feed volume ratio. It is limited by backwash and cleaning volumes for MF and UF, and by the maximum concentration in a module for NF and RO.

Energy costs are comparable or lower than the cost of ferric chloride (with the exception of RO due to osmotic effects due to high salt rejection). This does not include sludge treatment or the

consideration that energy can be provided from a renewable source which further supports the environmental argument for using NF when organic removal is important.

Finally, Table 10 shows a comparison of costs which originate from membranes, energy and chemicals addition. Costs are in US\$ per  $1000 \text{ m}^3$ . Membrane costs are based on a membrane life of 5 years.

The cost range for MF and open UF is the range of without pretreatment at the lower end and pretreatment with lowest cost ferric chloride at a dosage of  $100 \text{ mgL}^{-1}$  at the upper end. Costs will increase if higher quality coagulant is used or if the plant is at some distance to the ferric chloride supplier. The results show that chemical pretreatment costs effect treatment costs considerably and NF appears to be the choice for a stable water quality and cost.

## CONCLUSIONS

This study demonstrates that membranes with tighter pore sizes are superior to more porous membranes in terms of rejection and membrane costs where such costs include capital and maintenance costs of the membrane installation, costs of chemicals used for pretreatment and energy costs.

This contradicts the conventional belief that a hybrid process consisting of chemical treatment and MF is cheaper than NF. While NF produces waters with a guaranteed and relatively stable quality, the effectiveness of chemical pretreatment depends strongly on the organic type and solution chemistry. Costs for chemical pretreatment are above the energy costs for NF if a substantial amount of organics is to be removed.

However, it is appreciated that for an application only requiring removal of turbidity (including microorganisms) MF or loose UF have a clear cost advantage.

A cost comparison of chemicals addition and energy consumption revealed that the additional energy required to operate NF is cheaper than the chemicals required to achieve a comparable organics removal with MF. While a more complete analysis is required including a complete assessment of environmental impact the results obtained should encourage some rethinking of current water treatment practices.

# ACKNOWLEDGEMENTS

The Cooperative Research Centre for Water Quality & Treatment (Adelaide, Australia) is thanked for project funding. The assistance of Martina Fischer, Ursula Schwicker and Emmanuelle Aoustin with experimental work is appreciated.

Material support from Fluid Systems (now Koch Membrane Systems, San Diego, USA) and Millipore (Australia) is also acknowledged.

## REFERENCES

Aoustin, E., Schäfer, A.I., Fane, A.G. and Waite, T.D. (2000), Effect of humic substance and colloid interactions on ultrafiltration behaviour *Separation and Purification Technology*, (in press).

Childress, A.E. and Elimelech, M. (1996), Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes *Journal of Membrane Science* **119** 253-268.

Crozes, G., White, P. and Marshall, M. (1995) Enhanced coagulation: its effect on NOM removal and chemical costs *Journal AWWA* 87 78-89.

Fane, A.G. (1996) Membranes for water production and waste water reuse Desalination 106 1-9.

Ho, W.S.W. and Sirkar, K.K. (1992) Membrane Handbook, Chapman & Hall, New York.

Jacangelo, J.G., Adham, S.S. and Laîné, J.-M. (1995) Mechanisms of *Cryptosporidium*, *Giardia*, and *MS2* virus removal by MF and UF *Journal AWWA* **07** 107-121.

Johnson, W.T. (1999) Recent advances in microfiltration for drinking water treatment AWWA Annual Meeting Chicago June '99.

Leslie, G. personal communication (10/1999).

Schäfer, A.I. (1999) Natural organics removal using membranes, PhD Thesis, University of NSW, Chemical Engineering, Sydney, ISBN 0 7334 06 521.

Schäfer, A.I., Fane, A.G. and Waite, T.D. (1998) Nanofiltration of natural organic matter: Removal, fouling and the influence of multivalent ions *Desalination* **118** 109-122.

Schäfer, A.I., Schwicker, U., Fischer, M.M., Fane, A.G. and Waite, T.D. (2000) Microfiltration of Colloids and Natural Organic Matter *J Membrane Science* **171**(2) 151-172.

Takigawa, D., personal communication (07/1999).

Worch, E. (1993) A new equation for the calulation of diffusion coefficients of solutes (Eine neue Gleichung zur Berechnung von Diffusionskoeffizienten gelöster Stoffe) *Vom Wasser* **81** 289-297.

8

# **FIGURE CAPTIONS**

Figure 1 Rejection of DOC as a function of calculated pore diameter (see Table 2 for membrane characterisation). Experimental conditions pH 7-8, 5-15 mgL<sup>-1</sup> as DOC organics, 0.5 mM CaCl<sub>2</sub>, 1 mM NaHCO<sub>3</sub>, stirred at 270 to 400 rpm, transmembrane pressures 1 bar (MF and UF 30-100 kDa), 3 bar (UF 1-10 kDa), and 5 bar (NF).

Figure 2 UV<sub>254</sub> rejection as a function of pore diameter. The DOC curve is adapted from Figure 1. Experimental conditions as in Figure 1.

Figure 3 Rejection at fouling conditions (12.5 mgL<sup>-1</sup> as DOC IHSS HA, 2.5 mM  $CaCl_2$ , pH 8) as a function of pore diameter. The line graphs are rejection results of unfouled membranes adapted from Figure 1 and Figure 2.

Figure 4 DOC rejection as a function of pore diameter with coagulation pretreatment compared to rejection with no pretreatment (shown as a line). Experimental conditions pH 7-8, 5-15 mgL<sup>-1</sup> as DOC organics,  $0.5 \text{ mM CaCl}_2$ , 1 mM NaHCO<sub>3</sub>.

Figure 5 Ferric chloride addition in microfiltration (GVWP membrane, 2.5 mM CaCl<sub>2</sub>, pH 7-8, 1 mM NaHCO<sub>3</sub>, 20 mM NaCl, 5 mgL<sup>-1</sup> DOC IHSS HA).

Figure 6 Ferric chloride addition in ultrafiltration (100 kDa, 30 kDa and 10 kDa membranes, 0.5 mM CaCl<sub>2</sub>, pH 7-8, 1 mM NaHCO<sub>3</sub>, 20 mM NaCl, 5 mgL<sup>-1</sup> DOC IHSS FA).

Figure 7 Ferric chloride addition at fouling conditions in nanofiltration (TFC-SR membrane, 2.5 mM CaCl<sub>2</sub>, pH 7-8, 1 mM NaHCO<sub>3</sub>, 20 mM NaCl, 12.5 mgL<sup>-1</sup> DOC IHSS HA).

Figure 8 Water quality parameter as a function of clean membrane pore diameter. Values adapted from Table 4.

Figure 9 Membrane cost per 1000 m<sup>3</sup>/d capacity at clean water conditions over water quality parameter. Membranes are 1-GVWP at high flux, 2-GVWP at low flux, 3-100kDa UF, 4-30 kDa UF, 5-10 kDa UF, 6-5 kDa UF, 7-3 kDa UF, 8-1 kDa UF, 9-CA-UF, 10-TFC-SR, 11-TFC-S, 12-TFC-ULP.

Figure 10 Membrane cost per 1000 m<sup>3</sup>/d capacity at fouling conditions over water quality parameter. Membranes are 1-GVWP at high flux, 2-GVWP at low flux, 3-100kDa UF, 4-30 kDa UF, 5-10 kDa UF, 6-5 kDa UF, 7-3 kDa UF, 8-1 kDa UF, 9-CA-UF, 10-TFC-SR, 11-TFC-S, 12-TFC-ULP.

Figure 11 Membrane cost per 1000  $m^3/d$  capacity as a function of WQP. Membranes with no ferric chloride as shown in Figure 9. 1-GVWP high flux & low dose, 100kDa UF and 30kDa UF, 2- GVWP low flux & low dose and 10 kDa UF, 3-GVWP low flux, 4-30kDa UF<GVWP low flux and high dose<100kDa UF<10kDa UF, 5-TFC-SR.

# FIGURES

Figure 1







Schäfer, A.I.; Fane, A.G.; Waite, T.D. (2001) Cost Factors and Chemical Pretreatment Effects in the Membrane Filtration of Waters containing Natural Organic Matter, Water Research 35, 6, 1509-1517. doi:10.1016/S0043-1354(00)00418-8











Figure 6







Schäfer, A.I.; Fane, A.G.; Waite, T.D. (2001) Cost Factors and Chemical Pretreatment Effects in the Membrane Filtration of Waters containing Natural Organic Matter, Water Research 35, 6, 1509-1517. doi:10.1016/S0043-1354(00)00418-8













Figure 11



#

# TABLES

Table 1 Solution composition as used in experiments.

	pН	NaHCO <sub>3</sub>	CaCl <sub>2</sub>	NaCl	Natural Organics1	Inorganic
	[-]	[mM], [mgL <sup>-1</sup> ]	[mM], [mgL-1]	[mM], [mgL <sup>-1</sup> ]	[mgL <sup>-1</sup> as DOC]	Colloids <sup>2</sup> [mgL <sup>-1</sup> ]
Rejection	7-8	1,84	0.5, 56	20, 2 935	5 - 12.5	10
Experiments Fouling	7-8	1,84	2.5, 280	20, 2935	5 – 12.5	10
Experiments						

<sup>1</sup> Natural organics were humic acid, fulvic acid, natural organic matter or fractions of those.

<sup>2</sup> Inorganic colloids were monodispersed, spherical hematite colloids (diameters 40, 75, 250 and 500 nm).

Table 2 Pure water membrane characteristics (flux, permeability, applied transmembrane pressure, membrane resistance, molecular weight cut-off (MWCO) and pore diameter) of the MF, UF and NF membranes used in experiments.

Process	Membrane	Pure Water	Water	Pressure	Membrane	MWCO	Pore
		Flux	Permeability	[bar]	Resistance	[kDa]	Diameter
		$[Lm^{-2}h^{-1}]$	[Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> ]		$[m^{-1}]$		[nm]
MF	GVWP	$7968 \pm 288$	7968	1	$4.51 \cdot 10^{7}$	-	$220^{*}$
MF	GVHP	$7803\pm308$	7803	1	$4.60 \cdot 10^{7}$	-	$220^{*}$
UF	PLHK	$1320\pm40$	1320	1	$0.03 \cdot 10^{10}$	$100^{*}$	18.20
UF	PLTK	$390 \pm 20$	390	1	$0.09 \cdot 10^{10}$	$30^{*}$	9.62
UF	PLGC	$65 \pm 5$	21.7	3	$1.66 \cdot 10^{10}$	$10^{*}$	5.18
UF	PLCC	$28 \pm 3$	9.3	3	$3.85 \cdot 10^{10}$	5*	3.72
UF	PLBC	$22\pm2$	7.3	3	$4.90 \cdot 10^{10}$	3*	2.84
UF	PLAC	$15 \pm 2$	5.0	3	$7.18 \cdot 10^{10}$	$1^{*}$	1.88
NF	CA-UF	$49.9\pm4.2$	10.0	5	$3.6 \cdot 10^{10}$	5#	3.72
NF	TFC-SR	$45.8\pm6.1$	9.2	5	$3.9 \cdot 10^{10}$	$< 0.18^{\#}$	< 0.64
NF	TFC-S	$49.4\pm5.9$	9.9	5	$3.6 \cdot 10^{10}$	$< 0.18^{\#}$	< 0.64
NF	TFC-ULP	$19.4\pm2.6$	3.9	5	$9.3 \cdot 10^{10}$	$< 0.18^{\#}$	< 0.64

information supplied by Millipore.

<sup>#</sup> determined by Fluid Systems using lactose marker tests. Rejections for MWCO as >90% at 1% glucose in MilliQ (TFC Series). CA-UF determined with 5 kDa dextran at 100 mgL<sup>-1</sup> (Takigawa (1999)).

Table 3 Cation rejection as a function of membrane pore size in the absence of organics (0.5 mM CaCl<sub>2</sub>, pH 7-8, 1 mM NaHCO<sub>3</sub>, 20 mM NaCl).

Pore Size [nm]	220	18.2	9.6	5.2	3.7	2.8
Sodium [%]	0	0	0	0	0	0
Calcium [%]	0	0	2.8	2.6	2.0	13.6
Pore Size [nm]	1.9	3.7	< 0.64	< 0.64	< 0.64	
Sodium [%]	0	12.6	37.4	82.0	85.0	
Calcium [%]	13.2	14.4	67.6	94.4	90.4	

Table 4 Water quality criteria for process evaluation and water quality parameter. The numbers are fractions of the rejection achieved. The sum of each parameter suite of 100 corresponds to a rejection of 100% of all fractions. Experimental conditions were pH 7-8, 5-15 mgL<sup>-1</sup> organic as DOC, 0.5 mM CaCl<sub>2</sub> (except for MF where calcium concentration is 2.5 mM). The values will depend on time (or permeate volume) and stirring regime. Membrane cost estimate based on pure water flux and a plant capacity of 1000 m<sup>3</sup>/d.

	Colloids				DOC			ns	TOTAL	Membrane	
											Cost Clean
	40	75	250	500	HA	FA	NOM	$Na^+$	Ca <sup>2+</sup>	WQP	[US\$]
	nm	nm	nm	nm						(300 max)	
MF GVWP	0	2.1	20.8	23.3	3.4	2.4	5.7	0	0	58	325
UF 100 kDa	25	25	25	25	2.0	2.8	3.0	0	0	108	1 185
UF 30 kDa	25	25	25	25	3.7	4.0	3.3	0	1.4	112	2 740
UF 10 kDa	25	25	25	25	22.0	18.7	17.0	0	1.3	159	20 466
UF 5 kDa	25	25	25	25	29.3	27.3	24.7	0	1.0	182	24 851
UF 3 kDa	25	25	25	25	28.7	28.0	25.7	0	6.8	189	31 629
UF 1 kDa	25	25	25	25	30.0	29.0	28.7	0	6.6	194	46 389
NF CA-UF	25	25	25	25	25.3	23.6	19.1	6.3	7.2	182	17 333
NF TFC-SR	25	25	25	25	24.7	31.3	23.0	18.7	33.8	232	18 841
NF TFC-S	25	25	25	25	30.0	27.9	31.8	41.0	47.2	278	17 687
NF TFC-ULP	25	25	25	25	25.2	26.8	31.8	42.5	45.2	272	45 614

Table 5 Water quality parameter for fouling conditions (2.5 mM CaCl<sub>2</sub>, pH 7-8, IHSS HA). Plant capacity for cost estimate  $1000 \text{ m}^3/\text{d}$ .

			Quality and Cost					
Process	Total Colloids <sup>*</sup>	DOC	UV <sub>254nm</sub>	Ca <sup>2+</sup>	$Na^+$	WQP [-]	Membrane Cost Clean [US\$]	Membrane Cost Fouled [US\$]
MF GVWP	46	10	4	0	0	56	325	1488
MF GVWP#	46	10	4	0	0	56	3250	14880
UF 100kDa	100	57	70	0	0	157	1185	8698
UF 10 kDa	100	70	87	6	4	175	20466	21745
NF CA-UF	100	74	89	21	20	195	17333	20635
NF TFC-SR	100	93	100	55	24	233	18841	25490
NF TFC-S	100	94	99	96	80	282	17687	45614
NF TFC-ULP	100	87	98	98	91	282	45614	72222

values adapted from Table 4 as fouling with calcium and organics only considered here.

flux values corrected for low flux by a factor 10 from experimental value (1750 to 175 Lm<sup>-2</sup>h<sup>-1</sup>) due to lower permeate pressure drop of flat sheet membranes.

Table 6 Water quality parameter for pretreatment with ferric chloride (2.5 mM  $CaCl_2$ , pH 7-8, IHSS HA). Plant capacity for cost estimate 1000 m<sup>3</sup>/d.

		Rejection [%]	Quality and Cost					
Process	Total	DOC	Ca <sup>2+</sup>	$Na^+$	WQP	Membrane	Membrane Cost Fouled [US\$] 25 mgL <sup>-1</sup> /100 mgL <sup>-1</sup> FeCl <sub>3</sub>	
	Colloids	25 mgL <sup>-1</sup> /100 mgL <sup>-1</sup> FeCl <sub>3</sub>	_		[-]	[US\$]		
MF GVWP	100	10-39 / 48-83 <sup>*</sup>	0	0	110-183	325	1525 / 8710	
MF GVWP#	100	10-39 / 48-83	0	0	110-183	3250	15250 / 87100	
UF 100kDa	100	35-90 / 77	0	0	135-177	1185	1183 / 11794	
UF 30 kDa	100	50 / 94	0	0	150-194	2740	2433 / 6213	
UF 10 kDa	100	67-84 / 86	6	4	172-191	20466	13129 / 14201	
NF TFC-SR	100	94 / 79	83 - 99	3-43	222-265	18841	19697 / 23424	

range depending on organic type.

flux values corrected for low flux by a factor 10 from experimental value (1750 to 175 Lm<sup>-2</sup>h<sup>-1</sup>) due to lower permeate pressure drop of flat sheet membranes.

Table 7 Membrane cost based on Water Factory 21 Experience (Leslie (1999)).

Process	Module Size	Average Module	Membrane Cost
	[m <sup>2</sup> ]	Cost [US\$]	$[US\$/m^2]$
MF Polypropylene	31	650	21.0
MF PVDF	40	2500	62.5
UF CA	90	1500	16.7
NF Polyamide	48	750 - 1000	15.6 - 20.8
RO Polyamide	50	< 500	< 10
RO CA	50	< 500	< 10

Table 8 Ferric chloride cost as a function of dosage for a 1000  $m^3$ /day plant capacity. Range of costs of ferric chloride used was 0.29 to 7.1 US\$/kg depending on largely location of water treatment plant and coagulant quality.

	Ferric Chloride [m	Dosage as FeCl <sub>3</sub>
Ferric Chloride	25	100
Consumption [kg/d]	25	100
Cost [US\$/d]	7.3-177.5	29.4-710.0
Cost [US\$/m3]	0.007-0.18	0.029- 0.71

Table 9 Typical recoveries, transmembrane pressures, power requirements, consumption and resulting energy costs based on applied pressures with an overall motor/pump efficiency of 40%. Assumed energy cost 0.05 US\$/kWh.

	Recovery	Pressure	Consumption	Energy cost
	[%]	[kPa]	[kWh/d]	[US\$/m <sup>3</sup> ]
MF	90 - 98	100	77.5 - 70.8	0.004 - 0.0035
UF	90 - 98	100	77.5 - 70.8	0.004 - 0.0035
UF	90 - 98	300	231.5 - 212.5	0.012 - 0.011
NF	75 - 95	500	463.3 - 365.5	0.023 - 0.018
RO	50 - 80	1000	1389 - 868.3	0.070 - 0.043

Table 10 Comparison of WQP as well as membrane, energy and chemical costs for selected membranes. It has been assumed that membranes last for 5 years.

COSTS	WQP [ - ]	Clean	Fouled	FeCl3 Fouled	Energy	FeCl <sub>3</sub> Cost	FeCl <sub>3</sub> Cost	Total*
[US\$/1000m <sup>3</sup> ]		Membrane	Membrane	Membrane	Cost	25 mgL <sup>-1</sup>	100 mgL <sup>-1</sup>	
MF GVWP	58 - 183	0.18	0.82	4.88	1.5 - 1.4	7.34 - 177.5	29.4 - 710	2.2 - 35.8
MF GVWP <sup>#</sup>	58 - 183	1.78	8.15	47.7	0.15 - 0.14	7.34 - 177.5	29.4 - 710	8.3 - 77.3
UF 100 kDa	108 - 177	0.65	4.77	6.46	1.5 - 1.4	7.34 – 177.5	29.4 - 710	6.2 - 37.4
UF 30 kDa	112 - 194	1.50	3.40	3.40	1.5 - 1.4	7.34 - 177.5	29.4 - 710	4.8 - 34.3
UF 10 kDa	159 - 191	11.2	11.9	7.78	4.6 - 4.2	7.34 - 177.5	29.4 - 710	16.1 - 41.8
UF 5 kDa	182	13.6	14.1	-	4.6 - 4.2	-	-	18.5
UF kDa	189	17.3	18.2	-	4.6 - 4.2	-	-	22.6
UF 1 kDa	194	25.4	27.2	-	4.6 - 4.2	-	-	31.6
NF CA-UF	182	9.5	11.3	-	9.3 – 9.7	-	-	20.8
NF TFC-SR	232	10.3	14.0	-	9.3 – 9.7	-	-	23.5
NF TFC-S	278	9.7	25.0	-	9.3 – 9.7	-	-	34.5
NF TFC-ULP	272	25.0	39.6	-	9.3 – 9.7	-	-	49.1

 $^{\#}$  Flux and pressure reduced by a factor of 10.

\* Cost calculated for lowest ferric chloride quality and cost. Range is cost without pretreatment to pretreatment with lowest cost ferric chloride at a dosage of 100 mgL<sup>-1</sup>.