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Effects of caustic cleaning on pore size of nanofiltration membranes and their rejection of trace organic chemicals

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Abstract

The aim of this study was to assess the impact of caustic cleaning on the rejection of three different trace organic chemical (TrOC) groups (i.e. neutral hydrophilic, neutral hydrophobic and negatively charged) by two nanofiltration (NF) membranes - namely NF270 and NF90. Chemical cleaning was simulated by exposing virgin membrane samples to commercial caustic cleaning formulations as well as sodium hydroxide solutions containing analytical grade additives such as sodium dodecyl sulfate or ethylenediaminetetraacetic acid. The membrane average pore size before and after exposure to a commercially available caustic cleaning formulation was determined based on the pore transport model. The results show that caustic chemical cleaning could cause an increase in the membrane pore size, leading to an increase in permeability and decrease in rejection of conductivity. The impact of caustic cleaning on the pore size and solute rejection was a function of the membrane active skin layer and the chemistry of the cleaning formulation. Caustic cleaning led to a small increase in pore size of the NF270 membrane and resulted in a notable increase in the permeability and salt passage. By contrast, the impact on the NF90 membrane was negligible. The influence of caustic cleaning on TrOC rejection was dependent on physical characteristics of each TrOC including their molecular size, charge, and hydrophobicity. The rejection of neutral and hydrophobic TrOC by the NF270 membrane decreased significantly after exposure to caustic cleaning formulation. However, because the rejection of negatively charged TrOC is governed mostly by electrostatic interaction, their rejection was not significantly affected by caustic cleaning.

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Abstract

The aim of this study was to assess the impact of caustic cleaning on the rejection of three different trace organic chemical (TrOC) groups (i.e. neutral hydrophilic, neutral hydrophobic and negatively charged) by two nanofiltration (NF) membranes □ namely NF270 and NF90. Chemical cleaning was simulated by exposing virgin membrane samples to commercial caustic cleaning formulations as well as sodium hydroxide solutions containing analytical grade additives such as sodium dodecyl sulfate or ethylenediaminetetraacetic acid. The membrane average pore size before and after exposure to a commercially available caustic cleaning formulation was determined based on the pore transport model. The results show that caustic chemical cleaning could cause an increase in the membrane pore size, leading to an increase in permeability and decrease in rejection of conductivity. The impact of caustic cleaning on the pore size and solute rejection was a function of the membrane active skin layer and the chemistry of the cleaning formulation. Caustic cleaning led to a small increase in pore size of the NF270 membrane and resulted in a notable increase in the permeability and salt passage. By contrast, the impact on the NF90 membrane was negligible. The influence of caustic cleaning on TrOC rejection was dependent on physical characteristics of each TrOC including their molecular size, charge, and hydrophobicity. The rejection of neutral and hydrophobic TrOC by the NF270 membrane decreased significantly after exposure to caustic cleaning formulation. However, because the rejection of negatively charged TrOC is governed mostly by electrostatic interaction, their rejection was not significantly affected by caustic cleaning.

Keywords: Nanofiltration, trace organic chemicals (TrOC), physicochemical properties, caustic cleaning, pore size.

1   Introduction

Trace organic chemicals (TrOC) such as pharmaceutically active compounds, endocrine disrupting compounds, and pesticides are continuously released – either directly or indirectly – into municipal sewers. Some of these TrOC are poorly removed by conventional wastewater treatment processes and thus they can be detected in surface water [1-3] and in some rare cases even in drinking water [4, 5]. Although these TrOC usually occur in the aquatic environment and drinking water at concentrations well below the minimum acute therapeutic dose or toxicity level, their potential impact on human health and the environment over an extended period is largely unknown and is of significant concern to the public and scientific community [6]. Therefore, reliable removal of TrOC from municipal wastewater is essential for the protection of public health, particularly when effluent is intended for water reuse applications.

Driven by growing population densities, urbanisation, and the freshwater pollution, water reuse (or recycling) has become a pragmatic and sustainable approach to secure a stable supply of clean water beyond what is available from the hydrological cycle. Water reuse involves a range of advanced treatment processes such as nanofiltration (NF) or reverse osmosis (RO) membrane filtration, ozonation, activated carbon adsorption and/or UV oxidation. Among these technologies, NF/RO membrane applications have become an integral component of many water reuse schemes around the world [7]. Although NF/RO membrane processes can remove most TrOC reliably by steric hindrance (size exclusion), adsorption and/or electrostatic interaction (charge exclusion), TrOC removal in full-scale applications can be affected by inevitable membrane fouling (caused by deposition of organic and inorganic matter and/or the formation of biofilms) which necessitates periodic chemical cleaning [8-10]. However, to date, little is known about the impact of chemical cleaning on the rejection of TrOC by NF/RO membranes [11, 12].

Commonly used membrane cleaning reagents include acidic, caustic, surfactants and metal chelating reagents, which are often used in combination or in sequence to restore the membrane performance. Among these reagents, caustic formulations have been shown to exert a considerable impact on membrane performance immediately after chemical cleaning [9, 10, 13, 14]. This phenomenon has been recently explained by conformational rearrangements of polymeric chains in the membrane active skin layer (membrane swelling) as a response to the deprotonation of the membranes functional groups in a high pH environment [9]. Due to hysteresis, the polyamide chains do not immediately return to their normal position when the

membranes are subsequently used at near neutral pH. In addition, when used in a combination with a caustic reagent, metal chelating reagents and surfactants can adsorb and/or complex to the membrane polymer, which can further aggravate the impact of chemical cleaning on membrane performance [9, 13]. In fact, chemical cleaning with commercial caustic cleaning formulations, which usually contain a range of cleaning additives (i.e. surfactants and metal chelating reagents), have been often observed to recover the membrane flux to values above 100% of that achieved prior to cleaning [9, 13, 15, 16].

The aim of this study was to investigate the impact of caustic cleaning formulations on the rejection of TrOC by two NF membranes. These caustic cleaning formulation are usually used to control organic fouling, which is the predominant type of membrane fouling in water-reuse and surface water filtration applications [17]. Chemical cleaning was simulated by exposing virgin membrane samples to analytical grade and commercial cleaning formulations. Changes in membrane average pore size, surface hydrophobicity and permeability, were systematically correlated to the variation in the rejection and physico-chemical properties of the TrOC. The mechanisms underlining the influence of chemical cleaning on TrOC rejection were elucidated and discussed.

2   Materials and Methods

2.1   Membranes

Two thin film composite nanofiltration membranes – namely NF270 and NF90 (Dow FilmTec, Minneapolis, MN, USA) – were tested. These membranes have a semi-aromatic polyamide piperazine and a fully aromatic polyamide membrane active skin layer, respectively, on top of a porous polysulphone supporting structure [18]. The active skin layer thickness of the NF270 and NF90 membrane is 21 ± 5 nm and 218 ± 40 nm, respectively [19]. According to the manufacturer, the molecular weight cut-offs of the NF270 and NF90 membranes are 300-400 and 200 Daltons, respectively. The nominal permeate fluxes are 52 and 32 L/m^2h, respectively. The recommended operational pH range of the NF270 membrane is between pH 3 and 10 and that of the NF90 membrane is between pH 2 and 11. A more caustic (i.e. pH 12) or acidic condition (i.e. pH 1) can be used for cleaning 30 min or less [20].

2.2 Cleaning formulations

Two commercially available caustic cleaning formulations – namely MC11 (IMCD, Mulgrave, VIC, Australia) and PC98 (NALCO, Botany, NSW, Australia) – were used. The MC11 and PC98 were supplied in powder and liquid form, respectively. Chemical cleaning solutions were prepared according to the specifications of the manufacturer by separately dissolving 25 g/L of the MC11 and 4% (wt/wt) of the PC98 in Milli-Q water to obtain the final working solutions with a pH of 11.2 and 11.0 at 20 ± 1 °C, respectively. Although the exact compositions of these chemical cleaning formulations are proprietary information, it is understood that the MC11 formulation is a blend of detergent builders, pH buffers, and metal chelating reagents such as ethylenediaminetetraacetic acid (EDTA), sodium tripolyphosphate (STP) and trisodium phosphate (TSP). On the other hand, PC98 contains amphoteric surfactants and the chelating reagent EDTA.

Two additional caustic cleaning formulations were also prepared using analytical grade chemicals to obtain 5.4 mM EDTA or 10 mM sodium dodecyl sulfate (SDS) in a NaOH solution at pH 11.5. These cleaning solutions were designated as NaOH+SDS and NaOH+EDTA. It is noteworthy that no specifications from the membrane manufacturers could be found in the literature regarding the concentration limits of surfactants or metal chelating reagents in cleaning solutions despite their common use as key ingredients in commercial cleaning formulations.

2.3 Model trace organic contaminants

A set of 35 TrOC with molecular weights ranging from 138 to 376 Daltons and a wide range of physico-chemical properties were used for this study (Table 1). These compounds were purchased from Sigma Aldrich (Castle Hill, NSW, Australia) as analytical standards. Based on their physico-chemical properties, these TrOC could be classified into three groups: neutral hydrophilic (log D < 3), neutral hydrophobic (log D ≥ 3), and negatively charged (Table 1). Log D is defined as the effective log n-octanol–water distribution ratio, which takes into account the speciation of the compound as a function of the solution pH [21]. A stock solution containing 5 mg/L of each TrOC was prepared with methanol, stored at − 18 °C in the dark, and used within 1 month.

Table 1: Key physico-chemical properties of the TrOC.

	Compound	Chemical Formula[a]	MW[a] (Dalton)	Equivalent width (nm)[b]	Log D at pH 8 [a]	pK$_a$[a]
Neutral hydrophilic	Paracetamol	$C_8H_9NO_2$	151.16	0.60	0.33	9.86; 1.72
	Triamterene	$C_{12}H_{11}N_7$	253.26	0.61	1.15	-1.2; 6.28
	Caffeine	$C_8H_{10}N_4O_2$	194.19	0.70	−0.13	0.73
	Estriol	$C_{18}H_{24}O_3$	288.4	0.70	2.94	10.25
	Androstenedione	$C_{19}H_{26}O_2$	286.4	0.74	2.9	8.78
	Carbamazepine	$C_{15}H_{12}N_2O$	236.27	0.76	1.89	13.94; −0.49
	Atrazine	$C_8H_{14}ClN_5$	215.68	0.79	2.63	2.35
	Primidone	$C_{12}H_{14}N_2O_2$	218.25	0.79	0.4	12.26; −1.07
	Dilantin	$C_{15}H_{12}N_2O_2$	252.27	0.80	2.36	8.33; −2.81
	Fluoxetine	$C_{17}H_{18}F_3NO$	309.22	0.85	1.91	10.05
	Meprobamate	$C_9H_{18}N_2O_4$	218.25	0.86	0.7	13.09; −1.09
	Trimethoprim	$C_{14}H_{18}N_4O_3$	290.32	0.88	0.73	1.32; 7.45
	Omeprazole	$C_{17}H_{19}N_3O_3S$	345.42	0.92	2.33	4.72; 8.78
Neutral hydrophobic	Testosterone	$C_{19}H_{28}O_2$	288.4	0.63	3.47	15.06
	Triclosan	$C_{12}H_7Cl_3O_2$	289.54	0.64	4.76	7.8
	Etiocholanolone	$C_{19}H_{30}O_2$	290.4	0.65	3.75	15.13
	Androsterone	$C_{19}H_{30}O_2$	290.4	0.65	3.93	15.14
	Linuron	$C_9H_{10}Cl_2N_2O_2$	249.09	0.70	3.2	12.13; −1.04
	17a-estradiol	$C_{18}H_{24}O_2$	272.4	0.74	4.15	10.27
	17b-estradiol	$C_{18}H_{24}O_2$	272.4	0.74	4.13	10.27
	Estrone	$C_{18}H_{22}O_2$	270.4	0.76	3.68	10.25
	t-Octylphenol	$C_{14}H_{22}O$	206.32	0.84	4.93	10.15
	17a-ethynylestradiol	$C_{20}H_{24}O_2$	296.4	0.85	4.1	10.24
	Clozapine	$C_{18}H_{19}ClN_4$	326.28	0.90	3.8	7.33
	Amitriptyline	$C_{20}H_{23}N$	277.4	0.92	3.72	9.18
Negatively charged	Salicilic Acid	$C_7H_6O_3$	138.12	0.26	-1.14	3.01
	Ibuprofen	$C_{13}H_{18}O_2$	206.28	0.64	0.36	4.41
	Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	253.28	0.64	−0.9	5.81; 1.39
	Naproxen	$C_{14}H_{14}O_3$	230.25	0.76	−0.06	4.84
	TCEP	$C_9H_{15}O_6P$	250.91	0.78	-5.97	4.05
	Gemfibrozil	$C_{15}H_{22}O_3$	250.33	0.78	1.26	4.75
	Diclofenac	$C_{14}H_{11}Cl_2NO_2$	296.14	0.78	0.57	4.18; −2.25
	DEET	$C_{12}H_{17}NO$	191.27	0.81	1.96	−1.37
	Ketoprofen	$C_{16}H_{14}O_3$	254.28	0.83	−0.64	4.23
	Enalapril	$C_{20}H_{28}N_2O_5$	376.45	1.24	-0.45	3.15; 5.43

[a]Based on SciFinder Scholar

[b]Calculated using Molecular Modelling Pro

2.4 Filtration protocol

A laboratory-scale cross-flow NF/RO filtration system was used and consisted of a cross flow stainless steel cell, a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN), a

temperature control unit (Neslab RTE 7), a digital flow meter (Optiflow 1000, Agilent Technologies, Palo Alto, CA) connected to a PC, and a rotameter to measure the concentrate flow. The cross flow cell had an effective membrane area of 40 cm^2 (4 cm$\times$10 cm) and a channel height of 2 mm. Further details of this filtration system are available elsewhere [22].

Prior to each experiment, the membrane samples were rinsed with Milli-Q water to remove any protective chemicals. They were then compacted for one hour with Milli-Q water at 18 bar. To determine the rejection of TrOC, 10 litre of a background electrolyte solution containing 1 mM $CaCl_2$, 20 mM NaCl and 1 mM $NaHCO_3$ (pH = 8) was used. The stock solution of TrOC was added to the feed solution to obtain approximately 750 ng/L of each compound. The filtration was then conducted at a permeate flux, temperature and cross-flow velocity of 42 L/m^{2}h, 20 $\pm$ 0.1 °C and 23.6 cm/s, respectively. Permeate and feed samples (500 mL each) were collected for analysis after 1 and 24 h of filtration. The observed rejection (R_{ob}) is calculated by:

$$R_{ob} = 1 - \frac{c_p}{c_f}$$

(1)

Where c_f and c_p are the solute concentration in the feed and permeate solution, respectively.

2.5 Cleaning simulation protocol

Chemical cleaning was simulated by immersing the membrane samples in the cleaning solution for 18 h. The cleaning solution was kept at 35 $\pm$ 1 °C and was constantly agitated using a shaking water bath (SWB20, Ratek Instruments, Victoria, Australia). The membrane samples were removed from the cleaning solution, gently rinsed with Milli-Q water and used for filtration experiments on the same day. For comparison purposes, virgin (without chemical cleaning) membrane samples were also immersed in Milli-Q water at 35 $\pm$ 1 °C for 18 h prior to any filtration experiment. This chemical cleaning simulation represents one cleaning event for a severely fouled membrane as recommended by the manufacturer [23]. It can also represent a series of routine preventative chemical cleaning protocols of 1 h either every 3 or 6 months over 4.5 years, as suggested by BWA water additives (the manufacturer of the cleaning formulation MC11) [24]. In practice, there is a fouling layer on the membrane surface before chemical cleaning is required. To some extent, the fouling layer could shield the membrane surface from direct exposure to the cleaning solution. On the other hand, foulant residues on the membrane surface after chemical cleaning may also interfere with the measurement of the membrane surface

properties [16]. Thus, the cleaning procedure simulated in this study allows for a systematic examination of any changes in the membrane properties and separation efficiency without any interference of the foulant residues on the membrane surface. This cleaning protocol has been used successfully by several other research groups [15, 25-27].

2.6   Trace organic compound analyses

The analysis of the TrOC was based on a previously developed analytical method involving a solid phase extraction (SPE) procedure followed by determination using a liquid chromatography tandem mass spectrometry (LC-MS/MS) system [28]. Prior to the extraction, 50 ng of an isotopically labelled version of each analyte was added to 500 mL of sample. The analytes were then extracted using 5 mL, 200 mg hydrophilic/lipophilic balance (HLB) SPE cartridges (WAT106202, Oasis, Ohio, USA). The cartridges were pre-conditioned with 5 mL of tert-butyl methyl ether, 5 mL of methanol and 5 mL of Milli-Q water. Sample extraction was carried out at a flow rate of approximately 3 mL/min. Subsequently, the cartridges were rinsed with 5 mL Milli-Q water and dried for 30 min using high purity nitrogen. The loaded cartridges were stored in a sealed plastic bag at −18 °C in the dark until elution for LC-MS/MS analysis. The LC-MS/MS system consisted of an Agilent (Palo Alto, CA, USA) 1200 series high-performance liquid chromatography (HPLC) system, which was equipped with a Luna C18 (Phenomenex, Torrence CA, USA) column and an API 4000 triple quadruple mass spectrometer (Applied Biosystems, Foster City, CA, USA).

2.7   Membrane characterisation

2.7.1   Contact angle

The hydrophobicity of the membrane surface was measured using a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ) following the standard sessile drop method. Prior to each measurement, the membrane sample was air-dried. Milli-Q water was used as the reference solvent. At least 5 Milli-Q water droplets were applied to each membrane sample and the contact angle was immediately measured on both sides of the droplet.

2.7.2   Membrane permeability

A bench scale dead-end filtration system was used to measure the permeability of virgin and chemically cleaned membrane [29]. The system consisted of a stainless steel stirred cell with an active membrane surface area of 21.2 cm^2. A digital balance (Model Mettler Toledo, Ohio, USA)

connected to a personal computer was used to monitor the permeate flow. The membrane was initially compacted for 1 h using Milli-Q water at 6 bar and permeability measurement was then conducted for 1 h at 5 bar and room temperature (25 ± 1 °C).

2.7.3 Estimating the average membrane pore radius

Analytical grade dextrose, xylose, erythritol and dioxane were purchased from Sigma Aldrich (Castle Hill, NSW, Australia) and used as reference organic solutes to determine the membrane pore size (Table 1). These are hydrophilic organic compounds and thus they do not adsorb to the membrane. Prior to the filtration tests, the membranes were compacted at 18 bar until the flux reached a stable value. The Milli-Q water used for compaction was replaced with 10 L Milli-Q water containing a reference organic solute at concentration equivalent to 80 mg/L of total organic carbon (TOC). The filtration experiment was then conducted at 4, 6, 8, 10 and 12 bar. At each pressure, the system was stabilized for at least 1 h prior to the collection of feed and permeate samples (25 mL) for TOC analysis using a Shimadzu TOC V_{CSH} Analyser.

Table 2: Properties of the reference organic solutes.

Reference organic solutes	MW	Stokes radius (nm) [a]	Diffusivity (10^{-10} m^2/s) [a]
Dioxane	88	0.234	9.1
Erythritol	120	0.263	8.1
Xylose	150	0.290	7.4
Dextrose	180	0.324	6.6

[a] Reference: [27].

The average pore radius of virgin and chemically cleaned membrane was determined from the rejection data of the reference solutes and the pore transport model that incorporates hindered convection (size exclusion) and diffusion. This method has been widely used to determine the average pore size of nanofiltration membranes [30-32]. It is assumed in the pore transport model that the membrane pores are uniform and cylindrical and the solutes are spherical. Thus, the solute ratio (r_s) to pore size (r_p), $\lambda = r_s / r_p$, is associated to the partition coefficient Φ as:

$$\Phi = (1 - \lambda)^2 \tag{2}$$

The real rejection (R_r) can be expressed as a function of the Peclet number (Pe) and the convective hindrance factor (ΦK_c) for spherical solutes:

$$R_r = 1 - \left(\frac{\Phi K_c}{1 - (1 - \Phi K_c) \times \exp(-Pe)} \right) \tag{3}$$

ΦK_c can be calculated from λ and the detailed derivation is available elsewhere [33]. The real rejection can be calculated from the observed rejection (R_{ob}) value by taking into account the concentration polarisation phenomenon using the thin-film theory. R_r can be expressed as a function of the solute concentration on the membrane surface (c_m) and permeate (c_p), or the measured solvent flux (J_v), the mass transfer coefficient (k_f) and R_{ob}:

$$R_r = 1 - \frac{c_p}{c_m} = \frac{R_{ob} \times \exp\left(\frac{J_v}{k_f} \right)}{R_{ob} \times \exp\left(\frac{J_v}{k_f} \right) - R_{ob} + 1} \tag{4}$$

In this study, the mass transfer coefficient (k_f) was determined experimentally based on the variation of the membrane flux caused by the addition of a salt solution to a pure water feed [34]. Because the net driving pressure is influenced by the osmotic pressure of the feed solution established on the membrane surface, changes in the permeate flux allows for the determination of the salt concentration on the membrane surface and subsequently the mass transfer coefficient k_f. Filtration experiments were conducted at a cross-flow velocity and solution temperature of 23.6 cm/s and 20 ± 1 °C, respectively. Firstly, the volumetric water flux ($J_{v\,(water)}$) was measured using Milli-Q water. Subsequently NaCl was added to the feed reservoir to obtain 2000 mg/L and the solute flux ($J_{v\,(salt)}$) was measured. This procedure was conducted at two different applied pressures (ΔP) 10 and 14 bar. Knowing the salt concentration of the feed and permeate (and thus, the osmotic pressure of the feed (π_f) and the permeate (π_p)), the mass transfer coefficient can be calculated by [34]:

$$k_f = \frac{J_{v\,(salt)}}{\ln\left[\frac{\Delta P}{\pi_f - \pi_p} \left(1 - \frac{J_{v\,(salt)}}{J_{v\,(water)}} \right) \right]} \tag{5}$$

3   Results and discussion

3.1   Impact of caustic cleaning formulations on membrane properties

3.1.1   Membrane permeability

Exposure to a caustic cleaning formulation resulted in a considerable increase in the permeability of the NF270 membrane. A smaller but still notable increase in the permeability of the NF90 membranes could also be observed as a result of caustic cleaning (Figure 1). The more significant increase in the permeability of the NF270 can possibly be attributed to its larger membrane pore size and much thinner active skin layer [35] in comparison to the NF90 membrane. Results in Figure 1 are in good agreement with the literature, which reported that a combination of EDTA and/or SDS and caustic cleaning could lead to permeate flux recovery of more than 100% compared to the flux prior to cleaning [9, 13, 15, 36].
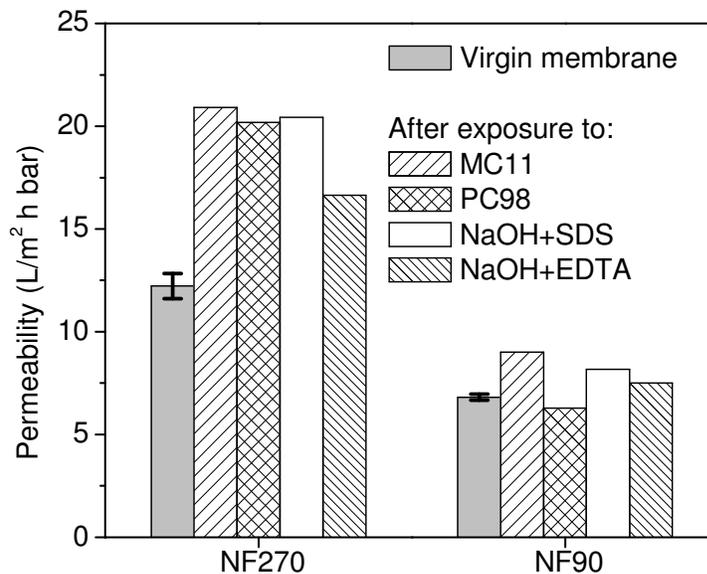

Figure 1

Figure 1: Permeability of the NF270 and NF90 membranes before and after exposure to MC11 (pH 11.2), PC98 (pH 11), NaOH+SDS (pH 11.5) and NaOH+EDTA (pH 11.5). The measurement was conducted with Milli-Q water at 5 bar and 25 ±1 °C.The error bars show the standard deviation of three repetitive measurements.

Recent investigations suggests that two mechanisms can be responsible, either individually or simultaneously, for an increase in permeability after exposing the NF membranes to a caustic cleaning solution. Li and Elimelech conducted cleaning experiments of the NF270 membrane fouled with humic acids using EDTA and SDS at pH 11 and reported a slightly over 100% permeate flux recovery [36]. The authors postulated that the residual EDTA or SDS on the membrane surface could render the membrane more hydrophilic, leading to a permeate flux value slightly higher than that of the virgin membrane. Variation in the membrane permeability due to chemical cleaning can also be driven by conformational changes in the polymeric matrix of the membrane active skin layer. Simon *et al.* [9] suggested that, when exposed to a strong caustic cleaning solution, the functional groups (i.e. COOH and NH) can further deprotonate to form more negatively charged moieties within the membrane active skin layer. Therefore, enhanced electrostatic interaction amongst these negatively charged moieties could cause conformational rearrangements of the polyamide structure resulting in an increase in pore size and/or membrane porosity. Due to hysteresis, a considerable increase in permeability after caustic cleaning could be observed, particularly if the membrane has a very thin active skin layer [9]. This study simultaneously examined the impact of caustic cleaning on the membrane surface hydrophilicity and pore size and the results are presented in the next two sections.

3.1.2   Surface hydrophobicity

Chemical cleaning using the four different cleaning formulations induced a notable influence on hydrophobicity (or contact angle) of the surface of the NF270 and NF90 membranes (Figure 2). The observed changes in the surface hydrophobicity were dependent on the initial contact angle of the virgin membrane and composition of the chemical cleaning formulation. Chemical cleaning with the PC98 and NaOH+SDS formulations resulted in a significant decrease in the contact angle of both the NF270 and NF90 membranes. The PC98 formulation contained amphoteric surfactants, thus, the decrease in the contact angle of the membrane surface observed in Figure 2 could be attributed to the adsorption of surfactant onto the membrane surface. By contrast, when the NF270 and NF90 membranes were exposed to the MC11 and NaOH+EDTA cleaning formulations, which do not contain any surfactants, the impact on the membrane surface hydrophobicity was not significant. A small but discernible increase in the surface hydrophobicity of the NF270 membrane could be observed as a result of exposure to the MC11 and NaOH+EDTA cleaning formulations. On the other hand, because the virgin NF90 is moderately

hydrophobic, a small decrease in hydrophobicity of the NF90 membrane was observed.
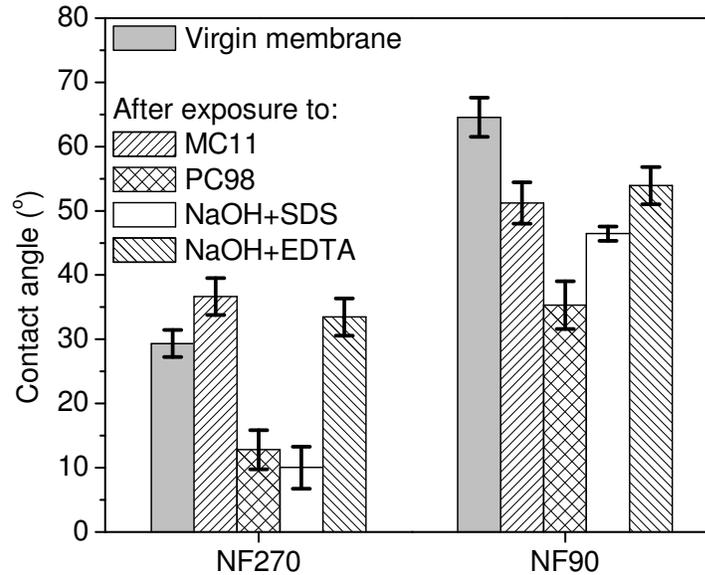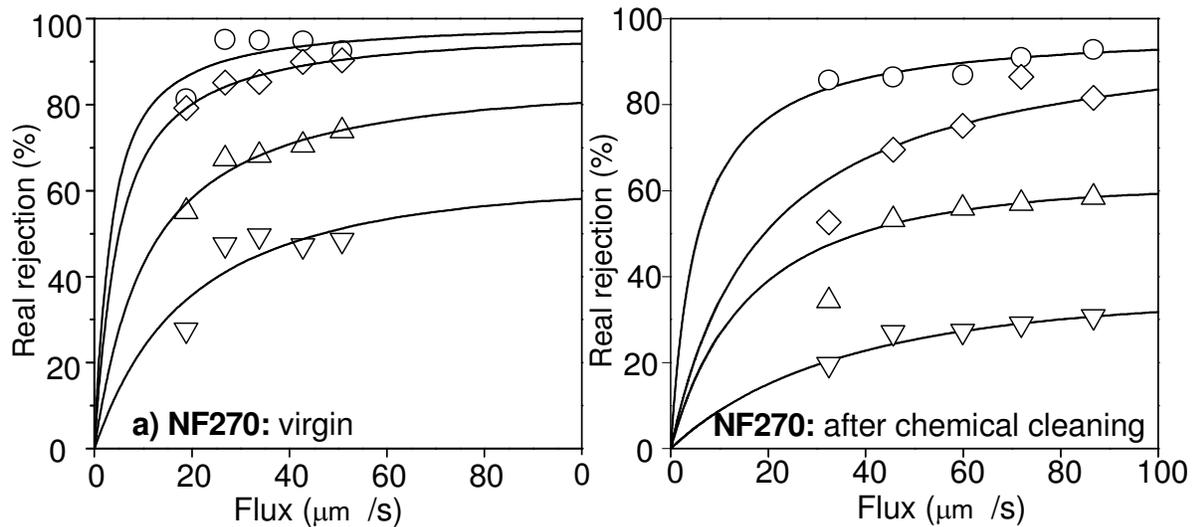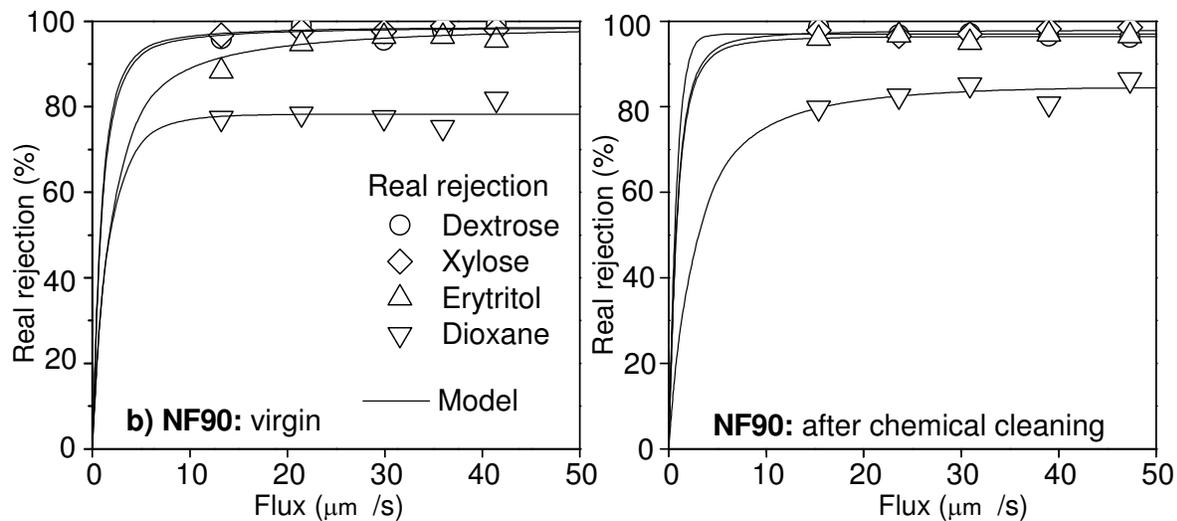

Figure 2

Figure 2: Contact angle of the NF270 and NF90 membranes before and after exposure to MC11 (pH 11.2), PC98 (pH 11), NaOH+SDS (pH 11.5) and NaOH+EDTA (pH 11.5). The error bars show the standard deviation of measurements obtained from five droplets on the membrane surface.

Membrane pore size

To determine the average pore size of the NF270 and NF90 membranes, the real rejection of each reference organic solute was calculated from the observed rejection after taking into account concentration polarisation effects (Eq. 4) and the mass tr ansfer coefficient (Eq. 5). Because the model parameters ΦK_c and Pe/J_v are uniquely related to the real rejection, they can be determined by fitting the real rejection data to the model (Eq. 3) using an optimisation program (Solver, Microsoft® Excel). The parameters ΦK_c and Pe/J_v are a function of the variable λ (ratio of solute radius to membrane pore radius, r_s/r_p). Thus, the membrane pore radius was calculated from the λ value for each reference solute used in this study. The real rejection of the reference organic solutes of the NF270 and NF90 membranes in virgin condition and after exposure to the caustic cleaning formulation MC11 is presented in Figure 3 and the average pore radii are

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presented in Table 3. In this study, the estimated average pore radius of the virgin NF270 was 0.38 nm while that of the virgin NF90 was 0.31 nm (Table 3). The pore size of membrane samples exposed to the MC11 cleaning formulation was also determined to evaluate the effect caustic cleaning on the membrane surface porosity. Exposure to the MC11 cleaning formulation resulted in a small increase in the average pore radius of the NF270 membrane. By contrast, the MC11 formulation did not result in any significant variation in the pore size of the NF90 membrane. These results are consistent with the changes in the membrane permeability and surface hydrophobicity reported above. Indeed, the increase in pore size of the NF270 observed here could explain the significant increase in the membrane permeability after caustic cleaning. On the other hand, because the average pore size of the NF90 membrane was not affected by caustic cleaning, the small increase in permeability of the membrane after exposure to the caustic cleaning formulation can be explained by an increase in the membrane surface hydrophilicity (Figure 2). In addition, the opening of pores smaller than the average pore size could also have affected the increase in the membrane permeability of both membranes.

Figure 3

Figure 3: Real rejection as a function of the permeate flux of the a) virgin and cleaned NF270 and b) virgin and cleaned NF90 membrane. **Cross-flow velocity, pH and temperature were 23.6 cm/s, pH 6 and 20 ± 0.1 °C, respectively**.

Table 3: Average pore radius of the NF270 and NF90 membranes before and after exposure to the MC11 cleaning formulation.

Reference organic solutes	Pore radius (nm)			
	Virgin NF270	NF270 after exposure to MC11	Virgin NF90	NF90 after exposure to MC11
Dextrose	0.37	0.37	–	–
Xylose	0.37	0.43	0.29	0.30
Erythritol	0.38	0.37	0.31	0.29
Dioxane	0.39	0.41	0.34	0.31
Average pore radius (nm)	0.38	0.40	0.31	0.30

3.2 Impact of caustic cleaning formulations on solute rejection

3.2.1 Rejection of conductivity

Caustic chemical cleaning led to a significant decrease in salt rejection (measured by conductivity) by the NF270 membrane, whereas no impact on the conductivity rejection by the NF90 membrane was found (Figure 4). These results are consistent with the impact of caustic cleaning with the MC11 reagent on the average pore size of both the NF270 and NF90 membrane reported in the previous section. Steric hindrance and electrostatic interactions can govern the rejection of ionic solutes by NF membranes [18]. In good agreement with previous studies [9, 10], the impact of caustic cleaning on the surface charge (zeta potential) of both membranes (data not shown) and thus, electrostatic interaction between ionic solutes and the membrane surface, was insignificant. As a result, any changes in conductivity rejection due to caustic chemical cleaning could be due to variation in the membrane pore size. In other words, the significant decrease in conductivity rejection by the NF270 membrane after exposing to caustic cleaning formulation may be due to the enlargement in its pore size as reported in section 3.1.3. Because chemical cleaning did not result in any significant impact on the pore size of the NF90 membrane (section 3.1.3), no discernible variations in conductivity rejection by the NF90 membrane could be observed after the membrane was exposed to various caustic cleaning formulations. It appears that the impact of caustic cleaning formulation was dependent not only on the cleaning pH but also ingredients of the cleaning formulations. Indeed, the four cleaning formulations caused slightly different effects on conductivity rejection by the NF270 membrane (Figure 4).
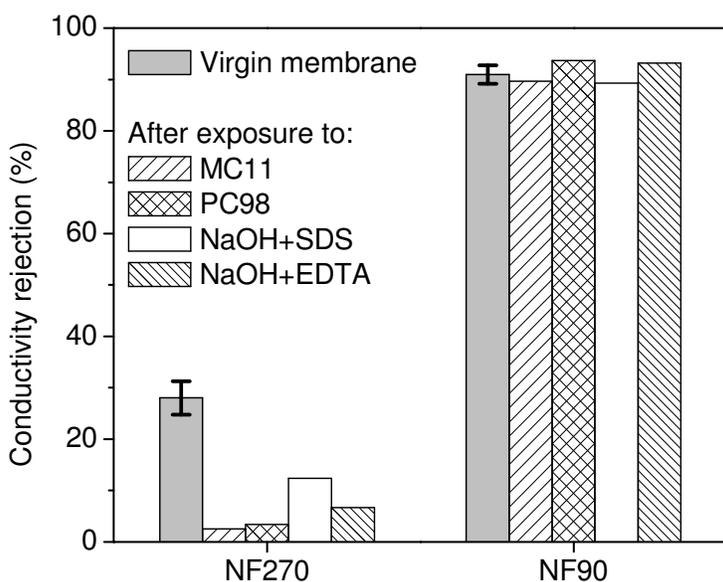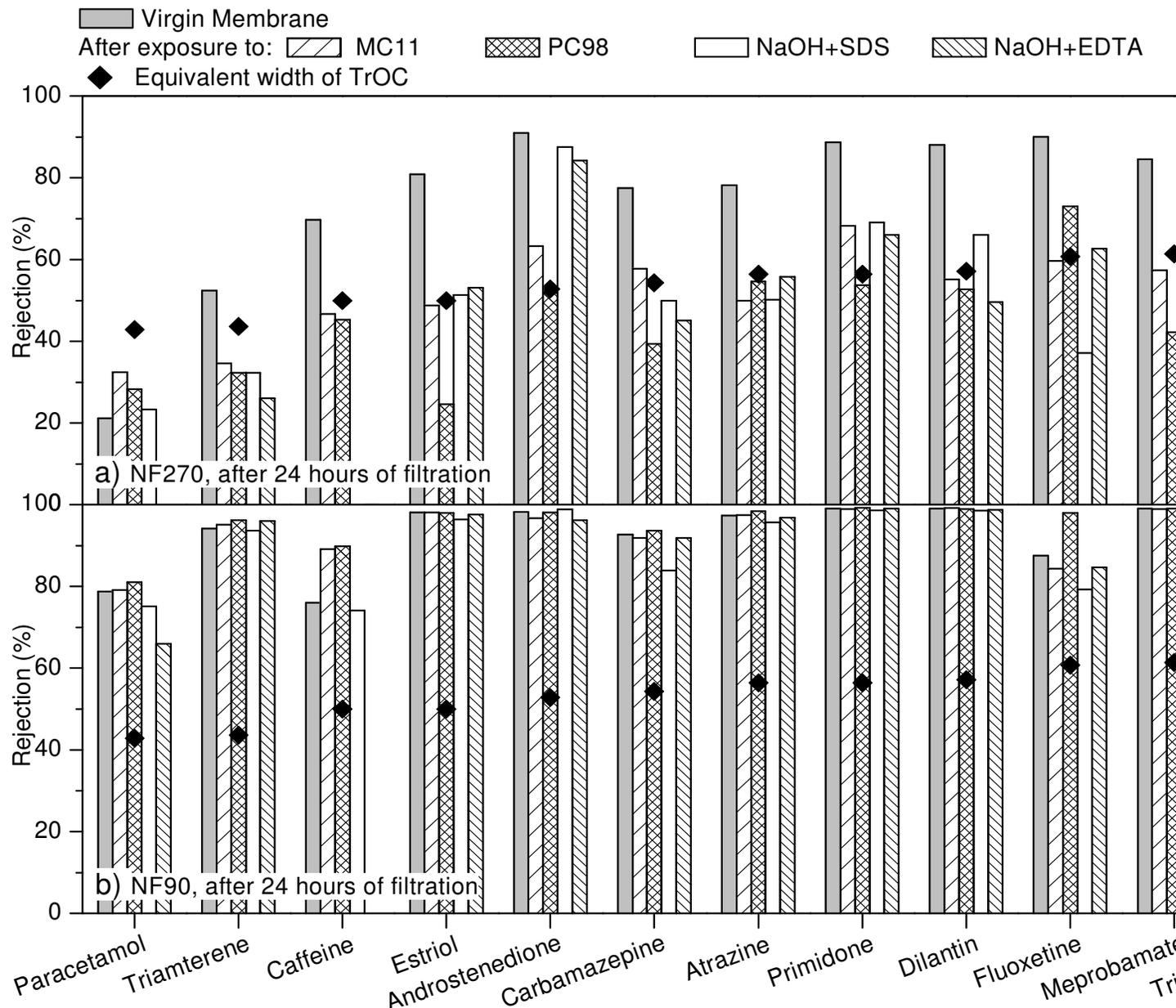
Figure 4

Figure 4: Conductivity rejection of the NF270 and NF90 membranes at pH 8 before and after exposure to MC11 (pH 11.2), PC98 (pH 11), NaOH+SDS (pH 11.5) and NaOH+EDTA (pH 11.5). The feed solution contained 1 mM $CaCl_2$, 20 mM NaCl and 1 mM $NaHCO_3$. Cross-flow velocity, permeate flow and temperature were 23.6 cm/s, 42 L/m^{2}h and 20 ± 1 °C, respectively. The error bars show the standard deviation of three measurements.

3.2.2   Rejection of neutral hydrophilic TrOC

The membrane porosity and the MW of the TrOC predominantly governed the rejection of hydrophilic and moderately hydrophilic neutral TrOC (log D < 3) by the NF270 and NF90 membranes. However, the rejection of TrOC can also be influenced by their molecular dimensions [37-39]. Therefore, the equivalent width (defined as $\sqrt{S}/2$, where S is the surface of rectangle of minimum area enclosing the projection of the molecule on the plane perpendicular to the length-axis) of the TrOC was used in this study to compare their rejection values by the NF270 and NF90 membranes. As shown in Figure 5, the equivalent width of the selected neutral hydrophilic TrOC ranged from 0.60 to 0.93 nm and the rejection of this group of TrOC by NF increased with their equivalent width by steric hindrance.

Caustic cleaning formulations led to a significant decrease in the rejection of neutral hydrophilic TrOC by the NF270 membrane (Figure 5a), consistent with a previous study [9]. As discussed before, the NF270 membrane is sensitive to chemical cleaning due to its very thin and loose active skin layer. Therefore, caustic chemical cleaning could affect the average pore size of the NF270 membrane, causing significant variation in the rejection of neutral hydrophilic TrOC (Figure 5a). By contrast, caustic cleaning had no impact on the average pore size and consequently rejection of neutral-hydrophobic TrOC by the NF90 membrane (Figure 5b) because of its thicker active skin layer (section 3.1.3). In addition, for the NF270 membrane, the effect of caustic cleaning on the rejection of TrOC was more significant as their equivalent width decreased. For example, the decrease in rejection of caffeine and estriol by the NF270 due to caustic cleaning was more severe than that of trimethoprim and omeprazole (which have larger equivalent molecular width than the former two compounds) (Figure 5a). It is probable that the increase in pore size of the NF270 membrane due to caustic chemical cleaning affects the convection transport of molecules with small equivalent width. This hypothesis is also consistent with the notable increase in the membrane permeability of the NF270 membrane after exposing to caustic cleaning formulations (Figure 1).
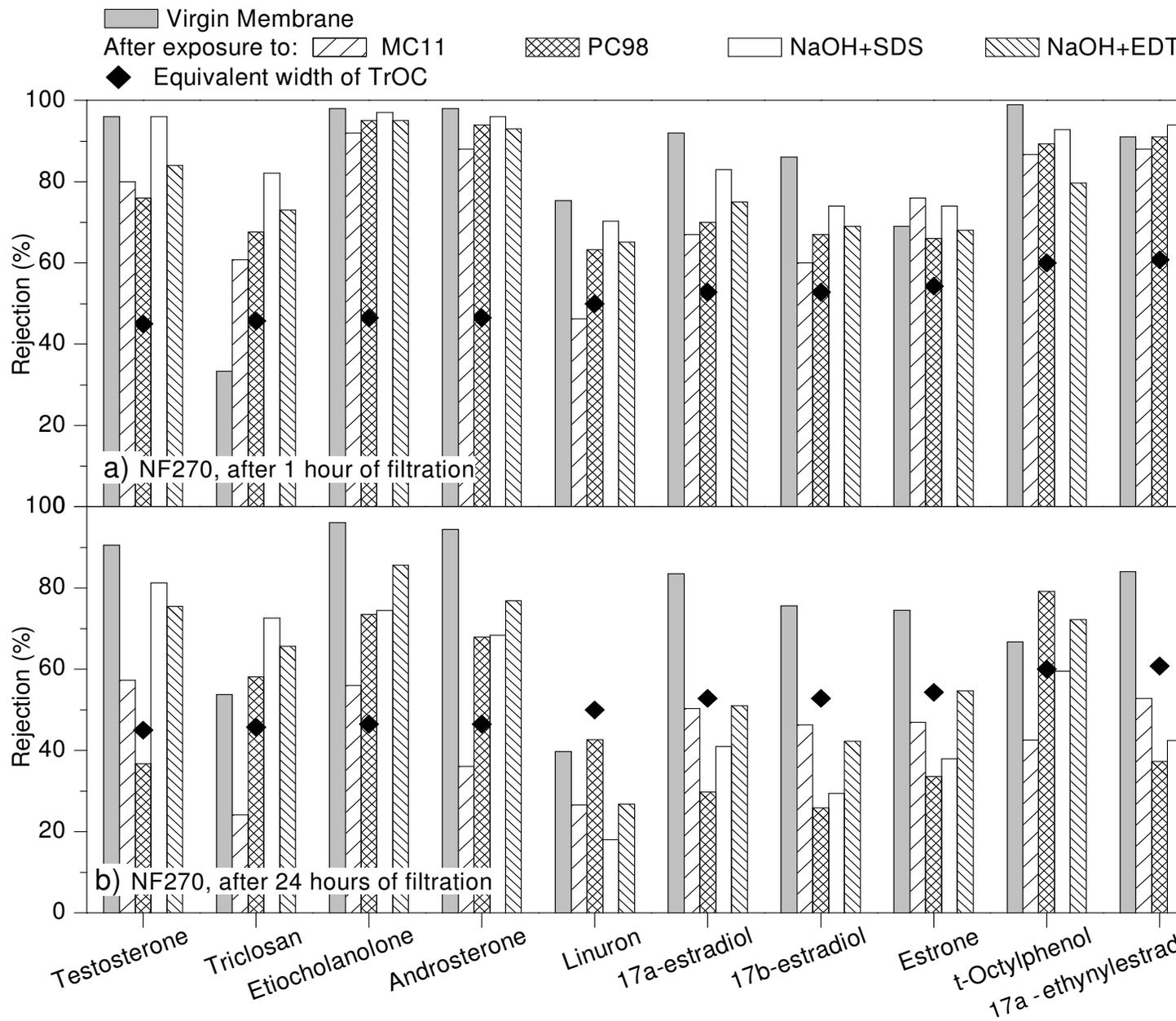
Figure 5

Figure 5: Rejection of neutral hydrophilic TrOC (Log D < 3) after 24 h of filtration as a function of the compounds equivalent width by the virgin and cleaned a) NF270 and b) NF90 membrane. Filtration conditions were as in Figure 3.

3.2.3 Rejection of neutral hydrophobic TrOC

As shown in Figure 6, at the beginning of the filtration process (i.e. after 1 h of filtration), adsorption of neutral hydrophobic TrOC (i.e. Log D $\geq$ 3) to the NF270 membrane could

contribute to their overall removal efficiency. However, as the membrane became saturated and the adsorption capacity for these neutral hydrophobic TrOC diminished, the rejection of neutral hydrophobic TrOC after 24 h of filtration decreased as both convection and diffusion through the NF270 membrane increased. The concentrations of all hydrophobic TrOC in the feed solution were also considerably decreased after 24 h of filtration (data not shown), which was in good agreement with the literature and indicated the adsorption of these compounds to the membrane [30, 40, 41].

Of the three groups of TrOC investigated here (i.e. neutral hydrophilic, neutral hydrophobic and negatively charged), caustic cleaning had the most significant impact on the rejection of neutral hydrophobic TrOC by the NF270 membrane (Figure 6). It is noteworthy that the impact of caustic cleaning on rejection of a number of hydrophobic TrOC by the NF270 membrane was only marginal after one hour of filtration. On the other hand, after 24 h of filtration, the rejection of all hydrophobic TrOC decreased considerably. This phenomenon can be explained by the high initial adsorption rate of hydrophobic TrOC to the membrane polymer, resulting in high retention of these TrOC, regardless of any changes in the membrane pore size due to chemical cleaning. However, after 24 h of filtration, the rejection of these hydrophobic TrOC by the NF270 membrane was predominantly controlled by size exclusion and the increase in the average membrane pore size of the NF270 membrane in response to the caustic formulated cleaning led to a substantial decrease in the neutral hydrophobic TrOC rejection. In addition, the increase in the membrane hydrophilicity (Figure 2) and/or pore size (Table 3) following caustic cleaning can impact the rate of adsorption and the total possible mass adsorption of TrOC to the NF270 membrane, which could also explain the observed enhanced diffusion of hydrophobic TrOC through the membrane after 24 h of filtration (Figure 6b) [42, 43]. No impact of chemical cleaning on the rejection of hydrophobic TrOC by the NF90 membrane was found in this study (data not shown), which was also consistent with the little or no variation in the pore size.
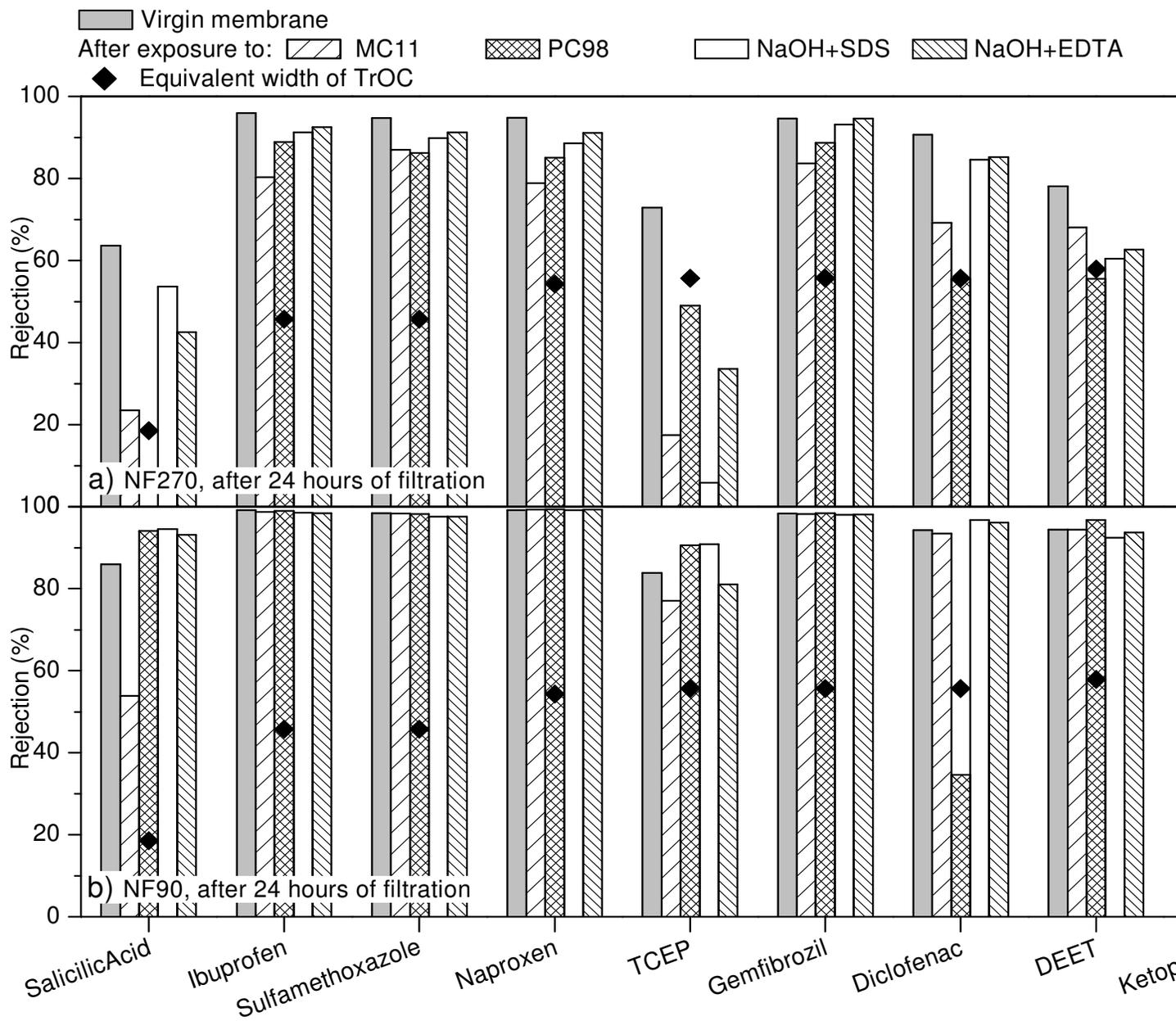
Figure 6

Figure 6: Rejection of neutral hydrophobic TrOC (Log D ≥ 3) as a function of the compounds equivalent width by the virgin and cleaned NF270 membrane after a) one hour and b) 24 h of filtration. Filtration conditions were as in Figure 3.

3.2.4 Rejection of negatively charged TrOC

The rejection of negatively charged TrOC (negatively charged in aqueous solutions at pH above their pK_a values) is governed by size and charge exclusion [38]. Because both the NF90 and

NF270 membranes are also negatively charged under normal pH conditions (i.e. pH 6 – 9) due to acidic functional groups in the membrane polymer [9], they reject negatively charged TrOC by not only size exclusion but also electrostatic repulsion. Consequently, the rejection of negatively charged TrOC by the NF270 and NF90 membrane was the highest among the three groups of TrOC (i.e. neutral hydrophilic, neutral hydrophobic, negatively charged) investigated here (Figure 7). In addition, when comparing the impact of chemical cleaning on the rejection values of the three groups of TrOC (Figure 5 – 7), it appears that the impact of caustic cleaning on negatively charged TrOC rejection was the least pronounced. Nevertheless, a small but discerniable decrease in the rejection of negatively charged TrOC by the NF270 membrane could be observed after it was exposed to caustic cleaning formulations (Figure 7a). As mentioned before (section 3.2.1), no impact of chemical cleaning chemical cleaning on the charge of the NF270 and NF90 membranes was found in previous studies [9, 10]. Consequently, observed variations on negatively charged TrOC rejection by the caustic cleaned NF270 membrane could be attributed predominantly to the enlargement of the membrane pore size. Once again, no discernible effect on the rejection of negatively charged TrOC by the NF90 membrane was observed (Figure 7b). This observation is consistent with the impact of caustic cleaning on the pore size of the NF90 membrane (section 3.1.3).

Figure 7

Figure 7: Rejection of negatively charged TrOC after 24 h of filtration as a function of the compounds equivalent width by the virgin and cleaned a) NF270 and b) NF90 membrane. Filtration conditions were as in Figure 3.

4   Conclusion

The impact of caustic cleaning on the pore size and solute rejection was found to be a function of the membrane active skin layer and the chemistry of the cleaning formulation. Caustic cleaning

led to a small increase in pore size of the NF270 membrane (which has a loose and thin active skin layer), resulting in a notable increase in the permeability and salt passage. By contrast, caustic cleaning did not exert any significant impact on the NF90 membrane (which has a thicker active skin layer). The influence of caustic cleaning on TrOC rejection was shown to be dependent on their molecular size, charge, and hydrophobicity. The rejection of neutral and hydrophobic TrOC by the NF270 membrane decreased significantly after exposure to caustic cleaning formulation, which is attributed to the increased membrane pore size and hydrophobic interaction with the active skin layer. On the other hand, because the rejection of negatively charged TrOC is predominantly controlled by electrostatic interaction, their rejection was less affected by caustic cleaning.

Acknowledgements

List of symbols

c_f	Solute concentration in feed (kg/m^3)
c_m	Solute concentration on the membrane surface in feed side (kg/m^3)
c_p	Solute concentration in permeate (kg/m^3)
J_v	Solvent flux (L/m^2 s)
$J_{v\,(salt)}$	Salt flux (kg/m^2 s)
$J_{v\,(water)}$	Water flux (L/m^2 s)
k_f	Mass transfer coefficient (m/s)
Pe	Peclet number (dimensionless)
R_{ob}	Observed rejection (%)
r_p	Pore radius (m)
R_r	Real rejection (%)
r_s	Solute radius (m)
π_f	Osmotic pressure feed ($Kg/m\ s^2$)
π_p	Osmotic pressure permeate ($Kg/m\ s^2$)
ΔP	Applied pressure ($Kg/m\ s^2$)
λ	Lambda (dimensionless)

| Φ | Partition coefficient (dimensionless) |
| ΦK_c | Convective hindrance factor (dimensionless) |

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