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Removal of organic micro-pollutants during drinking water treatment by nanofiltration and reverse osmosis

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ABSTRACT

A study on a flat sheet membrane test unit for nanofiltration (NF) and reverse osmosis (RO) with synthetic and natural waters was carried out in order to evaluate the performance of four NF/RO membranes for the removal of selected organic micro-pollutants. The influence of molecular weight and membrane material on removal efficiencies was shown. Perfluorinated compounds and X-ray contrast agents with molecular weights larger than 300 g/mol are rejected to a percentage of more than 90%. Pharmaceuticals and antibiotics show rejection values larger than 60%. For the substances with a molecular weight between 100 and 200 g/mol there is a large range of rejection values depending on the membrane type. RO membranes usually achieve higher rejection values than NF membranes. Rejection also depends on the type of organic micro-pollutant. Although NF/RO membranes do not reject substances selectively, NF/RO is a suitable treatment technology for their removal if this is desired. However, it has to be considered that water composition is changed drastically by NF/RO such that a post treatment of the permeate may be required to keep up with the drinking water standards. For full-scale application also the dosage of antiscalants has to be taken into account. In Germany there is a lively discussion about the discharge of concentrates when authorities have to decide on the realization of NF/RO plants.

Keywords: NF; Flat sheet membrane test unit; Organic micro-pollutants; Concentrate; Antiscalant

1. Introduction

Organic micro-pollutants like complexing agents, X-ray contrast agents, pharmaceuticals (incl. antibiotics), methyl-tertiary-butyl ether (MTBE), or pesticide metabolites like chloridazon-desphenyl or N,N-dimethylsulfamide (DMS) are undesired substances in drinking waters as they might have a negative impact on human health. It is well known, however, that raw waters used for drinking water production might be contaminated by such compounds and thus removal by subsequent treatment becomes necessary [1–6]. Many of these substances are easily removed by activated carbon adsorption, which is one of the traditionally applied treatment processes in drinking water supply in Western Europe [1]. However there is a wide range of substances with a low adsorption affinity. Especially polar substances like DMS, MTBE, the complexing agents or the X-ray contrast agents are not easily removed by activated carbon. If raw waters containing these substances are treated by activated carbon adsorption a breakthrough occurs after very short operation times such as 10 m^3/kg [2]. This is in contrast to well adsorbed substances like polycyclic aromatic hydrocarbons or some pesticides where breakthrough occurs only after more than 50–100 m^3/kg [7].

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Activated carbon adsorption is also limited by the content of natural organic matter (NOM) in the water, because adsorption sites are occupied by NOM which is present in the water in much higher concentrations than the organic micro-pollutants [3,8].

As for those polar and low adsorbing substances activated carbon adsorption cannot be operated economically with short operation times until breakthrough, other treatment processes have to be considered. In the present article nanofiltration (NF) and reverse osmosis (RO) have been investigated as treatment processes for the removal of organic micropollutants. Especially such substances have been selected that show low adsorption affinity onto activated carbon and where yet no or only few values for the rejection by NF/RO are known.

The main application of NF/RO in Germany is softening of groundwaters exhibiting a rather high hardness. A recent survey showed that there are around 30 NF/RO-plants in operation or under construction in public drinking water supply in Germany [9]. However, there is a lot of discussion about using these processes for the removal of micro-pollutants. Especially hard groundwaters that also show a contamination with pesticides caused by agricultural land use in the catchment area may be treated by NF/RO. Additionally river bank filtrate used for drinking water production along the major German rivers might contain organic micro-pollutants like MTBE, X-ray contrast agents or pharmaceutical residues [4]. For pesticides, e.g. the concentrations in groundwaters or riverbank filtrates might even exceed the limiting value according to the Drinking Water Directive such that the waters have to be suitably treated in order to be able to use them for drinking water purposes.

As methods for the removal of organic pollutants the membrane processes NF and RO as well as adsorption to activated carbon and advanced oxidation processes are taken into account. Depending on the type of contaminant that has to be removed one or the other process is favoured also considering other site conditions.

In order to check which treatment process shows the best removal efficiency for a certain micropollutant laboratory-scale tests can be carried out. With such tests it is possible to roughly estimate the technological possibilities of the processes named. For the NF/RO-process a membrane test unit can be operated with different membrane types and the concentrations of the contaminants are measured in permeate and concentrate samples during test runs under defined conditions. The test solutions contain the contaminants under investigation in concentrations close to the ones in environmental samples. However, for practical application of the technologies tested in laboratory-scale also other aspects like the need for antiscalants and the discharge of the concentrate have to be thought over carefully. All these items will be discussed in the present article.

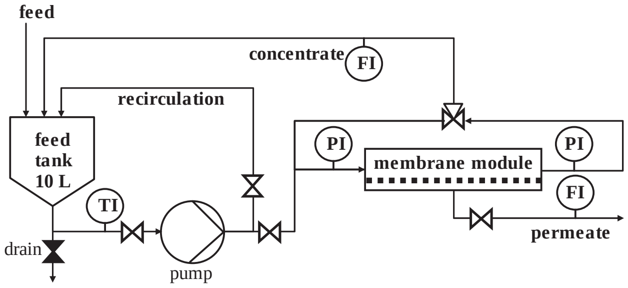

Fig. 1. Schematic illustration of the membrane test unit.

2. Materials and methods

2.1. Membrane test unit

The membrane test unit (CSM, Landau, Germany) mainly consists of a plate and frame membrane module of 0.008 m^2 membrane area, a high pressure pump and a raw water reservoir (volume 10 L). A schematic illustration of the test unit is shown in Fig. 1. The operation pressure was adjusted in the range of 6–8 bar according to practical conditions. The permeate flow ranged between 0.1 and 0.7 L/h depending on the type of membrane. Flux is similar to practical conditions in the range of 20–50 $L/m^2/h$. This results in values for the permeability of the tested membranes in the range of 5–15 $L/m^2/h/bar$. As the test unit has no automatic control unit, flow and pressure had to be readjusted regularly during long-term operation. Values of all operation conditions had to be manually documented. Excess energy of the circulation pump caused a temperature increase of the solution in the feed tank. A cooling coil in the feed tank helped to keep the operation temperature in a range between 22 and 28 °C. During data calculation permeability was corrected to a temperature of 20 °C. Temperature during test runs is higher than it would be during large scale application in water works. Rejection is less at higher temperature than at water work conditions. This means that rejections achieved during test runs are values standing for worst case conditions. According to the small membrane area the percentage of permeate related to the feed flowing across the membrane is also small (<1%) which is in contrast to the conditions in spiral wound modules. The cross flow velocity (around 2 m/s) is also much higher than in spiral wound modules and keeps the concentration polarization layer small. This means that

Table 1
Membrane specifications

Membrane type	XLE	NF90	NF200	NF270
Manufacturer	DOW FILMTEC	DOW FILMTEC	DOW FILMTEC	DOW FILMTEC
Material of active layer	Polyamide	Polyamide	Polyamide	Polypiperazine amide
MWCO*, Da	100	200	290-360	200-300
Contact angle				
Sessile drop, °	94.5 ± 14.1	68.4 ± 4.4	30.1 ± 4.6	34.7 ± 2.6
Captive bubble, °	45.6 ± 4.1	47.7 ± 4.0	49.3 ± 5.3	43.4 ± 2.7
Permeate flux, L/m^2/h	30–40	50–60	10–20	50–70
Permeability (20 °C)				
(clear water), L/m^2/h/bar	6–7	6–9	6–7	11–13
Operation pressure, bar	8	6–7	7	4–6
Salt retention, %	98–99	88–97	30–70	30–60

*molecular weight cut off.

concentration in the feed tank nearly corresponds to the concentration at the membrane surface.

Membranes were provided by DOW FILMTEC, a company that is one of the major membrane manufacturers. From a variety of available membrane types, four types were chosen that are used in practical applications for the treatment of groundwaters for drinking water supply. The membranes were characterized with regard to material, molecular weight cut off (MWCO), surface properties (contact angle) and permeability. Details are given in Table 1.

The RO membrane tested is not a typical sea water RO membrane but a low pressure RO membrane that can be operated at pressures far below 1 MPa. NF is used to remove multivalent ions and organic compounds. Compared to RO the rejection for monovalent ions is less pronounced. NF membranes are operated with lower pressure than RO membranes. With regard to the removal of organic compounds the rejection of lower molecular weight substances is smaller with NF membranes than with RO membranes. In special applications membrane manufacturers are able to adapt membrane properties to a certain removal task. In the case of a NF-plant at Méry-sur-Oise, e.g. DOW chemical company had developed a NF membrane, NF200B, which had a high rejection for pesticides and a lower rejection for the salts [10].

Test runs were carried out for at least 5 h in order to avoid any influence of compaction or adsorption effects. Before each test run the new membrane was rinsed with demineralized water for at least 2 h in order to remove any conserving chemical from the membrane. Each test run was started with the determination of the clear water permeability. In order to determine the removal of organic micro-pollutants by NF/RO corresponding samples were taken from the feed tank and the permeate. Mixtures of several substances were always taken as feed assuming that there is no interaction between them. Tests have been repeated with the different membrane types. As rejection of organic compounds is influenced by size exclusion, electrostatic repulsion and aromaticity of the compounds and ionic strength of the solution has an influence on rejection as it interacts with the membrane surface, test runs were performed with two defined water compositions.

2.2. Calculation of membrane process parameters

Rejection (R) is calculated according to Eq. (1) where $c_{P(i)}$ is the concentration of a substance (i) on the permeate side and $c_{F(i)}$ its concentration on the feed side of the membrane. In case of high yields the feed side concentration has to be corrected by the concentration in the concentrate. However in the presented cases Eq. (1) is correct.

$$R = 100 \times \left(1 - c_{P(i)}/c_{F(i)}\right) \text{ in } \% \quad (1)$$

Yield (Y) or water conversion factor is defined according to Eq. (2) with Q_P and Q_F standing for the flow rates of Permeate and Feed respectively.

$$Y = Q_P/Q_F \quad (2)$$

The driving force for NF or RO is the pressure difference across the membrane. This transmembrane pressure (TMP) is calculated according to Eq. (3). p_F is the pressure on the feed side, p_C the pressure on the concentrate and p_P on the permeate side.

$$\text{TMP} = (p_F + p_C)/2 - p_P \quad (3)$$

From TMP and Q_P permeability (J_P) may be calculated according to Eq. (4).

$$J_P(20\,^\circ C) = Q_P/\mathrm{TMP} \times f \tag{4}$$

$$f = exp(0.0239 \times (20 - t)) \tag{5}$$

It has to be noted that temperature has a strong influence on the membrane filtration process: TMP increases by 3% per degree C during decreasing temperature according to Arrhenius [11]. Therefore the values for TMP or J_P have to be corrected for a defined temperature in order to be able to compare results from different experiments. In Eq. (5) the temperature correction factor (f) for a temperature of 20 °C has been defined with t being the actual temperature of the experiment.

2.3. Raw waters

The experiments were carried out with two types of waters. In most test runs a 1:1 mixture of tap water (Karlsruhe) with demineralized water was used and the micro-pollutants were added in concentrations as detected in environmental water samples. The mixture had a pH of 7.4 and an electrical conductivity of around 38 mS/m. Some test runs were carried out with natural groundwaters that already contained some of the micro-pollutants in significant concentrations. Corresponding values are given below.

2.4. Chemicals

All reference compounds (Table 2) were of highest purity available. N,N-Dimethylsulfamide (>98%) was purchased from ABCR (Karlsruhe, Germany). Chloridazon-desphenyl (100 ng/µL solution in acetonitrile), bromacil (>99%) and mecoprop (>99%) were from Dr. Ehrenstorfer (Augsburg, Germany). All pharmaceutical compounds under investigation were of analytical grade (>90%) and purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany (amitriptyline, amoxicillin, bezafibrate, caffeine, carbamazepine, clofibric acid, dapson, diazepam, fenofibrate, fenoprofen, gemfibrozil, indometacine, ketoprofen, metformin, naproxen, pentoxifylline, phenacetine, sulfadiazine, triamterene and verapamil), Fluka Chemie AG, Buchs Switzerland (chloroamphenicol) or Promochem GmbH, Wesel, Germany (diclofenac, ibuprofen and piracetam). Fenofibric acid was synthesised by saponification of fenofibrate and subsequent purification by recrystallisation in acetone [5]. The synthesized fenofibric acid was free of fenofibrate impurities as was checked by GC-MS analysis. Most of the X-ray contrast agents (iodipamide, iohexol, iopamidol, iopanoic acid, iotalamic acid, ioxaglic acid and ioxitalamic acid) were purchased from Promochem while amidotrizoic acid (diatrizoic acid) was from Sigma-Aldrich Chemie. An iomeprol standard was provided as a courtesy by Byk Gulden (Konstanz, Germany), and an iopromide standard by Schering (Berlin, Germany). Benzotriazole and 5-methyltriazole as well as diglyme (diethylene glycol dimethyl ether) and triglyme (triethylene glycol dimethyl ether) were of >98% purity and were also purchased from Sigma-Aldrich. The perfluorinated compounds perfluorobutanoic acid (PFBA), perfluorobutane sulfonate (PFBS), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) provided by Wellington Laboratories (Southgate, ON, Canada) as 5 µg/ml solutions in methanol. Ethylenediaminetetraacetic acid (EDTA) and methyl tertiary-butyl ether (MTBE) were purchased as pure standards from Fluka Chemie AG.

The deuterated compounds carbamazepine-d10, diclofenac-d4 and ibuprofen-d3 used as internal standards for the HPLC-MS-MS method were purchased from Dr. Ehrenstorfer GmbH and were of >99% chemical purity.

From all target compounds, 1 g/L stock solutions in methanol (analytical grade, VWR International) were prepared. These stock solutions were stored in a refrigerator at −18 °C and proved to be stable for at least 12 months. From these stock solutions, 1 mg/L solutions were prepared by further diluting the stock solutions with methanol. These diluted solutions were used for a maximum time period of three months. All solvents used for sample preparation and as mobile HPLC phase were of analytical grade and were obtained from VWR International. Ultrapure water was provided by an Arium 611 laboratory water purification system (Sartorius AG, Göttingen, Germany).

2.5. Analytical methods

Contact angle was measured using an optical measuring system (OCA 15 Plus, Dataphysics GmbH, Filderstadt, Germany). A static captive bubble method as well as the sessile drop method was applied [12].

Analysis of DMS as well as analysis of the Perfluorinated compounds was done by high-p erformance liquid chromatography (HPLC) coupled to tandem mass spectrometry (HPLC-MS-MS) after solid-phase extraction. Instrumentation consisted of a high performance liquid chromatograph HPLC 1090, Series II from Agilent Technologies, Waldbronn, Germany coupled via an electrospray interface to an API 2000 tandem mass spectrometer from PE Sciex, Langen, Germany. Detection limit for this compound was

Table 2
List of investigated compounds, CASRN[1], molecular weight (MW) and chemical composition

Category	Compound	CASRN	MW, g/mol	Chemical composition
Pesticides and Metabolites	N,N-Dimethylsulfamide (DMS)	3984-14-3	124	$C_2H_8N_2O_2S$
	Chloridazon-desphenyl	6339-19-1	145	$C_4H_3N_3ClO$
	Bromacil	314-40-9	261	$C_9H_{13}N_2BrO_2$
	Mecoprop	93-65-2	215	$C_{10}H_{11}ClO_3$
X-ray contrast media	Amidotrizoic acid	117-96-4	614	$C_{11}H_9I_3N_2O_4$
	Iodipamide	606-17-7	1140	$C_{20}H_{14}I_6N_2O_6$
	Iohexol	66108-95-0	821	$C_{19}H_{26}I_3N_3O_9$
	Iomeprol	78649-41-9	777	$C_{17}H_{22}I_3N_3O_8$
	Iopamidol	60166-93-0	777	$C_{17}H_{22}I_3N_3O_8$
	Iopanoic acid	96-83-3	571	$C_{11}H_{12}I_3NO_2$
	Iopromide	73334-04-3	791	$C_{18}H_{24}I_3N_3O_8$
	Iotalamic acid	2276-90-6	614	$C_{11}H_9I_3N_2O_4$
	Ioxaglic acid	59017-64-0	1269	$C_{24}H_{21}I_6N_5O_8$
	Ioxitalamic acid	28179-44-4	644	$C_{12}H_{11}I_3N_2O_5$
Pharmaceuticals	Bezafibrate	41859-67-0	362	$C_{19}H_{20}ClNO_4$
	Carbamazepine	298-46-4	236	$C_{15}H_{12}N_2O$
	Clofibric acid	882-09-7	215	$C_{10}H_{11}ClO_3$
	Diazepam	439-14-5	285	$C_{16}H_{13}ClN_2O$
	Diclofenac	15307-86-5	296	$C_{14}H_{11}Cl_2NO_2$
	Fenofibrate	49562-28-9	361	$C_{20}H_{21}ClO_4$
	Fenofibric acid	42017-89-0	319	$C_{17}H_{15}ClO_4$
	Fenoprofen	31879-05-7	242	$C_{15}H_{14}O_3$
	Gemfibrozil	25812-30-0	250	$C_{15}H_{22}O_3$
	Ibuprofen	15687-27-1	208	$C_{13}H_{18}O_2$
	Indometacine	53-86-1	358	$C_{19}H_{16}ClNO_4$
	Ketoprofen	22071-15-4	254	$C_{16}H_{14}O_3$
	Naproxen	22204-53-1	230	$C_{14}H_{14}O_3$
	Pentoxifylline	6493-05-6	278	$C_{13}H_{18}N_4O_3$
	Phenacetin	62-44-2	179	$C_{10}H_{13}NO_2$
	Caffeine	58-08-2	194	$C_8H_{10}N_4O_2$
	Amitriptyline	50-48-6	277	$C_{20}H_{23}N$
	Metformin	657-24-9	129	$C_4H_{11}N_5$
	Piracetam	7491-74-9	142	$C_6H_{10}N_2O_2$
	Triamterene	396-01-0	253	$C_{12}H_{11}N_7$
	Verapamil	52-53-9	454	$C_{27}H_{38}N_2O_4$
Antibiotics	Amoxicillin	26787-78-0	365	$C_{16}H_{19}N_3O_5S$
	Chloroamphenicol	56-75-7	323	$C_{11}H_{12}Cl_2N_2O_5$
	Dapson	80-08-0	248	$C_{12}H_{12}N_2O_2S$
	Sulfadiazine	68-35-9	250	$C_{10}H_{10}N_4O_2S$
Perfluorinated chemicals	Perfluorobutanoic acid PFBA	375-22-4	214	$C_4HF_7O_2$
	Perfluorobutane sulfonate PFBS	375-73-5	300	$C_4HF_9O_3S$
	Perfluorooctanoic acid PFOA	335-67-1	414	$C_8HF_{15}O_2$
	Perfluorooctane sulfonate PFOS	1763-23-1	500	$C_8HF_{17}O_3S$
Others	EDTA	60-00-4	292	$C_{10}H_{16}N_2O_8$
	MTBE	1634-04-4	88	$C_5H_{12}O$
	Benzotriazole	95-14-7	119	$C_6H_5N_3$
	5-Methylbenzotriazole	136-85-6	156	$C_7H_7N_3$
	Triglyme	112-49-2	178	$C_8H_{18}O_4$
	Diglyme	111-96-6	134	$C_6H_{14}O_3$

[1] CASRN: Chemical Abstracts Service Registry Number.

10 ng/L. Details of the analytical method for DMS determination are described in [13]. Analysis of chloridazon-desphenyl was also done by HPLC-MS-MS after solid-phase extraction onto a polymeric material. All measurements were carried out using a 1200 HPLC system from Agilent Technologies coupled to a 4000 Q-Trap Triple-Quadrupole mass spectrometer from Applied Biosystems/MDS Sciex Instruments, Concord, ON, Canada with an electrospray interface operated in positive ionisation mode. Detection limit was 50 ng/L for chloridazon-desphenyl. Determination of bromacil (detection limit 30 ng/L) was performed by liquid chromatography and diode-array detection (Agilent 1110 liquid chromatograph) following solid-phase extraction onto RP-C18 material according to ISO 11369 [14]. Analysis of pharmaceutical residues and X-ray contrast media was also done by HPLC-MS-MS after solid-phase extraction onto various materials. The detection limit of X-ray contrast media was 10 ng/L. Details of the analytical procedures as well as of the instrumentation are described elsewhere [5,6].

EDTA was analysed by gas chromatography after derivatisation of the analyte according to ISO 16588 [15]. Analysis was done on a HP 5890 gas chromatograph from Agilent Technologies equipped with a nitrogen/phosphorous sensitive detector. MTBE analysis was done by a PTA-3000 purge&trap unit from IMT Innovative Messtechnik (Moosbach, Germany) and a TraceGC gaschromatograph coupled to a DSQ mass spectrometer from ThermoFinnigan (Bremen, Germany). Details of the method are described in [16].

3. Results and discussion

3.1. Removal of micro-pollutants by NF/RO

The analytical results from the laboratory-scale experiments for the tested substances are listed in Tables 3–7. The values for rejection are plotted versus molecular weight of the substances in Fig. 2. In general it can be seen that substances with low molecular weight show a lower rejection than substances with larger molecular weight. In Fig. 2 several groups of substances are indicated with corresponding symbols. Perfluorinated compounds and X-ray contrast agents with molecular weights larger than 300 g/mol are rejected to a percentage of more than 90%. Pharmaceuticals and antibiotics show rejection values larger than 60%. For the substances with a molecular weight between 100 and 200 g/mol there is a large range of rejection values. This is because different membranes have been used for the test runs. Fig. 3 shows the same data as Fig. 2 but indicates the membrane types used. It can be seen from this graph that the dense RO type membrane (XLE) shows larger rejection for the same substances than the membrane NF90. As expected the loose NF membranes NF200 and NF270 show even lower rejection values. Thus, it is not only the molecular weight of the substances but also specific interactions between substance and membrane surface that influence the rejection behaviour. This is consistent with findings of others [17–23]. In the case of chloridazon-desphenyl it can be seen from Table 4 that rejection by NF90 is also depending on the concentration of the micro-pollutant. At higher concentrations rejection seems to be lower than at lower concentration.

Each test run was started with the determination of the clear water permeability. Membranes were also characterized by their surface properties (contact angle). As can be seen from results in Table 1 there are differences between the membranes regarding permeability and contact angle. Smaller values of contact angle stand for more hydrophilic surface characteristics. Therefore NF270 is the most hydrophilic membrane which also results in the highest water permeability of the tested membranes (see data in Table 1). A further operative advantage of this membrane is the low operation pressure. However, the rejection of some organic micro-pollutants like DMS is rather low (see Table 3 and Fig. 2). This means that if DMS or other low molecular weight organic micro-pollutants have to be removed from a raw water denser membranes than NF270 have to be chosen in order to guarantee a higher rejection.

A comparison of DMS rejection values for three membranes is given in Fig. 4. XLE/NF90 and NF270 showed rejection values of 90% / 80% and 30%, respectively. Those values were achieved during short term runs of less than 10 h. For two of the membranes (NF90 and NF270) long term runs of 65–75 h were additionally carried out in order to check whether there is a change of rejection during operation time. As can be seen from Fig. 5 rejection slightly increases with time for the NF90 while rejection seems to stay constant or to only slightly decrease with time for the NF270. In both long term runs permeability slightly decreased with operation time showing that there might be some fouling layer build-up, that influences the rejection behaviour of the membrane. The only difference in both runs was the electrical conductivity of the feed water which was almost double in the NF270 run than in the NF90 run.

After the long-term run the membrane has been removed from the test unit and thoroughly rinsed with demineralized water. After 48 h of contact time 100 ng/L DMS has been detected in the rinsing solution. This shows that there is desorption occurring

Table 3
Rejection of organic micro-pollutants by different NF/RO membranes

Compound	Unit	Feed	Permeate	Rejection, %	Membrane	Run time, hours
Pharmaceuticals						
Bezafibrate	ng/L	140	<10	>93	XLE	10
Carbamazepine	ng/L	180	<10	>94	XLE	10
Clofibric acid	ng/L	190	<10	>95	XLE	10
Clofibric acid	ng/L	150	<10	>93	NF90	10
Clofibric acid	ng/L	150	14	91	NF270	10
Diazepam	ng/L	130	<10	>92	XLE	10
Diclofenac	ng/L	160	<10	>94	XLE	10
Fenofibric acid	ng/L	120	<10	>92	XLE	10
Fenoprofen	ng/L	130	<10	>92	XLE	10
Fenoprofen	ng/L	150	<10	>93	NF90	10
Fenoprofen	ng/L	110	15	86	NF270	10
Gemfibrozil	ng/L	170	<10	>94	XLE	10
Ibuprofen	ng/L	160	<10	>94	XLE	10
Ibuprofen	ng/L	150	<10	>93	NF90	10
Ibuprofen	ng/L	160	<10	>94	NF90	10
Indometacine	ng/L	140	<10	>96	XLE	10
Ketoprofen	ng/L	210	<10	>95	XLE	10
Naproxen	ng/L	130	<10	>92	XLE	10
Naproxen	ng/L	130	<10	>92	NF90	10
Naproxen	ng/L	92	<10	>89	NF90	10
Pentoxifylline	ng/L	59	<10	>83	XLE	10
Phenacetin	ng/L	130	24	82	XLE	10
Caffeine	ng/L	125	30	76	NF200B	2
Amitriptyline	ng/L	261	63	76	XLE	8
Amitriptyline	ng/L	402	50	88	NF90	8
Metformin	ng/L	352	61	83	XLE	8
Metformin	ng/L	520	227	56	NF90	8
Pentoxifylline	ng/L	642	<50	>92	XLE	8
Pentoxifylline	ng/L	457	92	80	NF90	8
Piracetam	ng/L	540	<150	>72	XLE	8
Piracetam	ng/L	397	<150	62	NF90	8
Triamterene	ng/L	650	<50	>92	XLE	8
Triamterene	ng/L	603	81	87	NF90	8
Verapamil	ng/L	303	74	76	XLE	8
Verapamil	ng/L	525	<50	>91	NF90	8

after the concentration of DMS in the solution is low. A similar effect has been observed by Zhang et al. for bisphenol A [21]. Further research should help to evaluate this effect.

In cases where the rejection of a single micro-pollutant is high enough for all tested membranes and a low rejection of other water compounds is desired, the NF270 membrane is preferred. Table 8 shows results of the test runs for some of the parameters measured. Mecoprop was added to the model solutions. It was retained by all three membranes beyond detection limit.

In order to check long term behaviour a pilot plant with a NF270-membrane was operated for 12 weeks resulting in a permeability (20 °C) of 5.5 L/m^2/h/bar at an operation pressure of 5 bar and a yield of 80% [23]. At a feed concentration of 2.3 μg/L mecoprop and a concentrate concentration of 15 μg/L mecoprop was rejected to a concentration of 0.1 μg/L in the permeate, corresponding to a rejection value of 95%. There was no deterioration of rejection observed even at higher yield of 85%. For stable conditions a yield of 80% was chosen. Under such conditions rejection values of other parameters were as shown in Table 9.

As can be seen from these results monovalent ions showed low rejection whereas multivalent ions showed higher values. With increasing MWCO of the membranes rejection of ions decreased (NF90 > NF200 > NF270).

Table 4
Rejection of organic micro-pollutants by different NF/RO membranes

Compound	Unit	Feed	Permeate	Rejection, %	Membrane	Run time, hours
Pesticides and Metabolites						
Bromacil	μg/L	2.7	0.008	99.7	XLE	13
Bromacil	μg/L	1.9	0.03	97–98	NF90	6
Bromacil	μg/L	2.1	0.16	92–94	NF200B	6
Bromacil	μg/L	2.8	0.28	87–90	NF270	6
Chloridazon-desphenyl	ng/L	330	<50	>85	XLE	10
Chloridazon-desphenyl	ng/L	450	150	66.7	NF90	8
Chloridazon-desphenyl	ng/L	170–180	23–72	58–87	NF90	10
Chloridazon-desphenyl	ng/L	1500	560	63	NF90	8
DMS	μg/L	15.5	1	94	XLE	6
DMS	μg/L	10–25	2–6	69–83	NF90	60
DMS	μg/L	11–13	8–9	28–34	NF270	65
Mecoprop	μg/L	1.2	<0.05	>95	NF90	8
Mecoprop	μg/L	1.2	<0.05	>95	NF200	8
Mecoprop	μg/L	1.2–2.3	0.06–0.1	95–96	NF270	720
Antibiotics						
Amoxicillin	ng/L	32	1	97	NF200B	7
Chloroamphenicol	ng/L	157	15	90	NF200B	7
Dapson	ng/L	111	38	66	NF200B	7
Sulfadiazine	ng/L	108	0.9	99	NF200B	7
Others						
Benzotriazole	ng/L	290–330	170–260	21–41	NF90	5
5-Methylbenzotriazole	ng/L	240–300	140–200	33–42	NF90	5
Triglyme	ng/L	90	70–80	11–22	NF90	5
Diglyme	ng/L	74–77	25–43	44–66	NF90	5

Over this long-term run no deterioration was observed. As rejection behaviour is influenced by several factors some pollutants show stable rejection while others show a decrease [20]. Klüpfel et al. also showed that especially alkaline chemical cleaning of NF270 membranes reduced the rejection of some organic micro-pollutants significantly depending on the presence of other water compounds [20].

Table 5
Rejection of perfluorinated substances by different NF/RO membranes

Compound	Unit	Feed	Permeate	Rejection, %	Membrane	Run time, hours
PFBA	ng/L	3500	2	99.9	XLE	8
PFBS	ng/L	5100	6–10	99.8	XLE	8
PFOA	ng/L	3500	3–6	99.9	XLE	8
PFOS	ng/L	2100	2–3	99.9	XLE	8
PFBA	ng/L	600	5–16	97–99	NF90	6
PFBS	ng/L	3800	4–6	99.8	NF90	6
PFOA	ng/L	2900	4–6	99.8	NF90	6
PFOS	ng/L	3000	1	100	NF90	6
PFBA	ng/L	700	23–29	96.7	NF200B	6
PFBS	ng/L	4200	150	96.4	NF200B	6
PFOA	ng/L	2900	86–110	97	NF200B	6
PFOS	ng/L	2700	1–4	99.9	NF200B	6
PFBA	ng/L	600	13–23	96–98	NF270	6
PFBS	ng/L	3800	180	95	NF270	6
PFOA	ng/L	3100	150	95.5	NF270	6
PFOS	ng/L	3300	7	99.8	NF270	6

Table 6
Rejection of X-ray contrast agents by different NF/RO membranes

Compound	Unit	Feed	Permeate	Rejection, %	Membrane	Run time, hours
Amidotrizoic acid	ng/L	270	<10	>96	XLE	8
Amidotrizoic acid	ng/L	600	<10	>98	NF90	8
Amidotrizoic acid	ng/L	67–5500	4–290	94–95	NF200B	20
Iodipamide	ng/L	320	<10	>97	XLE	8
Iodipamide	ng/L	770	<10	>99	NF90	8
Iodipamide	ng/L	33–6800	1–110	97–98	NF200B	20
Iohexol	ng/L	280	<10	>96	XLE	8
Iohexol	ng/L	500	<10	>98	NF90	8
Iohexol	ng/L	60–6400	5–420	92–93	NF200B	20
Iomeprol	ng/L	270	<10	>96	XLE	8
Iomeprol	ng/L	570	<10	>98	NF90	8
Iomeprol	ng/L	70–6900	4–450	93–94	NF200B	20
Iopamidol	ng/L	280	<10	>96	XLE	8
Iopamidol	ng/L	510	<10	>98	NF90	8
Iopamidol	ng/L	63–7960	6.3	90–98	NF200B	20
Iopanoic acid	ng/L	63–4300	1–140	97–98	NF200B	20
Iopromide	ng/L	260	<10	>96	XLE	8
Iopromide	ng/L	470	<10	>98	NF90	8
Iopromide	ng/L	47–7200	4–400	91–94	NF200B	20
Iotalamic acid	ng/L	240	<10	>96	XLE	8
Iotalamic acid	ng/L	570	<10	>98	NF90	8
Iotalamic acid	ng/L	71–6400	4–300	95–96	NF200B	20
Ioxaglic acid	ng/L	280	<10	>96	XLE	8
Ioxaglic acid	ng/L	600	<10	>98	NF90	8
Ioxaglic acid	ng/L	56–6370	2–280	95–96	NF200B	20
Ioxitalamic acid	ng/L	260	<10	>96	XLE	8
Ioxitalamic acid	ng/L	530	<10	>98	NF90	8
Ioxitalamic acid	ng/L	56–5800	2–273	95–96	NF200B	20

Chemical impact changes the surface properties and therefore causes a change in rejection behaviour. This effect was also observed by Urase and Sato [24].

The discussion showed that the rejection of micropollutants is influenced by a lot of factors that have to be thoroughly studied before a large scale NF/RO-plant is realized. The following chapter will discuss other important operational aspects that have to be considered before RO/NF is chosen as drinking water treatment process for the removal of organic micropollutants.

3.2. Important considerations for NF/RO operation

3.2.1. Antiscalant

With increasing yield the concentration at the membrane surface increases such that hardly soluble salts like carbonates or sulphates start to precipitate

Table 7
Rejection of EDTA and MTBE by different NF/RO membranes

Compound	Unit	Feed	Permeate	Rejection, %	Membrane	Run time, hours
EDTA	µg/L	54	<0.5	99	XLE	10
EDTA	µg/L	91	<0.5	99.5	NF90	8
EDTA	µg/L	4–29	0.5–1	87–97	NF200B	25
MTBE	µg/L	1.1	1.2	0	XLE	10
MTBE	µg/L	1.5	0.56	63	NF90	8
MTBE	µg/L	0.45	0.15	67	NF90	8
MTBE	µg/L	3–10	0.04–1.0	88–99	NF90	17

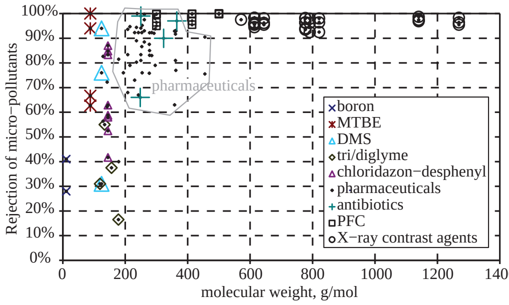

Fig. 2. Rejection of micro-pollutants depending on molecular weight (data given in Tables 3–7).

and form a scaling layer which blocks the transport of water through the membranes. In order to avoid the precipitation of carbonates, acid is added to the feed of the NF/RO-plant. In the case of sulfate scaling, complexing chemicals (antiscalants) like phosphates or phosphonates have to be added to prevent scaling. In the public drinking water supply in Germany only substances are allowed to add which are listed in the standard for drinking water [25]. In Table 10 the listed antiscalants are given. During the NF/RO process these compounds are concentrated by a factor of 4–5. In the case of sodiumtripolyphosphates as antiscalant the increase in phosphor concentration limits the dosage to the feed if the concentrate is discharged to the river. The discharge of concentrate to surface waters is limited to a concentration of 1–2 mg/L P (phosphorus), which means that the dosage to the feed has to be less than 0.2–0.5 ppm P. Depending on the water composition this might not be enough to completely prevent scaling. For example in one case the dosage is adjusted to 4.4 ppm phosphate resulting in 11 mg/L P in the concentrate. However in this special case the concentrate discharge is to the sewer with no cost and the waste water treatment plant operates a P-elimination plant [26].

In order to minimize P-content in the concentrates other products containing phosphonates or polycarboxylates or mixtures were developed and tested with regard to their applicability. With phosphonates lower dosages can be realized. For polycarboxylates this has been tested during a pilot experiment. With a mixture of phosphonate and polycarboxylate stable operation conditions were achieved in a case study. Further research will be carried out to evaluate this finding also for other water qualities.

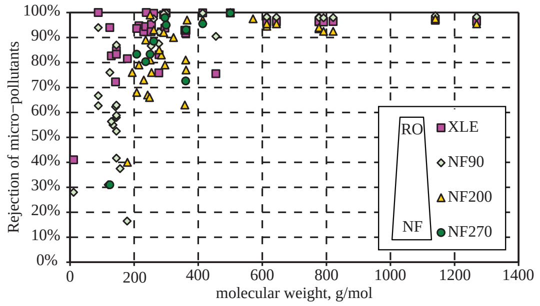

Fig. 3. Rejection of micro-pollutants depending on molecular weight and membrane type (data given in Tables 3–7).

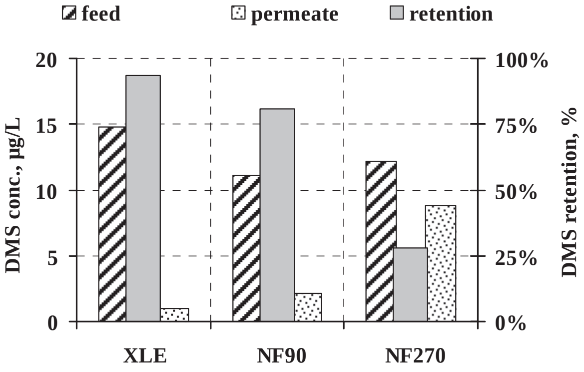

Fig. 4. Elimination of DMS by three different membranes.

3.2.2. Concentrate issue

With increasing applications of NF plants as a suitable process to remove hardness and organic pollutants, the concentrate issue has to be discussed [9,27,28].

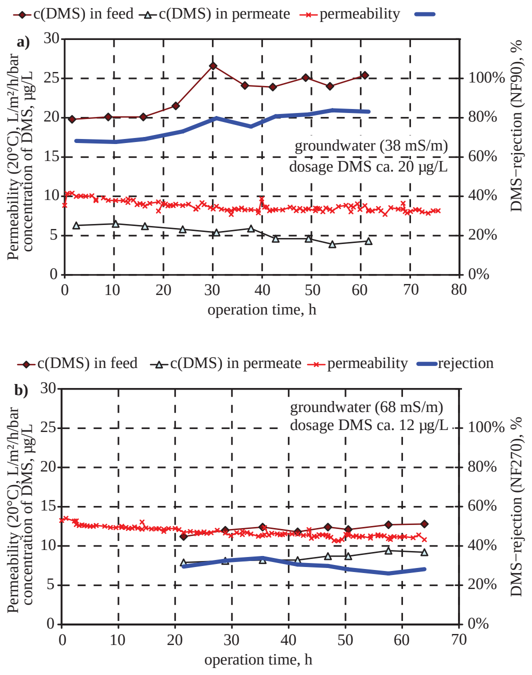

Fig. 5. Elimination of DMS during Nanofiltration for two different membranes a) NF90 and b) NF270.

Table 8
Rejection during short-term operation in the test unit for three membranes

		Feed	Filtrate	Filtrate	Filtrate
			NF90	NF200	NF270
Mecoprop	μg/L	1.2	<0.05	<0.05	<0.05
Calcium	mg/L	63.3	6.6	19.7	24.2
Magnesium	mg/L	7.6	0.8	2.2	2.7
Chloride	mg/L	18.4	5	13.9	15.3
Hydrogencarbonate	mmol/L	3.9	0.22	1.26	1.69

Further research should therefore focus on the biodegradation and adsorption possibilities for further treatment of the concentrates. A research project has just only started which evaluates the possibilities of a sustainable operation of NF/RO processes. In the working packages processes will be tested to further treat the concentrates in order to be able to discharge them into small surface waters of a protected area. It also looks at the technical possibilities to minimize antiscalant dosage.

It has been tested at a pilot plant, that the dosage of antiscalants can be minimized by a factor 4 with still acceptable operation conditions.

3.2.3. Treatment of permeate

When treating drinking water, it has to be taken into account that NF/RO is not a selective process for the removal of certain compounds as membranes usually retain all compounds larger than their cut off. This means that besides organic compounds also ions are removed. The resulting product is therefore more or less demineralised water and additional treatment options have to be applied to the permeate in order to produce a drinking water that complies with regulation. In many large scale NF plants this is done by mixing permeate with untreated raw water until reaching the desired value for hardness for example. In the case of raw waters with a contamination by micropollutants this is not feasible. Therefore another permeate treatment process has to be chosen like for example lime stone filtration. This type of treatment is often applied during sea water desalination. In some cases also a combination of lime stone filtration, CO_2 stripping and mixing with raw water is chosen [26].

Table 9
Rejection during long-term operation of NF270 (yield 80%)

Rejection	%
Mecoprop	95
Electr. conductivity	30
Calcium	35
Magnesium	50
Sodium	14
Potassium	17
Hydrogencarbonate	30
Chloride	4
Nitrate	0
Sulfate	>95
Total organic carbon (TOC)	>90
UV-adsorption at 254 nm	>95

3.2.4. Choice of membrane

For a full-scale application of membrane technologies, it has to be taken into account that the membrane material has an important influence on the removal efficiency and that smaller molecules like DMS and polar compounds are better removed by RO than by NF membranes. Such results have to be considered for the decision about the chosen process.

4. Conclusions

As NF/RO are known to be useful processes to remove organic micro-pollutants test runs with different NF/RO-membranes have been carried out with a membrane test unit in order to be able to further

Table 10
List of antiscalants

Antiscalant	CASRN	Allowed dosage
Sodiumpolyphosphate	68915-31-1	2.2 mg/L P
Sodiumtripolyphosphate	7758-29-4	2.2 mg/L P
Phosphonic acid[1]	6419-19-8	–
Polycarbonic acid[2]	9003-01-4 9003-06-9 29132-58-9	–

[1] Time limit for general application: 30.06.09.

[2] Time limit for individual application: 30.06.09.

elucidate the rejection behaviour for different organic micro-pollutants. It has been shown that rejection of micro-pollutants is dependent on membrane type with RO membranes having a higher rejection than NF membranes (XLE > NF90 > NF200 > NF270). Molecular weight (MW) of organic micro-pollutants plays an important role. Substances with MW larger than 200 g/mol show a good rejection. However, substances with MW in the range of 150–200 g/mol may show low rejection. Some substances exhibit only insufficient rejection.

However, when MW is close to the membranes cut-off also other factors like surface charge have an impact on rejection behaviour. Some substances absorb to the membrane and therefore the potential for desorption is increased when concentrations fluctuate. For large scale applications it has to be considered that NF/RO membranes do not reject organic micro-pollutants specifically. Other larger molecules and multivalent ions are removed to a large percentage too. The resulting permeate is depleted of minerals and does not comply with the standard for drinking water. Therefore, processes to stabilize the water for drinking water supply purposes have to be implemented after NF/RO. Moreover the concentrate issue has to be considered carefully. Further research is necessary on these issues [29].

References

[1] B. Van der Bruggen and C. Vandecasteele, Removal of pollutants from surface water and ground water by nanofiltration: overview of possible applications in the drinking water industry, Environ. Pollut., 122 (2003) 435-445.

[2] C. Baus, H. Hung, F. Sacher, M. Fleig and H.-J. Brauch, MTBE in drinking water production – Occurrence and efficiency of treatment technologies, Acta Hydrochim. Hydrobiol., 33 (2005) 118-132.

[3] Th. A. Ternes, M. Meisenheimer, D. McDowell, F. Sacher, H.-J. Brauch, B. Haist-Gulde, G. Preuss, U. Willme and N. Zullei-Seibert, Removal of pharmaceuticals during drinking water treatment, Environ. Sci. Technol., 36 (2002) 3855-3863.

[4] F. Sacher and H.-J. Brauch, Experiences on the fate of organic micro-pollutants during riverbank filtration, in: C. Ray (Ed.), Understanding Contaminant Biogeochemistry and Pathogen Removal, Kluwer Academic Publishers, The Netherlands, 2002, pp. 135-151.

[5] F. Sacher, F. Th. Lange, H.-J. Brauch and I. Blankenhorn, Pharmaceuticals in groundwaters – Analytical methods and results of a monitoring program in Baden-Württemberg, Germany, J. Chrom. A, 938(1–2) (2001) 199-210.

[6] F. Sacher, M. Ehmann, S. Gabriel, C. Graf and H.-J. Brauch, Pharmaceutical residues in the river Rhine – results of a one-decade monitoring programme, J. Environ. Monit., 10 (2008) 664-670.

[7] B. Haist-Gulde, Entfernung von Arzneimittelstoffen und iodierten Röntgenkontrastmitteln in Aktivkohlefiltern, TZW Schriftenreihe ISSN 1434-5765, 30 (2006) 105-122.

[8] H.-W. Hung, T.-F. Lin, C. Baus, F. Sacher and H.-J. Brauch, Competitive and hindering effects of natural organic matter on the adsorption of MTBE onto activated carbons and zeolites, Environ. Tech., 26 (2005) 1371-1382.

[9] U. Müller, B. Baldauf, S. Osmera and R. Göttsche, Erfassung und Bewertung von Nanofiltrations- und Niederdruckumkehrosmoseanlagen in der öffentlichen Wasserversorgung in Deutschland, TZW Schriftenreihe 39 (2009) ISSN 1434-5765.

[10] C. Ventresque and G. Bablon The integrated nanofiltration system of the Méry-sur-Oise surface treatment plant (37 mgd), Desalination, 113(2–3) (1997) 263-266.

[11] http://en.wikipedia.org/wiki/Arrhenius_equation.

[12] W. Zhang, M. Wahlgren and B. Sivik, Membrane characterization by the contact angle technique II. Characterization of UF-membranes and comparison between the captive bubble and sessile drop as methods to obtain water contact angles, Desalination 72 (1989) 263.

[13] C. Schmidt, Transformationsprodukte von Pflanzenschutzmittel-Metaboliten, GIT Labor-Fachzeitschrift, 10 (2007) 817-819.

[14] International Organisation for Standardization, Water quality – Determination of selected plant treatment agents – Method using high performance liquid chromatography with UV detection after solid-liquid extraction, International Standard ISO 11369, Geneva, Switzerland, 1997.

[15] International Organisation for Standardization, Water quality – Determination of six complexing agents – Gas-chromatographic method, International Standard ISO 16588, Geneva, Switzerland, 2002.

[16] J. Klinger, C. Stieler, F. Sacher and H.-J. Brauch, MTBE (methyl tertiary-butyl ether) in groundwaters: monitoring results from Germany, J. Environ. Monit., 4 (2002) 276-279.

[17] A.R.D. Verliefde, S.G.J. Heijman, E.R. Cornelissen, G.Amy, B. van der Bruggen and J.C. van Dijk, Influence of electrostatic interactions on the rejection with NF and assessment of the removal efficiency during NF/GAC treatment of pharmaceutical active compounds in surface water, Water Res. 41 (2007) 3227-3240.

[18] A. Verliefde, H. van Dijk, E. Cornelissen, B. Heijman and B. van der Bruggen, Rejection of pharmaceutically active compounds with NF: influence of hydrophobicity, charge and fouling. 7. Aachener Tagung ''Wasser und Membranen'', W9 (2007) 1-12.

[19] Y. Miyashita, Removal of N-Nitrosamines by NF and RO membranes, PhD thesis, Georgia Institute of Technology, USA, 2007.

[20] A. Klüpfel, F.H. Frimmel, Einflussfaktoren auf den Rückhalt polarer organischer Mikroverunreinigungen bei der Nanofiltration, Vom Wasser, 107 (2009) 19-24.

[21] Y. Zhang, C. Causserand, P. Aimar and J.P. Cravedi, Removal of bisphenol A by nanofiltration membrane in view of drinking water production, Water Res. 40 (2006) 3793-3799.

[22] D. Skutlarek, M. Exner and H. Färber, Perfluorinated surfactants in surface and drinking waters, Environ. Sci. Pollut. Res., 13(5) (2006) 299-307.

[23] S. Stauder, Removal of mecoprop by nanofiltration – case study, Unpublished, 2008.

[24] T. Urase and K. Sato, The effect of deterioration of nanofiltration membrane on retention of pharmaceuticals, Desalination, 202 (2007) 385-391.

[25] The Drinking Water Ordinance (TrinkwV 2001).

[26] S. Stauder, J. Klinger, G. Baldauf and H. Mück, Einsatz der Membrantechnik zur Entsalzung eines harten, chlorid- und selenhaltigen Grundwassers, Energie | Wasser-Praxis, 6 (2007) 10-15.

[27] M.M. Nederlof, J.A.M. van Paassen and R. Jong, Nanofiltration concentrate disposal. Experiences in the Netherlands, Desalination, 178 (2005) 303-312.

[28] M.M. Nederlof and J.H. Hoogendoorn, Desalination of brackish groundwater: the concentrate dilemma, Desalination, 182 (2005) 441-447.

[29] A. Verliefde, Rejection of organic micro-pollutants by high pressure membranes (NF/RO), PhD thesis, Technical University Delft, Water Management Academic Press, 2008, ISBN 978-90-8957-005-5.