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The rejection of trihalomethanes by nanofiltration membranes: influences of adsorption and NOM fouling

Di Peng[a], Florencia Saravia[b], Kristina Bock[b], Marcel Pelikan[b], Gudrun Abbt-Braun[b], Harald Horn[a,b,]*

[a]DVGW Research Laboratories at the Engler-Bunte-Institut, Water Chemistry and Water Technology, Engler-Bunte-Ring 9, Karlsruhe 76131, Germany, Tel. +49 721 608 42580; emails: harald.horn@kit.edu (H. Horn), di.peng@kit.edu (D. Peng)
[b]Karlsruhe Institute of Technology, Engler-Bunte-Institut, Water Chemistry and Water Technology, Engler-Bunte-Ring 9, Karlsruhe 76131, Germany, emails: florencia.saravia@kit.edu (F. Saravia), Kristinabock@gmx.de (K. Bock), marcel.peliokan@gmx.de (M. Pelikan), gudrun.abbt-braun@kit.edu (G. Abbt-Braun)

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ABSTRACT

Nanofiltration (NF) can be considered as an interesting alternative to remove disinfection by-products especially trihalomethanes (THM). However, the results have been contradictory in the literature regarding THM rejection. In this work, the rejection of four THM by three commercial NF membranes of different materials was investigated, including the effect of adsorption and organic fouling on rejection performance. Results indicated that in general NF membranes have actually limited rejection of THM, even when the molecular weight was larger than the molecular weight cut-off of the membrane. Adsorption has significant influence on rejection, facilitating the mass transport of THM through NF membrane. NF90, the tightest investigated membrane showed a steady-state rejection of 33%, 36%, 42% and 49% for chloroform, bromodichloromethane, dibromochloromethane and bromoform, respectively. Membrane material plays a substantial role in adsorption and, consequently, influences rejection. The cellulose acetate membrane (SB90) showed little adsorption capacity of THM but at the same time THM could pass cellulose acetate very quickly. Availability of the adsorption sites in the membrane plays a significant role in how the adsorption facilitates the transport of molecules through the membrane, decreasing membrane rejection. Natural organic matter in feed solution and organic fouling layer had little effects on THM rejection.

Keywords: Trihalomethanes; Nanofiltration; Adsorption; Organic fouling; Membrane material

1. Introduction

Chlorination is the most common disinfection process and one of the most important processes for water treatment. But free chlorine reacts with organic matter or bromide in water and produces disinfection by-products (DBP), which could induce health consequences. Chlorinated DBP have been intensively studied in recent decades. Trihalomethanes (THM) are the most typical DBP in chlorinated waters such as drinking water or swimming pool water and are regulated in many countries. The four mostly studied THM are chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and bromoform ($CHBr_3$). The European Communities (Drinking Water) (No. 2) Regulations implemented the limit for total THM at 100 μg/L from December 2008 [1]. In Germany, the limit of THM in drinking water regulation is 50 μg/L [2]. The U.S. Environmental Protection Agency (EPA) issued the "Stage 1 Disinfectants/Disinfection By-Products Rule (D/DBP)" in 1998 giving the maximum allowable annual average level for total THM at 80 μg/L [3]. According to the German Pool Water Standard [4], the recommended concentration for THM in swimming pool water is 20 μg/L.

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* Corresponding author.

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Activated carbon adsorption is one of the common treatments for controlling THM. But the capacity is limited and new activated carbon has to be replaced regularly. Nanofiltration (NF) has become an interesting alternative for DBP elimination in water. Most commercial NF membranes have a molecular weight cut-off (MWCO) of about 200–2,000 Da. Therefore, NF has a high rejection rate of dissolved organic matter [5]. The removal of precursors before the disinfection procedure could reduce the DBP formation potential in drinking water [6–8]. For systems with previously chlorinated water which already contains DBP, NF is an attractive option to directly reject THM. However, literature concerning the rejection behavior of THM by NF has been a matter of contradictions, ranging from little to 95% in rejection [5,9–12]. Most of the studies were short-term experiments. The variety of experimental conditions is also limited, mostly in deionized water prepared in the laboratory which does not consider the other natural occurring organic and inorganic water constituents. Some studies often had unrealistic high concentration of THM in the model solution, which would have huge impact on the diffusion process through membrane. Moreover, the volatility of THM makes the actual aqueous concentration during experiments difficult to control. However, only one work [10] mentioned special experimental set-up to avoid the volatilization.

THM belong to micropollutants and are relatively small organic molecules with the molecular weight of 119–253 g/mol. Some work has been done to study the rejection of micropollutants such as pharmaceuticals, pesticides, personal care products or DBP by NF [13–15]. Previous studies showed that most organic micropollutants could be effectively rejected by NF [16]. In general, neutral and small molecules are often associated with low rejection. To date no accepted method is known to predict the rejection of organic solute by polymeric membranes [17].

Rejection of organic pollutants by NF membranes includes different mechanisms. The well accepted major rejection mechanism in NF is steric exclusion of solutes which are larger than the membrane MWCO [18]. It is also recognized as the primary mechanism in the rejection of organic micropollutants by NF [16]. NF membranes are intermediate between ultrafiltration membranes and reverse osmosis (RO) membranes. So both convection through pores (defects) and solution-diffusion are involved for mass transport of solutes. Nghiem et al. [19] found out that the application of pore transport model lead to an overestimation of the rejection of natural hormones, probably because the hormones could pass the membrane both through convection and adsorption-dissolving-partitioning. Another study illustrated that the assumption of steric exclusion as the exclusive rejection mechanism led to an overestimation of rejection for solutes which have strong affinity to membrane material [17].

Solute–membrane interactions such as electrostatic effects and "solute–membrane affinity" play also a significant role in NF rejection. NF membranes are able to effectively remove natural organic matter (NOM) through a combination of size exclusion and physical–chemical interactions such as charge repulsion [20]. For negatively charged membranes, electrostatic repulsion can increase the rejection of negatively charged solutes and electrostatic attraction can decrease the rejection of positively charged solutes [21]. It was even discovered that negatively charged solutes do not engage in hydrophobic interactions since they cannot approach the membrane surface. THM present in water are neutral so the electrostatic effects should not play a role in rejection. Solute–membrane affinity has been a term which includes many different factors other than the widely studied electrostatic effects, such as the size, charge, hydrophobicity, hydrogen bonding and dipole moment, which may affect the solute–membrane interactions. This has been broadly investigated but was not well understood. The influences of these factors become especially more important for low molecular weight organic compounds [16,22].

Adsorption of solutes to the membrane is an important solute–membrane interaction. Neutral micropollutants which have high *n*-octanol/water partition coefficient (log K_{ow}) or hydrogen bonding capacity usually can adsorb to the membrane [23]. Adsorption can affect the mass transport of the solutes so as to the rejection. First, high initial rejection due to adsorption followed by decrease of rejection over time has been already observed for different organic micropollutants [23–25]. An accurate evaluation of the rejection of hydrophobic compound should be done only after the adsorption reaches the steady state or the "saturation." Once the sorption capacity of the membrane is exhausted, rejection is supposed to be dominated by the mechanisms regarding diffusion through the membrane. Adsorption might also have indirect effects on the steady-state rejection, because adsorption of solutes in the membrane separating layer may significantly affect the properties of the membrane with respect to its rejection performance. Adsorption of organic molecules to the membrane seemed to facilitate the diffusion transport of solutes through membrane and hence decreases the rejection [25,26].

Rejection mechanisms of micropollutants by NF membranes in real water matrices (i.e., in the presence of organic macromolecules) are very complex. The reported overall rejection value and effects of different feed water matrices vary significantly. Moreover, the presence of high content of organics in water often leads to organic fouling, which is a common problem in aquatic membrane filtration. Fouling could change the membrane surface properties and alter the interactions between solutes and membrane. The influence of water matrices and fouling on NF membrane performance is not completely understood. Different effects of fouling on the rejection were reported. One study showed that fouling by filtrated secondary effluent increased rejection of hydrophobic non-ionic organic solutes but facilitated organic transport through cellulose triacetate membranes [24]. Agenson and Urase [27] determined the change in membrane performance after organic fouling by sludge and landfill leachate using 36 neutral trace organic matters filtrated with aromatic polyamide NF and RO membranes. A lowered rejection of higher molecular weight solutes was observed. The given explanation was that the attachment of foulants on membrane polymer and subsequent diffusion of the large solute molecules through the membrane facilitated the transport [27], whilst fouling could also decrease the solute rejection by the phenomenon cake-enhanced concentration polarization, in which solutes with small diffusion coefficients are affected [28].

The aim of this study is to investigate the THM rejection by NF and the effect of adsorption and organic fouling on the rejection performance. According to the volatility of

THM, filtration experiments were carried out in a closed set-up using pressure vessels and stirred cells. Three relatively tight NF membranes were applied. The membranes have similar or smaller MWCO than the molecular weight of THM. Additionally, fouling experiments were performed to study the effects of NOM in feed and the fouling layer on rejection performance. The THM adsorption on membranes was calculated by mass balance. Membrane material functional groups, surface morphology and hydrophobicity were characterized.

2. Materials and methods

2.1. Materials

Laboratory-scale filtration experiments were carried out by dead-end filtration (Fig. 1) using two stirred cells Amicon M2000 (Millipore), which allows an effective membrane area of 0.017 m^2 and a volume of approx. 2.5 L. Nitrogen gas and stainless steel pressure vessels (Amicon) were used to provide the feed pressure. Permeate flow was measured by a balance (Sartorius).

Three commercial NF membranes made of different materials were used. NF90 is a high-flux thin-film composite membrane with an aromatic polyamide separating layer and a supporting layer made of polysulfone on polyester. NTR-7470pHT and SB90 are made of sulfonated polyethersulfone (PES) and cellulose acetate blend, respectively. Table 1 summarizes the most relevant characteristics provided by the manufacturers or measured in the laboratory. The average pore radius of membrane was only found for NF90 [29]. MWCO of the membranes was determined using nine neutral organic compounds (ethanol, ethylene glycol, glycerin, glucose, maltose, raffinose and polyethylene glycols in different molecular weight) with a molecular weight range between 46 and 1,550 g/mol.

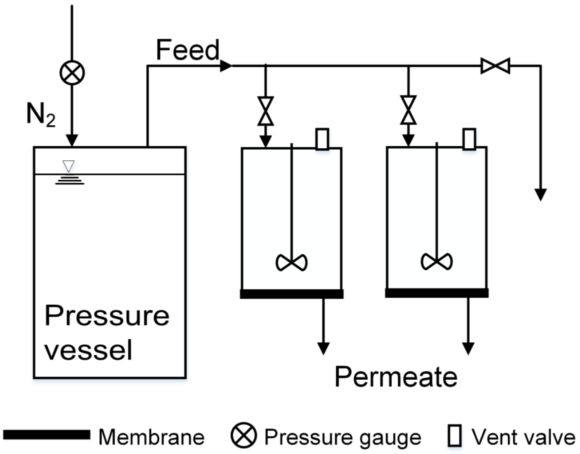

Fig. 1. Schematic diagram of the experimental set-up for dead-end filtration: pressure vessel and two stirred cells.

Feed solutions were made with demineralized water (electrical conductivity = 8.9 µS/cm). For fouling experiments, the NOM-rich water (brown water lake Hohloh, Germany, 0.45 µm filtrated using PES membrane, β(DOC) = 22 mg/L) which has low ion content (electrical conductivity = 33 µS/cm) was used instead of demineralized water as solvent. Chloroform and bromoform (Merck, Ph. Eur., Germany), bromodichloromethane (≥97%) and dibromochloromethane (≥98%) (Sigma-Aldrich, USA), were used as target compounds. The relevant properties of the four used THM for filtration experiments are summarized in Table 2 [5,30,31]. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) from company VWR (Germany), both of p.a. quality, were used to adjust the pH value. Sodium chloride (NaCl) was used as background electrolyte (section 2.2).

2.2. Experiments

To investigate the THM rejection and the potential effect of adsorption on rejection, separate filtration experiments either with 100 µg/L chloroform or with four THM mix ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$, each 100 µg/L) in the feed solution were carried out for each membrane. Feed solution was prepared with THM dissolved in demineralized water. 3 mM NaCl was dosed for an electrical conductivity of around 360–400 µS/cm. HCl and NaOH were added to keep the pH value at 7. Filtration experiments were carried out at approx. 6 bar and over 6 d. Samples of feed and permeate were taken intermittently. Feed samples were taken directly out of stirred cells through the valve to measure the actual feed THM concentration. To reduce volatilization of THM a closed set-up was essential in these experiments: (1) closed pressure vessels for feed solution were filled full to the brim; (2) by means of the air valve the stirred cells were always filled to the top without air bubbles and (3) feed solution in the pressure vessel was replaced every day.

Additionally, NOM fouling experiments were performed to study the fouling effect on THM rejection and adsorption. The feed solution was prepared using Hohloh lake water (section 2.1 Materials) instead of demineralized water. All the other parameters remained the same (see paragraph above). The effect of NOM fouling on THM

Table 1
Properties of used nanofiltration membranes

	Manufacturer	Membrane type	NaCl rejection[a]	MWCO[b] (Da)	Average pore radius (nm)
NF90	DOW/Filmtec	Polyamide thin film composite	90%	100	0.34 ± 0.04
NTR-7470pHT	Hydranautics/Nitto-Denko	Sulfonated polyethersulfone	50%	500	No data
SB90	TriSep	Cellulose acetate blend	80%	200	No data

Test conditions: [a]2,000 mg/L NaCl in demineralized water, ambient temperature, dead-end filtration at 6 bar. [b]25°C, cross-flow filtration at 8 bar, $V_{crossflow}$ = 0.22 m/s, neutral organic compounds such as sugars and polyethylene glycols in demineralized water.

rejection was investigated during the fouling layer formation and compared with the results in demineralized water tests.

Rejection of solutes was determined as:

$$\text{Rejection} = 1 - \frac{C_p}{C_f} \tag{1}$$

where c_f and c_p are the solute concentration in the feed and the permeate samples. THM samples were taken in duplicates in 40-mL glass vials which were capped with polytetrafluoroethylene-faced silica septum. Besides THM rejection, permeability decline, salt and organic matter rejection and membrane hydrophobicity (contact angle measurement) were used to analyze the membrane performance.

The amount of adsorbed THM to membranes was determined by mass balance:

$$m_{\text{adsorbed}} = m_{\text{feed}} - m_{\text{rejected}} - m_{\text{permeate}} \tag{2}$$

The mass of feed and permeate was calculated through integration from the filtrated volume and concentration measured intermittently. The rejected mass was calculated from the volume and concentration measured in the remaining retentate in the stirred cells when the experiments finished.

Furthermore, static adsorption experiments were carried out parallel to the filtration experiments to confirm the adsorption of THM to the membrane. A membrane with the same active area as in the filtration experiments was submerged in the same feed solution with four THM mix in demineralized water as in the filtration experiments in 1-L brown glass bottles. The adsorbed amount was determined by the difference between the concentration of THM in the solution before and after 6 d contact time.

Table 3 shows an overview of the experiments for each membrane. Each test was carried out with new membrane samples in duplicates in parallel. Prior to the tests all membranes were cleaned with demineralized water for 24 h, under operating conditions at 6 bar. All the experiments were performed at $T = 22°C \pm 1°C$.

2.3. Analytical methods

Electrical conductivity and pH were measured using a multiparameter instrument MultiLab P4 (WTW) with the electrodes TetraCon® 325 and SenTix 41. Dissolved organic carbon (DOC) was measured by a Total Carbon Analyzer TOC-V CSN (Shimadzu, Japan) using combustion catalytic oxidation method with the limit of detection 0.2 mg/L. THM in feed and permeate samples was determined using a headspace sampling capillary gas chromatograph (Agilent HP 6890, column DB-5MS) with electron capture detection with purge- and trap-process. The limit of detection was 0.4 μg/L for chloroform, 0.2 μg/L for bromodichloromethane, 0.5 μg/L for dibromochloromethane and 0.7 μg/L for bromoform. Each THM sample was measured at least twice.

Contact angle of air dried membranes was measured using the sessile drop method. An optical contact angle measurement system (OCA 20, Dataphysics, Germany) with integrated video and analysis function was used. At least 15 spots of each membrane sample were measured and averaged. Surface morphology was analyzed by a scanning electron microscope (SEM) (Leo 1530, Zeiss, Germany) with the software SmartSEM V05.03.01. Functional group characteristics of air dried membrane were measured using a Vertex 70 Fourier transform infrared (FTIR) spectrometer (Bruker, Germany) with an attenuated total reflection (ATR) element of diamond crystal and a deuterated-triglycine sulfate detector. The spectra were recorded by a single reflection method with 128 scans collected from 600 to 4,000 cm^{-1} at a wave number resolution of 4 cm^{-1}. A blank measurement was taken to justify the differences in instrument response and the atmospheric environment and subtracted from the measurement.

Table 2
Properties of used trihalomethanes

	M (g/mol)	Molecular width [5] (nm)	Molecular length [5] (nm)	Dipole moment [29] (D)	log K_{ow} [30]
$CHCl_3$	119.38	0.176	0.450	1.16	1.97
$CHCl_2Br$	163.83	0.180	0.473	1.07	2.10
$CHClBr_2$	208.28	0.185	0.495	0.99	2.24
$CHBr_3$	252.73	0.191	0.495	0.91	2.38

Table 3
Overview of experiments for each membrane

Number	THM in feed	THM concentration (μg/L)	Solvent	Experiment
1	$CHCl_3$	100	Demineralized water	Filtration
2	4 THM mix	100 each	Demineralized water	Filtration
3	$CHCl_3$	100	Hohloh lake water	Filtration
4	4 THM mix	100 each	Hohloh lake water	Filtration
5	$CHCl_3$	100	Demineralized water	Static adsorption
6	4 THM mix	100 each	Demineralized water	Static adsorption

3. Results

3.1. Rejection of THM

Fig. 2 shows the results of the THM rejection over permeate volume from the filtration experiments with THM in demineralized water for the three membranes. (a) to (c) are the experiments with $CHCl_3$ alone (experiment number 1). Membranes NF90 and NTR-7470pHT showed a high initial $CHCl_3$ rejection (>90%), whereas SB90 presented an initial rejection of about 30%. Rejection value by all membranes decreased quickly during filtration and reached steady state after different filtrated volume. The rejection decline was significantly more quick for SB90 (10 h) and most slow for NTR-7470pHT (50 h). The rapid decline of initial rejection indicates adsorption of $CHCl_3$ to membranes. At steady state, NF90 rejected 30% of $CHCl_3$ and the other two membranes had no $CHCl_3$ rejection.

Figs. 2(d) and (e) are the experiments with the four THM mix in the feed (experiment number 2). Similar to the results of $CHCl_3$, the rejection of all four THM appeared to decrease from the beginning of filtration for all membranes. The rejection decline profiles of four THM were well separated from each other for NF90 and NTR-7470pHT. The more brominated the THM were, the later the rejection reached the steady state and the higher adsorption capacity the membrane has. The rejection of $CHBr_3$ reached the steady state even after 5 d for NF90 and NTR-7470pHT. Comparing the results of $CHCl_3$ alone and of $CHCl_3$ in the THM mix, the $CHCl_3$ rejection reached the steady state sooner when it was in the THM mix than when it was alone. This "acceleration" due to presence of other THM was most apparent for NTR-7470pHT. NF90 had the steady-state rejection of 33%, 36%, 42% and 49% for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ respectively. NTR-7470pHT and SB90 showed no rejection of THM at steady state.

During fouling experiments (experiment numbers 3 and 4) DOC from NOM-rich lake water was well rejected (>90%) and at the end of each fouling experiment the organic fouling layer on the membrane was obvious (Fig. S1). But the profile of rejection over permeate volume was very close to those in the experiments 1 and 2 with demineralized water (Fig. S2). THM were little influenced by the presence of NOM or fouling.

3.2. Adsorption of THM

The absorbed amount of THM during filtration experiments is shown in Table 4. Adsorption to the filtration device (stirred cells) can be neglected considering the quick saturation of SB90. The more brominated the THM, the higher the

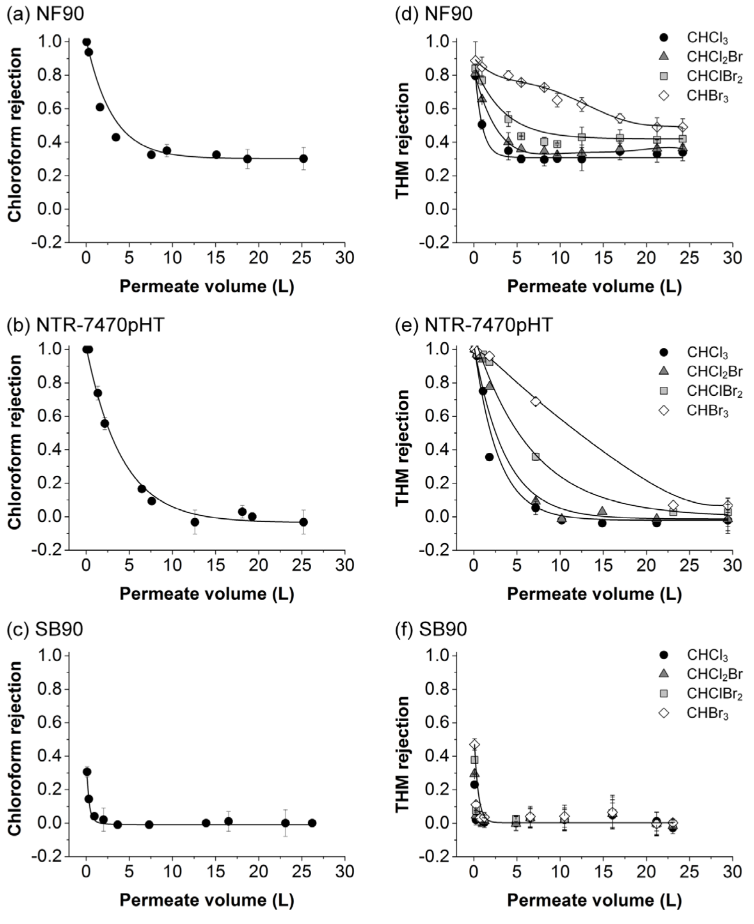

Fig. 2. Rejection of chloroform by (a) NF90, (b) NTR-7470pHT and (c) SB90 and rejection of four THM by (d) NF90, (e) NTR-7470pHT and (f) SB90 (experiment numbers 1 and 2).

adsorption, which confirmed the results of rejection decline profiles in which $CHBr_3$ reached the steady state at the latest. According to the molecular properties of THM (Table 2), molecular weight, length and width as well as log K_{ow} all exhibited a positive correlation with the adsorption. NF90 presented the highest THM adsorption capacity followed by NTR-7470pHT. The amount of THM adsorbed to SB90 was less than 10% of the amount adsorbed to NF90 and thus corresponded to the much quicker rejection decline of SB90.

Comparing the results of $CHCl_3$ alone and THM mix during filtration experiments with demineralized water, the adsorbed mass of $CHCl_3$ was nearly the same for the membrane NF90. Interestingly, for the membrane NTR-7470pHT, when the feed contains $CHCl_3$ alone, $CHCl_3$ adsorbed 60% more than when it was present in the THM mix. Similar phenomenon was also observed for the membrane SB90 but only to a lesser extent. A possible explanation can be that competitive adsorption between four THM molecules led to less adsorption of $CHCl_3$.

The influence of fouling on adsorption was also studied and compared with the experiments with demineralized water. When there was $CHCl_3$ alone, organic fouling did not change the adsorbed amount obviously. In the case of THM mix, the three membranes showed different behaviors. For NF90, $CHCl_3$ and $CHCl_2Br$ adsorbed less when there was organic fouling. NTR-7470pHT did not present a difference in adsorption with or without fouling. For SB90, the adsorption seemed to increase when there was fouling except for $CHBr_3$.

Static adsorption test was performed to quantify the adsorption of THM to the membranes only from the surface contact with membrane. The same feed solution with four THM mix in demineralized water was used. Table 5 presents the adsorbed amounts of $CHCl_3$ and the THM mix. Similar to the results of filtration experiments for NTR-7470pHT (Table 4), the adsorbed $CHCl_3$ was higher when it was alone than when it was in the THM mix. For the other two membranes this trend was minimal. Generally the adsorbed THM mass in the membrane during the static adsorption test was much lower than those in the filtration experiments, thus the competitive adsorption between the different THM and the trend with increasing bromide content were less obvious. In static adsorption experiments, the molecular diffusion was the only driving force and the concentration of THM in the solution decreases with time. Therefore, the driving force was lower than in the filtration experiments, in which fresh feed solution was always added to the system and the THM concentration was constant with time.

3.3. Characterization of membranes

SEM images (Fig. 3) showed the significant rougher surface of NF90 and the smooth surface of NTR-7470pHT and SB90. Roughness data of the membrane surface were found in literature [32–35] and the hydrophobicity of the surface of membranes, by measuring the contact angle, was analyzed (Table 6). As expected from the SEM images, NF90 presented higher roughness values than SB90. Although no information for NTR-7470 was found, according to SEM pictures we can expect that the roughness should be similar as SB90. Hydrophobicity of virgin membranes was similar for all investigated membranes. After fouling, all membranes became more hydrophobic and the contact angles were still close to each other. The high deviation of contact angles for NF90 after fouling was probably due to the uneven distribution of the fouling layer. Unfortunately, these surface properties could not be correlated to the adsorption capacity of the membranes.

Infrared spectroscopy was measured for virgin membranes and presented in Fig. 4. The functional groups of membrane polymer were interpreted based on wave number. For NF90 amide I (C=O stretching, 1,663 cm^{-1}), aromatic amide (1,609 cm^{-1}) and amide II (N–H bending, 1,543 cm^{-1}) peaks belong to the main features of polyamide [36,37]. Since the ATR-FTIR measurement penetrates the membrane to 6–10 μm and goes through the thin polyamide layer of NF90 to the polysulfone layer underneath, NF90 and NTR-7470pHT presented, except for the amide groups, very

Table 4
Results of adsorbed THM during filtration experiments

Membrane	Exp. number	THM in feed	Adsorbed mass (mg/m^2)			
			$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
NF90	1	$CHCl_3$	27 ± 3			
	2	THM mix	29 ± 2	37 ± 2	49 ± 2	83 ± 4
	3	$CHCl_3$, fouling	25 ± 3			
	4	THM mix, fouling	18 ± 2	32 ± 2	47 ± 2	86 ± 4
NTR-7470pHT	1	$CHCl_3$	24 ± 1			
	2	THM mix	15 ± 1	18 ± 1	42 ± 2	74 ± 4
	3	$CHCl_3$, fouling	25 ± 2			
	4	THM mix, fouling	13 ± 1	18 ± 1	38 ± 2	73 ± 4
SB90	1	$CHCl_3$	1.6 ± 0.1			
	2	THM mix	1.2 ± 0.1	2.5 ± 0.1	3.8 ± 0.2	5.4 ± 0.3
	3	$CHCl_3$, fouling	1.8 ± 0.2			
	4	THM mix, fouling	1.3 ± 0.1	3.1 ± 0.1	5.0 ± 0.2	4.4 ± 0.2

Table 5
Results of static adsorption experiments

Membrane	Exp. number	THM in feed	Adsorbed mass (mg/m^2)			
			$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
NF90	5	$CHCl_3$	3.9 ± 0.1			
	6	THM mix	3.7 ± 0.1	4.6 ± 0.1	5.0 ± 0.1	5.6 ± 0.1
NTR-7470pHT	5	$CHCl_3$	4.8 ± 0.6			
	6	THM mix	3.5 ± 0.1	4.0 ± 0.1	4.1 ± 0.1	4.6 ± 0.1
SB90	5	$CHCl_3$	0.7 ± 0.1			
	6	THM mix	0.6 ± 0.1	0.4 ± 0.1	0.5 ± 0.2	0.8 ± 0.2

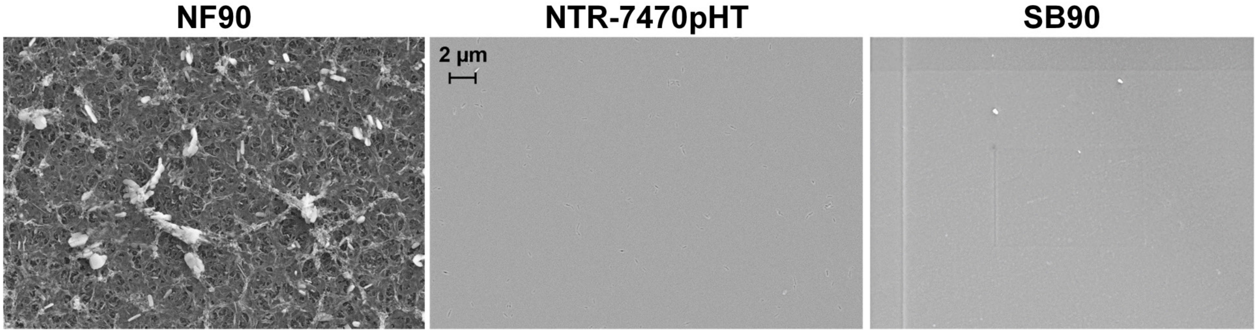

Fig. 3. SEM measurement of the three nanofiltration membranes (virgin).

Table 6
Characterization of membranes

	Roughness (nm)	Contact angle[a] (deg)	
		Virgin membrane	After fouling experiments
NF90	63–77 [31–33]	66 ± 3	85 ± 12
NTR-7470pHT	No data	62 ± 3	95 ± 6
SB90	9.8 [34]	59 ± 4	95 ± 4

[a] Sessile drop method.

similar spectra. Polysulfone and polyethersulfone share common structures featuring the Ar–SO_2– and Ar–O– functional groups, which was revealed by aromatic ether band (1,240 and 1,107 cm^{-1}) [35], aromatic ring (C–C stretching motion, 1,585, 1,487 and 1,169 cm^{-1}) and symmetric O=S=O stretching (1,152 cm^{-1}). And the asymmetric O=S=O vibrations at around 1,325 cm^{-1} should split into three bands, 1,324, 1,307 and 1,294 cm^{-1} for polysulfone in NF90 and 1,324, 1,295 and 1,289 cm^{-1} (shoulder, not apparent here) for polyethersulfone in NTR-7470pHT [36]. SB90 presented a completely different spectrum, which is distinguished by an ester carbonyl with C=O stretching (1,736 cm^{-1}), methyl groups on the acetate group (1,369 cm^{-1}), a strong C–O–C stretching (1,219 cm^{-1}) and pyranose ether band (1,036 cm^{-1}) [36,38]. ATR-FTIR results showed that both NF90 and NTR-7470pHT which had high adsorption THM capacity also have similar functional groups in terms of membrane/membrane support material.

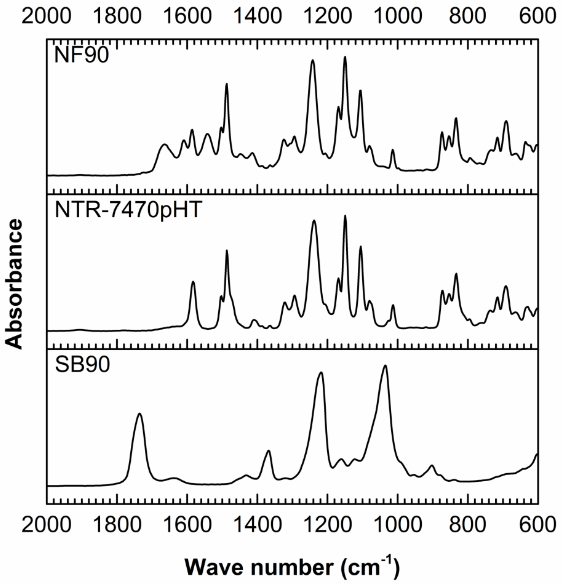

Fig. 4. ATR-FTIR spectra of the three nanofiltration membranes (virgin) over 600–200 cm^{-1}.

4. Discussion

4.1. Effect of molecular properties on adsorption

The amounts of adsorbed THM to NF90 and NTR-7470pHT, compared with similar studies found for organic compounds adsorption [25], were relatively high. As previously mentioned, less polar and hydrophobic compounds tend to adsorb to the hydrophobic membrane polymer. All four THM have hydrophobic characteristics with log $K_{ow} > 2$ [23] and are relatively less polar. Both features increased adsorption potential to the NF membranes.

$CHBr_3$ was the most preferentially adsorbed onto membrane, followed by $CHCl_2Br$, $CHClBr_2$ and then $CHCl_3$. For SB90, the steady state was reached soon (lower adsorption capacity). Therefore, it could only be seen that at the beginning of the experiment higher molecular weight THM had a higher adsorption than smaller THM. The tendency agreed that adsorption to membranes was preferable for THMs with higher molecular weight, higher hydrophobicity (log K_{ow}) and less polarity (dipole moment). Similar tendency was observed in THM adsorption to activated carbon, because generally the adsorption capacity of activated carbon increases with the higher molecular weight or less polarity of the compound [39,40]. A study showed that the extent of adsorption of phenolic compounds was promoted by hydrophobic interactions between them and the membrane structure [26]. Another study indicated that although the log K_{ow} was the best parameter to describe the hydrophobic adsorption. The relationship between molecular size or weight of the solute and the pore size of membrane also plays an important role [41].

4.2. Effect of membrane material on adsorption

Membranes of different materials showed highly different behaviors for THM adsorption. The different "saturation times" revealed highly different characteristics and capacity of three membranes for THM adsorption. At a realistic THM concentration range, NF90 and NTR-7470pHT could adsorb significant amount of THM which led first to an overestimation of rejection and then to a continuous rejection decline over up to 5 d. The rejection declines of four THM were all clearly quicker for SB90 than for the other two membranes. Steady state was reached already after 6 L permeate volume (about 6 h). Possible reason can be that different membrane properties in material or surface which affect the interaction between membranes and THM. A static adsorption study of perfluorinated compounds and thin-film composite polyamide NF membranes also showed that the adsorption depended strongly on the material of the active membrane layer [42].

The hydrophobicity of the three membranes shown by contact angles was similar. NF90 has significantly rough surface while the other two membranes have very smooth surface. ATR-FTIR results, in comparison, demonstrated the comparable spectra for NF90 and NTR-7470pHT and completely different spectra for SB90. The results indicated that the common structures Ar–SO_2– and Ar–O– shared by polysulfone and polyethersulfone in NF90 and NTR-7470pHT, respectively, could be the key for the THM adsorption. According to Kiso [43], the dominant effect on adsorption to cellulose acetate material is the hydrophobic interaction between cellulose acetate and the solute molecule, which is mainly through the acetyl groups of cellulose acetate and the alkyl chains of the solute. Cellulose acetate is less hydrophobic compared with polysulfone/polyethersulfone. Thus it can be assumed that cellulose acetate has less adsorption capacity for THM.

4.3. Effect of THM adsorption on rejection

Adsorption of THM to NTR-7470pHT and NF90 needed a considerable time period to reach a steady state, which can result in serious overestimation of rejection in short-term experiments. After the rejection reached the steady state, NF90 could maximally reject $CHBr_3$ at 49% and NTR-7470pHT and SB90 could not reject THM. From both series of experiments either with $CHCl_3$ or four THM mix, the THM rejection was generally lower than what was expected based on the MWCO of the membranes (Table 1), especially in the case of NF90 and SB90. Since NF90 is one of the tightest commercial NF membranes, we can conclude that NF serves only as a limited barrier for THM. Bellona et al. [44] have investigated NF90 for chloroform rejection and reported also poor rejection (25%–30%).

THM and the small molecules used in the MWCO determination were compared in Table 7 together with the corresponding steady-state rejection by each membrane. Diffusivity was calculated with the Wilke and Chang equation [45]. Molecular radii of THM and used organic substances were calculated with the Stokes–Einstein equation [46]. The molecular radii of all listed substances were smaller than the pore radius of NF90, the tightest membrane (Table 1). Compared with THM, substances such as ethylene glycol and glycerol which are smaller than THM could be better rejected by the NF membranes. One hypothesis for this behavior is

Table 7
Solute properties and membrane rejection

	M (g/mol)	Diffusivity (10^{-9} m²/s)	Molecular radius (nm)	Rejection		
				NF90	NTR-7470pHT	SB90
Chloroform	119.38	1.04	0.209	33%	0	0
Bromodichloromethane	163.83	1.02	0.212	36%	0	0
Dibromochloromethane	208.28	1.01	0.215	42%	0	0
Bromoform	252.73	0.99	0.218	49%	0	0
Ethanol	46.07	1.35	0.160	39%	0	7%
Ethylene glycol	62.07	1.26	0.171	87%	8%	19%
Glycerol	92.09	1.09	0.198	91%	22%	59%
Glucose	180.16	0.76	0.286	93%	60%	92%

that the adsorbed THM in the membrane matrix facilitates the transport. According to the solution-diffusion model, solute is first dissolved in the membrane and then moves across the membrane by diffusion or convection. The adsorbed THM may affect this process by influencing the diffusion into membrane bulk. Previous studies also proposed that solute with a high affinity to the membrane material adsorbs to the membrane matrix more easily and thus facilitating diffusion though the membrane [26,47]. According to Steinle-Darling et al. [25], steady-state rejection is lower when the adsorption is higher for the same solute. Another study also indicated higher hydrophobicity led to increase of adsorption and decrease of rejection for NF membranes, while the influence of hydrophobicity decreased when the molecular size (above the MWCO of the membrane) increases [48].

However, the fact that SB90 could not reject THM at all is still interesting. Low rejection of THM by cellulose acetate membrane was observed in previous studies. The rejection of different trace organics including THM by a full-scale RO plant was studied by Reinhard et al. [49]. Smaller chlorinated compounds could be rejected to some extent by polyamide membranes but passed through cellulose acetate membranes. It was also reported that cellulose acetate RO membrane has lower THM rejection (11%–18%) than aliphatic polyamide RO membranes (40%–66%) and especially aromatic polyamide RO (70%–90%) [50]. Meanwhile, in this study SB90 adsorbed much less THM than the other two membranes but the rejection was the poorest considering the MWCO. So we can conclude that it is not only the high amount adsorbed in the membrane structure which leads to more permeation of the solute but probably it is the adsorption capacity of the membrane material which plays an additional role. Cellulose acetate has low THM adsorption capacity so that it is soon saturated, which has fully favored the transport of THM.

Solute–membrane affinity plays dominantly in the mechanisms for the THM rejection by NF membranes. MWCO and pore/molecular radius are not always reliable for choosing membranes for specific target such as organic micropollutants even for less polar and neutral organics.

4.4. Competitive adsorption and effect of fouling

Compared with filtration experiments with $CHCl_3$ alone in feed, reaching the steady state was accelerated for $CHCl_3$ in the THM mix. This acceleration due to presence of other THM was most apparent for NTR-7470pHT. Meanwhile, in both filtration and static adsorption experiments the adsorbed $CHCl_3$ to NTR-7470pHT was higher when it was alone than in the THM mix. This could be the phenomenon of the competitive adsorption among four THM molecules which led to less adsorption $CHCl_3$. Competitive sorption was also observed for NF270, a polyamide NF membrane [25].

In fouling experiments, the less brominated THM – $CHCl_3$ and $CHCl_2Br$ – adsorbed less for NF90. This could be attributed to (1) the competitive adsorption between THM and NOM as background organics or (2) membrane blocking by organic fouling layer which occupies the available adsorption positions and reduces THM adsorption. During fouling experiments, the presence of NOM did not affect the THM rejection profiles for the three membranes. Obviously, there was no effect on a possible interaction of the hydrophobic THM with NOM, which might have influenced the adsorption of THM on the fouling layer. So the competition from NOM should be minimal. Zhang and Minear [51] applied the size-exclusion chromatograms and pointed out that THM were not bound to Suwannee River fulvic acid. Since THM do not adsorb to NOM fouling layer, the blocking of membrane by organic fouling layer could reduce the THM adsorption by covering the membrane surface. This phenomenon was not observed in the experiments with the other two membranes, probably because the extent of membrane surface reduction due to fouling layer was much more significant on the much rougher surface of NF90 (Fig. 3). So blocking should be the main reason here for the decrease of THM adsorption after fouling. The less adsorptive the molecule is, the more the adsorption was affected. Consequently, the reduction of $CHCl_3$ and $CHCl_2Br$ was observed and $CHCl_3$ was to the largest extent.

5. Conclusions

THM rejection by three NF membranes of different materials was studied over 6 d. NF has actually limited rejection of THM (maximum 30%–50%). Large extent of THM adsorption to membrane leads to severe overestimation of rejection in short-term experiments. Investigation of THM rejection by NF needs sufficient filtration volume/time. Adsorption has significant influence on rejection mechanism, facilitating the mass transport of THM through NF membrane. Membrane material plays a substantial role in adsorption and, consequently, has the impact on rejection. Competitive adsorption among THM was observed. NOM in the feed solution and organic fouling layer had little effects on rejection performance. Organic fouling lowered the adsorption of less adsorptive THM due to blocking of the membrane surface.

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Supplementary information

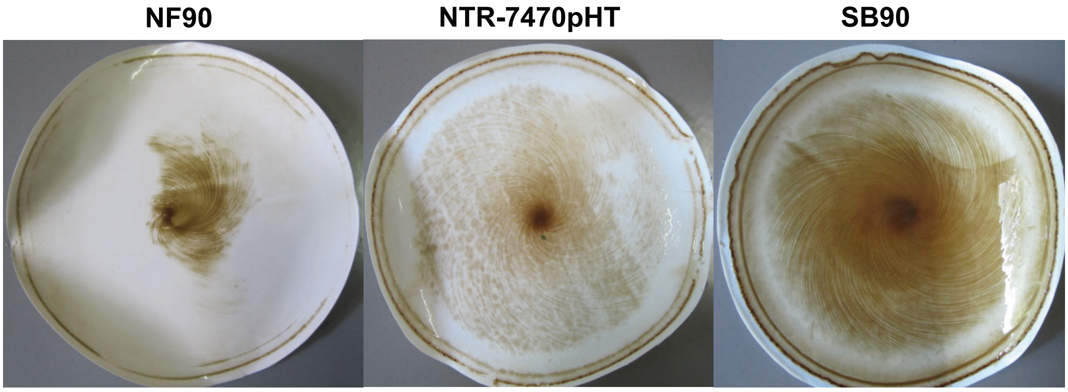

Fig. S1. Nanofiltration membranes fouled by NOM-rich lake water.

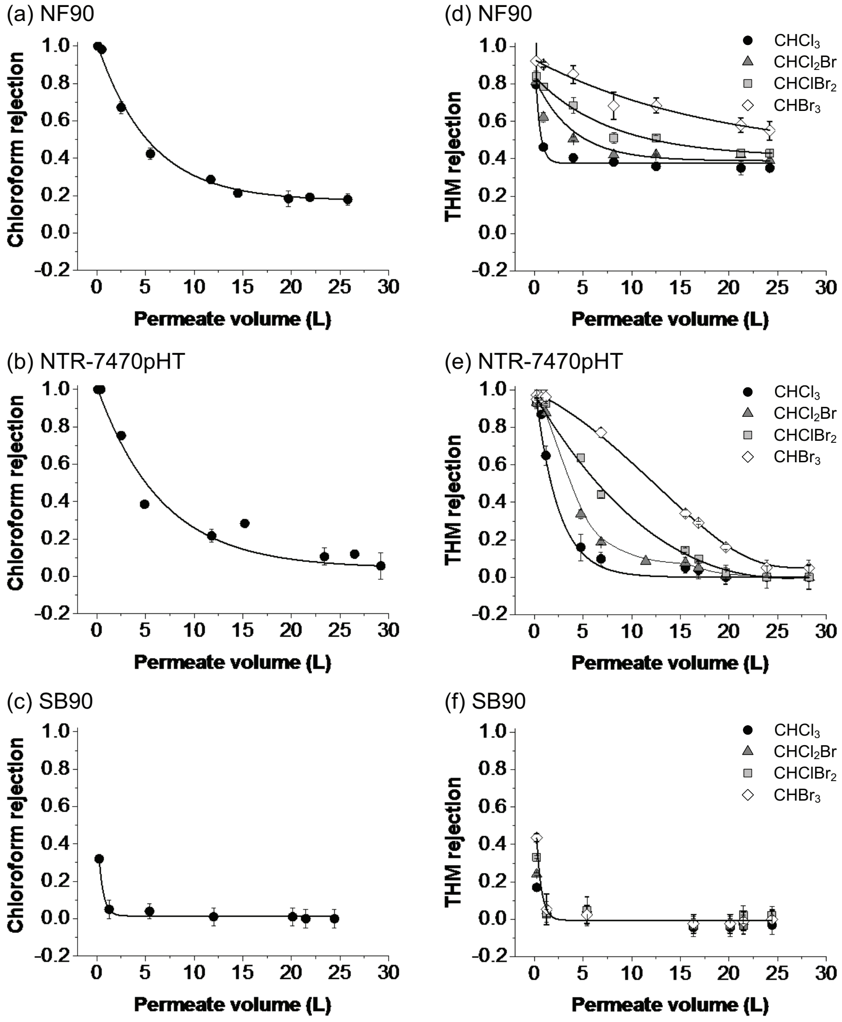

Fig. S2. Rejection of chloroform by (a) NF90, (b) NTR-7470pHT and (c) SB90 and rejection of four THM by (d) NF90, (e) NTR-7470pHT and (f) SB90 in fouling experiments with NOM-rich lake water (experiment numbers 3 and 4).