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ADVANCED TREATMENT COMBINATION FOR GROUNDWATER RECHARGE OF MUNICIPAL WASTEWATER BY NANOFILTRATION AND OZONATION

M. Ernst and M. Jekel

Technical University of Berlin, Department of Water Quality Control (DWQC),
Secr. KF4, Strasse des 17. Juni 135, D-10623 Berlin, Germany

ABSTRACT

This paper presents the results of research undertaken on an advanced treatment combination for polishing municipal wastewater with the purpose of a safe groundwater recharge. The results of a former study of DWQC initiated this research. It is envisaged that tertiary effluent is nanofiltrated to reject dissolved organic carbon (DOC) and adsorbable organic halogens (AOX) to concentrations less than 2-3 mg DOC/L respectively <20 μg AOX/L. The brine will be given back in a recycling process to the sewage treatment plant after passing an oxidation step. To avoid rising scaling potentials and other negative impacts due to increasing salinity, the rejection characteristics of several NF-membranes were investigated. They show a strong dependence between DOC and sulfate removal. Biofouling on the membrane surface (Desal DK5) can be controlled by higher cross-flow velocities (CFV) of about 1 m/s, however, a suitable pre-treatment like slow sand filtration is required. High water conversion factors result in moderately higher biofouling. This shows that water quality is the main factor responsible for fouling and not the concentration of constituents. Ozonation experiments with the concentrate confirmed an enhanced biodegradability of refractory DOC. At a specific ozone consumption of 1,7 mg O_3/mg DOC_0 the DOC reduction by micro-organisms (aerobic bio-test) reaches its maximum after 14 days of biodegradation with a total reduction rate of 60%. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Aerobic biotest; adsorbable organic halogens (AOX); biofouling; dissolved organic carbon (DOC); groundwater recharge; nanofiltration; oxidation.

INTRODUCTION

The reuse of municipal wastewater for groundwater recharge is increasingly being viewed as a valuable method to overcome the lack of naturally accumulated groundwater especially in dry regions. It is sometimes the only feasible method to meet the increasing demands for drinking water in the growing urban areas. Even though wastewater is already indirectly reused in some regions as part of the natural water cycle due to bank filtration of river water that often contains high amounts of treated municipal wastewater, the direct groundwater recharge with tertiary effluent ensures that water quality is controlled and that higher infiltration rates than through river bank filtration are achieved. A shorter water cycle will lead to a more effective use of wastewater which in turn makes tightened monitoring of problematic substances such as micro-organisms, heavy metals and organic compounds absolutely necessary.

Situation in the Berlin region - background

The City of Berlin has to meet its water needs without access to water supplies from other areas. The reclamation of clarified wastewater is being considered as one option to compensate for the lack of water supply which would be a result of a possible fall of the groundwater level caused by the decrease of water provided by the river Spree to the City. More than 60% of the river Spree consists of pumped groundwater from lignite mining in the Lausitz region. However, this process will be ceased in the near future because of economical reasons. The DWQC of the TU Berlin has been conducting research on refractory organic substances in tertiary effluents during groundwater recharge for many years. In order to reach an acceptable wastewater reuse, the dissolved organic carbon (DOC) or adsorable organic halogens (AOX) parameter respectively must be reduced to a certain level before reaching the groundwater which should be in a similar range to the natural background concentrations in the local aquifer. Even if this criterion is not a toxicological one, concentrations of 3 mg DOC/L and 20 µg AOX/L are considered as the limits for a sustainable groundwater recharge in the Berlin area. These figures are the typical concentrations in the raw potable water that is up to 60% derived from bank filtered water from the rivers Havel and Spree.

Treatment combination

The results of the DWQC study have shown that mainly the DOC, but also the AOX are poorly adsorbable on activated carbon in the effluent of the Berlin wastewater treatment plant Ruhleben. Furthermore, a concentration of 10 - 11 mg DOC/L of the total concentration of 15 mg DOC/L was found to be non-biodegradable through soil aquifer treatment (SAT) (Drewes, 1997). To reject this part of refractory DOC which is mainly formed by compounds smaller than 1000 Dalton, an advanced treatment combination was designed. The tertiary effluent is filtrated by a membrane step (NF or tight UF) suitable to cut off large amounts of poorly biodegradable and adsorbable DOC and AOX compounds. This membrane process with a high water conversion factor will produce a purified permeate that can be used for groundwater recharge within the mentioned limits.

The brine of the membrane process is subsequently oxidised. By ozonation or combined oxidation (O_3 and H_2O_2) the refractory DOC is converted into bio-available organic compounds which can be mineralised by bacteria when being recycled into the wastewater treatment plant.

METHODS

A number of important aspects in relation to the implementation of the advanced treatment combination will be discussed in the following:

1. Because of the high content of colloidal matter, bacteria and nutrients (nitrogen, phosphorus, organic substances) in the tertiary effluent, the water cannot be filtered by a membrane process like NF without any pre-treatment. The fouling potential (especially the biofouling potential) of the effluent has to be decreased by an appropriate technique to avoid the blocking of the membrane.
2. NF Membranes usually have a cut off in the range of 300-1000 Dalton which allows us to obtain high rejection rates for DOC and AOX but also for double charged ions, such as Ca^{2+}, Mg^{2+}, Br^{2+}, SO_4^{2-} and CO_3^{2-}. These ions can only escape the treatment cycle by the permeate or the sludge.
3. The salt concentration in the cycle will depend on the rejection characteristic of the chosen membrane and the water conversion factor. High concentrations of sulfate or calcium may influence the oxidation process, the performance of the bioreactor and the membrane process. Furthermore, the precipitation of salts (scaling) can occur by reaching the solubility product and block the membrane.
4. If high concentrations of DOC are oxidised in the concentrate by ozone or perozone, the bio-availability of the dissolved organic substances is enhanced. However, AOX or other problematic by-products might be produced in the concentrate.

Fouling and rejection behaviour

A bench-scale NF plant equipped with a testing cell for membrane sheets (Fig. 1) was constructed for the experiments. Hydraulic conditions were adjusted to those of spiral wound elements assigned for pilot testing.

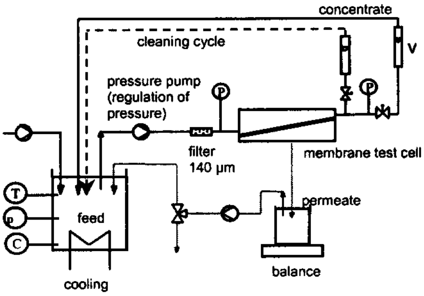

Figure 1: Flow diagram of the bench-scale NF-Plant.

The small membrane area of 117 cm^2 is sufficient to collect samples for rejection experiments but it requires a long time to achieve a notable recovery for fouling experiments. Because of this a bigger testing plant with a spiral wound modul (Osmonics, DK5) was built to supply feedwater with high water conversion factors for fouling experiments in the bench scale plant. Process parameters like transmembrane pressure, permeate flux, temperature (T), pH-value and conductivity (C) were continuously recorded. The temperature of the feed was regulated by a cooler, minor variation was allowed for by a correction of the permeate flux according to Yesselman and Sharpe (1997, cited in Hong *et al.*, 1996). Permeate flux was standardised to 7 bar.

Membrane material and pre-treatment: At the beginning of the research, a membrane screening of 9 nano- and ultrafiltration membranes was carried out to find an appropriate membrane capable of reducing DOC and AOX from tertiary effluent below the desired thresholds. Membranes form Desal, Hydranautics/Nitto Denko, Celgard (former Hoechst), DOW, TechSep and TriSep were tested. The membrane Desal DK5 was chosen for the fouling experiments because of its rejection properties and permeate flux identified as well as its availability on the market.

Prior to the experiments a new membrane is treated with deionisated (d.i.) water for 24 h in order to achieve a constant permeate flux. Therefore, the same operational parameters as for the following experiments with tertiary effluent were used (temperature: 20°C, feed flow rate 62 l/h respectively 200 l/h equivalent to a cross-flow velocity (CFV) of 0.3 m/s respectively 1 m/s). Subsequently, the MTC_w (pure water permeability coefficient) was determined in [$ms^{-1}Pa^{-1}$].

Oxidation and aerobic biotest

The oxidation tests were conducted in a 6L -batch glass reactor, 200 mm in diameter and height. The ozone gas was introduced into the reactor by a perforated teflon ring located under a high frequency stirrer to ensure a good mass transfer of ozone into the water. In order to determine the specific ozone consumption, ozone gas concentrations in the inlet and outlet of the reactor were measured simultaneously using UV-spectrophotometers (BMT 961). The fluid ozone concentration was determined by an electro-chemical ozone sensor (Obisphere Modell 3600). The pH-value and the temperature (20°C) were fixed by automated control. After oxidation the samples were prepared for a subsequent aerobic biodegradation test, carried out in 250 ml flasks according to the ISO 7827 guideline on ultimate biodegradability. As inoculum, mixed cultures from the municipal wastewater treatment plant Berlin Ruhleben were employed. Samples were taken every third, seventh and fourteenth day and filtrated through 0.45 μm to determine SAC, DOC and COD. Reduction rates of DOC are calculated and shown as:

$$\alpha = \frac{DOC_0 - DOC_{red}\,(z_{spec.})}{DOC_0}$$

Analytic

The following parameters were analysed to characterise the samples:

- DOC and TIC as NPOC (non-purgeable organic carbon)/TIC with HighTOCAnalyser, Elementar GmbH, Hanau. Concerning the DOC analysis the proportion of volatile organic compounds was considered negligible
- UV/VIS-absorbance as Specific Absorbance Coefficient (SAC 254 nm and 436 nm), Perkin Elmer Lambda 2 spectrophotometer
- AOX (column method according to German standard DIN 38409-H14), Ströhlein Coulomat 702Cl
- Anions (SO_4^{2-}, NO_3^-, Cl^-), ion chromatography, Dionex DX 100, USA
- Ca^{2+}, Mg^{2+}, AAS Varian 400 and hardness by titration (DIN 38406)
- Electrical conductivity, WTW LF95

Feedwater characteristic

Table 1. Average composition of tertiary effluent [mg/L], plant Berlin Ruhleben (Drewes, 1997)

	COD/BOD_5	DOC	AOX	NH_4^+-N	NO_3^--N	O-PO_4^{3-}	Cl^-	SO_4^{2-}
tert. effl.	45/4	15.1	0.05	0.3	8	0.15	170	154

RESULTS AND DISCUSSION

Rejection properties

Table 2 shows the rejection properties of a selection of different membrane types and materials. In the following the chosen operating parameters for the bench-scale plant are listed: cross-flow velocity (CFV)=0.3 m/s, pH=7.5, T=20°C, transmembrane pressure (Δp)=7 bar. The feedwater was tertiary effluent slow sand filtrated by 1.4 m/d.

Table 2. Average NF-membrane rejection rates [%] for tertiary effluent

Manufacturer	DESAL OSMONICS	DOW FILMTEC	Celgard (HOECHST)	TechSep
Typ	DK5	NF200B	NF-PES10	N400
Material	Polysulfone + Polypiperazinamid	Polypiperazine	Polyethersulfone	ZrO_2
MTC_0 [$ms^{-1}Pa^{-1}$].	1.50E-11	1.61E-11	3.41E-11	2.77E-11
conductivity	42	44	14	4
SAC 254	98	97	75	28
DOC	96	95	67	15
AOX	99	97	60	21
TIC	52	54	10	8
sulfate	99	99	56	9
chloride	6	26	4	4
calcium	68	60	24	11
Magnesium	55	57	20	1

All four presented membranes are called NF-membranes by the manufacturers, even though their rejection properties differ greatly. Desal DK5 and DOW NF200 show a nearly similar characteristic in regard to the organic parameters. The NPOC rejection of 96% or 95% respectively is high enough to achieve permeate concentrations of less than 3 mg DOC/L even at recoveries rates of 80%. The concentration of 20 µg AOX/L aimed at can be met as well. However, their high rejection rates for calcium and especially for sulfate are a problem for the treatment combination. The NF200 is offered by DOW as a low rejection membrane for Ca^{2+} (Ventresque, 1997).

PES10 and N400 are examples of more open NF-membranes. The moderate or low rejection rates for sulfate and hardness of these membranes are combined with a weak performance regarding DOC and AOX. These two membranes are not able to reach the desired concentrations for organic substances. It also has to be taken into account that the rejection rates for an industrial plant will be a little bit lower depending on recovery and the given membrane rejection characteristics.

Biofouling/pretreatment

To guarantee a stable filtration rate in the membrane process, a further treatment between the sewage plant and the membrane step is necessary. For this reason, different kinds of pretreatment, such as filtration, rapid filtration, soil aquifer treatment (SAT) and microfiltration were conducted with DK 5 to investigate the resulting fouling potential. The SAT, with low infiltration rates (0,2 m/d) has been a successful treatment to control biofouling during the investigation period of 350 h (Ernst *et al.*, 1999). In addition to the pretreatment, membrane process parameters also have a big influence on fouling behaviour. Figures 2 and 3 show the dependence of CFV and WCF on the forming of the biofouling layer shown as relative flux decline.

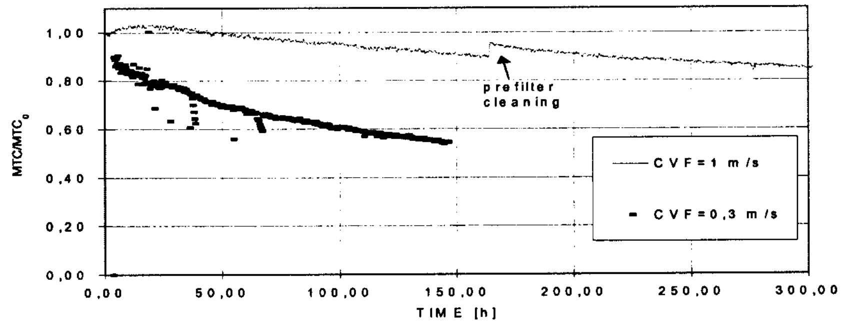

Figure 2. Flux decline in dependence of the CFV, Feed: ultrafiltrated tert. effl., WCF=0, Δp=7bar, DK 5.

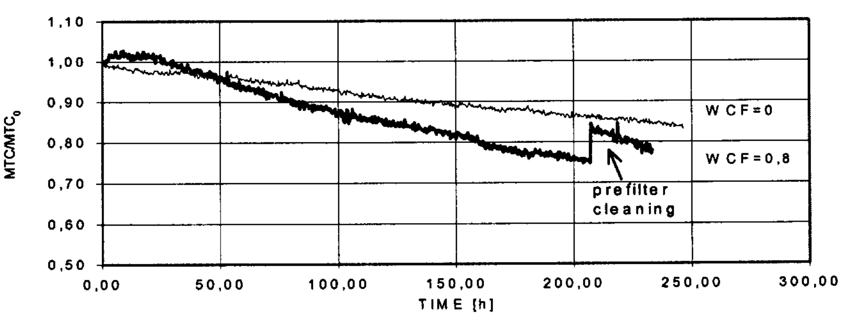

Figure 3. Flux decline in dependence of the WCF, Feed: SAT 1.4 m/d, CFV=1 m/s, Δp=7 bar, DK 5.

The CFV has a strong influence on the fouling potential.. At cross-flow velocities of 1 m/s the flux decline of the membrane process can be controlled during 300 h of operation. The performance is similar to the pre-treatment with SAT at 0.17 m/d at a CFV of 0.3 m/s (Ernst *et al.*, 1999). The experiment simulates the fouling characteristics at WCF=0, similar to the first modul in an industrial plant. Fig. 3 describes the range of biofouling between the first and last module in a WCF=0.8 filtration process. The increase of fouling potential is moderate compared to WCF=0, yet the stucture of the biofouling layer differs from lower WCF. The results of this recycling experiment correspond with online tests in spiral wound element configuration (Chellam *et al.*, 1997).

Oxidation/biodegradation

Tertiary effluent after SAT at 0.17 m/d was concentrated in a recycling spiral wound modul plant to WCF=0.8. Prior to ozonation the initial DOC was around 20-30 mg/L after membrane filtration. AOX reached approximately 150 μg AOX/L. Figure 4 shows the dependence of direct mineralisation as a function of pH-value and specific ozone consumption.

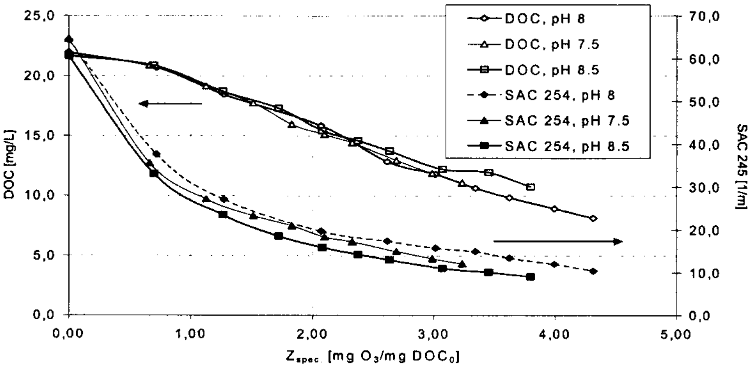

Figure 4. Oxidation of DOC and SAC_{254} in NF-concentrates of tertiary effluent (WCF=0.8), dependence of pH and Z_{spec}.

The retentate does not show a significant dependence on the pH-value during direct mineralisation. Up to $Z_{spec.}$=0.7 mg O_3/mg DOC_0 there is only a slight reduction of DOC while the SAC_{254} value decreases rapidly. Ozone first attacks chromophoric functions and C-double bindings responsible for the formation of SAC_{254}. At a specific ozone consumption of 1 mg O_3/mg DOC_0, the SAC_{254}/DOC value reaches a relatively stable level between 1.2-1.4 and the DOC subsequently decreases linearly independently of the adjusted pH-value. Figure 5 shows the effect of direct mineralisation and conversion of refractory DOC to bioavailable organic substances.

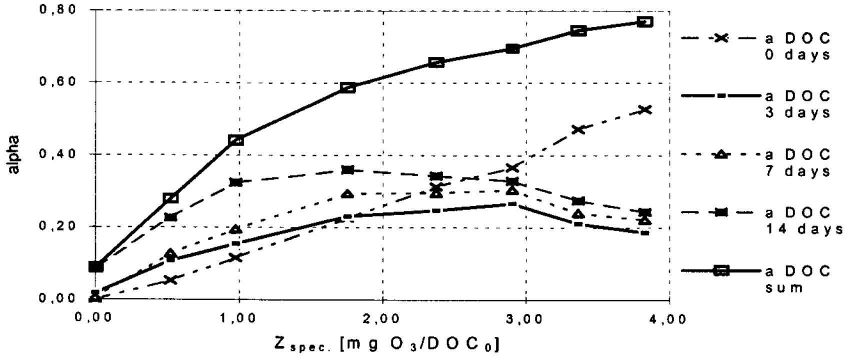

Figure 5. DOC reduction rate α due to ozonation and subsequent aerobic biotest, WCF=0.8.

The "0-day" line displays the reduction of direct mineralisation of DOC by ozone. Due to the input of O_2 into organic substances, the refractory DOC is converted into bioavailable substances with increasing specific ozone consumption. The "7 day" biotest line shows a maximum of the DOC reduction at $Z_{spec.}$=1,7 O_3 mg/mg DOC_0. This result was verified by the "14 day" line as well. There, the DOC reduction rate caused by micro-organisms achieves about 35% of the DOC_0. In conjunction with the direct conversion of DOC to CO_2 caused by ozone, this results in a total decrease of about 60% of the initial DOC. Similar tests with higher concentrations of SO_4^{2-} and Ca^{2+} (up to 3 g/L) did not show any influence on the position and range of the maximum. The oxidation and biological treatment step will therefore not be influenced negatively by concentrations of scaling builders in this range. For the membrane step it could be shown that up to concentrations of 7 g/L sulfate in the feedwater no precipitation occurs.

Another important aspect is the concentration of AOX during ozonation. Figure 6 points out that with increasing $Z_{spec.}$ the AOX-values also increase.

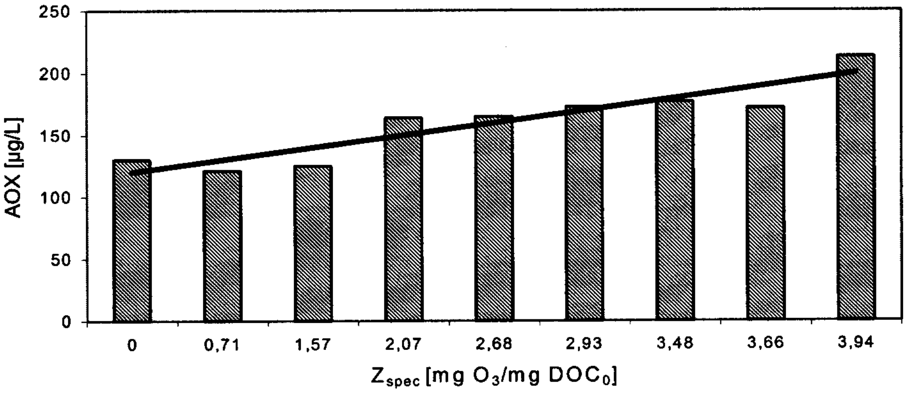

Figure 6. c(AOX) vs. $Z_{spec.}$, NF-concentrate of tertiary effluent, pre-treatment SAT at 1.4 m/d, DK5.

The figure above shows that the conversion of refractory DOC to bioavailable organic matter by ozone can produce AOX in significant amounts at the same time. This behaviour, however, is not very distinctive up to $Z_{spec.}$=2 mg O_3/mg DOC_0 so that it would hardly effect the quality of the permeate by rising halogens in the recycling cycle. The increase of AOX value might be caused by the formation of organo bromine compounds during the oxidation of the brine (Van Gunten *et al.*, 1998). This will be investigated by further specification of the AOX-species in the near future.

CONCLUSIONS

It was confirmed that by nanofiltration of tertiary effluent with appropriate membranes (Desal DK5, DOW NF 200) the desired concentration of < 2-3 mg DOC/L and < 20 µg AOX/L for artificial groundwater recharge can be achieved. However, in a recycling treatment combination 'municipal sewage plant - membrane process – oxidation', "tight" NF-membranes will produce an increased sulfate and calcium concentration in the recycling cycle. The high salinity of the resulting concentrate might have negative consequences for its further treatment (scaling). Furthermore, the high biofouling potential of the tertiary effluent needs to be controlled by pre-treatment as well as by membrane process parameters like CFV or WCF. An increase of CFV from 0.3 m/s to 1 m/s results during a 300 h test in a significant reduction of the specific flux decline. This positive effect however requires six times more energy because of the square dependence of kinetic energy. Higher recoveries rates (WCF=0 to WCF=0.8) result in moderately higher biofouling which proves that water quality is mainly responsible for fouling and not the concentration of constituents.

The conversion from refactory DOC to bioavailable organic matter through ozonation was also confirmed. A specific ozone consumption of 1.7 mg O_3/mg DOC_0 results in an optimal reduction of DOC by aerobic micro-organisms. This ozone dosage produces a ratio of approx. 1.5 between the biodegraded DOC and directly mineralised DOC after 7 days of aerobic biotesting. A total reduction of 60% of the DOC_0 after ozonation and biodegradation (14d) will result in increasing DOC concentrations in the recycling cycle which will influence permeate quality and might have an effect on the AOX formation in the oxidation step. To achieve higher total reduction rates further studies are necessary.

One option to overcome problems of accumulation of double charged ions as well as of organic compounds in the recycling cycle could be the use of wider membranes. However, the quality of permeate concerning DOC and AOX will not meet the mentioned quality standards for groundwater recharge directly. If these substances can not be degraded by SAT during infiltration, a further treatment of these permeates is necessary.

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS / ABBREVIATIONS

α	DOC reduction rate
$DOC_{0\,/\,red}$ [mg/L]	Initial DOC / after reduction by O_3 or aerobic biotest
AOX [μg/L]	adsorbable organic halogens
COD [mg/L]	chemical oxygen demand
BOD_5 [mg/L]	biological oxygen demand in a 5 days biotest
MTC_0 [$ms^{-1}Pa^{-1}$]	Mass transfer coefficient, pure water permeability
CFV [ms^{-1}]	Cross flow velocity
WCF	Water conversion factor, yield
$Z_{spec.}$ [mg O_3/mg DOC_0]	Specific ozone consumption: O_3 that has been used neither by breakup of O_3 or oxidation of water compounds
SAT	Soil aquifer treatment

REFERENCES

Chellam, S., Jacangelo, J. G., Bonacquisti, T. P. and Schauer, B. A. (1997). Effect of pretreatment on surface water nanofiltration. *J. AWWA*, **89**(10), 77-89.

Drewes, J. E. (1997) Untersuchungen zum Verhalten organischer Abwasserinhaltsstoffe bei der Wiederverwendung kommunaler Kläranlagenabläufe zur künstlichen Grundwasseranreicherung (Investigations of the behavior of DOC in the effluent of municipal wastewater, when reused at artifical groundwater recharge). PhD thesis, Reihe 15 Umwelttechnik, Nr. 174, VDI Verlag Düsseldorf

Ernst, M., Blöcher, C., Schläger, J. and Jekel, M. (1999). Removal of dissolved organic matter from tertiary effluent by nanofiltration with respect to pre-treatment, fouling behaviour and membrane cleaning. *VOM WASSER 99* (in press).

Hong, S. and Elimelech, M. (1996). Chemical and physical aspects of natural organic matter fouling of nanofiltration membranes. American Chemical Society, Division of Environmental Chemistry, 212th ACS National Meeting, 25-29 Aug. 1996, Orlando, Florida. Preprints of papers 36/2, 89-91

Van Gunten, U. and Oliverus, Y. (1998) Advanced oxidation of bromide containing waters: Bromide formation mechanisms. *Environ. Sci. Technol.*, **32**, 63-70.

Ventresque, C. and Bablon, G. (1997). The integrated nanofiltration system of the Méry-sur-Oise surface water treatment plant (37 mgd). *Desalination*, **113**(2-3), 263-267.