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N-nitrosamine rejection by reverse osmosis: Effects of membrane exposure to chemical cleaning reagents

Takahiro Fujioka
University of Wollongong, takahiro@uow.edu.au

Stuart Khan
University of New South Wales, s.khan@unsw.edu.au

James McDonald
University of New South Wales

Annalie Roux
Seqwater

Yvan Poussade
Veolia Water Australia, yvan.poussade@veoliawater.com.au

See next page for additional authors

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Authors
Takahiro Fujioka, Stuart Khan, James McDonald, Annalie Roux, Yvan Poussade, Jorg Drewes, and Long Nghiem

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Takahiro Fujioka [1], Stuart J. Khan [2], James A. McDonald [2], Annalie Roux [3], Yvan Poussade [4], and Jörg E. Drewes [2, 5], Long D. Nghiem [1,*]

[1] Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental Engineering, The University of Wollongong, NSW 2522, Australia

[2] UNSW Water Research Centre, School of Civil and Environmental Engineering, The University of New South Wales, NSW 2052, Australia

[3] Seqwater, Level 2, 240 Margaret St, Brisbane, QLD 4000, Australia

[4] Veolia Water Australia, Level 15, 127 Creek Street, Brisbane, QLD 4000, Australia

[5] Chair of Urban Water Systems Engineering, Technische Universität München, 85748 Garching, Germany

* Corresponding author: Long Duc Nghiem, Email: longn@uow.edu.au, Ph +61 2 4221 4590

Abstract

The impact of chemical cleaning on the removal of N-nitrosamines by low pressure reverse osmosis (RO) membranes was investigated. The results show that caustic chemical cleaning resulted in an increase in membrane permeability but caused a notable decrease in the rejection of N-nitrosamines. The impact of caustic chemical cleaning was particularly obvious for N-nitrosodimethylamine (NDMA) and N-nitrosomethylethylamine (NMEA), which have the lowest molecular weight amongst the N-nitrosamines investigated in this study. A correlation between the increase in permeability and the decrease in the rejection of either NDMA or NMEA could be observed. The rejection of conductivity also decreased as the membrane permeability increased, indicating that conductivity rejection can be an indicative parameter of predicting changes in NDMA and NMEA rejection during RO plant operation. The impact of caustic cleaning was not permanent and could be significantly reduced by a subsequent acidic cleaning step.

Keywords: Water reuse; N-nitrosamines; reverse osmosis (RO); chemical cleaning; N-nitrosodimethylamine (NDMA).

1. Introduction

Potable water reuse has been recognised as an effective and reliable measure to augment the supply of drinking water in many parts of the world where fresh water resources are under severe stress [1]. In this practice, reservoirs or underground aquifers are replenished with high quality reclaimed water. The reclamation of water for potable purposes is accomplished by an array of several advanced treatment processes such as reverse osmosis (RO), activated carbon adsorption, and advanced oxidation [1, 2]. The deployment of these advanced treatment processes is to ensure effective removal of pathogenic agents and trace organic chemicals of concern. Notable examples of these trace organic chemicals are N-nitrosodimethylamine (NDMA) and several other N-nitrosamines. Other N-nitrosamines that have previously been reported in treated wastewater include N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine (NDEA), N-nitrosodipropylamine (NDPA), N-nitrosodi-n-butylamine (NDBA), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR), and N-Nitrosodiphenylamine (NDPhA) [3-7]. Some of these N-nitrosamines have also been identified as potential human carcinogens and their concentrations in reclaimed water intended for potable reuse have been regulated in Australia and several other countries at 10 ng/L or less [8].

RO is a key treatment process in water reclamation applications for the removal of organic matter, inorganic salts and trace organic chemicals [9-11]. Due to its high performance on solute separation, RO process in water reclamation plants is also accounted for some degrees of N-nitrosamine removal from the reclaimed water which is used for the augmentation of drinking water source. Nevertheless, the removal of NDMA by the RO process appears to be highly variable. For example, NDMA rejections by the same type of RO membranes reported

from pilot- and full-scale studies range from negligible to 86% [12]. On the other hand, NDMA rejections by RO membranes obtained from laboratory-scale experiments varied from 50 to 70% [13-15]. In recent studies, Fujioka et al. [16] reported that changes in pH, ionic strength and temperature of the feed as well as membrane fouling can significantly affect NDMA rejection by RO membranes. These results can account for some but not all of the discrepancy in the rejection values of NDMA by RO membranes reported in the literature.

In addition to feed solution characteristics and operating conditions, the separation performance of RO membranes may also be affected by the alteration of membrane surface characteristics particularly caused by chemical cleaning. Because membrane fouling is an inherent phenomenon in almost all pressure driven membrane processes, chemical cleaning is inevitable. Typical cleaning chemicals include sodium hydroxide (NaOH) citric acid (CA), hydrochloric acid (HCl) and ethylenediaminetetraacetic acid (EDTA) [17, 18]. Although chemical cleaning can frequently restore the performance of RO membranes exposed to wastewater foulants [19, 20], these chemicals may also modify polyamide membrane structures, resulting in an increase in permeability or decrease in salt rejection [17]. Simon et al. [21] recently investigated the effects of chemical cleaning by exposing a NF270 nanofiltration membrane to several cleaning reagents (i.e., NaOH, CA, sodium dodecyl sulphate (SDS) and EDTA) and reported that these chemical cleaning agents (with the exception of CA) increased membrane permeability by up to 30%. Simon et al. [21] reported that the rejection of neutral solutes was more significantly affected by chemical cleaning than that of charged compounds. When the NF270 membrane was exposed to NaOH solution (pH 12), its permeability increased by 30% and the rejection of carbamazepine (molecular weight 253.3 g/mol) decreased from 80 to 50%. Thus, periodical chemical cleaning can potentially lead to a decrease in the rejection of N-nitrosamines including NDMA in full-scale RO

installations. Nevertheless, to date, the impact of chemical cleaning on the rejection of N-nitrosamines by RO membranes has not been fully understood.

The aim of this study was to provide a comprehensive understanding of the effects of chemical cleaning on the rejection of N-nitrosamines by RO membranes. The cleaning agents used in this investigation include three general cleaning chemical solutions (NaOH, HCl, CA) and three proprietary cleaning solutions. The impact of chemical cleaning was elucidated by examining the membrane pure water permeability, surface charge through zeta potential measurements, and separation performances of salts and select organic solutes.

2. Materials and methods

2.1. RO membranes

Two low pressure RO membranes – namely TFC-HR (Koch Membrane Systems, San Diego, CA, USA) and ESPA2 (Hydranautics, Oceanside, CA, USA) – were used in this study. They are classified as thin-film composite membranes that consist of an ultrathin polyamide active layer on top of a porous polysulfone support layer. These membranes are commonly deployed in several full-scale RO plants for potable water reuse applications in the USA and Australia [22, 23].

2.2. Chemicals

Eight N-nitrosamines (Supplementary Material Figure S1) were purchased from Sigma-Aldrich (St Louis, MO, USA) as analytical grade standards. Their molecular weight ranges from 74 to 158 g/mol. Further description of their physicochemical properties can be found elsewhere [13]. An N-nitrosamine stock solution containing 10 mg/L of each N-nitrosamine

was prepared in pure methanol. A surrogate stock solution of 100 µg/L of each deuterated N-nitrosamines (N-nitrosodimethylamine-D6, N-nitrosomethylethylamine-D3, N-nitrosopyrrolidine-D8, N-nitrosodiethylamine-D10, N-nitrosopiperidine-D10, N-nitrosomorpholine-D8, N-nitrosodipropylamine-D14 and N-nitrosodi-n-butylamine-D9) was also prepared in pure methanol. The deuterated N-nitrosamines supplied by CDN isotopes (Pointe-Claire, Quebec, Canada). These stock solutions were kept at -18 ºC in the dark and were used within 1 month of preparation.

Six chemical cleaning agents were used in this investigation (Table 1). Analytical grade NaOH, HCl and CA from Ajax Finechem (Taren Point, NSW, Australia) were used as cleaning reagents based on recommendations from the membrane manufacturers (Supplementary Material Table S2). The cleaning solution was prepared by dissolving the reagent in Milli-Q water. Three proprietary formulations designed for membrane cleaning in full-scale RO plants were also used. They are referred to as MC3, MC11 and PC98. Floclean® MC3 is an acidic based while Floclean® MC11 and PermaClean® PC98 are caustic based chemical cleaning formulations. MC3 and MC11 were supplied in powder form and the cleaning solution was prepared at 25 g/L as recommended by the manufacturer. PC98 was supplied in liquid form and was prepared at 4% (w/w) as recommended by the manufacturer.

[Table 1]

2.3. Membrane filtration system

A laboratory scale cross-flow RO filtration system was used for this investigation (Supplementary Material Figure S3). The membrane cell was made of stainless steel and could hold a 4 cm × 10 cm flat sheet membrane sample. The channel height of the cell was 2

mm. The feed solution was fed from a stainless steel reservoir to the membrane cell by a high pressure pump (Hydra-Cell, Wanner Engineering Inc., Minneapolis, MN, USA). The permeate flow rate and cross flow velocity were regulated by adjusting a bypass valve and back-pressure valve (Swagelok, Solon, OH, USA). The permeate flow was continuously monitored with a digital flow meter (FlowCal, GJC Instruments Ltd, Cheshire, UK) and the retentate flow was monitored with a rotameter. Feed solution temperature was controlled in the feed reservoir using stainless steel heat exchanging pipes connected to a chillier/heater unit (Neslab RTE 7, Thermo Scientific Inc., Waltham, MA, USA).

2.4. Simulated chemical cleaning protocols

Chemical cleaning was simulated by immersing a membrane sample in a glass container containing a cleaning chemical solution. The flat sheet membrane samples were first rinsed with Milli-Q water to remove any preservative materials from the membrane surface. In addition to these cleaning chemical solutions, Milli-Q water was also used for cleaning to obtain control membrane samples, and these control samples are designated as virgin membrane in this study. The containers were submerged in a temperature-controlled water bath (SWB1, Stuart®, Staffordshire, UK) and the temperature was maintained at 30±0.5 ºC according to the membrane manufacturer's recommendation (Supplementary Material Table S2). The simulated cleaning was carried out for 25 h. This cleaning simulation over 25 h corresponds to the cumulative chemical cleaning period of typical three-year operation comprising six months of chemical cleaning frequency and approximately 4 h of each cleaning. After the chemical cleaning procedure, the membrane samples were rinsed with a copious amount of Milli-Q water and stored (in Milli-Q water) at 4 ºC in the dark until they were used for further experiments. To evaluate the impact of a two-step cleaning procedure,

the membrane sample was first immersed into a NaOH solution for 25 h followed by a CA solution for 25 h. For the evaluation of effects of each cleaning solution, two membrane samples were prepared.

A general chemical cleaning procedure in full-scale RO plants is based on a sequential cycle of the first recirculation of chemical solution, 1-8 h soaking, second recirculation of chemical solution at an elevated temperature (e.g. 30 – 35 ºC), rinsing with clean water and flushing with feed water (Supplementary Material Table S2). Although the first recirculation using chemical solution is effective to remove fouling layer from the membrane surface, the membrane surface might still be partially covered by a fouling layer compromising direct exposure of the top skin layer of the membrane to chemical cleaning solution. Moreover, the effectiveness of chemical cleaning in full-scale RO plants is generally enhanced by higher cross-flow velocities [24]. Despite the difference in the impact of chemical cleaning from full-scale RO plants, the simulated chemical cleaning procedure used in this study enables a systematic investigation for the impact of each chemical cleaning solution on the separation performance of RO membranes. In fact, similar experimental protocols on chemical cleaning were previously reported in the literature [21, 25, 26].

2.5. Filtration experiments

Prior to each filtration experiment, the membrane was compacted at 1,800 kPa using Milli-Q as the feed until the permeate flux stabilised. Following the compaction stage, the permeability of each membrane sample was measured at feed pressure of 1,000 kPa. The Milli-Q water in the feed was then conditioned with 20 mM NaCl, 1 mM $CaCl_2$ and 1 mM $NaHCO_3$ to simulate the background electrolyte composition typically found in secondary or tertiary treated effluent. The stock solution of N-nitrosamines was also spiked into the feed to

make up 250 ng/L of each target compound. The permeate flux was then adjusted to 20 L/m^{2}h, and the system was operated for at the least 2 h before the first samples of the feed and permeate were taken for analysis. A previous study revealed no significant changes in the rejection of almost all N-nitrosamines after 1 h filtration [13]. The cross flow velocity and feed temperature during tests were kept at 0.42 m/s and 20±0.1°C, respectively.

2.6. Analytical methods

2.6.1. N-nitrosamine analytical technique

N-nitrosamine concentrations were determined using an analytical method published by McDonald et al. [27]. This method involves the solid phase extraction (SPE) of the analysts to a 2 g Supelclean^{TM} Coconut Charcoal cartridge (Supelco, St Louis, MO, USA) followed by quantification using an Agilent gas chromatography tandem mass spectrometry (GC-MS/MS) system with electron ionisation. Prior to the SPE process, 100 µL of a 0.1 mg/L surrogate stock solution was added to each 200 mL sample to obtain 50 ng/L of each deuterated N-nitrosamine surrogate. The SPE cartridges were conditioned with 6 mL dichloromethane, 6 mL methanol and 12 mL of Milli-Q water. N-nitrosamines in the sample were then extracted to the SPE cartridge at a flow rate of approximately 5 mL/min. The SPE cartridges were then rinsed with 3 mL Milli-Q water and dried with a gentle stream of high purity nitrogen gas for at least 60 minutes. N-nitrosamines in the dried SPE cartridges were eluted using 12 mL dichloromethane. After the eluent was added with 50 µL of toluene, it was concentrated to 1 mL with a Turbovap LV (Caliper Life Sciences, Hopkinton, MA, USA) under a gentle nitrogen gas stream. The concentration of N-nitrosamines was quantified using an Agilent 7890A gas chromatograph (GC) coupled with an Agilent 7000B triple quadrupole mass spectrometer (MS/MS) using electron ionisation. The detection limits of N-nitrosamines

established for this analytical method are 5 ng/L for NDMA, NDEA, NPIP, and NMOR, and 10 ng/L for NMEA, NPYR, NDPA, and NDBA.

2.6.2. Surface chemistry

Functional groups of RO membranes were analysed obtaining Fourier transform infrared spectroscopy (FTIR) spectra using a IRAffinity-1 (Shimazu, Kyoto, Japan) equipped with a diamond crystal plate. The active skin layer of each dried membrane sample was fixed on the diamond crystal plate with the same press force. The spectrum was obtained in the range of 400-4000 cm^{-1} at 2 cm^{-1} resolution.

2.6.3. Zeta potential measurement

The streaming potential of the membrane surface was measured using a SurPASS electrokinetic analyser (Anton Paar GmbH, Graz, Austria). The measurement of the streaming potential was performed in 1 mM KCl background electrolyte solution. The background solution was first adjusted to pH 9.5 using a KOH (0.1 M) solution. Subsequently, the background pH was reduced to pH 3 by a stepwise automatic titration using HCl (0.1 M) solution. The zeta potential of the membrane surface was calculated with the measured streaming potential using the Fairbrother-Mastin method [28]. During the analysis, the background solution temperature was maintained at 22±1 °C.

3. Results and discussion

3.1. Effects of membrane cleaning on membrane characteristics

Caustic chemical cleaning caused a significant increase in membrane permeability for both the TFC-HR and ESPA2 membranes (Figure 1). In comparison to caustic cleaning, the

impact of acidic chemical cleaning on the membrane permeability was much less discernible (Figure 1). Changes in the membrane permeability could occur via several mechanisms. A previous study by Kim et al. [29] suggested that under extreme conditions, the polyamide active akin layer can be hydrolysed to carboxylic acid derivatives, resulting in an increase in water permeability and surface hydrophilicity. Both acidic and caustic cleaning resulted in some variation in the membrane hydrophilicity and impact was specific to each membrane and the individual cleaning reagent (Supplementary Material Figure S4). There was no evidence to suggest that the membrane was hydrolysed under the experimental conditions of this study. The increase in permeability can also be attributed to some extent to adsorption of cleaning additives such as chelating reagents and surfactants in the proprietary cleaning formulations on the membrane surface. A previous study by Ang et al. [24] suggested that a small amount of residual chemical reagent (e.g. EDTA) on the membrane surface makes the active skin layer more hydrophilic, leading to more water passage through the membrane. Indeed, the proprietary cleaning formulations MC11 (pH 11) and PC98 (pH 10.7) resulted in a similar increase in permeability of the TFC-HR membrane in comparison to the NaOH (pH 12) solution (Figure 1a).

[Figure 1]

FTIR spectra of the virgin and several cleaned membranes in the range of 1750-750 cm^{-1} revealed the bonding structure of the polyamide active skin layer and the polysulfone supporting layer (Supplementary Material Figure S5). The polyamide active skin layer exhibit peaks at 1663, 1609 and 1541 cm^{-1}, which represent C-O and C-N stretching and C-C-N deformation vibration (amide I), N-H deformation vibration and C=C ring stretching vibration of aromatic amide, and N-H in-place bending and N-C stretching vibration of a -

CO-NH- group (amide II), respectively [30, 31]. Details of the other peaks associated with polysulfone supporting layer can be found elsewhere [30]. The FTIR spectra exhibited no discernible variations in these peaks (i.e. 1663, 1609 and 1541 cm^{-1}) after exposing the membranes to chemical cleaning reagents (Supplementary Material Figure S5). These results suggest that hydrolysis of the polyamide skin layer did not occur and that other mechanisms are responsible for the increase in permeability after caustic chemical cleaning.

Several previous studies have reported that changes in the membrane charge density can lead to conformational changes in the polymeric matrix due to a reduced electrostatic repulsion amongst charged functional group, which can result in a variation in the membrane pore and thus permeability [32, 33]. In this study, zeta potential of the virgin and chemically cleaned RO membranes was measured to substantiate any impact on permeability that may be caused by the changes in the membrane surface charge. The results reveal that acidic chemical cleaning (i.e., using HCl, CA and MC3 solutions) did not result in any discernible impact on zeta potential of the polyamide RO membranes (Figure 2a and c). Although caustic chemical cleaning (i.e., using NaOH, MC11 and PC98 solutions) could slightly alter the membrane zeta potential (Figure 2b and d), such changes did not cause any discernible influence on the membrane permeability (Supplementary Material Figure S6). Thus, changes in membrane surface charge are not likely to be a cause of changes in membrane permeability.

[Figure 2]

3.2. Effects of chemical cleaning on rejection performance of RO membranes

Caustic chemical cleaning resulted in a notable decrease in the rejection of N-nitrosamines by the TFC-HR and ESPA2 membranes while impact of acidic cleaning was not significant

(Figure 3). The impact of chemical cleaning was more apparent for low molecular weight N-nitrosamines (i.e., NDMA and NMEA). On the other hand, negligible impact was observed for high molecular weight N-nitrosamines (i.e., NDPA and NDBA).

[Figure 3]

Results reported here are in agreement with the changes in the membrane permeability due to chemical cleaning reported in section 3.1.1. A correlation was observed between permeability and the rejection of NDMA (R^2 = 0.86 and 0.87) and NMEA (R^2 = 0.93 and 0.86) for the TFC-HR and ESPA2 membranes, respectively (Figure 4). These results indicate that the rejection of low molecular weight N-nitrosamines (i.e., NDMA and NMEA) by RO membranes decrease significantly in accordance with the degree of the permeability increase caused by chemical cleaning, while the rejection of high molecular weight N-nitrosamines is not affected by chemical cleaning. Water permeability and solute passage increase when the void volume within the active skin layer increases and effective thickness of the active skin layer decreases [34]. Al-Amoudi [35] recently used the positron annihilation spectroscopy technique to measure the change in membrane pore volume due to chemical cleaning and reported that the pore volume increased slightly after chemical cleaning. Simon et al. [36] hypothesized that the enlargement of the membrane pore size immediately after caustic cleaning can be attributed to the increased electrostatic interactions at high pH among the deprotonated carboxylic functional groups of the polyamide active skin layer. Due to the hysteresis effect, the membrane pore size can only return to the normal condition after a sufficient period.

[Figure 4]

It is also notable that in addition to N-nitrosamines rejection, a correlation (R^2 = 0.79 and 0.80 for the TFC-HR and ESPA2 membranes, respectively) between permeability and conductivity rejection was also observed (Figure 4). These results also suggest that changes in conductivity rejection, which is monitored online in full-scale plants, also correspond to some extend to variations in the rejection of low molecular weight N-nitrosamines.

3.3. Sequential cleaning

A sequential cleaning procedure using caustic followed by acidic chemicals are also used at water reclamation plants. This two-step cleaning procedure is particularly common for the third stage of an RO plant where both organic and inorganic fouling occurs [37]. In this study, permeability measured after a sequential cleaning (NaOH solution at pH 12 followed by CA solution at pH 2.1) was lower than that measured after a single cleaning using NaOH solution only (Figure 5). Likewise, the sequential cleaning also mitigated the impact of a single NaOH cleaning on NDMA and NMEA rejection, and the rejections of sequentially cleaned membranes were similar to those of CA cleaned membranes (Figure 6). The results reported here confirm the hypothesis proposed by Simon et al. [36] indicating that the interactions between membrane matrix and cleaning chemicals are reversible. Thus, the impact of caustic chemical cleaning on membrane separation performance could be alleviated by a sequence of caustic cleaning followed by acidic cleaning.

[Figure 5]

[Figure 6]

4. Conclusions

The effect of chemical cleaning on the rejection of N-nitrosamines by two RO membranes was investigated at bench-scale using six different caustic and acidic cleaning chemicals. Caustic chemical cleaning resulted in a considerable increase in the membrane permeability and the impact was much more significant than that of acidic cleaning. After exposure to caustic cleaning reagents, notable decrease in the rejection of low molecular weight N-nitrosamines (i.e., NDMA and NMEA) was observed. On the other hand, the rejection of larger molecular weight N-nitrosamines exhibited no discernible changes after chemical cleaning. The sequence of caustic followed by acidic cleaning could alleviate the impact of caustic chemical cleaning on permeability and N-nitrosamine rejection despite the fact that the additional cleaning leads to an increase in operational cost. This suggests that the impact of caustic cleaning on water permeation and transport of small molecular weight solutes is reversible and is not permanent. Indeed, FTIR analysis of the membrane surface before and after exposure to various chemical cleaning reagents did not show any discernible changes in the bonding structure of the polyamide skin layer.

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N-nitrosamine rejection by reverse osmosis: effects of membrane exposure to chemical cleaning reagents

Takahiro Fujioka [1], Stuart J. Khan [2], James A. McDonald [2], Annalie Roux [3], Yvan Poussade [4], and Jörg E. Drewes [2, 5], Long D. Nghiem [1,*]

[1] Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental Engineering, The University of Wollongong, NSW 2522, Australia

[2] UNSW Water Research Centre, School of Civil and Environmental Engineering, The University of New South Wales, NSW 2052, Australia

[3] Seqwater, Level 2, 240 Margaret St, Brisbane, QLD 4000, Australia

[4] Veolia Water Australia, Level 15, 127 Creek Street, Brisbane, QLD 4000, Australia

[5] Chair of Urban Water Systems Engineering, Technische Universität München, 85748 Garching, Germany

SUPPLEMENTARY MATERIAL

* Corresponding author: Long Duc Nghiem, Email: longn@uow.edu.au, Ph +61 2 4221 4590

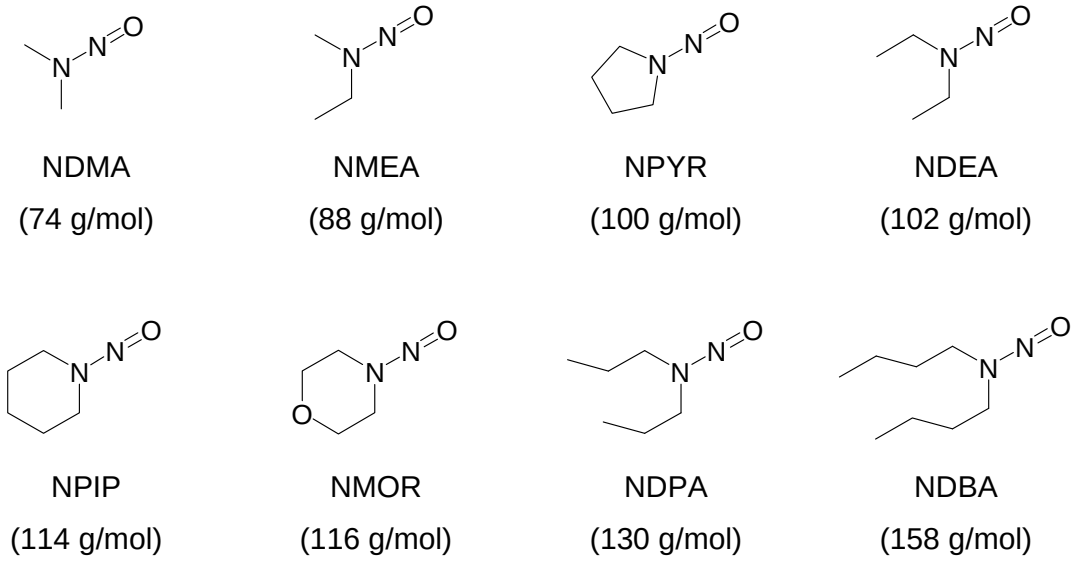

Figure S1: Molecular structure and molecular weight of the selected N-nitrosamines.

Table S2: Typical chemical cleaning for RO membrane elements recommended by the membrane manufacturer.

Frequency	3-12 months
Caustic	NaOH (pH = 11.5 and 30 °C)
	NaOH + SDS (pH = 11.5 and 30 °C)
	Na-EDTA + sodium tripolyphosphate (pH 10 and 40 °C)
Acid	2% Citric acid (40 °C)
	HCl (pH = 2.5 and 35 °C)
Cleaning period	1-8 h/stage

* Hydranautics, Foulants and Cleaning Procedures for composite polyamide RO Membrane Elements (ESPA, ESNA, CPA, LFC, NANO and SWC), Technical Service Bulletin, (2010).

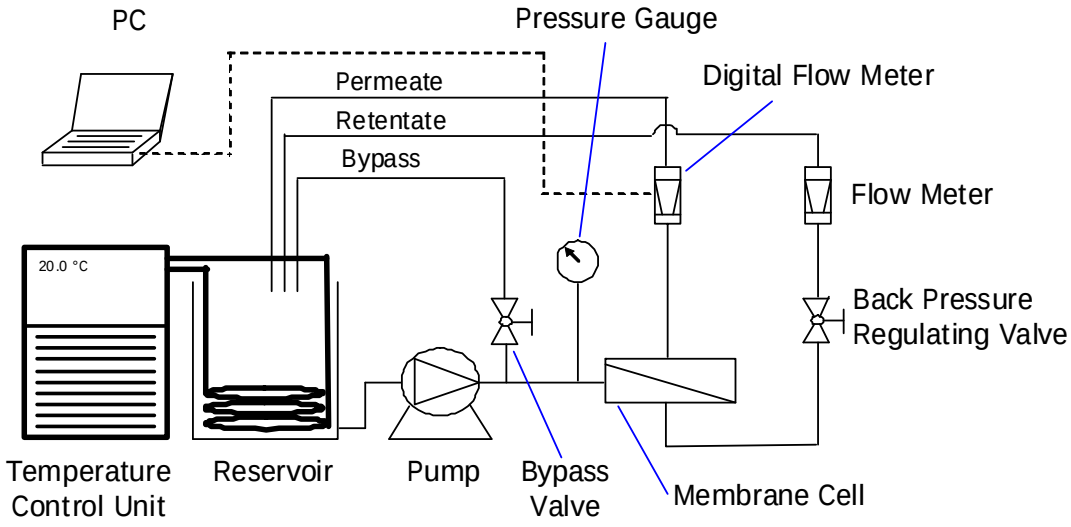

Figure S3: Schematic diagram of the cross flow filtration system.

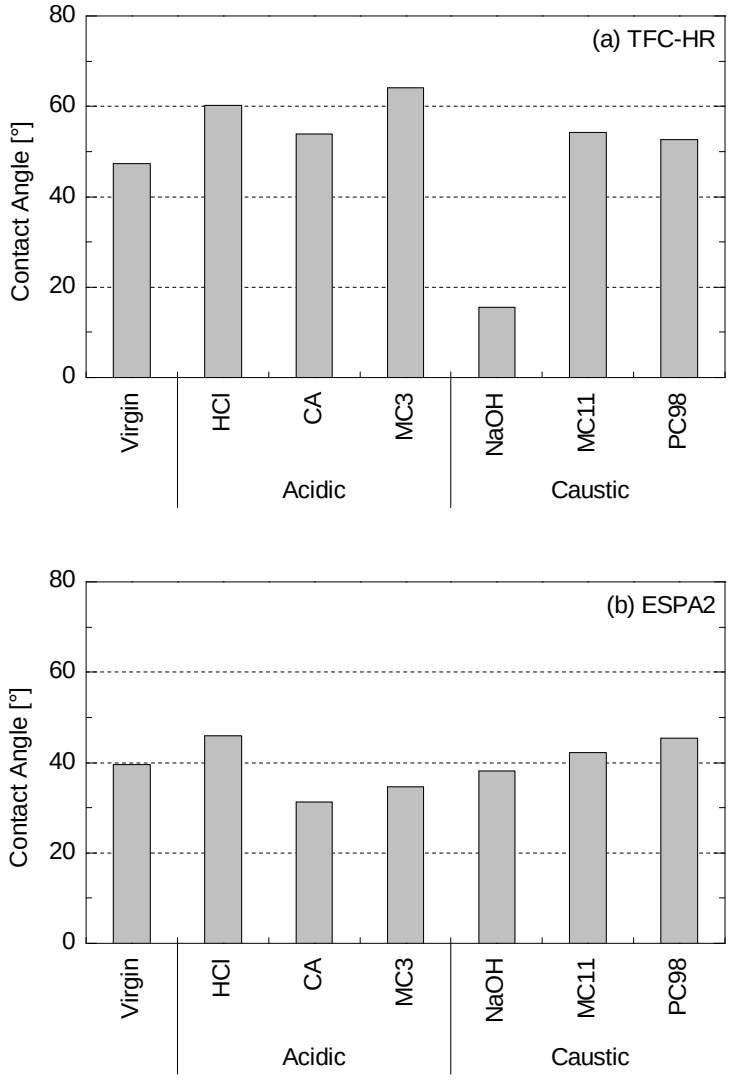

Figure S4: Hydrophobicity of the (a) TFC-HR and (b) ESPA2 membranes before and after being exposed to permeability of TFC-HR membrane before and after being exposed to cleaning solutions for 25 hours at 30 °C.

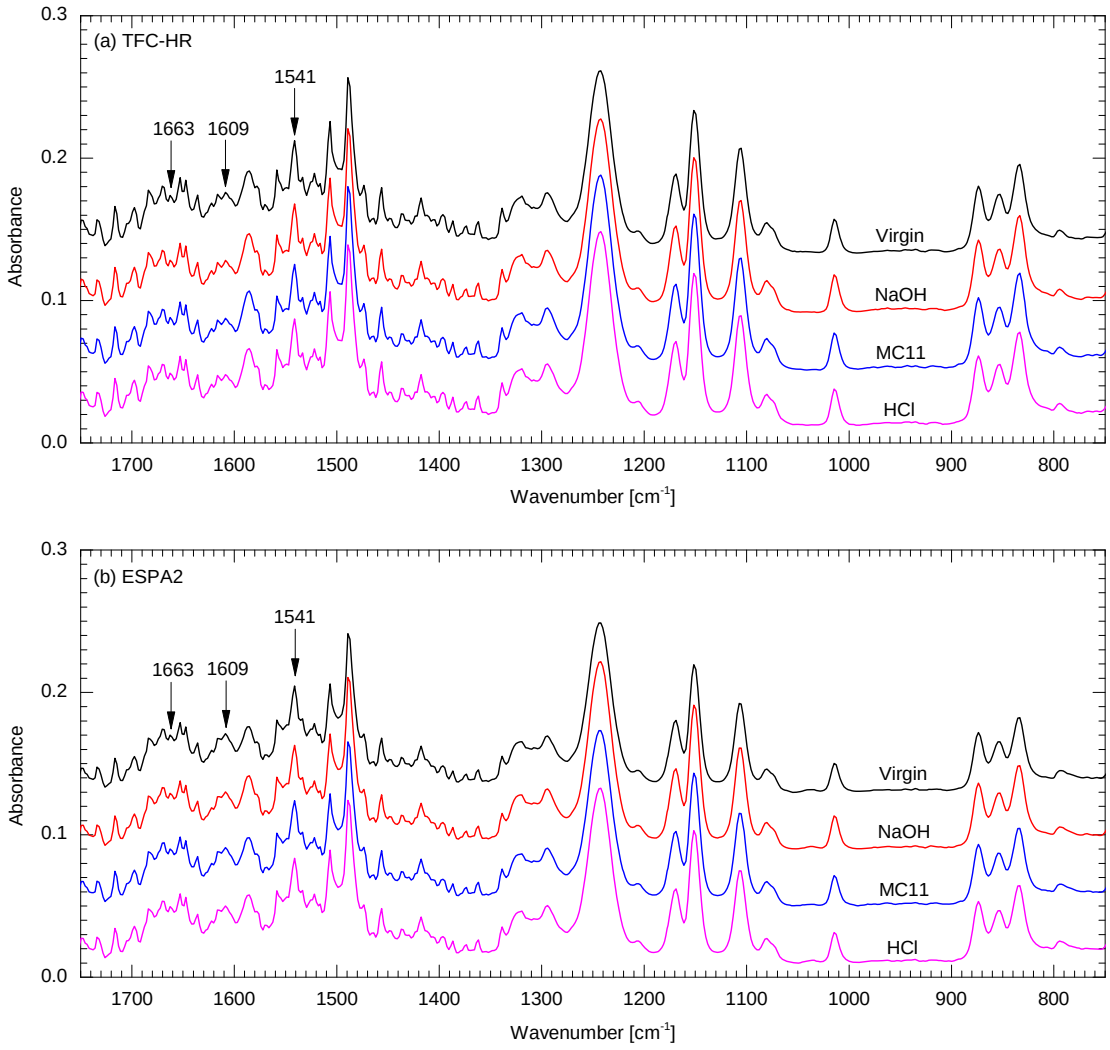

Figure S5: FTIR spectra of the (a) TFC-HR and (b) ESPA2 membranes before and after being exposed to the cleaning solutions NaOH, MC11 and HCl for 25 h at 30 °C.

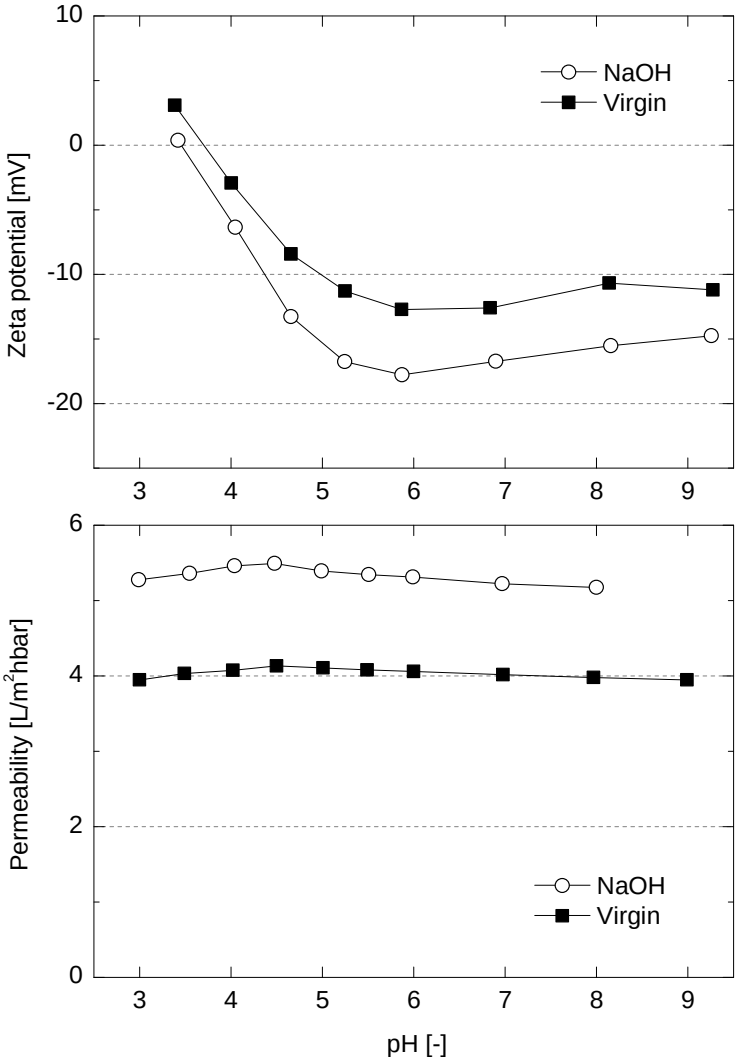

Figure S6: (a) Zeta potential and (b) permeability of TFC-HR membrane before and after being exposed to NaOH (pH 12) solution for 25 hours at 30 °C. The analysis of zeta potential was carried out in 1mM KCl solution. Pure water permeability was determined with Milli-Q water at 1,000 kPa and 20°C feed temperature.

Table S7: Rejection of N-nitrosamines by the virgin and chemical cleaned TFC-HR and ESPA2 membranes and their membrane permeability after being exposed to chemical solutions for 25 h at 30 °C.

Membrane	Parameter	Virgin	HCl	CA	MC3	NaOH	MC11	PC98
TFC-HR	Permeability [L/m^{2}hbar]	3.8 ± 0.2	4.2 ± 0.2	4.6 ± 0.3	4.3 ± 0.2	5.8 ± 0.1	5.5 ± 0.4	6.1 ± 0.1
	Conductivity [%]	99.3 ± 0.1	99.2 ± 0.1	98.6 ± 0.3	99.1 ± 0	98.6 ± 0	98.7 ± 0	98.3 ± 0.1
	NDMA [%]	54.2 ± 1.1	48.8 ± 0.4	42.3 ± 1	56.1 ± 3.9	35.1 ± 1.5	39.9 ± 1.1	31.4 ± 9.6
	NMEA [%]	83.1 ± 2.2	78.7 ± 2.1	73.1 ± 2.7	81 ± 0.9	66.9 ± 4.6	71.1 ± 3	64 ± 2.8
	NPYR [%]	90.8 ± 2.9	89.4 ± 3.4	88.3 ± 2.4	91.4 ± 2.8	85.2 ± 0.1	87 ± 1.1	81.2 ± 4
	NDEA [%]	96.2 ± 0.9	94.6 ± 0.5	92.1 ± 1.3	95.5 ± 0	89.7 ± 2.5	90.2 ± 2.2	85.6 ± 2
	NPIP [%]	97.9 ± 0.4	96.4 ± 1.3	95.7 ± 0.4	98.3 ± 0.2	96.6 ± 0.7	96.8 ± 0.5	94.8 ± 0.4
	NMOR [%]	92.6 ± 3.7	90.1 ± 1.5	84.1 ± 2.7	93.3 ± 0.8	89.4 ± 3.8	89 ± 0.7	82.2 ± 0.6
	NDPA [%]	95.5 ± 1.4	92.9 ± 4.1	93 ± 2.9	96.5 ± 0.2	96.4 ± 0.1	96.7 ± 0.5	94.7 ± 0.8
	NDBA [%]	94.6 ± 1.5	91.7 ± 3.7	91.4 ± 5.1	95.5 ± 0.2	96.1 ± 0.1	95.6 ± 0.5	95.2 ± 0.1
ESPA2	Permeability [L/m^{2}hbar]	4.8 ± 0.3	5 ± 0.1	5.3 ± 0.1	5.1 ± 0.1	6.7 ± 0	6.5 ± 0.1	6.2 ± 0.1
	Conductivity [%]	98.2 ± 0.4	97.1 ± 0.1	97.5 ± 0.3	97.5 ± 0.3	95.4 ± 0.5	96.5 ± 1	96 ± 0.7
	NDMA [%]	36.2 ± 0	37.5 ± 0.4	35.4 ± 3.4	35.6 ± 3.2	17.7 ± 3	25.2 ± 1.1	20 ± 2.5
	NMEA [%]	75.7 ± 3	69.5 ± 0.1	68.4 ± 4.8	64.3 ± 2.6	50.4 ± 5.2	45.5 ± 2.1	47.7 ± 4.1
	NPYR [%]	87 ± 5.6	80.9 ± 0.4	83 ± 5.7	80.3 ± 3	68.6 ± 1.2	64.2 ± 1.7	62.3 ± 7.1
	NDEA [%]	90.2 ± 3.1	77.2 ± 0.2	90.2 ± 1.7	82.4 ± 6.7	77.1 ± 0.8	75.2 ± 1.1	77.5 ± 0
	NPIP [%]	95 ± 1.1	92 ± 0.5	95.8 ± 1.1	93.5 ± 1	89.9 ± 1	87.8 ± 0.3	90.2 ± 0.1
	NMOR [%]	88.6 ± 4.9	89.3 ± 0	89 ± 0	88.8 ± 2.7	83.8 ± 1.2	77.2 ± 1.2	77.5 ± 0.4
	NDPA [%]	95.5 ± 0.4	93.4 ± 0.3	95.7 ± 1.1	95.3 ± 2	91.9 ± 0.2	91 ± 1.3	91.6 ± 0.3
	NDBA [%]	95.1 ± 0	97.8 ± 0.1	96.3 ± 0.4	95.9 ± 0	95.5 ± 0.4	95.1 ± 0.2	93.1 ± 0.7

Table S8: N-nitrosamine rejection and permeability of the virgin and chemical cleaned TFC-HR and ESPA2 membranes after being exposed to the NaOH solution or CA solution for 25 h at 30 ºC, and NaOH solution for 25 h at 30 ºC followed by CA solution for 25 h at 30 ºC.

Membrane	Parameter	CA	CA + NaOH	NaOH
TFC-HR	NDMA [%]	42.3 ± 1	42.6 ± 2.9	35.1 ± 1.5
	NMEA [%]	73.1 ± 2.7	72.3 ± 0.6	66.9 ± 4.6
	NPYR [%]	88.3 ± 2.4	87.1 ± 0.7	85.2 ± 0.1
	NDEA [%]	92.1 ± 1.3	92 ± 1	89.7 ± 2.5
	NPIP [%]	95.7 ± 0.4	96.3 ± 1.1	96.6 ± 0.7
	NMOR [%]	84.1 ± 2.7	86.8 ± 7.7	89.4 ± 3.8
	NDPA [%]	93 ± 2.9	93.7 ± 3.5	96.4 ± 0.1
	NDBA [%]	91.4 ± 5.1	91.7 ± 6.1	96.1 ± 0.1
ESPA2	NDMA [%]	35.4 ± 3.4	37.1 ± 3.1	17.7 ± 3
	NMEA [%]	68.4 ± 4.8	66.9 ± 1.3	50.4 ± 5.2
	NPYR [%]	83 ± 5.7	83.1 ± 2.6	68.6 ± 1.2
	NDEA [%]	90.2 ± 1.7	84 ± 8.6	77.1 ± 0.8
	NPIP [%]	95.8 ± 1.1	94.5 ± 0.9	89.9 ± 1
	NMOR [%]	89 ± 0	91.3 ± 0	83.8 ± 1.2
	NDPA [%]	95.7 ± 1.1	94.7 ± 0	91.9 ± 0.2
	NDBA [%]	96.3 ± 0.4	95.4 ± 0.2	95.5 ± 0.4

Table 1: Properties of the selected cleaning solutions.

Chemical	pH	Chemical formula/ingredients	Abbreviation
Sodium hydroxide	12.0	NaOH	NaOH
Chloridric acid	2.1	HCl	HCl
Citric acid	2.1	$C_6H_8O_7$	CA
Floclean® MC3	3.3	Organic acids and chelating agents containing tripolyphosphate (SDP)	MC3
Floclean® MC11	11	Detergent builders, pH buffer, chelating agents containing EDTA, SDP and sodium trisodium phosphate	MC11
PermaClean® PC98	10.7	Amphoteric surfactant and chelating agents containing EDTA	PC98

LIST OF FIGURES

cross flow velocity 40.2 cm/s, feed pH 8.0 ± 0.1, feed temperature 20.0 ± 0.1 °C). Values reported here are the average and ranges of duplicate results (Supplementary Material Table S8).

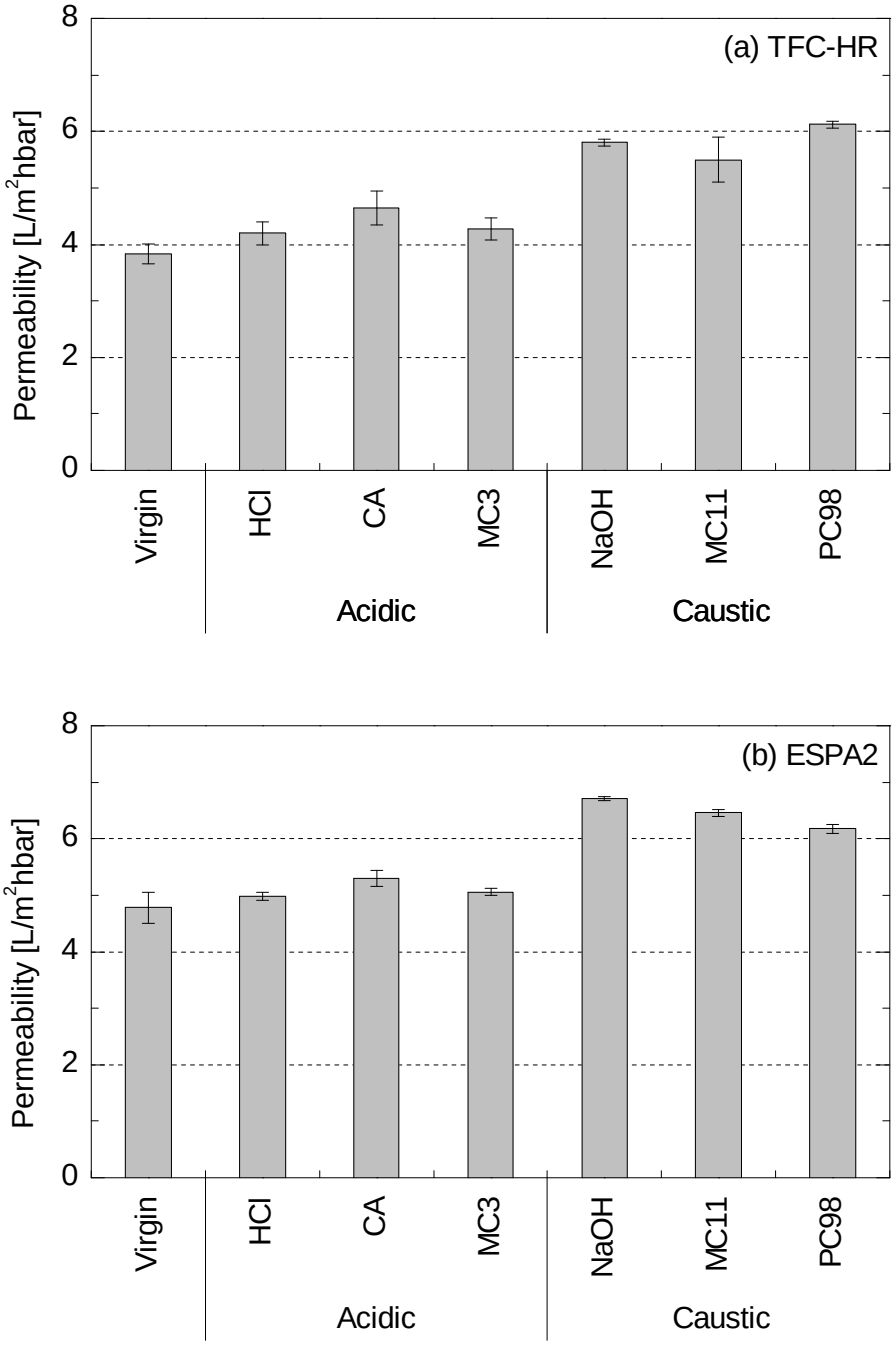
(a) TFC-HR
Permeability [L/m2hbar]
0
2
4
6
8
Virgin
HCl
CA
MC3
NaOH
MC11
PC98
Acidic
Caustic
(b) ESPA2
Permeability [L/m2hbar]
0
2
4
6
8
Virgin
HCl
CA
MC3
NaOH
MC11
PC98
Acidic
Caustic

Figure 1

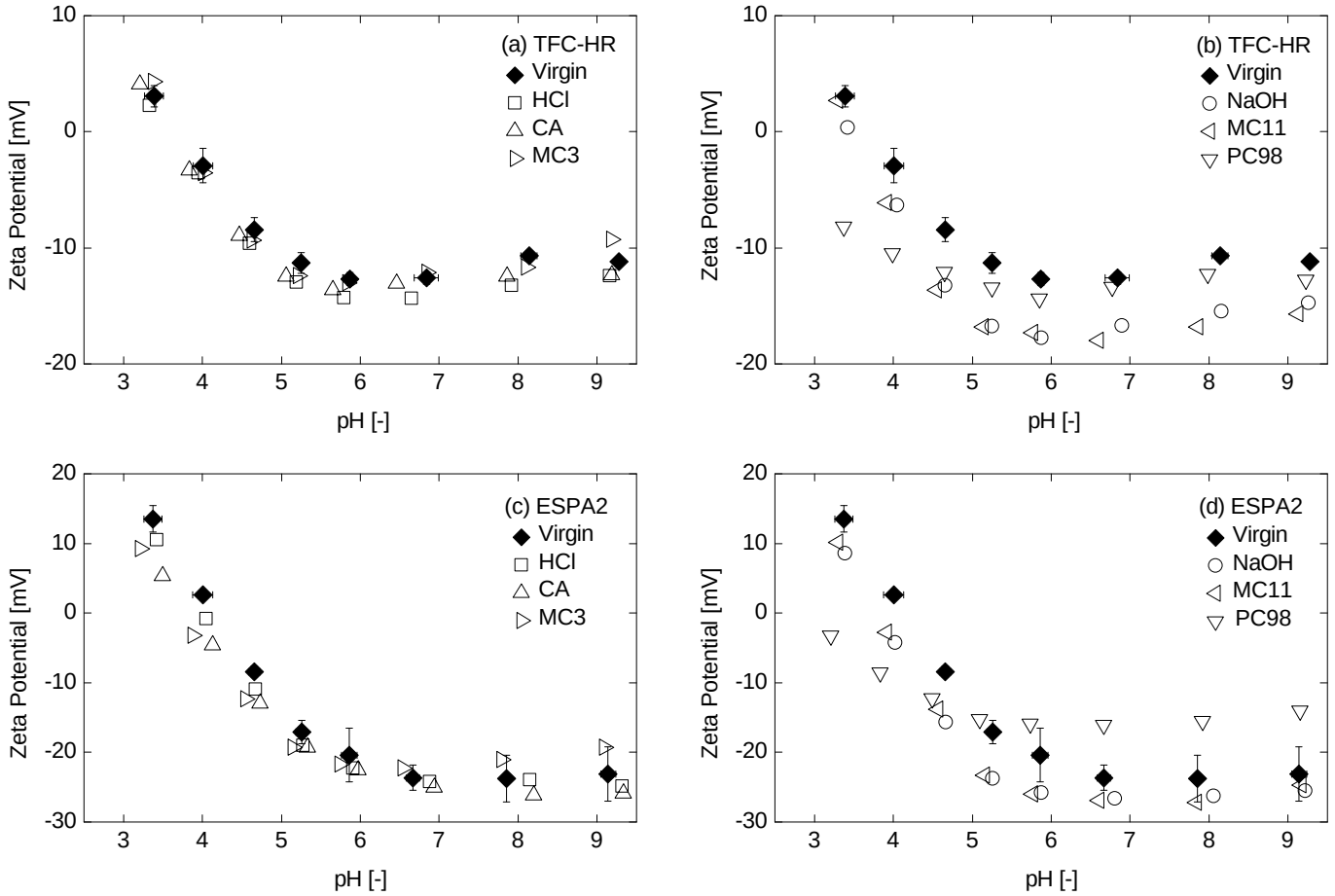
(a) TFC-HR
Virgin
HCl
CA
MC3
(b) TFC-HR
Virgin
NaOH
MC11
PC98
(c) ESPA2
Virgin
HCl
CA
MC3
(d) ESPA2
Virgin
NaOH
MC11
PC98
Zeta Potential [mV]
pH [-]

Figure 2

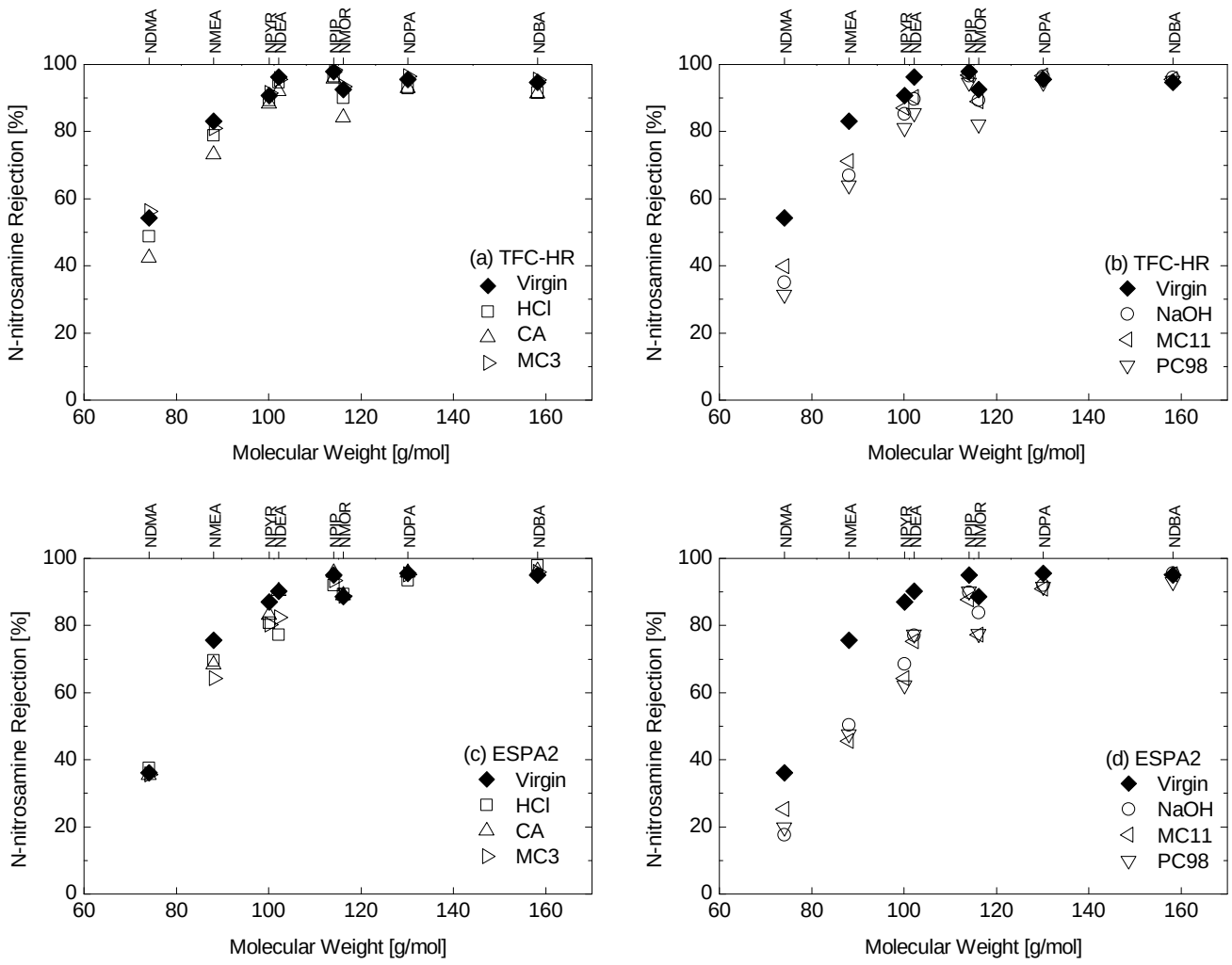
NDMA
NMEA
NPYR
NDEA
NPIP
NMOR
NDPA
NDBA
N-nitrosamine Rejection [%]
Molecular Weight [g/mol]
(a) TFC-HR
Virgin
HCl
CA
MC3
(b) TFC-HR
Virgin
NaOH
MC11
PC98
(c) ESPA2
Virgin
HCl
CA
MC3
(d) ESPA2
Virgin
NaOH
MC11
PC98

Figure 3

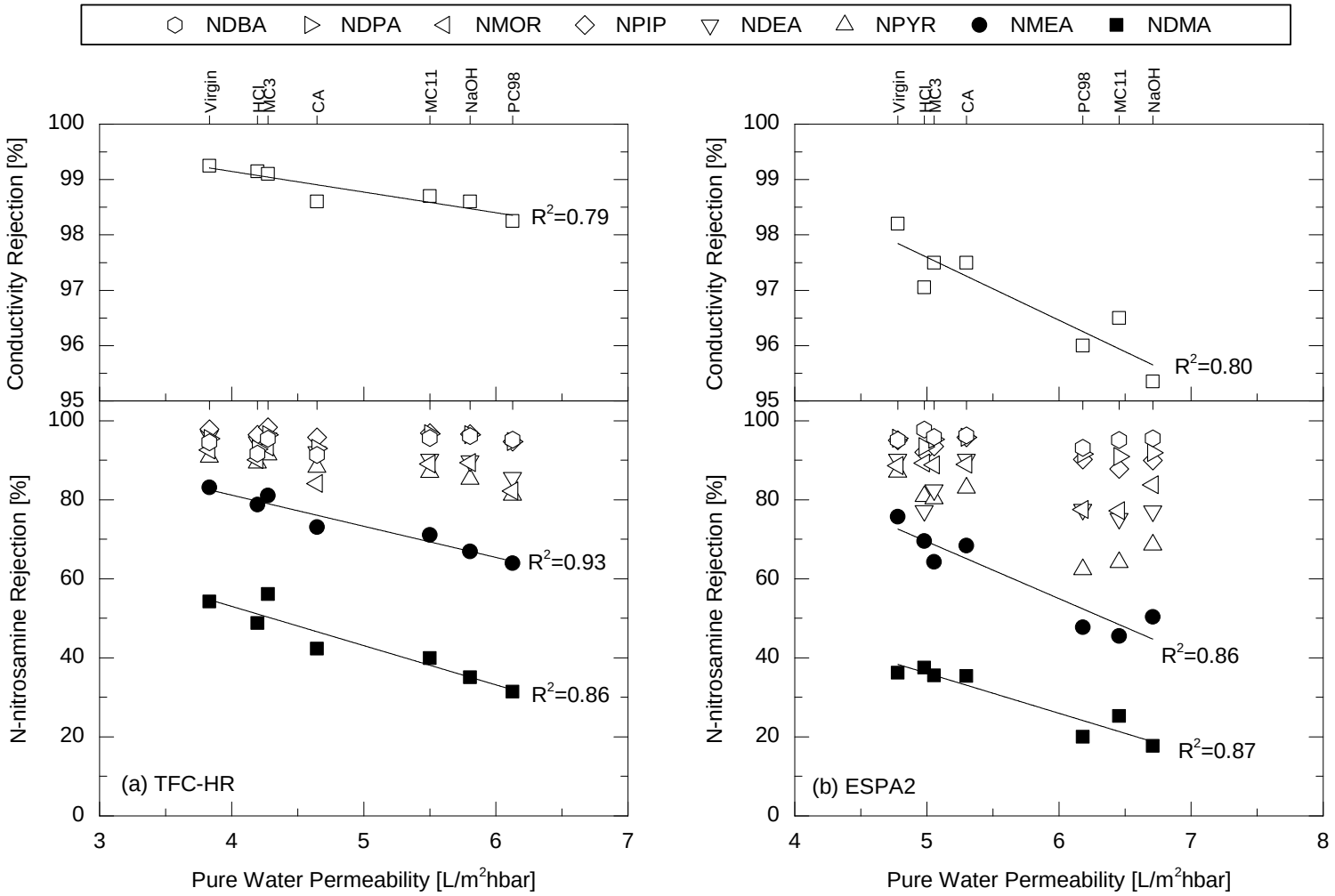
NDBA
NDPA
NMOR
NPIP
NDEA
NPYR
NMEA
NDMA
Virgin
HCl
MC3
CA
MC11
NaOH
PC98
Conductivity Rejection [%]
N-nitrosamine Rejection [%]
R2=0.79
R2=0.93
R2=0.86
(a) TFC-HR
Pure Water Permeability [L/m2hbar]
R2=0.80
R2=0.86
R2=0.87
(b) ESPA2

Figure 4

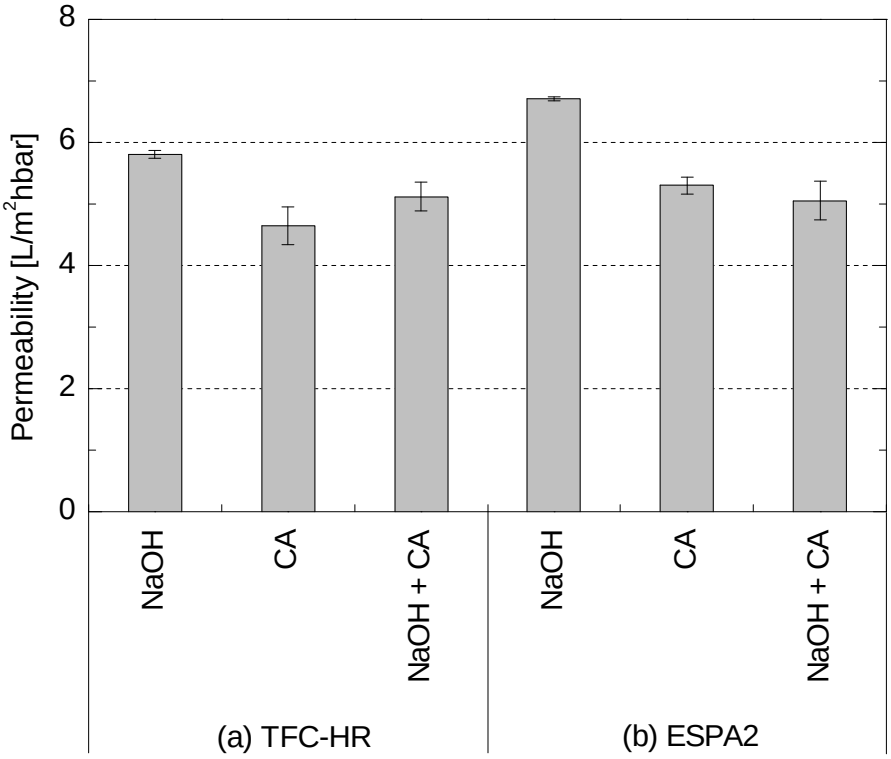
Permeability [L/m2hbar]
8
6
4
2
0
NaOH
CA
NaOH + CA
NaOH
CA
NaOH + CA
(a) TFC-HR
(b) ESPA2

Figure 5

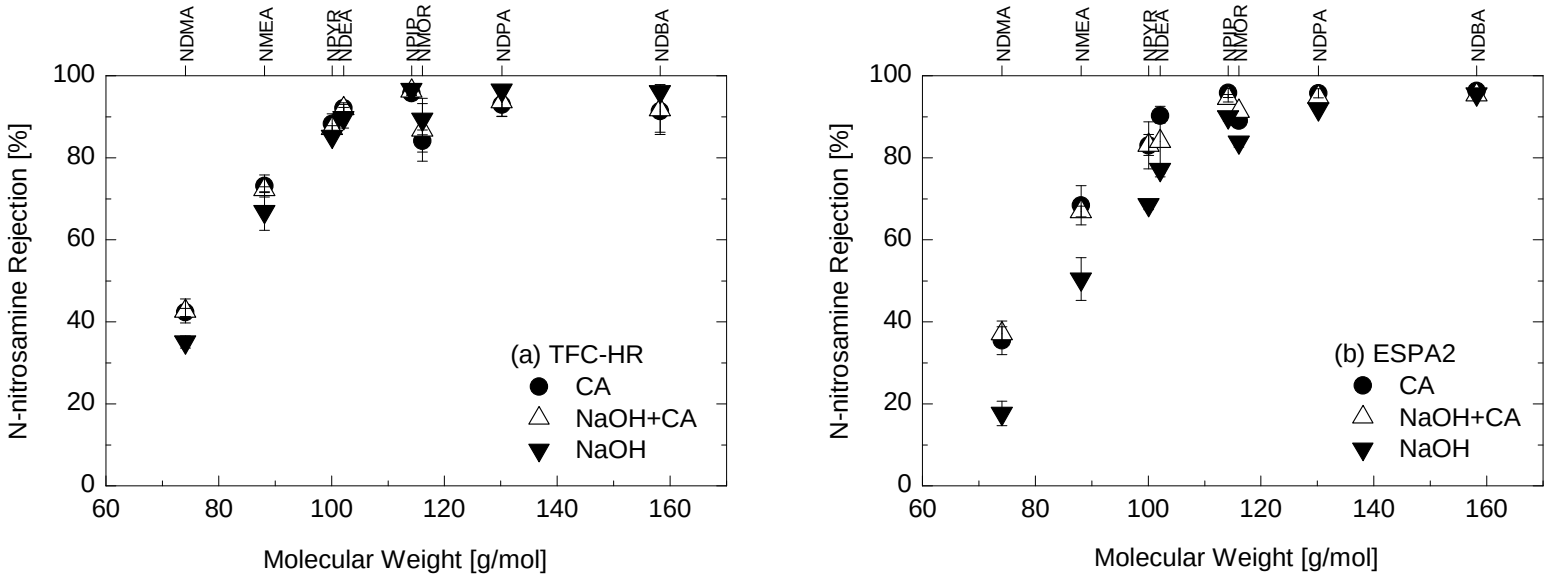
NDMA
NMEA
NPYR
NDEA
NPIP
NMOR
NDPA
NDBA
N-nitrosamine Rejection [%]
Molecular Weight [g/mol]
(a) TFC-HR
(b) ESPA2
CA
NaOH+CA
NaOH

Figure 6