



Recent developments in the preparation of improved nanofiltration membranes for extreme pH conditions

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ABSTRACT

Conventional commercially available nanofiltration (NF) membranes show limited stability at extreme pH conditions, whereas commercially available NF membranes that can cope with these conditions often show (too) low permeance or are relatively open. Since NF applications in many industrial sectors require pH stable NF membranes with a range of molecular weight cut-offs (MWCO), including tight NF membranes, substantial research and development efforts are being devoted to the research and development of these membranes. This review discusses these developments as reported in open literature, with a focus on the period between 2016 and 2021. Most developments relate to the use of interfacial polymerization to produce thin film composite membranes. Polyamine and polyurea membranes with good chemical stability for extreme pH conditions have been prepared. For polysulfonamide membranes indications for good chemical stability at low pH have been shown. These membrane types show improved stability compared to developed poly(aryl cyanurate), polyesteramide, poly(amide-sulfonamide), and polyamide membranes, which are more susceptible to hydrolysis and therefore less chemically stable at extreme pH. Furthermore, layer-by-layer coating using strong cation - and anion polyelectrolytes has led to new pH stable NF membranes. Despite the extension of the pH stable NF membrane portfolio, most of the developed membranes still do not meet the performance characteristics of the best commercially available NF membranes applicable for the common pH range between 2 and 11. Only a few layer-by-layer coated polyelectrolyte membranes combine high permeance, relatively low MWCO and stability at extreme pH. However, these membranes are not yet commercially available for full-scale applications requiring high pressure operation. Consequently, there is still room for research and development to further improve pH stable NF membranes.

1. Introduction

Nanofiltration is a pressure-driven membrane technology that is typically used for the separation of divalent ions and neutral components from monovalent ions in aqueous solutions [1]. Applications are typically found in the water purification [2], food [3], chemical [4], pulp and paper [5], and textile industries [6]. Most of these applications require membranes with a chemical stability in the pH range between 2 and 11. Several well-known commercially available membranes, such as NF-270 and NF-90 (DuPont - Filmtec), NE-40, NE-70, and NE-90 (Toray), Desal 5DL and Desal 5DK (SUEZ), NTR-7250 and NTR-7450 (Nitto Denko), and TS-80 and XN-45 (TriSep), fall in this category, some having a slightly more restricted pH stability range [7,8]. These membranes cover the typical nanofiltration molecular weight cut-off

(MWCO) range between 200 and 1000 Da. Several industrial applications, such as the recovery of alkaline cleaning solutions in the food industry [3], recovery and re-use of steeping lye for sustainable viscose fiber production [9], the recovery of acid solutions in mining applications [10], and the concentration of sulfuric acid solutions [10], require membranes with chemical stability outside of the pH = 2–11 range.

Nanofiltration membranes and processes have received a lot of attention from the scientific community, and numerous scientific papers regarding these topics have been published since the last decades of the previous century. Several research lines related to nanofiltration have also been reviewed extensively. These reviewed topics include:

- Membrane fouling [11]
- Modelling of nanofiltration [11,12]

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Nomenclature	
Symbols	
CF	Concentration factor(-)
IEC	Ion exchange capacity (meq·g ⁻¹)
IEP	Isoelectric point(-)
MW	Molecular weight (g·mol ⁻¹)
MWCO	Molecular weight cut-off (Da)
SD	Sulfonation degree(-)
Subscripts	
HDA	based on 1,6-hexanediamine crosslinking
PXDC	p-xylylene dichloride
x	Number of bi-layers coated on a support (ranges from 3 to 9)
XDA	based on <i>para</i> -xylenediamine crosslinking
y	Ion exchange capacity (IEC) of the membrane in meq·g ⁻¹
Abbreviations	
APTES	aminopropyl triethoxysilane
[AVIm]Cl	1-allyl-3-vinylimidazolium chloride
BADGE	bisphenol-A-diglycidyl ether
BCMBP	4,4'-bis(chloromethyl)-1,1'-biphenyl
BD	benzene-1,3-diol
BDSC	benzene-1,3-disulfonyl chloride
[BeMIm]Cl	1-benzyl-3-methylimidazolium chloride
BHPF	9,9-bis(4-hydroxyphenyl)fluorene
BN	boron nitride
BPTAB	3-bromopropyltrimethylammonium bromide
[BuMIm]Cl	1-butyl-3-methylimidazolium chloride
CC	cyanuric chloride
CIP	cleaning in place
COF	Covalent organic framework
DCBPS	4,4'-dichloro biphenyl sulfone
2,6-DFBN	2,6-difluorocyanophenyl
DETA	diethylene triamine
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
EDA	ethylene diamine
EPON	EPON™ Resin 1031, tetraphenolethane tetraglycidylether
GO	graphene oxide
HDA	1,6-hexanediamine
HDI	hexamethylene diisocyanate
Im	imidazolium
IP	interfacial polymerization
IPA	isopropyl alcohol
IPP	interfacial initiation of polymerization
LBL	layer-by-layer
MDI	diphenylmethane diisocyanate
Mel	melamine (2,4,6-triamino-1,3,5-triazine)
MPD	m-phenylene diamine
MPTES	3-mercaptopropyltriethoxysilane
MWCNT	multiwall carbon nanotube
NENP-1	nitrogen enriched nanoporous polytriazine
NF	nanofiltration
NMP	N-methyl-2-pyrrolidone
NTSC	naphthalene-1,3,6-trisulfonylchloride
o-SWNT	oxidized single-walled carbon nanotubes
PAA	poly(acrylate)
PAH	poly(allylamine hydrochloride)
PAH-Gu	poly(allylamine hydrochloride) functionalized with guanidine groups
PDADMAC	poly(diallyldimethylammoniumchloride)
PDI	1,4-phenylene diisocyanate
PE	polyethylene
PEG	polyethyleneglycol
PEHA	pentaethylene hexamine
PEI	polyethylenimine
PEM	polyelectrolyte multilayer
PES	polyethersulfone
Pip	piperazine
PPD	p-phenylenediamine
PPH-DMEA	N-(N,N-dimethylaminoethyl)-3,3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone
PXDC	p-xylylene dichloride
PSf	polysulfone
PScEN	poly(sulfone-co-ethernitrile)
PSS	poly(styrenesulfonate)
PTFE	poly(tetrafluoroethylene)
PVA	polyvinyl alcohol
PVDF	polyvinylidene fluoride
PVP	polyvinyl pyrrolidone
RO	reverse osmosis
SA	sulfanilamide
SDBS	sodium dodecyl benzenesulfonate
SDS	sodium dodecyl sulfate
SEM	scanning electron microscopy
SLS	sodium lauryl sulfonate
SMeIF	sulfonated melamine formaldehyde
SPEEK	sulfonated poly(ether ether ketone)
SPES	sulfonated polyethersulfone
SPSt	sulfonated polystyrene
TBMB	1,3,5- tris(bromomethyl)-benzene
TDI	toluene diisocyanate
TEPA	tetraethylene pentamine
TFC	thin film composite
TFPG	1,3,5-triformylphloroglucinol
TGIC	triglycidyl isocyanurate
THPE	1,1,1-tris(4-hydroxyphenyl)ethane
TMC	trimesoyl chloride
TOC	total organic carbon
Tris	Tris(hydroxymethyl)aminomethane
TCSP	2,4,6-(trichlorosulfonyl)phenol
UF	ultrafiltration
[VEIm]Br	1-vinyl-3-ethylimidazolium bromide
XDA	<i>para</i> -xylenediamine

- Progress and prospects in nanofiltration [13] and advanced materials for nanofiltration membranes [14]
- Drawbacks of nanofiltration [15]
- Nanofiltration fabrication and modification [16,17]
- Organic solvent nanofiltration [18]
- Cleaning of nanofiltration membranes used for water treatment [19]
- Effects of salt and pH on nanofiltration membrane performance [20]
- Nanofiltration for challenging environments [21]

These reviews discuss a broad number of topics related to nanofiltration membranes or solvent and solute transport during nanofiltration processes. However, only the reviews related to drawbacks of nanofiltration [15], nanofiltration membrane cleaning [19], and the effect of pH on nanofiltration membrane performance [20] are related to the continuous operation at harsh pH conditions to a limited extent. Luo and Wan [20] have reviewed the effect of pH variation on nanofiltration membrane performance during relatively short exposure times and

generally for a pH range between 2 and 11. Van der Bruggen et al. [15] and Liu et al. [19] both discuss the chemical resistance of nanofiltration during chemical cleaning using acid or alkaline solutions. However, even though membrane cleaning can be performed at a pH outside the conventional pH = 2–11 range, cleaning times are usually very short and cleaning frequencies are reduced to a minimum required to maximize the membrane lifetime. Therefore, for membranes used for continuous operation at extreme pH conditions, such as for several applications mentioned earlier, the pH stability is even more important. Han et al. [21] discussed nanofiltration membrane development for challenging environments but focused on organic solvent resistant nanofiltration, chlorine resistance and thermal stability. The development of membranes for extreme pH conditions was discussed only briefly, mentioning the recent developments of only a few membranes. Therefore, to the best of my knowledge, none of the publications reviewing nanofiltration topics extensively describe and review the development of nanofiltration membranes for applications where stability at extreme pH conditions outside of the conventional pH = 2–11 range is required during long-term continuous operation.

The common commercially available NF membranes, often composed of a polyamide top layer (see Table 1) which is largely responsible for the separation characteristics of the NF membrane, have limited chemical stability at extreme pH conditions (outside of the pH = 2 – 11 range). This limited stability is ascribed to the hydrolysis of the amide bonds present in the polyamide top layer [22,23]. Nevertheless, despite the chemical stability restrictions set by the membrane suppliers, several research studies have investigated the possibility to stretch the pH range of these commercially available membranes or have used these membranes as comparison for the pH stability of newly developed membranes based on new chemistries.

Only for a limited amount of nanofiltration membranes a broader applicable pH range (outside pH = 2 – 11) is claimed by the membrane suppliers. These membranes include MPF-34 (Koch), NP030 (Nadir), A-3012, A-3014 and B-4022 (all AMS Technologies) [24], and NF09081 (SolSep) [9]. For most of these membranes the composition of the membrane has not been provided and only typical membrane characteristics such as the permeance, molecular weight cut-off (MWCO), salt retention, and the pH stability range have been revealed (see Table 2). Compared to the commonly used nanofiltration membranes such as NF-270 and Desal 5DK, these more chemically stable nanofiltration membranes show a higher MWCO and/or a relatively low water permeance. Since a higher membrane permeance in combination with a lower or unchanged MWCO would result in a lower required membrane surface area and therefore usually lower investment costs, there is a clear incentive for the development of pH stable nanofiltration membranes with higher permeance in combination with a lower or unchanged

MWCO. Several research groups have investigated the possibility to develop improved pH stable NF membranes. These groups have used different chemistries and techniques to prepare the newly developed membranes. This review will focus on summarizing and discussing the developments that have taken place to generate better chemically stable NF membranes for processing of solutions with extreme pH (focusing on the time frame between 2016 and 2021).

Although the amount of relevant publications in open literature is still relatively small compared to the total number of publications in the area of nanofiltration membranes and technology, the number of manuscripts published each year is growing (see Fig. 1 (left)), especially since 2019. It should be noted that the number presented for 2021 refers to publications that were available on-line before August 1, 2021. The geographic spread of activities related to the development of nanofiltration membranes for harsh conditions is illustrated in Fig. 1 (right). Most active countries on this topic can be found in Asia and Europe, with China leading the list of relevant publications, followed by the Netherlands, Germany, Belgium and Iran (see Fig. 1 (right)). It should be noted that a single publication can be ascribed to multiple countries when the publication is written by authors employed by universities or institutes from different countries.

In the next sections, for a selected number of commercially available membranes with restricted pH stability, the results of experiments using solutions having a pH outside of the normal pH range between 2 and 11 will be discussed. Special attention will be paid to the chemical stability of these membranes for these challenging conditions. In subsequent sections similar studies with commercially available pH stable membranes will be summarized, and especially recent developments (focusing on the time frame between 2016 and 2021) to prepare pH stable membranes will be reviewed and discussed. The review and discussion related to the recently developed nanofiltration membranes, often based on new chemistries, is divided into sections based on the preparation method used. For each of the preparation methods subsections will describe the materials used to prepare the separation layer of the newly developed membranes (such as polyamines, polyurea etc.). This approach is graphically shown in Fig. 2. Within these subsections a division between different monomers used to prepare the separation layer material is made. The effect of the use of different monomers on the chemical stability and the separation performance for several separation layer materials is discussed in a separate sub-section. The progress made in developing new and improved pH stable NF membranes based on the results for all the separation layer materials and preparation methods is discussed in a final section, where all membrane materials and preparation methods are compared, prior to the conclusions.

Table 1

Membrane characteristics as provided by the suppliers (unless specified differently) for several commercially available NF membranes with a chemical stability within the pH = 2 – 11 range.

Membrane name	Supplier	Material	Water Permeance (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	MWCO (Da)	Claimed pH stability range
Desal 5DL	SUEZ	Polyamide TFC	5.7 [25]	400	2 – 11
Desal 5DK	SUEZ	Polypiperazine amide [26]	5.5 4.2 [7]	200	2 – 11
NE-40	Toray	Piperazine based polyamide [8]	8.3 ^a		2 – 11
NE-70	Toray	Piperazine based polyamide [8]	6.0 ^a		2 – 11
NE-90	Toray	m-phenylene diamine-based polyamide [8]	4.2 ^a		2 – 11
NF-270	DuPont – Filmtec	Piperazine based semi-aromatic polyamide [27,28]	11 ^b – 13 ^f	200 – 400	2 – 11
NF-90	DuPont – Filmtec	Fully aromatic polyamide [26,28]	6.4 ^c 9.6 [7]	200 – 400	2 – 11
XN-45	TriSep	Polypiperazine-amide	5 6.7 [7]	≈ 500	4 – 11

^a for a NaCl solution instead of water at T = 25 °C and P = 5 bar (for NE-40 and NE-70) or P = 7.5 bar (for NE-90)

^b for a MgSO₄ solution instead of demineralized water

^c for a CaCl₂ solution instead of demineralized water

Table 2
Membrane characteristics as provided by the suppliers (unless specified differently) for commercially available pH resistant NF membranes.

Membrane name	Supplier	Material	Water Permeance (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	MWCO (Da)	Claimed pH stability range
MPF-34	Koch	Proprietary [24]	1.5	200	0 – 14
NP030	Microdyn Nadir	Polyethersulfone [24]	1.7 4.4 [29]	400 [30] 520 [31]	0 – 14
NanoPro A-3012	AMS Technologies	Proprietary	2.1 ^a	≈ 200	0 – 12
NanoPro A-3014	AMS Technologies	Proprietary [24]	2.4 ^a	≈ 400	0 – 12
B-4022	AMS Technologies	Melamine-polyamine [24]	2.2 ^a	≈ 200	3 – 14
NF09081	SolSep	Probably sulfonated polyether ether ketone (SPEEK) [9]	1 – 2 [9]		Up to 14 [9]
Inopor nano	Inopor	Ceramic [24]	3.4 [32]	450	0 – 14
HydraCoRe 70pHT	Hydranautics	Sulfonated polyethersulfone	3.1 [33]	720 [33]	1 – 13.5 [33]
Desal KH (Duracid) [34]	SUEZ	Polypiperazine amide [26] Sulfonamide [35]	2.0 [26] (8.0 [24])	150 – 200 (400 [24])	0 – 9

^a at T = 30 °C and P = 40 bar.

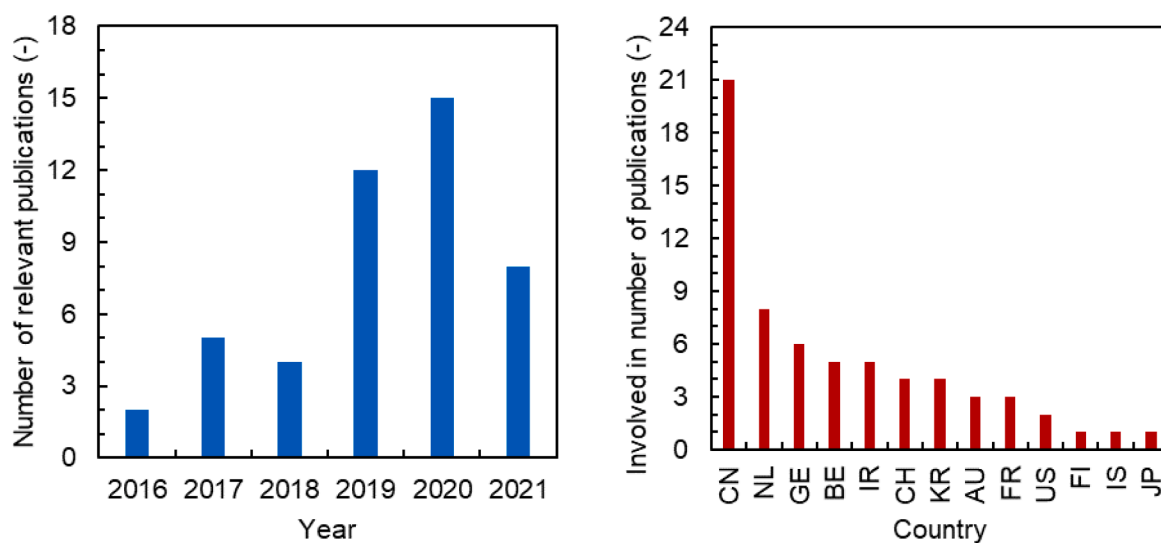


Fig. 1. The number of publications related to the development of new nanofiltration membranes for extreme pH conditions (outside the pH = 2 – 11 range) since 2016 (left) and the location (country) of the institute or company where authors of these publications are employed to indicate geographic activity on the topic (right). On the x-axis countries are abbreviated as CN (China), NL (The Netherlands), GE (Germany), BE (Belgium), IR (Iran), CH (Switzerland), KR (Republic of Korea), AU (Australia), FR (France), US (United States of America), FI (Finland), IS (Israel), JP (Japan).

2. pH stability of commercially available membranes outside of their specified pH range

In this section the chemical stability of a selection of commonly applied nanofiltration membranes outside of their pH stability range is reviewed and discussed. The characteristics of several of these membranes are listed in Table 1. Furthermore, in open literature a lot of contributions deal with the stability of (these) membranes in sulfuric acid (H₂SO₄) solutions. Some of these contributions only mention the pH of these solutions, whereas other contributions mention the sulfuric acid concentration or the weight fraction of the solution. For comparison sake, Fig. 3 shows the relation between the pH, the sulfuric acid concentration and the density of the solution. It should be noted that these relations apply for a pure sulfuric acid solution, which means that if substantial amounts of other compounds (e.g. sulfate salts) are present in the solution these relations (e.g. between H₂SO₄ concentration and density and between H₂SO₄ concentration and pH) can be different. These relations have furthermore been used to estimate the pH for sulfuric acid solutions for which this has not been mentioned by the authors of the reviewed publication.

2.1. Commercial polyamide nanofiltration membranes based on piperazine and trimesoylchloride

Immersion of NF-270, a piperazine (Pip) – trimesoylchloride (TMC) based NF membrane [16] with a claimed chemical stability in the pH = 3 – 10 range [7] or pH = 2 – 11 range [24], in a 15 %w H₂SO₄ solution (pH < 0) for four weeks resulted in a strongly increased membrane permeance and decreased MgSO₄ retention in intermittent membrane characterization tests at P = 10 bar and T = 25 °C [27]. For the first two weeks gradual changes in membrane performance were observed, while stronger changes occurred after two weeks of exposure. NF-270 was also not stable during nanofiltration of an 8 %w H₂SO₄ solution (pH ≈ 0.1) containing 25 g·L⁻¹ CuSO₄ at T = 40 °C as clearly indicated by a strong reduction in copper retention [37]. During nanofiltration of similar solutions, albeit with different H₂SO₄ concentrations (between 2 %w – 8 % w), at T = 30 °C for only limited time (2 h) NF-270 showed proper chemical stability [38]. Immersion of NF-270 in a 20 %w H₂SO₄ solution at T = 90 °C resulted in a very strong increase in pure water permeance and virtually absent Na₂SO₄ retention, clearly showing the instability of NF-270 for these conditions [39]. ATR-IR results confirmed chemical changes of the top layer. NF-270 showed very good chemical stability

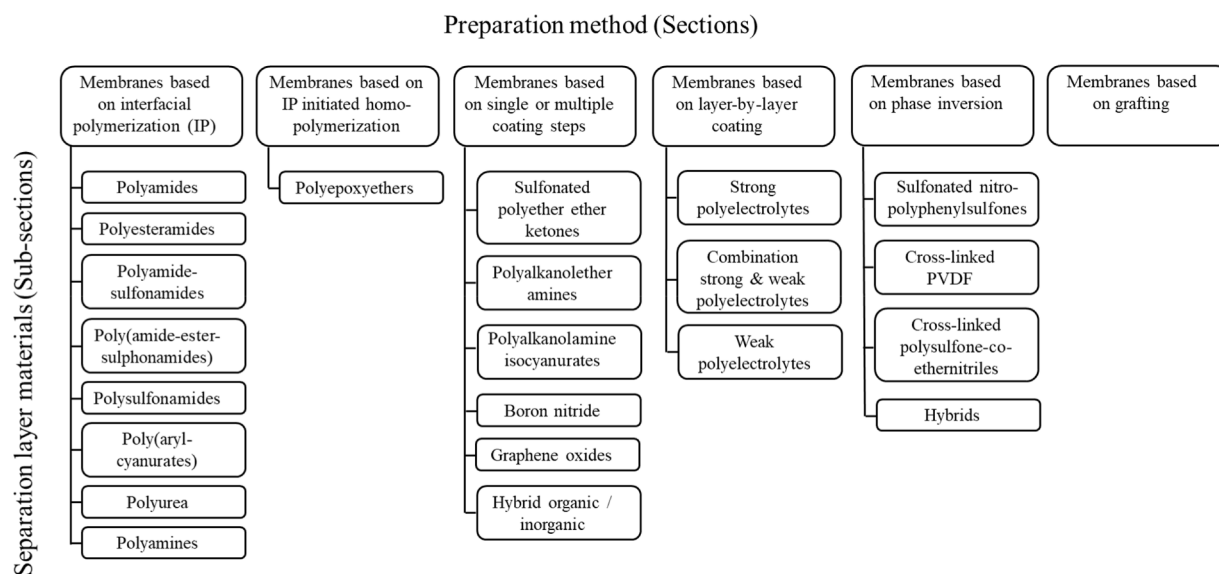


Fig. 2. Schematic overview of the lay-out of the sections related to the development of new pH stable membranes.

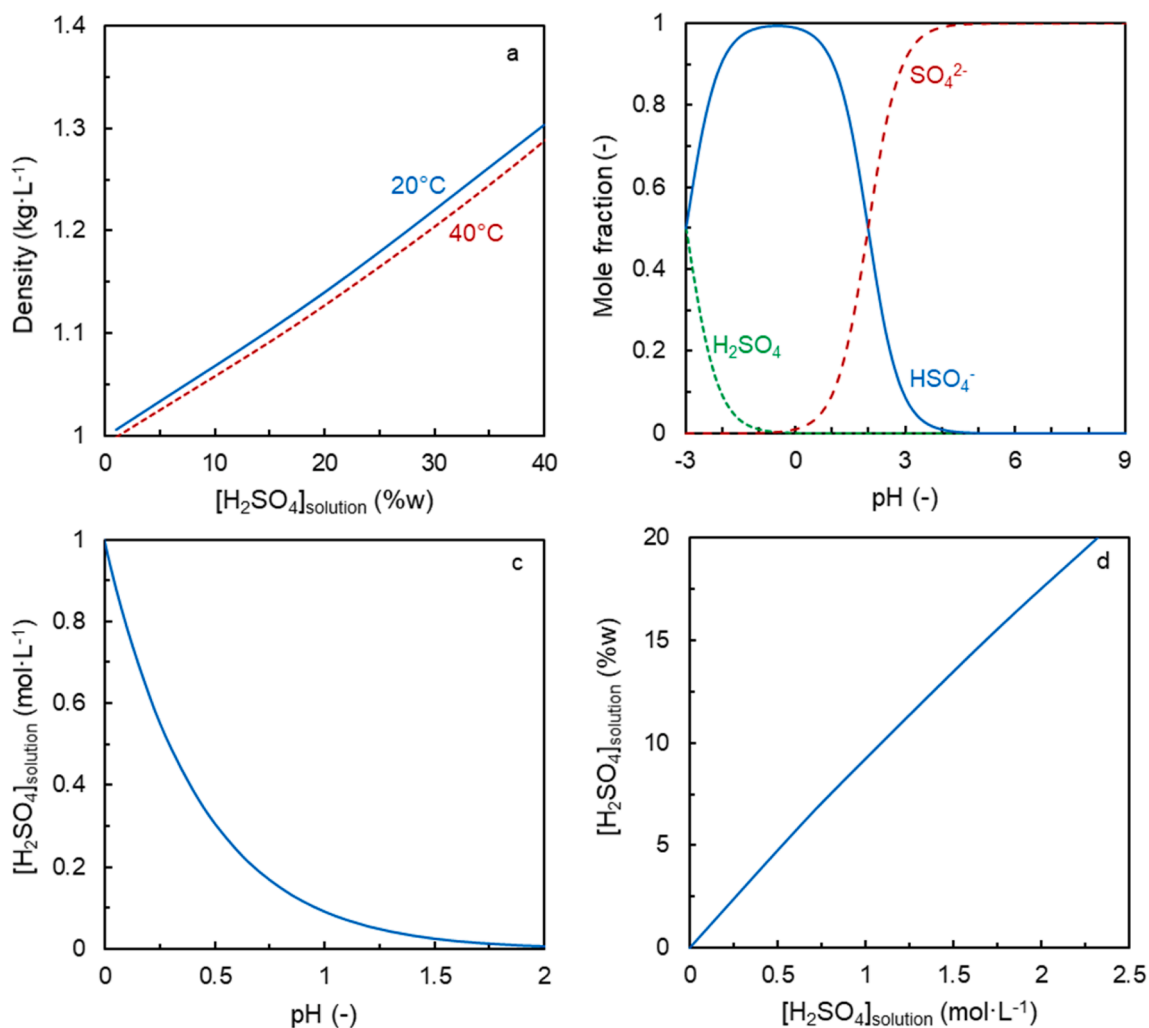


Fig. 3. The relation between sulfuric acid weight fraction and density at $T = 20^\circ\text{C}$ and $T = 40^\circ\text{C}$ [36] (a), pH and mole fraction for H_2SO_4 , HSO_4^- and SO_4^{2-} using $\text{p}K_{a,1} = -3$ and $\text{p}K_{a,2} = 1.97$ [36] (b), pH and sulfuric acid solution concentration (c), and sulfuric acid concentration and weight fraction at $T = 20^\circ\text{C}$ (d) for a pure sulfuric acid solution.

upon exposure to an acid solution with pH = 1.5 for six weeks, with stable phosphorous retention and stable flux based on characterization tests prior to and after exposure to the acid solution [40]. These studies all confirm the relatively poor stability of NF-270 under very acidic conditions [27], especially at high temperature, in line with the applicable pH range provided by the manufacturer. However, exposure to acidic conditions outside of the specified pH range for a limited time appears to be possible.

NF-270 showed a strong initial increase followed by a more gradual increase in permeance and a strong initial reduction followed by a more gradual reduction in glucose and MgSO₄ retention during 125 h exposure to a solution (pH = 11.5) based on P3-Ultrasil 112 at different temperatures (between T = 40 °C and T = 70 °C) [41]. This solution contains NaOH and alkyl benzyl sulfonate. The changes in membrane performance generated during 20 h exposure at T = 70 °C could be, at least partly, reversed after a recovery time of almost 145 h. After short term (1.5 h) exposure to a 0.01 mol·L⁻¹ NaOH solution (pH = 12) at ambient conditions, NF-270 showed higher MWCO and flux, and lower NaCl retention than after exposure to neutral conditions [42]. However, changes in performance were reversible, indicating that the performance of the membrane had not changed and NF-270 was chemically stable at these conditions for the limited (1.5 h) exposure time. NF-270 was also able to cope with short term operation at pH = 12.3 [43] and T = 30 °C, as indicated by its high sulfate retention of 98%, and could also cope with frequent short term pH excursions to values of pH > 11 during nanofiltration of a salt plant mother liquor saturated in both Na₂SO₄ and NaCl [43]. For exposure to a strong alkaline (pH = 13.5) solution for 6 weeks, characterization tests showed that the phosphorous retention for NF-270 reduced from 96.5% to 92.1%, even though the flux remained relatively stable [40]. Consequently, NF-270 is chemically unstable when exposed to these high pH conditions, especially in combination with a high temperature, for a longer time frame but can cope with short term exposure to conditions outside its specified alkaline pH limit.

Desal 5DL and Desal 5DK are Pip-TMC based nanofiltration membranes as well [16] with a claimed pH stability range between pH = 2 – 11 [7]. Like NF-270, Desal 5DK was also not stable during 2 months of continuous nanofiltration of an 8 %w H₂SO₄ solution (pH ≈ 0.1) containing 25 g·L⁻¹ CuSO₄ at T = 40 °C [37]. Nanofiltration of similar solutions, albeit with varied H₂SO₄ concentration (between 2 %w – 8 %w), for a short time (2 h) at P = 20 bar and T = 30 °C did not affect the membrane performance [38]. Furthermore, Desal 5DK appeared to be able to cope with short term nanofiltration in diafiltration mode of a hydrolysate with pH = 1 [26] and could cope with short term nanofiltration at pH = 12.3 [43], as indicated by its high sulfate retention of 98%. On the other hand, it was not able to cope with frequent short term pH excursions to values of pH > 11 during nanofiltration of a salt plant mother liquor saturated in both Na₂SO₄ and NaCl, where each excursion led to a stronger reduction in retention, and Desal DK showed worse stability than NF-270 for these pH excursions [43].

For nanofiltration of a salt plant mother liquor saturated in both Na₂SO₄ and NaCl, Desal 5DL showed relatively poor stability at pH = 12.3 as indicated by its low sulfate retention of 62 – 78 % [43] at a concentration factor of 1, T = 32 °C and P = 54 bar. Like NF-270, Desal 5DL showed a strong initial increase followed by a more gradual increase in permeance and a strong initial reduction followed by a more gradual reduction in glucose and MgSO₄ retention during 125 h exposure to a solution (pH = 11.5) based on P3-Ultrasil 112 at different temperatures (between 40 °C and T = 70 °C) [41]. Exposure to the solution with pH = 11.5 resulted in the detachment of the coating layers on Desal 5DL, changing its top layer color from yellow to white [41]. However, minor changes in chemical structure based on IR measurements were only reported after exposure of the membrane to T = 70 °C. Changes in permeance and retentions could mainly be attributed to conformational changes of the polymeric top layer and the effects appeared to be more substantial at higher temperature [41]. The changes in membrane performance generated during 20 h exposure at T

= 70 °C could, at least partly, be reversed after a recovery time of almost 145 h. For XN-45, another Pip-TMC based polyamide membrane [16] with a claimed pH stability range of pH = 4 – 11 [7], changes at T = 70 °C were less pronounced.

NE-40 and NE-70 (both Toray and formerly CSM) were exposed to a 15 %w/w H₂SO₄ solution (pH ≈ -0.2) during membrane immersion tests for 30 days [44]. Intermittent characterization tests of these membranes showed a steady water flux increase and MgSO₄ retention decrease, clearly showing the chemical instability of these membranes for this low pH solution. These results are in line with the results from a concise chemical stability evaluation of these membranes in a 15 %w/v H₂SO₄ solution (pH ≈ -0.2) at T = 25 °C for 63 days [8].

The results for these Pip – TMC based commercially available polyamide membranes clearly confirm the instability of the membranes outside of the pH = 2 – 11 range, confirming the membrane supplier claims. However, for several of these membranes short term excursions outside of this range hardly seem to affect the membrane characteristics or affect these only to a limited extent, at least for operation at or close to room temperature.

2.2. Commercial polyamide nanofiltration membranes based on *m*-phenylene diamine and trimesoylchloride

NF-90 (DuPont – Filmtec), a *m*-phenylene diamine (MPD) – TMC based membrane [28] with a claimed chemical stability in the range of pH = 2 – 11 showed very good stability for exposure to a strong acid (pH = 1.5) for 6 weeks [40] and is stable at this condition for this relatively limited time, like the Pip-TMC based NF-270 [28]. For nanofiltration at high pH (13.5), NF-90 showed a gradually decreasing phosphorous retention during intermittent characterization tests, with NF-90 being more stable than NF-270 under pH = 13.5 conditions [40]. The flux for NF-90 membranes remained relatively stable and higher than at pH = 1.5. Immersion of NF-90 in NaOH solutions with a pH = 13.0, pH = 13.5 or pH = 14.0 confirmed that this membrane is not fully stable at pH = 13.5 and higher [22]. An increase in the water permeance and MWCO, and a reduction in the NaCl retention were observed for 28 days immersion of NF-90 in NaOH solutions with a pH ≥ 13.5, as evidenced from intermittent membrane characterization experiments. Especially at pH = 14.0, the deterioration rate of the top layer was high with complete loss of performance after 7 days. NF-90 appeared to be stable for 28 days exposure to the NaOH solution with pH = 13.0 as evidenced by stable water permeance and NaCl retention during this time frame [22].

NE-90 (Toray), another MPD – TMC based membrane with a claimed chemical stability in the range of pH = 2 – 11, showed a permeance increase from 5.4 to 8.5 L·m⁻²·h⁻¹·bar⁻¹ (as determined from intermittent characterization experiments at P = 5 bar) during the first 10 days of exposure to a 15 %w/w H₂SO₄ solution (pH ≈ -0.2), followed by stable permeance during the next 20 days [44]. MgSO₄ retention changed from 96% to 85%, especially after 10 days. This membrane is therefore considered to be unstable in this low pH solution, but less unstable than its Pip – TMC based equivalents NE-40 and NE-70 (see Section 2.1), which have lower NaCl retention and are probably more open. The observation that NE-90 is more stable than NE-40 and NE-70 is in line with other results [8], where strong performance changes of NE-40 and NE-70 during characterization experiments were observed after immersion of the NE-40 and NE-70 membranes in 15 %w/v H₂SO₄ solution for 63 days, whereas NE-90 showed stable permeance and NaCl and MgSO₄ retentions. The reason why the Pip – TMC NE-40 and NE-70 membranes were less acid stable than the MPD – TMC based NE-90 was explained based on Gibbs free energy differences for the hydrolysis reaction [8]. Furthermore, it was suggested that the observed permeance and retention changes upon the 63 days immersion of NE-90 in an H₂SO₄ solution with a pH = 1 may have resulted from twisted hydrogen bonds between the hydrogen from the amine part of an amide group and the oxygen from another amide group within the membrane, leading to an increased permeance and reduced retention during characterization of

the membranes that had been exposed to the acid solution [45]. For a more concentrated H_2SO_4 solution with $\text{pH} = 0$, protonation of the oxygen or nitrogen within the amide group may have resulted in a substantially higher fraction of twisted hydrogen bonds, leading to membrane compaction as concluded from the observed lower permeance of the membrane exposed to the acid solution when pressurized during the characterization tests. In this case lower NaCl and MgSO_4 retentions were reported for the acid exposed NE-90 as well. Stability results for NE-90 in H_2SO_4 solutions in this study [45] seem to contradict with the good stability results for NE-90 reported in earlier work [8], and explanations for this contradiction have not been provided nor are evident. Immersion of NE-90 in a HCl, HI or HBr solution of $\text{pH} = 0$ may result in broken hydrogen bonds and a collapsing polymer network according to the authors [45].

Based on the results from the stability tests there are strong indications that the commercially available MPD – TMC based polyamide NF membranes are more stable at extreme pH conditions than the Pip – TMC based NF membranes, in line with conclusions reported in [16]. However, both membrane types lack sufficient stability for long term operation outside the $\text{pH} = 2 - 11$ range, in line with membrane manufacturer claims.

3. Evaluation of commercially available membranes with claimed pH stability

In this section a selected number of studies related to membranes with claimed chemical stability outside of the $\text{pH} = 2 - 11$ range are reviewed and briefly discussed. An overview of the characteristics of several of these membranes are listed in Table 2.

MPT-34, the tubular equivalent of MPF-34 (which is the flat sheet equivalent of MPS-34) was shown to be suitable for acid (HNO_3) and alkaline (NaOH) cleaning solution recovery in the food industry [3]. Short term nanofiltration tests with MPF-34 using feed solutions containing Ni^{2+} , Co^{2+} and sulfuric acid at different pH (between 0 and 4) showed proper Ni^{2+} and Co^{2+} retention for MPF-34 [46]. However, surprisingly, for exposure of MPF-34 to either a pressure oxidation acid goldmining effluent at a $\text{pH} = 1.46$ or to a $0.15 \text{ mol}\cdot\text{L}^{-1} \text{H}_2\text{SO}_4$ solution at room temperature for 8 weeks, intermittent characterization tests showed that the membrane was not completely stable. A gradual increase in water permeance from 2.9 to $8.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and a pore radius increase from 0.42 nm to 0.61 nm in 8 days were observed after immersion of MPF-34 in the pressure oxidation acid goldmining effluent. Immersion in the $0.15 \text{ mol}\cdot\text{L}^{-1} \text{H}_2\text{SO}_4$ solution ($\text{pH} \approx 0.8$)

resulted in even stronger membrane property changes [47]. On the other hand, immersion of MPF-34 in a 20 \%w/v HCl or a 20 \%w/v H_2SO_4 solution for 1 year resulted in a relatively small PEG ($\text{MW} = 200 \text{ g}\cdot\text{mol}^{-1}$) retention reduction from 93% to 87% and 85% , respectively. Furthermore, based on other intermittent characterization results, the MgSO_4 retention only reduced from 98% to 94% and 93% after 1 year immersion in the 20 \%w/v HCl and 20 \%w/v H_2SO_4 solutions, respectively, at an increase in permeance from $2.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ to $3.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and $3.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, respectively. These results show that MPF-34 is quite stable under these extreme conditions for a relatively long exposure time. Under alkaline conditions MPF-34 was practically stable during immersion in 20 \%w/v for 1 year with a minor reduction in MgSO_4 retention from 98% to 92% and an almost negligible permeance increase from $2.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ to $2.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. Furthermore, MPF-34 was found to be chemically stable during nanofiltration of a salt plant mother liquor saturated in both Na_2SO_4 and NaCl with a $\text{pH} = 12.3$ at $T = 30 \text{ }^\circ\text{C}$ and $P = 35 \text{ bar}$ [43], at least during the limited time of operation. The stability under alkaline conditions was confirmed by nanofiltration of an aqueous solution containing $260 \text{ g}\cdot\text{L}^{-1}$ NaCl and $70 \text{ g}\cdot\text{L}^{-1}$ Na_2SO_4 at $\text{pH} = 12$ for 450 h (following nanofiltration of the same solution at $\text{pH} = 8.5$ for 250 h and $\text{pH} = 9.8$ for 505 h) as indicated by an unchanged pure water permeance (see Fig. 4 (right)) prior to and following nanofiltration of the salt solution. However, despite the relatively high pressure ($P = 30 \text{ bar}$) used, the flux for MPF-34 was low, but comparable to the flux obtained at $\text{pH} = 8.5$ (see Fig. 4 (left)). Furthermore, MPF-34 was not stable during the processing of a 25 \%w NH_4OH solution containing organic acid (EDTA) and amine (EDA) contaminants at low concentration ($< 4 \text{ g}\cdot\text{kg}^{-1}$ in total), as indicated by the gradual increase in flux with time (see Fig. 5).

NP030 (Nadir), a sulfonated polyether sulfone (sPES) based membrane, is chemically stable in alkaline solutions with NaOH concentrations as high as (at least) $5 \text{ mol}\cdot\text{L}^{-1}$ [48]. A disadvantage of this membrane is the relatively low operating pressure that can be applied, limiting its use to low osmotic pressure feedstocks only. This disadvantage is illustrated in [26], where zero flux was reported for NP030 after pre-compacting the membrane with pure water at $P = 36 \text{ bar}$ and $T = 25 \text{ }^\circ\text{C}$. The pre-compaction was performed for the intended detoxification of a highly acidic hemicellulosic hydrolysate ($\text{pH} = 1$) with an osmotic pressure of 28 bar [26]. The sensitivity of NP030 to high pressure was confirmed for nanofiltration of a salt solution containing $260 \text{ g}\cdot\text{L}^{-1}$ NaCl and $70 \text{ g}\cdot\text{L}^{-1}$ Na_2SO_4 . This solution also needs to be processed at high pressure because of its high osmotic pressure. Nanofiltration at a pressure of 30 bar and a concentration factor of $\text{CF} = 1$ clearly shows

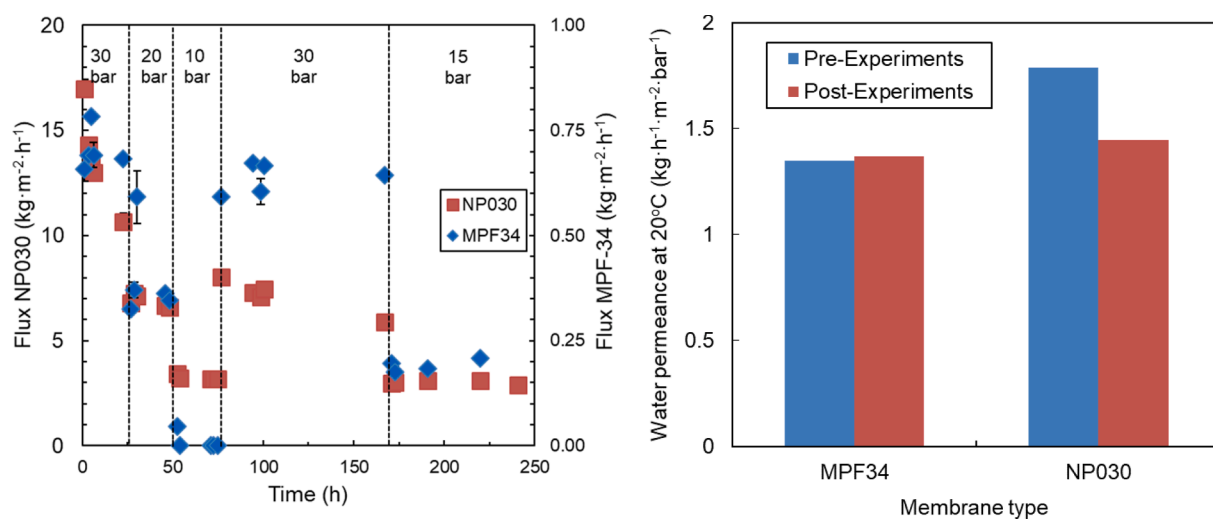


Fig. 4. Flux for NP030 and MPF-34 for nanofiltration of an aqueous solution (demineralized water) containing $260 \text{ g}\cdot\text{L}^{-1}$ pure NaCl and $70 \text{ g}\cdot\text{L}^{-1}$ pure Na_2SO_4 at $\text{pH} = 8.5$, $\text{CF} = 1$ and $T = 20 \text{ }^\circ\text{C}$ (left) and pure water permeance at $T = 20 \text{ }^\circ\text{C}$ and $P = 5 - 30 \text{ bar}$ prior to and following experiments at $\text{pH} = 8.5$, $\text{pH} = 9.8$ and $\text{pH} = 12$ during a total of 1205 h (right). Unpublished results of the author.

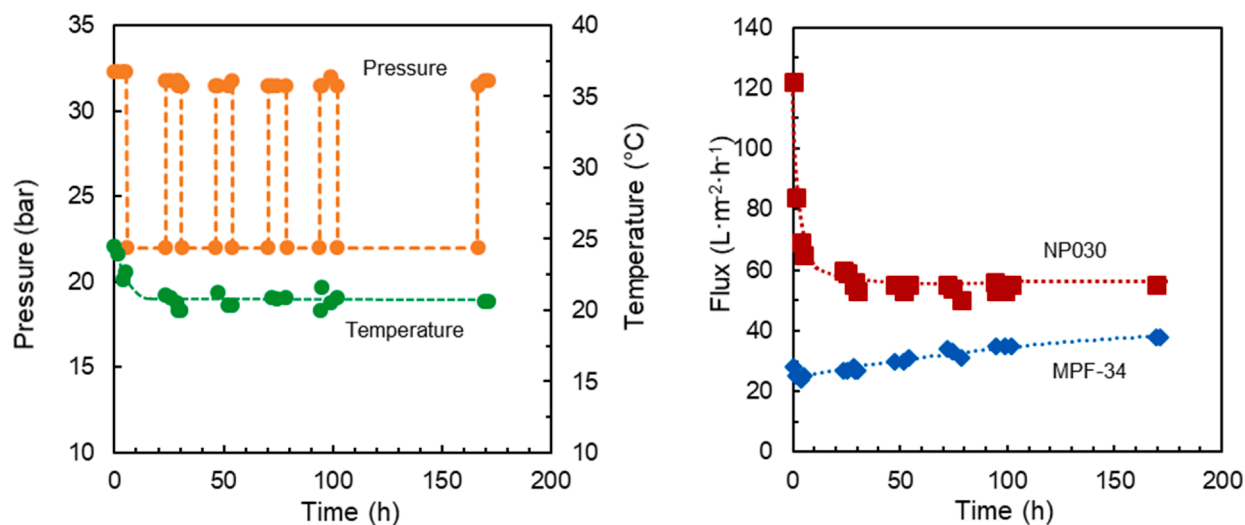


Fig. 5. Continuous nanofiltration of a 25% w NH_4OH solution at a concentration factor of $\text{CF} = 1$, using MPF-34 and NP030. Experimental conditions (left) and flux results (right). Unpublished results of the author.

reduction in membrane flux for NP030 (see Fig. 4 (left)) even though the solution is non-fouling. The observed compaction was confirmed by the reduced pure water permeance following nanofiltration of the salt solution at different pH levels for more than 1200 h in total (see Fig. 4 (right)). However, it should be noted that the decrease in water permeance was relatively low and membrane compaction appeared to be partly reversible. This membrane was evaluated for the recovery and reuse of steeping lye (with a $5.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH concentration) at pressures up to 35 bar and a temperature of 40°C as well [9]. For these conditions, membrane fluxes below $10 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ were obtained. Furthermore, NP030 appeared to be stable during the processing of a 25% w NH_4OH solution containing organic acid (EDTA) and amine (EDA) contaminants at low concentration ($<4 \text{ g}\cdot\text{kg}^{-1}$ in total). The flux for this membrane decreased initially due to the compaction behavior described earlier but was constant in the time frame between 30 and 170 h (see Fig. 5).

NF09081 (SolSep), a membrane stable at alkaline conditions, was also evaluated in experiments studying steeping lye recovery [9]. This membrane showed much higher flux than NP030 at the same conditions (between 10 and $35 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) at similar to higher hexoses, pentoses and total organic carbon (TOC) retentions.

Desal KH (SUEZ), a piperazine based polyamide membrane according to [26], showed proper pH resistance, as expected, during short-term nanofiltration in diafiltration mode using a hydrolysate containing $0.13 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 ($\text{pH} = 1$). However, due to its low MWCO and consequently high retention, the membrane was not suitable for the intended application because of the high osmotic pressure difference between the retentate and the permeate produced, causing low permeance [26] even at 36 bar operating pressure. Desal KH (Duracid) was also evaluated for batch concentration of synthetic sulfuric acid solutions with a pH between 0.6 and 1.6 containing several metal ions [35]. A concentration factor of 2 was reached with almost zero sulfuric acid retention for this membrane, characterized as a sulfonamide membrane by the authors. Stability of the membrane during a longer period was, unfortunately, not evaluated [35]. Good membrane stability for Desal KH was reported for 2 months of continuous nanofiltration of an 8% w H_2SO_4 solution ($\text{pH} \approx 0.1$) containing $25 \text{ g}\cdot\text{L}^{-1}$ CuSO_4 at $T = 40^\circ\text{C}$ [37]. Cu^{2+} retentions were stable (between 92 and 95%) in combination with a flux of $20 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ at $P = 30$ bar and an acid retention of 23–30% [37].

HydraCoRe 70pHT (Hydranautics) was evaluated for the recovery of rare earth elements from acidic mine waters [33]. Synthetic sulfuric acid solutions with a pH of 1.0 and 1.5 and varied salt concentrations were used in experiments performed at $T = 25^\circ\text{C}$. HydraCoRe 70pHT showed lower acid recovery and metal retention than Desal DL [33]. Long term

membrane stability was not evaluated.

A-3012 (AMS Technologies) was successfully evaluated in lab-scale batch concentration experiments for the recovery of phosphoric acid from a solution containing sewage sludge ash leachate with $\text{pH} = 1.15$ [49]. A-3012 showed low permeance ($0.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), a relatively high phosphate retention (in excess of 65%) and very high ($>99\%$) Fe^{3+} and Mg^{2+} retentions, which were maintained at higher concentration factor. In another study [50] A-3012 showed slightly lower permeance ($0.24 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), 97–98% Al^{3+} retention and 28–40% phosphorous retention, depending on the pressure used, for nanofiltration of a solution containing 10% phosphoric acid and $2 \text{ g}\cdot\text{L}^{-1}$ aluminum phosphate at $\text{pH} = 0.7$.

Summarizing, the commercially available membranes with claimed chemical stability for solutions with a pH outside of the $\text{pH} = 2 - 11$ range indeed seem to show stability at extreme pH, even though in some studies changes in membrane performance have been reported. This shows that these commercially available chemically stable membranes have their limitations in chemical stability as well. Their permeance is generally lower than the permeances reported for commercial membranes that can only cope with solution pH values between 2 and 11 (see Tables 1 and 2). Furthermore, some of these membranes are not able to cope with pressures as high as 30 or 40 bar, which is needed for the nanofiltration of solutions with a high osmotic pressure. Consequently, there is room for the development of more optimal pH resistant nanofiltration membranes. Recent developments in the production of these types of membranes will be discussed in the next sections.


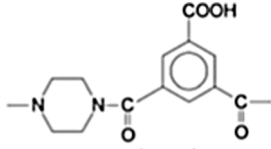
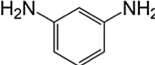
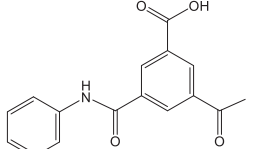
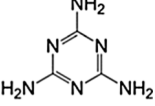
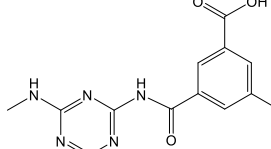
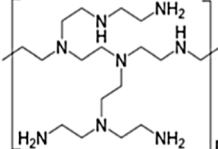
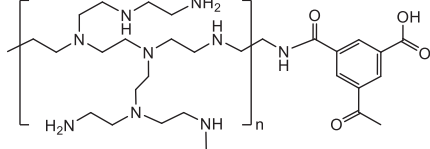
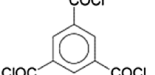
4. Acid and alkaline stability of newly developed membranes based on interfacial polymerization

Most thin film composite (TFC) nanofiltration membranes are produced via interfacial polymerization (IP). An overview and review of chemistries used for the preparation of these types of membranes can be found in [51]. This section provides an overview of recently developed IP based NF membranes that have been evaluated for the processing of solutions with a pH outside the standard $\text{pH} = 2 - 11$ range.

4.1. Polyamide membranes

A considerable amount of studies related to the preparation of IP thin film composite (TFC) polyamide NF membranes for extreme pH conditions involve membrane top layers based on trimesoylchloride (TMC) and either piperazine (Pip) or m-phenylene diamine (MPD) (see Table 3

Table 3
Typical molecules used in the preparation of polyamide IP TFC NF membranes.

Molecule (abbreviation)	Molecular structure monomer	Molecular structure polyamide based on trimesoylchloride
piperazine (Pip)		
m-phenylene diamine (MPD)		
melamine (Mel)		
polyethyleneimine (PEI)		
trimesoylchloride (TMC)		

for several amine monomers and resulting polyamide structures). The reason for the use of these compounds is that it is believed that a lot of the commercially available NF membranes have been prepared using these compounds [16,52,53], despite the fact that these commercially available membranes are usually not chemically stable in solutions having a pH outside of the 2 – 11 range. The described polyamide membranes have often been used as reference for stability evaluations of membranes based on different chemicals.

4.1.1. Piperazine-based polyamide membranes

Piperazine and trimesoylchloride based polyamide membranes were prepared on different ultrafiltration (UF) membrane supports such as polyethersulfone (PES), polyacrylonitrile (PAN), polysulfone (PSf), and poly(tetrafluoroethylene) (PTFE).

TFC polyamide membranes based on TMC and Pip on a porous PES support were produced via IP using a 0.1 %w/v TMC solution in hexane and a 2 %w/w aqueous solution of Pip [53]. The prepared (Pip/TMC)/PES membranes showed a low isoelectric point (IEP) of 3.3 [53]. After immersion in either a 10 %w/w H₂SO₄ (pH ≈ 0) or a 2.5 %w/w HNO₃ (pH ≈ 0.4) solution at T = 55 °C for 24 h, subsequent nanofiltration stirred cell tests at T = 25 °C and P = 5 bar using a solution containing 500 mg·L⁻¹ MgSO₄ in 5 %w/w H₂SO₄ revealed that the (Pip/TMC)/PES membrane appeared to be degraded completely as indicated by the extremely high flux and complete loss of MgSO₄ retention. Polyamide membranes produced from these types of amines are usually stable for the short-term processing of a 5 %w/w H₂SO₄ solution (pH ≈ 0.25) at room temperature, while a temperature increase to T > 40 °C strongly increases the hydrolysis rate of PA membranes exposed to strong acid solutions [54]. The relatively high temperature used during membrane immersion can therefore have (further) reduced its chemical stability [53]. The negative effect of a higher exposure temperature and further

reduced solution pH on the chemical stability of Pip/TMC based membranes is also illustrated by the immersion of (Pip/TMC)/PES membranes, prepared via IP using a 0.15 %w/v TMC solution in cyclohexane and a 1.0 %w/v Pip aqueous solution [39], in a 20 %w H₂SO₄ solution at T = 90 °C for 24 h. This exposure led to a strongly increased pure water permeance and almost complete loss of Na₂SO₄ retention determined from characterization experiments. The membrane instability was further confirmed based on ATR-IR analysis [39].

TFC NF membranes prepared via IP based on 1 %w Pip in water and 0.05 %w TMC in hexane on a polyacrylonitrile (PAN) ultrafiltration membrane support [55] (see Fig. 6 for illustration purposes) were evaluated in relatively short batch-wise membrane characterization tests in a pH range between 1 and 13, at room temperature and for pressures between 7 and 30 bar. A prepared (Pip/TMC)/PAN membrane showed an IEP of 4.2 and a pure water permeance of 7 L·m⁻²·h⁻¹·bar⁻¹, in between the permeances for NF-270 and Desal 5DK, and much higher than the pH stable MPF-34 membrane [55]. The NaCl retention of the produced membrane during NF of a 2.0 g·L⁻¹ NaCl solution at neutral pH was comparable to those for NF-270 and Desal 5DK at similar flux, whereas the NaCl retention for MPF-34 was considerably higher. MWCO measurements at different pH using polyethylene glycol (PEG) solutions clearly showed that the MWCO and the permeance of the (Pip/TMC)/PAN membrane was constant in the pH range from 1 – 11, whereas at pH = 12 and 13 (using either a NaOH or a HNO₃ solution for pH adjustment) the MWCO of the membrane became increasingly higher and the permeance increasingly lower. These changes appeared to be reversible [55], indicating membrane stability at the conditions and time frame used. However, based on the experience with PEI/TMC based NF membranes, as will be discussed later in this section, it is expected that at high pH the stability of the (Pip/TMC)/PAN membrane will be worse than at low pH. Based on the limited exposure time of the

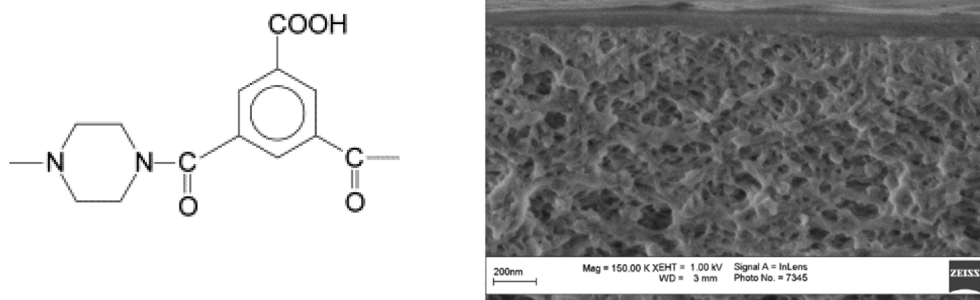


Fig. 6. Chemical representation of Pip/TMC polymer top layer (left) and scanning electron microscopy image of a (Pip/TMC)/PAN membrane (right) produced by Dalwani et al. [55]. Reproduced with permission of Elsevier.

membrane to these extreme pH conditions, firm conclusions about the stability of this membrane for prolonged exposure to solutions with an extreme pH cannot be drawn, although the performance of Pip/TMC based membranes on other supports clearly indicate poor chemical stability for longer exposure times.

A (Pip/TMC)/PSf TFC NF membrane based on IP using Pip and TMC as reactants on a polysulfone (PSf) UF membrane with a MWCO \approx 30 kDa (Development Center for Water Treatment Technology) as support showed a high permeance of $7.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and Na_2SO_4 , MgSO_4 and NaCl retentions of 97.6%, 95.0 and 54.2%, respectively, using $2.0 \text{ g}\cdot\text{L}^{-1}$ single salt solutions at $T = 25^\circ\text{C}$, $P = 6.9 \text{ bar}$ and neutral pH [56]. Exposure (ex-situ) of the membrane to a $0.05 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 solution ($\text{pH} \approx 1.2$) for a specific time up to 700 h showed a steady permeance increase from $7.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ to $15.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and a MgSO_4 retention reduction from 95% to 62% during intermittent characterization experiments [56], clearly showing insufficient chemical stability of (Pip/TMC)/PSf under these acidic conditions. A prepared (Pip/TMC)/PSf membrane using a PSf UF membrane (Toray Chemical Korea Inc) as support, having an IEP of around 4.0 [44], slightly higher than reported for (Pip/TMC)/PES [53] and slightly lower than reported for (Pip/TMC)/PAN [55] (*vide supra*), was not stable in a 15 %w/w H_2SO_4 solution ($\text{pH} < 0$) during membrane immersion tests for 30 days. Intermittent membrane characterization showed linearly increasing water permeance and reducing MgSO_4 retention (relatively slowly during the first 11 days, but more strongly afterwards). However, (Pip/TMC)/PSf appeared to be more stable than the commercially available NE-70 and NE-40 membranes from Toray (previously CSM) [44] (see Section 2.1). Immersion of a MWCO = 340 Da (Pip/TMC)/PSf membrane, having a PSf support prepared by Zhongke Rui Yang Membrane Technology Co., in an H_2SO_4 solution with $\text{pH} < 2$ (unspecified concentration) for 216 h, resulted in a gradually reducing Na_2SO_4 retention from 98.3% to 91.1% and an increasing water flux from $26.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $32.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at $P = 4 \text{ bar}$ and $T = 25^\circ\text{C}$ [57]. A similar trend was observed upon immersion of the membrane in a NaClO_3 solution ($\text{pH} > 11$) with an unspecified concentration for 110 h [57]. (Pip/TMC)/PSf membranes prepared on MWCO = 100 kDa PSf supports (LG Chem.) using an aqueous solution containing 4 %w Pip and 0.2 %w TMC in isoparaffin ISOL-C [58] and annealing the membranes at $T = 60^\circ\text{C}$ for 10 min were immersed in a 50 %w H_2SO_4 solution for 11 days [58]. The membranes were evaluated for acid stability using intermittent characterization tests at $P = 15.5 \text{ bar}$ and $T = 25^\circ\text{C}$ using a 2000 ppm MgSO_4 solution. At this extremely high acid concentration the membranes showed a strong reduction in retention (from almost 100% to below 30%) and a strong increase in flux. A hollow-fiber (Pip/TMC)/PSf membrane prepared using a 0.75 %w aqueous solution of Pip, a 0.15 %w TMC solution in hexane, a reaction time of 30 s., a curing time of 5 min at $T = 80^\circ\text{C}$ and a hollow-fiber 70 kDa PSf support (Solvay) [59] was exposed (ex-situ) to a $0.01 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution ($\text{pH} = 12$) for 120 h.

This (Pip/TMC)/PSf membrane was not stable with a permeance increase from 5.6 to $6.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and a Na_2SO_4 retention reduction from 92% to 81% after 120 h of ex-situ exposure as determined from characterization experiments using a $2000 \text{ mg}\cdot\text{L}^{-1}$ Na_2SO_4 solution at $P = 5 \text{ bar}$ and room temperature [59].

Intermittent characterization experiments of a (Pip/TMC)/PE membrane featuring a Pip/TMC layer on a polyethylene (PE) support from SK Innovation during immersion in a 15 %w H_2SO_4 solution (probably at room temperature, although this was not specified) for three weeks, showed a membrane permeance increase by a factor 70 and strongly decreased NaCl and MgSO_4 retentions to 0% [27]. This clearly indicates the poor stability of the (Pip/TMC)/PE membrane under these acidic conditions.

A (Pip/TMC)/PTFE NF membrane based on a bi-stretched (longitudinal and transverse) PTFE support [60] showed slight instability for immersion in a $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 solution ($\text{pH} \approx 0.3$) for 30 days, as indicated by the gradually increasing membrane flux (<10%) and reducing Na_2SO_4 retention (by several % absolute) during intermittent characterization tests using a $1.0 \text{ g}\cdot\text{L}^{-1}$ Na_2SO_4 solution at $P = 4 \text{ bar}$ and $T = 25^\circ\text{C}$. For this membrane a pure water permeability of $9.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ was claimed prior to exposure to the sulfuric acid solution [60]. However, the linear relation shown between the flux and the pressure results in a flux of $0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at approximately $P = 1 \text{ bar}$. The flux obtained at $P = 4.0 \text{ bar}$ for this membrane equaled $33 - 34 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, leading to a permeance of $8.2 - 8.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ at this pressure. The membrane showed Na_2SO_4 , MgSO_4 , NaCl and MgCl_2 retentions of 98.1%, 93.7%, 49.0% and 38.1%, respectively, for the processing of $1.0 \text{ g}\cdot\text{L}^{-1}$ single salt solutions, an IEP = 3.8 and a MWCO = 765 Da.

Consequently, the long-term stability tests of Zeng et al. [56], Shin et al. [27], Wei et al. [57], Park et al. [44] and Tang et al. [60] clearly show that even at room temperature the stability of Pip/TMC top layers at low pH conditions is limited, even though the change in performance during 30 days was relatively small for (Pip/TMC)/PTFE [60], and the observed chemical stability during the tests performed by Dalwani et al. [55] with (Pip/TMC)/PAN appeared to be good. However, the latter observation is most likely due to the limited time of exposure to the acid solution in that study. The instable behavior of Pip/TMC top layer membranes for exposure to H_2SO_4 solutions (at low pH) with different concentration and temperature combinations is illustrated in Fig. 7. All evaluated commercially available (Fig. 7a) and recently developed Pip/TMC based membranes (Fig. 7b) appear to be instable at the temperature - H_2SO_4 solution weight percentage combinations shown in this Figure. Furthermore, due to the instability of the top layer for extreme pH, the effect of the different supports used appears to be a secondary order effect for these polyamide membranes.

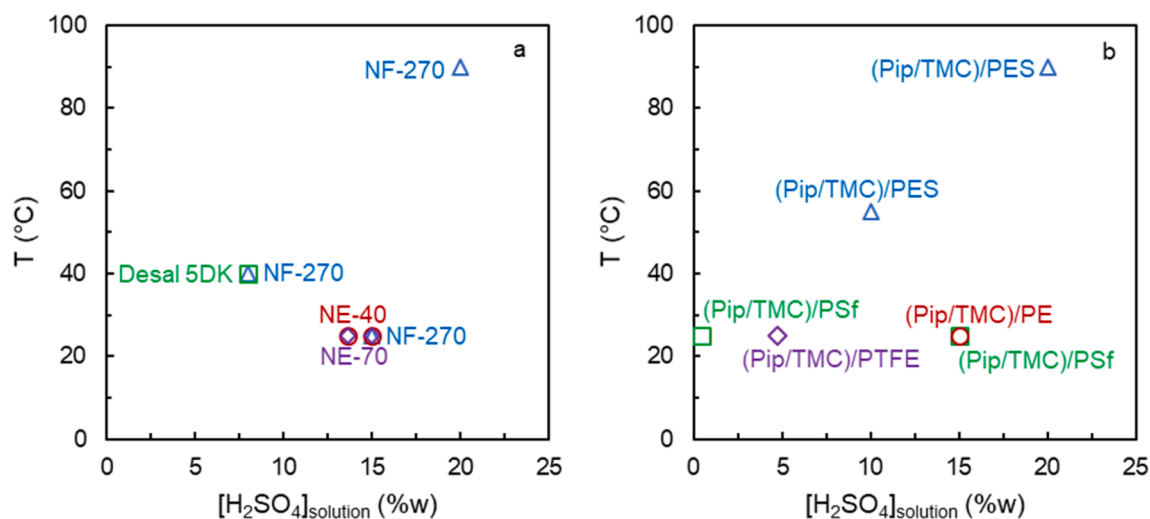


Fig. 7. Sulfuric acid concentration – temperature combinations for which commercially available (a) and recently developed (b) Pip/TMC based polyamide membranes were evaluated for pH stability. Open symbols indicate membrane instability at the sulfuric acid concentration – temperature combination shown.

4.1.2. *m*-Phenylene diamine-based polyamide membranes

TFC polyamide membranes based on trimesoylchloride (TMC) and *m*-phenylene diamine (MPD) on a porous PES support were evaluated at the same conditions as the (Pip/TMC)/PSf membrane prepared by the same authors [53,61] (*vide supra*). (MPD/TMC)/PES showed an IEP of 4.4, slightly higher than the (Pip/TMC)/PES membrane [53,61]. After exposure to a 10 %w/w H_2SO_4 (pH \approx 0) or 2.5 %w/w HNO_3 (pH \approx 0.4) solution at $T = 55\text{ }^\circ\text{C}$ for 24 h, comparable to the (Pip/TMC)/PES membrane (see Section 4.1.1), the (MPD/TMC)/PES membrane appeared to be degraded completely as well, as indicated by the extremely high flux and complete loss of $MgSO_4$ retention.

An (MPD/TMC)/PE membrane featuring an MPD/TMC layer on top of a PE support from SK Innovation had a water permeance of $1.7\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and showed typical reverse osmosis (RO) characteristics with a MWCO < 100 Da and 99.6% NaCl retention during characterization tests at $P = 10$ bar and $T = 25\text{ }^\circ\text{C}$ [27]. Intermittent characterization results showed that immersion in a 15 %w H_2SO_4 solution (pH < 0) under similar conditions as used for (Pip/TMC)/PE (see Section 4.1.1) for four weeks did not affect the membrane permeance nor the NaCl and $MgSO_4$ retentions, indicating good stability for (MPD/TMC)/PE under these acidic conditions [27]. The clear disadvantage of this membrane is that it cannot be used for nanofiltration applications due to its very low MWCO. Solvent activation of the prepared (MPD/TMC)/PE RO membrane using different aprotic solvents (dimethyl sulfoxide (DMSO), dimethylformamide (DMF) or *N*-methyl-2-pyrrolidone (NMP)) increased the MWCO and converted the RO membranes into NF membranes. The use of DMSO, the strongest solvent, created the strongest membrane performance changes with a water permeance and MWCO increase from 1.7 to $14.5\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and < 100 to 240 Da, respectively, and a NaCl retention decrease from 99.6 to 85.1% using a 1000 ppm NaCl solution at $P = 10$ bar and $T = 25\text{ }^\circ\text{C}$ [27]. Exposure of this solvent activated (MPD/TMC)/PE NF membrane to a 15 %w H_2SO_4 solution (probably at room temperature although this was not specified) for four weeks, did not change the water permeance nor the NaCl or $MgSO_4$ retention, proving that the solvent activated (MPD/TMC)/PE membrane was stable under these conditions. The results obtained for (MPD/TMC)/PE and (Pip/TMC)/PE [27] indicate that the stability of MPD based polyamide membranes appears to be better than for Pip based polyamide membranes, in line with results reported by Paul and Jones [16].

An (MPD/TMC)/PVDF membrane was prepared via interfacial polymerization using a 2 %w MPD aqueous solution, a 0.15 %w TMC in hexane solution, and a nanofibrous PVDF created by phase inversion as support [62]. The prepared membrane was modified using a 2 %w Tris

(hydroxymethyl)aminomethane (Tris) solution. The membrane was not stable during immersion in an acidic solution at pH = 1 (a $0.1\text{ mol}\cdot\text{L}^{-1}$ nitric acid solution) for one month, as indicated by its clearly lower salt retention and higher permeance in characterization tests using a 2000 ppm $MgSO_4$ solution and deionized water prior to and following immersion in the acid solution [62]. Immersion of this membrane in a $0.1\text{ mol}\cdot\text{L}^{-1}$ NaOH solution (pH = 13) for 1 month resulted in a strong decrease in the salt retention from 46% to 12% and a strong increase in water flux from $21.5\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $55\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 6 bar [62] as well, clearly showing the instability of the membrane under these alkaline conditions.

Apparently, conflicting acid stability results were obtained for the limited number of MPD/TMC based membranes developed. However, in this case the effect of higher exposure temperature (for the (MPD/TMC)/PES membrane versus the surface modified (MPD/TMC)/PE membrane) and the development of a more open membrane (the Tris modified (MPD/TMC)/PVDF membrane versus the (MPD/TMC)/PE membrane and its surface modified version) probably led to worse chemical stability in the acid solutions.

4.1.3. 1,3,5-(tris-piperazine)-triazine-based polyamide membranes

A (TPT/TMC)/PSf membrane, prepared using 1,3,5-(tris-piperazine)-triazine (TPT) and TMC as reactants on a polysulfone (PSf) UF membrane, showed a water permeance of $8.7\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and Na_2SO_4 , $MgSO_4$ and NaCl retentions of 98.6%, 97.0% and 40.5%, respectively at neutral pH conditions for NF of $2.0\text{ g}\cdot\text{L}^{-1}$ single salt solutions at $T = 25\text{ }^\circ\text{C}$ and $P = 6.9$ bar [56]. The permeance and retentions, apart from the NaCl retention, were higher than those for (Pip/TMC)/PSf prepared by the same authors (see Section 4.1.1). Exposure of the (TPT/TMC)/PSf membrane to $0.05\text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 solutions (pH \approx 1.2) led to a linearly increasing water permeance and an almost linearly decreasing $MgSO_4$ retention as function of the acid solution exposure time. After slightly more than 700 h of exposure characterization experiments revealed that the permeance was approximately 20% higher, while the salt retention was 5% (relative) lower than prior to the exposure. Additionally, significant changes in ATR spectra and SEM images were not found, indicating that the membrane was only slightly unstable under the acid test conditions. The poly(amide-*s*-triazine-amine) (TPT/TMC)/PSf membrane was therefore considerably more stable at low pH than the polyamide (Pip/TMC)/PSf membrane (see Section 4.1.1) [56].

4.1.4. Polyethyleneimine-based polyamide membranes

A membrane featuring a polyethyleneimine (PEI) and TMC based top

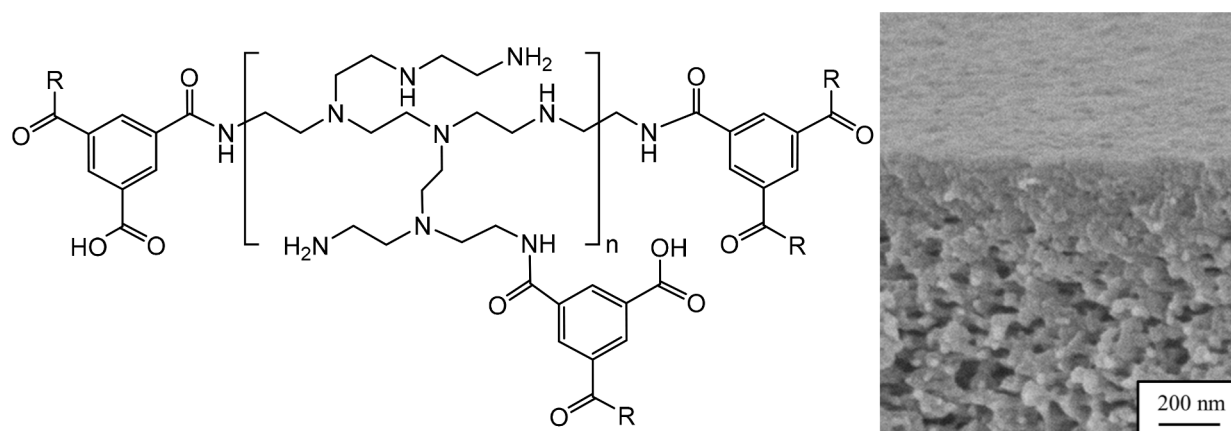


Fig. 8. Chemical representation of the PEI/TMC top layer (left, adapted from Lee et al. [24]) and a scanning electron microscopy image of a (PEI/TMC)/PES membrane produced by Lee et al. [24] (right). Reproduced with permission of Elsevier.

layer on a PES support ((PEI/TMC)/PES) [61], prepared according to the same procedure as described earlier for the preparation of (Pip/TMC)/PES and (MPD/TMC)/PES membranes [53,61], showed a relatively high isoelectric point (IEP) of 7.7, practically equal to the IEP reported by Lee et al. [24] for their (PEI/TMC)/PES membrane which will be discussed later in this section. Upon exposure of the membrane to either a 10 %w/w H₂SO₄ (pH ≈ 0) or a 2.5 %w/w HNO₃ (pH ≈ 0.4) solution at 55 °C for 24 h, the performance of (PEI/TMC)/PES changed, although not as much as that for (MPD/TMC)/PES. The (PEI/TMC)/PES performance changed less after immersion in a 2.5 %w/w HNO₃ solution than after immersion in a 10 %w/w H₂SO₄ solution [61]. TFC NF membranes based on IP reacting PEI with TMC on top of a flat sheet 30 kDa hydrophilized PES UH030 UF membrane from Microdyn Nadir were prepared as well [24] (see Fig. 8 for a scanning electron microscope image). A (PEI/TMC)/PES NF membrane prepared from solutions containing 1.25 g·L⁻¹ of PEI in water and 0.5 g·L⁻¹ of TMC in hexane using a reaction time of 30 s showed a pure water permeance of approximately 7.5 L·m⁻²·h⁻¹·bar⁻¹ and approximately 55% NaCl retention for nanofiltration of a 2.0 g·L⁻¹ NaCl solution at P = 10 bar and room temperature [24]. The pure water permeance increased slightly to 9 L·m⁻²·h⁻¹·bar⁻¹, whereas the NaCl retention remained constant upon ex-situ exposure of the membrane to a 0.1 mol·L⁻¹ HNO₃ (pH = 1) solution for 900 h, indicating reasonable but probably not full membrane stability for operation at pH = 1. Exposure of the (PEI/TMC)/PES membrane to a 0.1 mol·L⁻¹ NaOH (pH = 13) solution resulted in a steady strong increase in pure water permeance to 27 L·m⁻²·h⁻¹·bar⁻¹, and a strong reduction in NaCl retention to approximately 10% after an exposure of 900 h [24], clearly showing that this polyamide membrane was chemically unstable at pH = 13 conditions.

A (PEI/TMC)/PSf membrane produced by IP using 3.7 %w/w PEI in water and 0.25 %w/v TMC in hexane and a 30 kDa PSf UF support (Pureach Tech Ltd.) was not stable in a 0.1 mol·L⁻¹ HNO₃ (pH = 1) solution nor in a 0.1 mol·L⁻¹ NaOH (pH = 13) solution [63]. This was concluded from a strong increase in membrane flux from approximately 1 L·m⁻²·h⁻¹ to 25 L·m⁻²·h⁻¹ and a strong reduction in retention from approximately 95% to below 40% during membrane characterization using a 1 g·L⁻¹ MgCl₂ solution at P = 10 bar and room temperature after slightly more than 700 h exposure to the acid or the alkaline solution. Reasons for the observed differences in acid stability between the (PEI/TMC)/PES membranes produced by Lee et al. [24] and Hoseinpour et al. [61], and the (PEI/TMC)/PSf membrane produced by Jiang et al. [63] are not evident, but may be due to differences in membrane preparation procedures and differences in immersion temperature. The stability of all three PEI/TMC based membranes for strong alkaline solutions are similar and insufficient for their use under alkaline conditions [24,61,63].

4.1.5. Mixed amines-based polyamide membranes

The mixed amines-based polyamide membrane (Pip-Mel/TMC)/PSf, based on TMC and a mixture of Pip and melamine (Mel) on a PSf UF support (Toray Chemical Korea Inc.) showed better stability than (Pip/TMC)/PSf (see Section 4.1.1) upon immersion in a 15 %w/w H₂SO₄ solution for 30 days [44]. This was concluded from intermittent characterization tests showing stable water permeance for 10 days, followed by an increase of approximately 100% after the subsequent 10 days, and stable MgSO₄ retention during the first 5 days, followed by a gradual reduction during the next 15 days. The prepared membrane was not only more stable than the single amine based (Pip/TMC)/PSf polyamide membrane, but more stable than NE-40 and NE-70 (see Section 2.1) as well.

Another mixed amine-based membrane, (PEI-Mel/TMC)/PES, based on trimesoylchloride (TMC) and a PEI-Mel copolymer on a porous PES support was produced via IP using a 0.1 %w/v TMC solution in hexane, and an aqueous solution containing 2 %w/w PEI and 0.35 %w/w Mel [61]. Membrane preparation was performed according to the same method used for single amine based (Pip/TMC)/PES, (MPD/TMC)/PES and (PEI/TMC)/PES polyamide membranes prepared by the same authors [53,61] and described in earlier sections. The (PEI-Mel/TMC)/PES membrane had an even higher IEP of 10.2 than the other polyamide membranes [53,61], most likely due to the higher amount of amine groups present in the membrane. The performance of (PEI-Mel/TMC)/PES was slightly more stable than for (PEI/TMC)/PES and changed less after immersion in 2.5 %w/w HNO₃ (pH ≈ 0.4) compared to immersion in 10 %w/w H₂SO₄, as also found for (PEI/TMC)/PES [61].

Based on these observations there are indications that the use of a mixture of different amines in the production of polyamide membranes leads to improved membrane stability for nanofiltration of acidic solutions with low (<2) pH. This is at least proven for the use of Mel in combination with Pip or PEI. However, it must be noted that the mixed amine-based polyamide membranes produced were not compared to polyamide membranes based on Mel only, and a Mel based polyamide membrane could therefore perform better than the Pip-Mel or PEI-Mel based polyamide membranes.

4.1.6. Polyamide membranes with embedded nanosheets, nanotubes or silica particles

Polyamide membranes with embedded graphene oxide (GO) nanosheets or oxidized single-walled carbon nanotubes (o-SWNT) were prepared on MWCO = 100 kDa PSf supports (LG Chem.) using an aqueous solution containing 4 %w Pip and 20 ppm, 40 ppm or 300 ppm exfoliated GO nanosheets or o-SWNT, and 0.2 %w TMC in isoparaffin ISOL-C [58]. The membranes were annealed at T = 60 °C for 10 min. As reference (Pip/TMC)/PSf polyamide membranes without nanosheets or

Table 4
Stability of polyamide membranes at extreme pH conditions.

Membrane type and name	Acid stability	Alkaline stability
Polyamide (Pip/TMC)/PES	Unstable (completely degraded) for immersion in a 2.5 %w HNO ₃ solution at T = 55 °C for 24 h [53] Unstable (completely degraded) for immersion in a 10 %w H ₂ SO ₄ solution at T = 55 °C for 24 h [53] Unstable (completely degraded) for immersion in a 20 %w H ₂ SO ₄ solution at T = 90 °C for 24 h [39]	
Polyamide (Pip/TMC)/PSf	Unstable for ex-situ exposure to a 0.05 mol·L ⁻¹ H ₂ SO ₄ solution (pH ≈ 1.2) at room temperature for 700 h [56] Unstable for immersion in a 15 %w H ₂ SO ₄ (pH < 0) for 30 days [44] Unstable upon immersion in a 50 %w H ₂ SO ₄ solution for 11 days [58] Unstable for immersion in a H ₂ SO ₄ solution with pH < 2 (but unspecified concentration) for 216 h [57]	Unstable for immersion in a HClO ₃ solution with pH > 11 (but unspecified concentration) for 110 h [57] Unstable for immersion in a 0.01 mol·L ⁻¹ NaOH (pH = 12) solution for 120 h [59]
Polyamide (Pip/TMC)/PE	Unstable for immersion in a 15 %w H ₂ SO ₄ solution (probably at room temperature, although this was not specified) for three weeks [27]	
Polyamide (Pip/TMC)/PAN	Stable during short term membrane characterization experiment at pH = 1 (using a HNO ₃ solution for pH adjustment) [55]	Stable during short term membrane characterization experiment at pH = 13 (using a NaOH solution for pH adjustment) [55]
Polyamide (Pip/TMC)/PTFE	Slightly unstable in a 0.5 mol·L ⁻¹ H ₂ SO ₄ solution at T = 25 °C for 30 days [60]	
Polyamide (Pip/TMC/GO)/PSf	Unstable upon immersion in a 50 %w H ₂ SO ₄ solution for 11 days [58]	
Polyamide (Pip/TMC/o-SWNT)/PSf	Unstable upon immersion in a 50 %w H ₂ SO ₄ solution for 11 days [58]. Less stable than (Pip/TMC/GO)/PSf and similar stability as (Pip/TMC)/PSf [58]	
Polyamide (Pip/TMC/HGPN-SiO ₂)/PSf	Stable for immersion in a H ₂ SO ₄ solution with pH < 2 (but unspecified concentration) for 216 h [57]	Unstable for immersion in a HClO ₃ solution with pH > 11 (but unspecified concentration) for 110 h [57]
Polyamide (MPD/TMC)/PES	Unstable (completely degraded) for immersion in a 2.5 %w HNO ₃ solution at T = 55 °C for 24 h [53,61] Unstable (completely degraded) for immersion in a 10 %w H ₂ SO ₄ solution at T = 55 °C for 24 h [53,61]	
Polyamide (MPD/TMC)/PE	Stable for immersion in a 15 %w H ₂ SO ₄ solution (probably at room temperature, although this was not specified) for four weeks [27]. Membrane characterization indicates that the prepared membrane is a RO membrane rather than a NF membrane	
Polyamide (MPD/TMC)/PVDF	Unstable during ex-situ immersion in an acidic solution at pH = 1 (a 0.1 mol·L ⁻¹ HNO ₃ solution) for one month [62]	Unstable during ex-situ immersion in an alkaline solution at pH = 13 (a 0.1 mol·L ⁻¹ NaOH solution) for one month [62]
Polyamide (TPT/TMC)/PSf	Unstable for ex-situ exposure to a 0.05 mol·L ⁻¹ H ₂ SO ₄ solution (pH ≈ 1.2) at room temperature for 700 h, but more stable than (Pip/TMC)/PSf [56]	
Polyamide (PEI/TMC)/PES	Unstable for immersion in a 2.5 %w HNO ₃ solution at T = 55 °C for 24 h [61] Unstable for immersion in a 10 %w H ₂ SO ₄ solution (pH ≈ 0) at T = 55 °C for 24 h [61] Not fully stable for ex-situ exposure in a 0.1 mol·L ⁻¹ HNO ₃ solution for 900 h [24]	Unstable for ex-situ exposure in a 0.1 mol·L ⁻¹ NaOH solution for 900 h [24]
Polyamide (PEI/TMC)/PSf	Unstable for ex-situ exposure in a 0.1 mol·L ⁻¹ HNO ₃ solution for 700 h [63]	Unstable for ex-situ exposure in a 0.1 mol·L ⁻¹ NaOH solution for 700 h [63]
Polyamide (Pip-Mel/TMC)/PSf	Unstable for immersion in a 15 %w H ₂ SO ₄ (pH < 0) for 30 days, but more stable than (Pip/TMC)/PSf [44]	
Polyamide (PEI-Mel/TMC)/PES	Unstable for immersion in a 2.5 %w HNO ₃ solution at T = 55 °C for 24 h, but more stable than (PEI/TMC)/PES [61] Unstable for immersion in a 10 %w H ₂ SO ₄ solution (pH ≈ 0) at T = 55 °C for 24 h, but more stable than (PEI/TMC)/PES [61]	

nanotubes were prepared (see Section 4.1.1). Membranes were immersed in a 50 %w H₂SO₄ solution for 11 days and were evaluated for acid stability using intermittent characterization tests at P = 15.5 bar and T = 25 °C using a 2000 ppm MgSO₄ solution. A higher GO nanosheet concentration in the top layer of the polyamide membrane resulted in a slower increase in flux and reduction in retention MgSO₄. Nevertheless, the MgSO₄ retention for the polyamide membrane prepared from the Pip solution containing 40 ppm GO (Pip/TMC/GO₄₀)/PSf still reduced from almost 100% to 50% and the flux increased by >100% in only 11 days. Obviously, the H₂SO₄ concentration of the solution to which the membranes were exposed was extremely high. The use of 300 ppm exfoliated GO nanosheets in the Pip solution resulted in a more stable membrane with only small changes in flux and retention during the first 10 days, followed by a sudden drop in retention and increase in flux on the 11th day of exposure. The addition of o-SWNT (40 ppm at maximum) hardly affected the acid stability of the polyamide membrane. The difference in behavior between GO nanosheets and o-SWNT was attributed to the difference in shape and different barrier properties [58]. However, depending on the procedure used to treat the membranes after removal

from the strong acid solution, which was not described in detail, a different behavior of the different membranes to osmotic pressure shock (caused by the transfer of the membrane from the highly concentrated sulfuric acid solution with high osmotic pressure to the MgSO₄ solution with low osmotic pressure) may have had an impact as well. Consequently, inclusion of GO nanosheets in polyamide membranes is clearly beneficial for acid stability. However, since an accelerated aging test was used featuring the use of an extremely high sulfuric acid concentration and relatively short exposure time, the effect of the use of GO nanosheets to improve acid stability of polyamide membranes for lower (more practically relevant) acid concentrations is yet unclear.

Addition of hydrophilic SiO₂ nanoparticles (HGPN-SiO₂), with an average diameter of 15 nm and prepared by chemical vapor deposition, to the aqueous Pip solution used in combination with TMC in hexane to prepare polyamide IP NF membranes on a PSf support (Zhongke Rui Yang Membrane Technology Co) was also targeted [57]. The HGPN-SiO₂ reacted with the TMC and formed ester bonds in the polymer network. The HGPN-SiO₂ concentration in the aqueous solution was varied from 0 %w to 0.16 %w, while a 0.1 %w Pip aqueous solution and 0.05 %w

TMC in hexane were selected as optimal solutions for the preparation of the membranes. Other optimized preparation conditions can be found in the supplementary information of [57]. The (Pip/TMC/HGPN-SiO₂)/PSf membrane with the optimum HGPN-SiO₂ concentration of 0.08 %w and a MWCO = 454 Da showed better acid stability than its equivalent without nanoparticles (*vide supra*) with practically unchanged flux and Na₂SO₄ retention after 216 h exposure to an H₂SO₄ solution with pH < 2 (unspecified concentration). The stability upon exposure to the NaClO₃ solution (pH > 11 with unspecified concentration) of this membrane was worse than for its equivalent without nanoparticles [57]. Consequently, the addition of nanoparticles to a TFC NF membrane based on Pip and TMC may result in better stability for acid solutions, whereas for alkaline solutions this has not been shown.

4.1.7. Summarizing the pH stability of developed polyamide membranes

Observations regarding the acid and alkaline stability for all reported polyamide membranes have been summarized in Table 4. In general, it can be concluded that polyamide nanofiltration membranes are not highly stable at extreme acidic (pH < 2) or alkaline (pH > 11) conditions although the degradation rate of the prepared membranes does depend on the amine (combination) used for the prepared membrane. The only two membranes that have been reported to be stable at these extreme conditions, (Pip/TMC)/PAN [55] and (Pip/TMC/HGPN-SiO₂)/PSf, either featured evaluation at an extreme pH for a limited time only, or featured a hybrid membrane evaluated at unknown pH (still below 2) and sulfuric acid concentration. The proper stability of polyamide membranes at extreme pH during limited time is expected, as it is generally known that commercial polyamide membranes can generally be cleaned at extreme pH for limited time periods. Only (Pip/TMC/GO)/PSf may show proper stability for acid solutions with (limited) acid concentrations used in practical applications. However, due to the extremely high sulfuric acid concentration and the limited exposure time used during the immersion tests and the unspecified procedure used in between removal of the membrane from the acid solution and membrane characterization this is unclear at present. Furthermore, the production and use of exfoliated GO nanosheets is laborious and probably relatively expensive.

4.2. Polyesteramide membranes

Polyesteramide membranes were prepared based on MPD, TMC and 9,9-bis(4-hydroxyphenyl)fluorene (BHPF) or benzene-1,3-diol (BD) on a PSf support (Institute of Seawater Desalination and Utilization) [64]. The PSf support was immersed in an alkaline NaOH solution (pH = 13) containing 0.8 %w MPD and either 0.4 %w BHPF or 0.4 %w BD. After removal of excess liquid, the support was immersed in a 0.05 %w TMC containing hexane solution, subsequently using a crosslinking reaction time and temperature of 10 min and 60 °C, respectively. Only the produced (MPD-BHPF/TMC)/PSf membrane was immersed in a 5 %w HCl solution or in a 5 %w NaOH solution for 48 h to validate acid and alkaline stability. Immersion of the membrane in the 5 %w HCl solution resulted in a flux decrease for (MPD-BHPF/TMC)/PSf of approximately 10%, starting at 53 L·m⁻²·h⁻¹ prior to exposure to the acid solution as established from characterization tests using a 2000 ppm NaCl solution at P = 20 bar and T = 25 °C. The NaCl retention dropped by approximately 5% (relative), starting at 95.1% prior to exposure to the acid solution. The high initial NaCl retention indicates that the prepared membrane is a RO membrane rather than a NF membrane. Immersion of the prepared membrane in the alkaline solution for 28 h resulted in approximately 20% higher flux and 2% (relative) higher NaCl retention [64]. Ester and amide bond hydrolysis was concluded from contact angle measurements. Contact angle changes for (MPD-BHPF/TMC)/PSf from 73° prior to acid or alkaline solution exposure, to 59° and 56° after immersion in the acid and alkaline solutions, respectively were reported, indicating the formation of hydroxyl and carboxyl groups during acid and alkaline solution exposure. The produced polyesteramide

membrane was therefore unstable at these conditions, as expected by the authors [64].

4.3. Poly(amide-sulfonamide) membranes

4.3.1. Benzene-1,3-disulfonyl chloride – trimesoyl chloride-based membranes

Poly(amide-sulfonamide) membranes were prepared using either Pip or MPD in a 2 %w/w aqueous solution in combination with a mixture of 0.05 %w/v TMC and 0.05 %w/v benzene-1,3-disulfonyl chloride (BDSC) in Isopar G [53]. The IP process was performed using a PES support. The (Pip/BDSC-TMC)/PES and (MPD/BDSC-TMC)/PES membranes showed an IEC of 3.2 and 4.3, respectively, approximately 0.1 lower than their polyamide alternatives (see Sections 4.1.1 and 4.1.2, respectively). Upon exposure of the membranes to either a 10 %w/w H₂SO₄ (pH ≈ 0) or a 2.5 %w/w HNO₃ (pH ≈ 0.4) solution at 55 °C for 24 h, the (Pip/BDSC-TMC)/PES and (MPD/BDSC-TMC)/PES showed better stability than their polyamide alternatives (Pip/TMC)/PES and (MPD/TMC)/PES, respectively, but their performance (water permeance and salt retention) changed as well, with stronger changes for the MPD based membrane. Furthermore, for both membranes stronger changes were obtained upon exposure to the 10 %w/w H₂SO₄ solution than for exposure to the 2.5 %w/w HNO₃ solution [53].

4.4. Poly(amide-ester-sulfonamide) membranes

4.4.1. Piperazine, sulfonated melamine formaldehyde and sulfanilamide – trimesoyl chloride-based membranes

(Pip-SMelf-SA/TMC)/PSf, prepared from 0.1 %w TMC in hexane, an aqueous solution containing a mixture of 1.0 %w Pip, 0.3 %w sulfonated melamine formaldehyde (SMelf) and 0.05 %w sulfanilamide (SA), and a PSf UF support (Toray Chemical Korea Inc.), was immersed in a 15 %w H₂SO₄ (pH < 0) solution for 30 days. The membrane containing ester bonds next to amide and sulfonamide bonds, showed a good permeance stability during the first 20 days of exposure followed by a small increase during the subsequent 10 days, and a gradual reduction in MgSO₄ retention after 10 days of exposure (from approximately 96% to 90%) [44]. (Pip-SMelf-SA/TMC)/PSf was consequently not completely stable at these conditions but showed similar stability as NE-90 (see Section 2.2) and better stability than the polyamide membranes NE-40, NE-70, (Pip/TMC)/PSf and (Pip-Mel/TMC)/PSf (see Sections 2.1, 4.1.1 and 4.1.5) [44].

4.5. Polysulfonamide membranes

4.5.1. Benzene-1,3-disulfonyl chloride-based membranes

Polysulfonamide TFC NF membranes based on benzene-1,3-disulfonyl chloride (BDSC) and either MPD or Pip were prepared using either Pip or MPD in a 2 %w/w aqueous solution in combination with a mixture of 0.16 %w/v BDSC in Isopar G [53,61]. The NF membranes were produced on a PES support [53]. (Pip/BDSC)/PES and (MPD/BDSC)/PES showed marginally lower IEP than their poly(amide-sulfonamide) membrane alternatives, (Pip/BDSC-TMC)/PES and (MPD/BDSC-TMC)/PES, respectively [53,61]. Using the same acid exposure procedure as used for the polyamide (see Sections 4.1.1 and 4.1.2) and poly(amide-sulfonamide) membranes (see Section 4.3.1) it was found that the polysulfonamide (Pip/BDSC)/PES and (MPD/BDSC)/PES membranes were acid stable in the 10 %w/w H₂SO₄ (pH ≈ 0) and the 2.5 %w/w HNO₃ (pH ≈ 0.4) solution at 55 °C for 24 h.

Polysulfonamide top layer membranes based on BDSC and either PEI, or PEI in combination with an amine monomer (Pip or MPD) were produced as well [65]. The membranes were prepared by IP on a PVDF support that was produced via phase inversion according to the method described by Mertens et al. [66]. Membranes were immersed in either a 2.5% (w/w) HNO₃ solution (pH ≈ 0.4) or a 20.0%w/w H₂SO₄ aqueous solution at T = 70 ± 5 °C for 24 h, subsequently washed and

characterized for water permeance and dye retention at $P = 5$ bar and $T = 25$ °C. The pure water flux of (PEI/BDSC)/PVDF measured at $T = 25$ °C and $P = 5$ bar increased from $16 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $43 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ upon exposure to the 20.0%w/w H_2SO_4 solution ($\text{pH} \ll 0$) at $T = 70$ °C, while crystal violet and methyl orange (dye) retentions reduced from 95% to 92% and 90% to 89%, respectively. Exposure to the 2.5%w/w HNO_3 solution ($\text{pH} \approx 0.4$) at $T = 70$ °C resulted in a slightly lower flux increase, but a significantly higher reduction in dye retentions [65]. (PEI-MPD/BDSC)/PVDF was the least stable of the membranes produced, as indicated by the strong increase in water flux and strong reductions in dye retentions. (PEI-Pip/BDSC)/PVDF showed much better stability than (PEI-MPD/BDSC)/PVDF. It showed lower relative water flux increase upon exposure to the 20.0%w/w H_2SO_4 solution at $T = 70$ °C and the 2.5%w/w HNO_3 solution at $T = 70$ °C than (PEI/BDSC)/PVDF. Dye retention loss of (PEI/BDSC)/PVDF was similar to that of (PEI-Pip/BDSC)/PVDF for exposure to the 20.0%w/w H_2SO_4 solution ($\text{pH} \ll 0$) at $T = 70$ °C, whereas it was slightly higher for exposure to the 2.5%w/w HNO_3 solution at $T = 70$ °C. Out of the membranes produced (PEI-Pip/BDSC)/PVDF turned out to be the most stable, followed by (PEI/BDSC)/PVDF, with (PEI-MPD/BDSC)/PVDF being very unstable after exposure to these acid solutions at high temperature ($T = 70$ °C) during 24 h. The claim of Eslami et al. [65] that (PEI/BDSC)/PVDF has excellent stability against low pH solutions does not seem to be fully supported by their results showing a strong increase in pure water flux after exposure of the membrane to the acid solutions, even though the dye retention loss was indeed limited. Furthermore, it should be realized that at least part of the pure water flux increase can be due to the exposure of the membranes at a temperature of $T = 70$ °C during the immersion of the membrane in the acid solutions. The membrane characterized before the immersion in the acid solution had not been exposed to this high temperature, since characterization was performed at $T = 25$ °C. There are indications that hysteresis effects in membrane performance may occur when a polymeric nanofiltration membrane is exposed to temperatures as high as $T = 50$ °C in combination with the presence of salts and changed pH (in the range between $\text{pH} = 5$ and $\text{pH} = 9$) as shown for NFT-50, a polyamide membrane, by Nilsson et al. [67]. This hysteresis effect has been attributed to increased polymer flexibility at higher temperature opening new pathways for transport, which do not disappear if the membrane stays in a wetted state [67]. Manttari et al. [68] showed hysteresis effects in membrane performance for commercial NF membranes that were exposed to temperatures as high as 65 °C. However, in their case the increase in temperature led to a membrane flux loss for some of the membranes evaluated, possibly due to membrane compaction following increased polymer chain flexibility due to the high temperature exposure. Kallioinen et al. [41] also showed that increasing temperature under alkaline conditions ($\text{pH} = 11.5$) can lead to changes in membrane performance for commercially available polyamide membranes, but these performance changes could be (slowly) reversed in time and were ascribed to conformational changes in the polymer structure rather than chemical instability of the membrane (see Section 2.1). A fairer comparison of the membrane performance prior to and following exposure of the (PEI/BDSC)/PVDF membrane to the acid solutions in the study of Eslami et al. [65] would therefore have been when the membrane would have been exposed to $T = 70$ °C prior to membrane characterization and exposure to the acid solution, or when the membrane characterization prior to and following exposure to the acid solution would have been performed at $T = 70$ °C.

Polyallylamine hydrochloride (PAH) and BDSC were also used to prepare polysulfonamide membranes on a 30 kDa PES UF membrane (Zhongcorui Film Technology Co.) support [69]. The pH of the aqueous PAH solution used was varied from 8.5 to 9.7, yielding membranes with different characteristics. A membrane prepared using a 0.1 %w/v BDSC solution in Isopar G and a 0.7 %w/v PAH aqueous solution at $\text{pH} = 9.33$ with a soaking time of 25 min and a reaction time of 20 min resulted in a membrane ((PAH/BDSC)/PES) with a MWCO of approximately 720 Da and an IEP = 8.5 [69]. Upon exposure of the membrane to a 20 %w/v

H_2SO_4 solution at $T = 25$ °C for 30 days a slight reduction in retention was observed from 92.4 to 88.3% in combination with a slight flux increase from 34.1 to 38.6 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ based on intermittent characterization tests using a $1.0 \text{ g}\cdot\text{L}^{-1}$ MgCl_2 solution at $P = 5$ bar and room temperature [69]. This clearly indicates slight membrane instability at the evaluated extremely low pH conditions. To improve the (PAH/BDSC)/PES membrane the addition of hydrophilic triazine-structured covalent organic frameworks (nitrogen enriched nanoporous polytriazine, NENP-1) during the IP membrane preparation was tried [70]. NENP-1, a honeycomb structure linked by $-\text{NH}-$ groups, had been produced from cyanuric chloride (CC) and MeI and was mixed with the aqueous PAH solution with varied NENP-1 concentrations. A (NENP-1 – PAH/BDSC)/PES nanofiltration membrane with a MWCO = 620 Da (equivalent to a pore radius of 0.70 nm) was produced using a 0.15 %w/v BDSC solution in Isopar G and a 0.8 %w/v PAH aqueous solution at $\text{pH} = 9.35$ with a reaction time of 20 min. For this membrane a 0.1 %w/v NENP-1 concentration was used. Immersion of the prepared membrane in a 20 %w/v H_2SO_4 solution at $T = 25$ °C for 30 days resulted in a gradual practically linear reduction in retention from 93.0 to 90.9% in combination with a slight flux increase from 75.4 to 81.5 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ as determined from intermittent membrane characterization using $1.0 \text{ g}\cdot\text{L}^{-1}$ MgCl_2 solution at $P = 5$ bar and room temperature [70]. The stability of this membrane was therefore slightly better than for (PAH/BDSC)/PES [69], but the membrane was not completely stable.

4.5.2. Naphthalene-1,3,6-trisulfonylchloride-based membranes

Polysulfonamide membranes based on diethylenetriamine (DETA) and naphthalene-1,3,6-trisulfonylchloride (NTSC) were prepared on a commercial PSf membrane support ((DETA/NTSC)/PSf) [71]. Alternatively, a membrane with a sulfonated polyether ether ketone (SPEEK) intermediate layer ((DETA/NTSC)/SPEEK/PSf) was prepared [71]. The SPEEK used had a sulfonation degree (SD) of 0.69. The ((DETA/NTSC)/PSf) and ((DETA/NTSC)/SPEEK/PSf) membranes showed an IEP of 4.3 and 4.1, respectively. The membrane without the SPEEK intermittent layer had a MWCO of approximately 1500 Da (a tight UF membrane), whereas the membrane with the intermittent SPEEK layer was identified as an open NF membrane with a MWCO of approximately 800 Da. Immersion of the membranes in an 8 %w H_2SO_4 solution at 25 °C for 24 h did not affect the performance of ((DETA/NTSC)/PSf) with an unchanged water flux of $7.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and approximately 92% retention during membrane characterization using a $1.0 \text{ g}\cdot\text{L}^{-1}$ Na_2SO_4 solution at $P = 10$ bar and $T = 25$ °C. During characterization at the same conditions ((DETA/NTSC)/SPEEK/PSf) showed an increase in water flux from approximately $25 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ prior to its exposure to the acid solution to approximately $40 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ after its exposure to the acid solution [71]. Despite the relatively strong increase in permeance, the Na_2SO_4 retention remained almost constant at approximately 99% for 24 h. The stability of this polysulfonamide membrane with a SPEEK intermittent layer is therefore not completely clear.

4.5.3. 2,4,6-(Trisulfonyl)phenol-based membranes

Polysulfonamide membranes based on Pip and 2,4,6-(trisulfonyl)phenol (TCSP) were prepared on a PES support using spinning assisted multilayer IP [39]. A 5-layer (Pip/TCSP)/PES membrane showed an IEP = 3.1, a pure water permeance of $3.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and retentions for Na_2SO_4 , MgSO_4 , NaCl of 99.8%, 99.4% and 85.5%, respectively, during characterization experiments using $2.0 \text{ g}\cdot\text{L}^{-1}$ single salt solutions at $T = 25$ °C and $P = 10$ bar. A (Pip/TCSP)/PES membrane produced via a traditional IP procedure showed a pure water permeance of only $1.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and MgSO_4 and Na_2SO_4 retentions of 92.9% and 98.3%, respectively, at the same conditions. Immersion of the 5-layer (Pip/TCSP)/PES membrane in a 20 %w H_2SO_4 solution at $T = 90$ °C for 24 h led to a strong increase in pure water permeance to $5.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and a reduction in Na_2SO_4 retention to 96.6% after 6 h exposure. This change was followed by a small reduction in water permeance to $5.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and a

further reduction in Na₂SO₄ retention to 95.9% after 12 h exposure and unchanged performance during the next 12 h. The (Pip/TCSP)/PES membrane prepared via the traditional IP method showed a pure water permeance increase to 3.2 L·m⁻²·h⁻¹·bar⁻¹ and a Na₂SO₄ retention reduction to 96.0% after 24 h exposure of the membrane to the 20 %w H₂SO₄ solution at T = 90 °C. The pure water permeance changes were ascribed to dissolution of oligomers by the acid solution. Despite the changes in performance the membrane was claimed to show relatively good stability in the acid solution compared to a prepared (Pip/TMC)/PES polyamide membrane and NF-270, based on unchanged ATR-IR results indicating unchanged chemical composition and the limited reduction in Na₂SO₄ retention [39]. Especially when taken into account that the (Pip/TCSP)/PES polysulfonamide membranes were exposed to not only extreme pH conditions, but extreme temperature conditions as well, the relatively stable performance of the prepared membranes is remarkable, although it should also be noted that the exposure time was only 30 h. It should also be noted that the membrane had not been exposed to T = 90 °C during characterization prior to exposure to the acid solution, whereas this was the case during characterization following the exposure to the acid solution at T = 90 °C. As mentioned earlier, this may have caused the observed performance changes (higher permeance and lower retention), making a proper evaluation of the pH stability results at this high temperature more difficult.

4.5.4. Summarizing the pH stability of developed polysulfonamide membranes

Observations regarding the acid stability of the poly(amide-sulfonamide), poly(amide-sulfonamide-ester) and polysulfonamide membranes have been summarized in Table 5. Information on these membranes regarding alkaline stability has not been found. Based on the presented information (see Tables 4 and 5 and Fig. 9), poly(amide-sulfonamide), poly(amide-ester-sulfonamide) and polysulfonamide membranes seem to be more stable than their polyamide equivalents for extremely acidic conditions, with polysulfonamide membranes being the most stable out of these three membrane types. At extremely low pH some of the polysulfonamide membranes prepared appear to be fully stable for 24 h at an exposure temperature of T = 25 °C ((DETA/NTSC)/PSf, see Fig. 9 (right)) and even at an exposure temperature of T = 55 °C ((Pip/BDSC)/PES and (MPD/BDSC)/PES, see Fig. 9 (right)), in contrast

to their poly(amide-sulfonamide alternatives ((Pip/BDSC-TMC)/PES and (MPD/BDSC-TMC)/PES, see Fig. 9 (left)). Other membranes were not proven to be fully stable during longer term exposure to temperatures of T = 70 °C or higher, however, observed changes in performance may originate from the temperature change rather than from the extreme pH condition, since these membranes had not been exposed to high temperature prior to exposure to the acid solution. Furthermore, the extremely high sulfuric acid concentration of the solution (20 %w) at this condition may also have played a role. The instability of sulfonamide groups for acid and alkaline hydrolysis was reviewed by Searles and Nukina [72], who showed that these groups are quite stable under acid and alkaline conditions. They furthermore showed that HCl solutions caused protonation of the amine, turning it into a quaternary amine, followed by hydrolysis of the sulfonamide group. Baxter et al. [73] showed that alkaline based hydrolysis of a small sulfonamide is much slower than that of a similar amide, confirming the stability differences obtained in the studies discussed in this review.

4.6. Poly(aryl cyanurate) membranes

Other investigated alternatives for the poorly stable polyamide membranes were poly(aryl cyanurate) membranes based on IP using 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) and CC on a PES UF support [74]. It was anticipated that the membranes would be less susceptible to hydrolysis and therefore more stable at extreme pH conditions than polyamide membranes, since the prepared poly(aryl cyanurate) membranes do not contain a carbonyl group. However, the prepared membranes with a MWCO = 400 Da and a water permeance of 1.8 L·m⁻²·h⁻¹·bar⁻¹ were not stable in a 0.1 mol·L⁻¹ HNO₃ solution (pH = 1) nor in a 0.01 mol·L⁻¹ (pH = 12) or a 0.1 mol·L⁻¹ (pH = 13) NaOH solution for two months. The membrane performance during intermittent characterization tests seemed to be stable at pH = 12 for two weeks, but a strong permeance increase and a gradual MgSO₄ retention reduction was observed afterwards. The authors conclude that the aryl cyanurate bond behaves like an ester bond, which is susceptible to hydrolysis, as observed for polyesteramide NF membranes [64], and is the cause for the observed membrane degradation at low and high pH [74]. Another possible explanation for the observed degradation of these types of membranes is the presence of the ether bond adjacent to the aromatic

Table 5

Stability of poly(amide-sulfonamide), poly(amide-ester-sulfonamide) and polysulfonamide membranes at extreme acid conditions.

Membrane type and name	Acid stability
Poly(amide-sulfonamide) (Pip/BDSC-TMC)/PES	Unstable for immersion in a 2.5 %w HNO ₃ solution at T = 55 °C for 24 h, but more stable than (Pip/TMC)/PES [53]
Poly(amide-sulfonamide) (MPD/BDSC-TMC)/PES	Unstable for immersion in a 10 %w H ₂ SO ₄ solution at T = 55 °C for 24 h, but more stable than (Pip/TMC)/PES [53]
Poly(amide-ester-sulfonamide) (Pip-SMeF-SA/TMC)/PSf	Unstable for immersion in a 2.5 %w HNO ₃ solution at T = 55 °C for 24 h, but more stable than (MPD/TMC)/PES [53]
Polysulfonamide (Pip/BDSC)/PES	Unstable for immersion in a 10 %w H ₂ SO ₄ solution at T = 55 °C for 24 h, but more stable than (MPD/TMC)/PES [53]
Polysulfonamide (MPD/BDSC)/PES	Stable for immersion in a 10 %w H ₂ SO ₄ solution at T = 55 °C for 24 h [53]
Polysulfonamide (PEI/BDSC)/PVDF	Unstable for immersion in a 20 %w H ₂ SO ₄ solution at T = 70 °C for 24 h, but more stable than (PEI-MPD)/BDSC/PVDF [65]
Polysulfonamide (PEI-Pip/BDSC)/PVDF	Unstable for immersion in a 2.5 %w HNO ₃ solution at T = 70 °C for 24 h, but more stable than (PEI-MPD)/BDSC/PVDF [65]
Polysulfonamide (PEI-MPD/BDSC)/PVDF	Unstable for immersion in a 20 %w H ₂ SO ₄ solution at T = 70 °C for 24 h, but more stable than (PEI-MPD)/BDSC/PVDF [65]
Polysulfonamide (PAH/BDSC)/PES	Unstable for immersion in a 2.5 %w HNO ₃ solution at T = 70 °C for 24 h [65]
Polysulfonamide (NENP-1 - PAH/BDSC)/PES	Not fully stable for immersion in a 20 %w H ₂ SO ₄ solution at T = 25 °C for 30 days [69]
Polysulfonamide (DETA/NTSC)/PSf	Not fully stable for immersion in a 20 %w H ₂ SO ₄ solution at T = 25 °C for 30 days [70], but slightly more stable than (PAH/BDSC)/PES
Polysulfonamide (DETA/NTSC)/SPEEK/PSf	Stable for immersion in an 8 %w H ₂ SO ₄ solution at T = 25 °C for 24 h [71]
Polysulfonamide (Pip/TCSP)/PES	Possibly unstable for immersion in an 8 %w H ₂ SO ₄ solution at T = 25 °C for 24 h [71]
Polysulfonamide (Pip/TCSP)/PES	Possibly stable for immersion in an 8 %w H ₂ SO ₄ solution at T = 90 °C for 30 h [39]

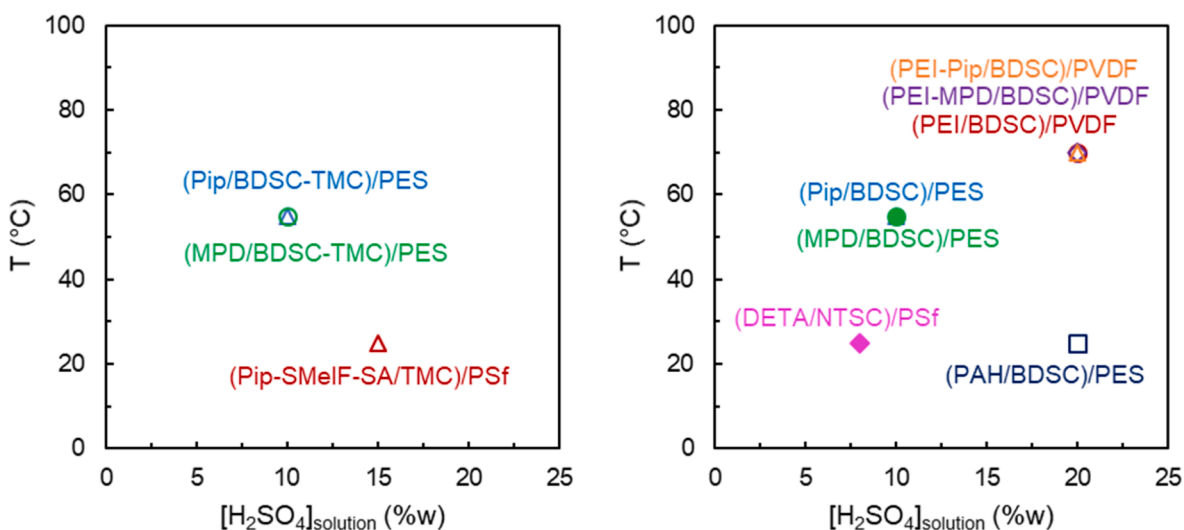


Fig. 9. Sulfuric acid solution concentration – temperature combinations for which recently developed poly(amide-sulfonamide) and poly(amide-ester-sulfonamide) membranes (left) and NTSC or BDSC based polysulfonamide membranes (right) were evaluated and found instable (open symbols) or stable (filled symbols).

ring in the polymer, which are mentioned to be susceptible to hydrolysis [75]. The occurrence of hydrolysis of aryl cyanurate bonds for highly crosslinked polyaromatic cyanate ester resins was proven by Marella et al. [76], who also explained the degradation path.

4.7. Polyurea membranes

IP-based polyurea membranes have been produced from a diisocyanate (hexamethylene diisocyanate (HDI), a diphenylmethane diisocyanate (MDI), a 1,4-phenylene diisocyanate (PDI) or a toluene diisocyanate (TDI)) and a combination of amines (branched PEI and Pip) on a PES support, which was prepared via non-solvent induced phase separation [77]. The diisocyanate concentration in the (unspecified) organic solvent was varied between 0.1 and 0.25 %w/v, while the concentration fraction of PEI was varied between 0 and 0.5 %w/v at a constant total amine concentration of 0.5 %w/v in the aqueous solution. Furthermore, all prepared polyurea membranes were annealed using a heat treatment at $T = 70\text{ }^{\circ}\text{C}$ for 3 min. (PEI_{0.4}-Pip_{0.1}/PDI_{0.2})/PES, (PEI_{0.4}-Pip_{0.1}/TDI_{0.2})/PES, (PEI_{0.4}-Pip_{0.1}/MDI_{0.2})/PES and (PEI_{0.4}-Pip_{0.1}/HDI_{0.2})/PES (where the subscript describes the concentration in the solution used to prepare the membrane) showed a PEG (200 g·mol⁻¹) retention of 90%, 89%, 64% and 26%, respectively. (PEI_{0.4}-Pip_{0.1}/PDI_{0.2})/PES and (PEI_{0.4}-Pip_{0.1}/TDI_{0.2})/PES have relatively low water permeance, 0.5 L·m⁻²·h⁻¹·bar⁻¹ and 1.0 L·m⁻²·h⁻¹·bar⁻¹, respectively. Both membranes, characterized as tight NF membranes, showed a higher MWCO in combination with a considerably lower permeance compared to MPF-34 [77]. (PEI_{0.4}-Pip_{0.1}/PDI_{0.2})/PES showed an IEP slightly in excess of IEP = 5.

(PEI_{0.1}-Pip_{0.4}/PDI_{0.2})/PES, a membrane with a 30% higher permeance than (PEI_{0.4}-Pip_{0.1}/PDI_{0.2})/PES and a similar MgSO₄ retention (around 97%) was evaluated for long-term acid stability by immersing the membrane into a 20 %w/v HCl, a 20 %w/v H₂SO₄, a 20 %w/v H₃PO₄, or a 15 %w/v acetic acid (CH₃COOH) solution at room temperature for 1 year. Intermediate characterization tests using a 2000 ppm MgSO₄ solution at $P = 20\text{ bar}$ and room temperature were performed to establish the stability of the membrane in these solutions. In all cases a gradual increase in permeance (of at least 100%, but in some cases even 400%) and a reduction in retention was obtained that continued even during the final months of exposure. However, for most cases the retention stayed in excess of 90%, which is remarkable for such a long exposure time at these extreme acid conditions. Only for immersion in the 20 %w/v H₂SO₄ solution a retention of only 87% was obtained after 1 year [77]. (PEI_{0.4}-Pip_{0.1}/PDI_{0.2})/PES and (PEI_{0.1}-Pip_{0.4}/

PDI_{0.2})/PES showed a similar behaviour regarding permeance and retention changes for immersion in either 20 %w/v HCl or 20 %w/v H₂SO₄, whereas for (PEI_{0.4}-Pip_{0.1}/TDI_{0.2})/PES and (PEI_{0.4}-Pip_{0.1}/PDI_{0.25})/PES the changes were significantly higher and lower, respectively. Although the permeance change for (PEI_{0.4}-Pip_{0.1}/PDI_{0.25})/PES was relatively small compared to the permeance change for (PEI_{0.4}-Pip_{0.1}/PDI_{0.2})/PES it should be noted that the initial permeance of (PEI_{0.4}-Pip_{0.1}/PDI_{0.25})/PES was more than 20% lower as well. Furthermore, the change in retention and permeance for MPF-34 was significantly smaller than for the polyurea membranes prepared, indicating that this membrane is more suitable for the treatment of these acid solutions. Nevertheless, PDI-based polyurea NF membranes can be produced with relatively high acid stability, especially taking the long immersion time and the limited change in retention into account. The urea (—NH—CO—NH—) bond consequently seems to be stronger than the amide (—NH—CO—) bond found in polyamide membranes, which appeared to be (far) less stable (see Section 4.1). The authors even claim that the membranes are fully stable and that the observed changes in performance stem from membrane swelling, since ATR-FTIR and SEM results of the membranes prior to and following immersion of the membranes in the acid solutions were the same [77]. However, the absorbance at 1656 cm⁻¹, representing the stretching of the carbonyl group in the urea group is relatively small, and limited changes due to hydrolysis or other membrane degradation mechanisms, such as due to an osmotic pressure shock after removal from the concentrated acid solution and washing with pure water, will hardly be visible in the transmittance figures. Since the change in permeance and retention continued even after 350 days, it is more likely that gradual hydrolysis or membrane degrading of the polyurea membranes occurred rather than membrane swelling. However, this does not change the conclusion that the membranes have relatively high stability and are considerably more acid stable than polyamide membranes. Long term filtration tests of (PEI_{0.4}-Pip_{0.1}/PDI_{0.25})/PES using an acid solution consisting of 20 % w/v H₂SO₄ and 2000 ppm Na₂SO₄ for 35 days resulted in stable retentions and a permeance increase of only 10%. This relatively good stability indicates that part of the performance change for this membrane in immersion tests may indeed have been caused by an osmotic pressure shock during removal from the acid solution and subsequent washing with pure water.

Immersion of (PEI_{0.1}-Pip_{0.4}/PDI_{0.2})/PES and (PEI_{0.4}-Pip_{0.1}/PDI_{0.25})/PES in a 20 %w/v NaOH solution also led to a strong gradual increase in permeance of 500% and 300%, respectively and a gradual MgSO₄ retention reduction from 97% to 84% and 98% to 91%, respectively in 1

year. The permeance increase and the retention reduction for MPF-34 was lower than for these polyurea membranes, but after immersion for 1 year (PEI_{0.4}-Pip_{0.1}/PDI_{0.25})/PES and MPF-34 showed the same permeance and retention. In this case, like for the immersion in acid solutions, the permeance and retention changes for the polyurea membranes are more likely caused by membrane degradation or hydrolysis than by membrane swelling. Long term filtration tests of (PEI_{0.4}-Pip_{0.1}/PDI_{0.25})/PES using an alkaline solution consisting of 5 %w/v NaOH and 2000 ppm Na₂SO₄ for 35 days resulted in stable retentions and a permeance increase of approximately 20%.

4.8. Polyamine membranes

IP based TFC polyamine membranes feature membrane top layers based on a multifunctional amine molecule (see for examples [Tables 5 and 6](#)) and either cyanuric chloride (CC) or 1,3,5-tris(bromomethyl)-

benzene (TBMB).

4.8.1. Cyanuric chloride-based membranes

TFC polyamine NF membranes based on interfacial polymerization were prepared by reacting either PEI or a multifunctional monomeric amine (Mel, MPD, ethylene diamine (EDA), DETA, Pip, tetraethylene pentamine (TEPA), see [Tables 5 and 6](#)) with cyanuric chloride (CC). As support either a flat sheet 30 kDa hydrophilized PES UH030 UF membrane (Microdyn Nadir) [[24,78](#)], a flat sheet 20 kDa PES UF membrane (Hagzhou Doa Mmc Co., Ltd) [[79](#)], a 30 kDa PES UF membrane (Advanced Membrane Technology Inc.) [[80](#)], a PSf membrane [[63](#)] or a crosslinked PVDF membrane using 1,6-hexanediamine (HDA) as cross-linker [[81](#)] were applied. For the preparation of polyamine membranes CC replaced TMC, which is commonly applied in the production of polyamide membranes for NF and reverse osmosis (RO) applications as shown in earlier sections.

Table 6
Typical molecules used in the preparation of polyamine IP TFC NF membranes.

Molecule (abbreviation)	Molecular structure monomer	Molecular structure polyamine based on cyanuric chloride
melamine (Mel)		
ethylene diamine (EDA)		
diethylene triamine (DETA)		
tetraethylene pentaamine (TEPA)		
(linear) polyethyleneimine (PEI)		
(branched) polyethyleneimine (PEI)		
cyanuric chloride (CC)		

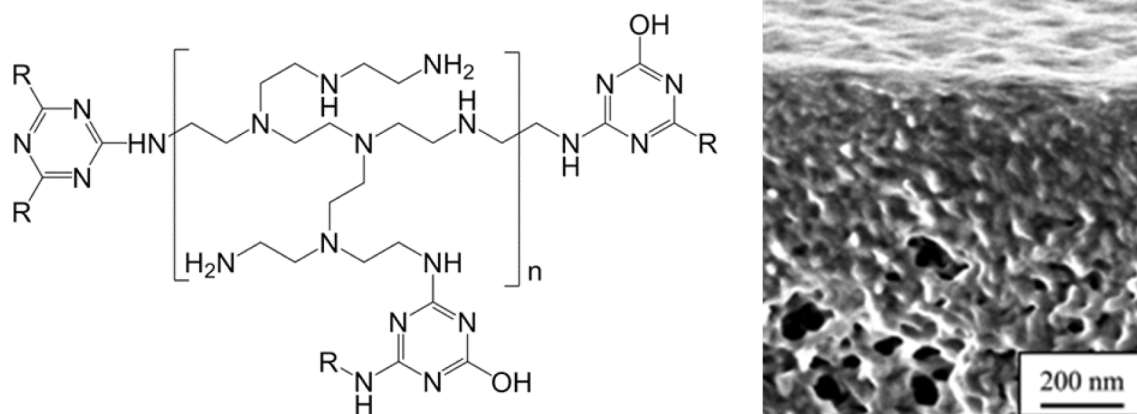


Fig. 10. Chemical representation of PEI/CC polymer top layer (left) and scanning electron microscopy image of a (PEI/CC)/PES membrane produced by Lee et al. [24] (right). Reproduced with permission of Elsevier.

Variation of PEI (MW = 25,000 mol·g⁻¹) and CC concentrations in water and hexane, respectively, led to (PEI/CC)/PES NF membranes with a permeance between 0.1 and 2.7 L·m⁻²·h⁻¹·bar⁻¹ and a NaCl retention between 95 and 50% for NF of a 2.0 g·L⁻¹ NaCl solution at P = 10 bar and room temperature [24]. A (PEI/CC)/PES NF membrane (see Fig. 10) prepared from 1.25 g·L⁻¹ PEI in water and 0.5 g·L⁻¹ CC in hexane, having a MWCO = 500 Da, showed stable performance for 900 h ex-situ exposure to a 0.1 mol·L⁻¹ NaOH solution at room temperature. Proper membrane stability was concluded based on a stable permeance close to 3 L·m⁻²·h⁻¹·bar⁻¹ (after an initial 30% change in permeance) and a stable (approximately 55 – 60%) NaCl retention during intermittent membrane characterization tests [24]. After 900 h exposure to a 0.1 mol·L⁻¹ HNO₃ solution at room temperature, the membrane appeared to be stable as well, showing slightly lower permeance and slightly higher NaCl retention compared to the membrane after exposure to a 0.1 mol·L⁻¹ NaOH solution [24]. (PEI/CC)/PES membranes based on different PES surface activation methods were evaluated as well [79], using either sodium dodecyl sulfate (SDS), sodium lauryl sulfonate (SLS) or sodium dodecyl benzenesulfonate (SDBS) as surfactant. The surfactant concentration was varied between 0 and 0.2 %w and an aqueous solution of 10 g·L⁻¹ PEI (MW = 1800 mol·g⁻¹) and 0.07 g·L⁻¹ CC in hexane were used to prepare the thin film composite layer on the PES UF support (MWCO = 20 kDa, Hagzhou Doa Mmc Co., Ltd). The resulting NF layer was cured at T = 80 °C for 5 min [79]. The most optimal membrane, based on water permeance and MgCl₂ retention, was produced based on (0.1 %w) SDS [79], which was also used by Lee et al. [24], albeit at slightly lower concentration (0.05 %w). The optimal (PEI/CC)/PES membrane showed a high pure water permeance (13.7 L·m⁻²·h⁻¹·bar⁻¹ at P = 10 bar) and a MgCl₂ retention as high as 92% at T = 25 °C and P = 10 bar using a 500 ppm MgCl₂ solution. As expected, a positively charged membrane was produced with an IEP ≫ 8, higher than the IEP = 7.5 as obtained by Lee et al. [24] for their (PEI/CC)/PES membrane, as also confirmed by the salt retention order of R MgCl₂ > R NaCl > R MgSO₄ > R Na₂SO₄. The optimal membrane, like membranes produced using either 0.05 %w or 0.2 %w SDS solutions, showed good acid stability at pH = 1 as determined from ex-situ exposure tests for 35 days as well as from in-situ nanofiltration tests at pH = 1 for 12 h using a 0.1 mol·L⁻¹ HNO₃ solution containing 1000 ppm MgCl₂. Especially for the membranes prepared using either 0.1 %w or 0.2 %w SDS solutions MgCl₂ retention was unaffected by the ex-situ exposure, while the (PEI/CC)/PES permeance gradually reduced with time and started at a lower value than obtained during the in-situ pH stability tests. During the in-situ pH stability tests for 12 h MgCl₂ retention was clearly lower and the permeance was clearly higher than obtained during the characterization tests performed following ex-situ exposure to the 0.1 mol·L⁻¹ HNO₃ solution. These differences may be caused by evaluation at different pressures (3 bar for the

in-situ tests vs 10 bar for characterization following ex-situ exposure [79]), leading to a different compaction behavior. Furthermore, at pH = 1 the presence of a high proton concentration related to the magnesium concentration resulted in substantially lower magnesium retentions due to reduced Donnan exclusion at higher chloride concentration. Obtained membrane permeances were considerably higher than reported by Lee et al. for their (PEI/CC)/PES membrane [24], albeit that a direct comparison cannot be made since the pore size or the MWCO of the membranes prepared by Bai et al. was not determined [79]. A similarly good stability was obtained for a (PEI/CC)/PSf membrane during exposure to a 0.1 mol·L⁻¹ HNO₃ solution or a 0.1 mol·L⁻¹ NaOH solution at ambient temperature [63]. (PEI/CC)/PSf showed a stable membrane flux (0.5 L·m⁻²·h⁻¹) and retention (90%), during membrane characterization using a 1 g·L⁻¹ MgCl₂ solution at P = 10 bar and room temperature, independent on whether the acid or the alkaline solution was used, for 720 h exposure to the extreme pH solutions [63]. In all cases, the PEI/CC top layer membranes were more stable than their PEI/TMC equivalents [24,61,63] which were discussed in Section 4.1.4. An effort was made [80] to (further) improve the PEI/CC top layer by creating a Janus type layer (with different properties in the top layer near the membrane surface and the part of the top layer close to the support) with higher permeance, using low CC concentrations and temperature curing. For the preparation of the (PEI/CC)/PES membrane a 10.0 g·L⁻¹ aqueous PEI solution was used, while the CC concentration in hexane was varied between 0.01 g·L⁻¹ and 2.0 g·L⁻¹ to study the optimal concentration. A 30 kDa PES UF membrane (Advanced Membrane Technology Inc.) was used as support. Relatively open NF and tight UF membranes were prepared with MWCO ranging from 680 to 1400 Da. Only membranes based on a CC concentration between 0.05 and 0.15 g·L⁻¹ showed a MgCl₂ retention in excess of 90% in combination with a permeance in excess of 2.5 L·m⁻²·h⁻¹·bar⁻¹. The Na₂SO₄ retention increased with an increasing CC concentration [80] from below 20% to almost 50% for a 0.05 g·L⁻¹ CC solution and a 0.15 g·L⁻¹ CC solution, respectively. The (PEI/CC)/PES membrane, produced from 0.15 g·L⁻¹ CC in hexane and cured at T = 70 °C for 5 min, with a MWCO close to 1000 Da showed very stable MgCl₂ retention (during intermittent characterization tests) for exposure to a 3 %w HCl solution at T = 25 °C for 1800 h. Exposure to the 3 %w HCl solution at T = 50 °C during 72 h resulted in a gradual decrease in MgCl₂ retention and an increase in water permeance from 2.5 L·m⁻²·h⁻¹·bar⁻¹ to approximately 6 L·m⁻²·h⁻¹·bar⁻¹ for membrane characterization at room temperature [80]. The permeance seemed to stabilize at 6 L·m⁻²·h⁻¹·bar⁻¹ after 48 h. For this case, the membrane had not been exposed to T = 50 °C during the characterization prior to exposure to the acid solution and hysteresis effects as discussed in Section 4.5.1 may have played a role here as well.

Membranes with NF layers consisting of EDA, MPD, Pip or Mel on a

PES UH030 membrane support showed very attractive permeances during characterization experiments with 2 g·L⁻¹ NaCl solutions at 10 bar pressure, but at the same time very low NaCl retentions (below 15%) [78]. Membranes with NF layers consisting of DETA or TEPA on the same support showed NaCl retentions in the NF range of 50 – 85% in combination with a relatively low permeance (around 2 L·m⁻²·h⁻¹·bar⁻¹ at maximum), which is partly caused by the relatively low permeance of the PES UH030 membrane support of only 30 L·m⁻²·h⁻¹·bar⁻¹. Out of these monomeric amines-based polyamine membranes a (DETA/CC)/PES membrane with a permeance of 1.5 L·m⁻²·h⁻¹·bar⁻¹, the most optimal amongst the membranes developed, was selected [78] for ex-situ exposure to extreme pH conditions. Intermittent characterization tests using pure water or a 2 g·L⁻¹ NaCl solution showed that the membrane stability at pH = 1 (0.1 mol·L⁻¹ HNO₃ solution) and pH = 13 (0.1 mol·L⁻¹ NaOH solution) for 1200 h exposure time was good with generally a stable permeance and NaCl retention at P = 10 bar. For one of the membrane samples exposed ex-situ to pH = 13 some increase in permeance was observed. In the flux range between 10 and 30 L·m⁻²·h⁻¹, a retention for PEG with an average molecular weight of MW = 200 g·mol⁻¹ (PEG 200) slightly in excess of 90% was obtained for a membrane that had been exposed to a 0.1 mol·L⁻¹ NaOH solution (pH = 13), while the retention for a membrane that had been exposed to a 0.1 mol·L⁻¹ HNO₃ solution (pH = 1) was even slightly higher in the same flux range. A NF membrane featuring a DETA/CC top layer on a crosslinked PVDF support produced using 1,6-hexanediamine (HDA) as crosslinker was evaluated for permeance and sucrose retention using a 5 g·L⁻¹ concentration at P = 10 bar in a stirred cell [81]. Prior to its exposure to alkaline or acid solutions, the membrane had a water permeance of approximately 0.7 L·m⁻²·h⁻¹·bar⁻¹ and a sucrose retention of 88%. After exposure to a 5 mol·L⁻¹ HCl solution for 5 days no significant change in sucrose retention was found, but a more than 100% increase in permeance was seen, in contrast to observations of Lee et al [78]. This difference in stability behavior between the (DETA/CC)/PVDF and (DETA/CC)/PES membranes was ascribed to the extremely high acid concentrations used in the work of Van Goethem et al. [81]. A small and insignificant permeance increase (to approximately 0.9 L·m⁻²·h⁻¹·bar⁻¹) was reported for the membrane after exposure to a 5 mol·L⁻¹ NaOH solution for 5 days. This change was ascribed to reversible physicochemical changes of the membrane, as also found by Lee et al. for extreme alkaline conditions [78,81]. However, an average sucrose retention of 80%, significantly lower than obtained prior to exposure to the alkaline solution, was found albeit with relatively high standard deviation [81]. This reduction in sucrose retention is not in line with the practically unchanged MWCO results reported for (DETA/CC)/PES after exposure to the 0.1 mol·L⁻¹ NaOH solution [78]. The chemical stability of the (DETA/CC)/PVDF membrane at these extremely high acid and alkaline concentrations is consequently doubtful.

4.8.2. Surface modified cyanuric chloride-based membranes

Surface modified polyamine membranes based on pentaethylene hexamine (PEHA) and CC via interfacial polymerization on a PVDF nanofibrous support created by phase inversion were produced using a 2 %w Tris solution [62]. Amongst others, the effect of reaction temperature was studied since this has a clear effect on the membrane properties due to the difference in reactivity between the first, second and third chloride group reacting. Although the authors claim that their optimized tris-grafted polyamine membrane does not show a significant performance change due to exposure to the 0.1 mol·L⁻¹ HNO₃ or the 0.1 mol·L⁻¹ NaOH solution for 30 days, their graphical results from membrane characterization experiments at P = 6 bar and unspecified temperature seem to show a minor reduction in MgSO₄ retention and a significant increase in water permeance, which is worse for the exposure to the alkaline solution (40% vs 20% increase). The increase in water flux may have resulted in the observed minor reduction of the MgSO₄ retention due to concentration polarization in the dead-end cell used for the characterization experiments. Furthermore, the increased

permeance may be a result of membrane swelling at the extreme pH conditions. In any case, the observed retention change was clearly lower than obtained for their surface modified polyamide alternatives (see Section 4.1.2).

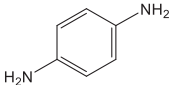
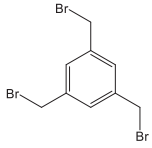
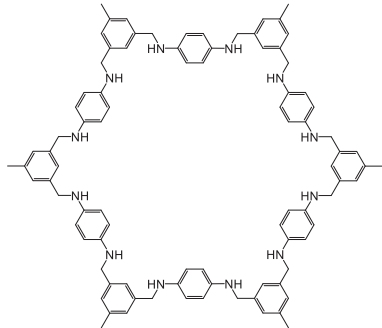
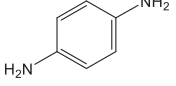
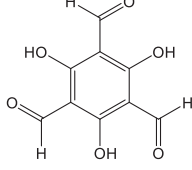
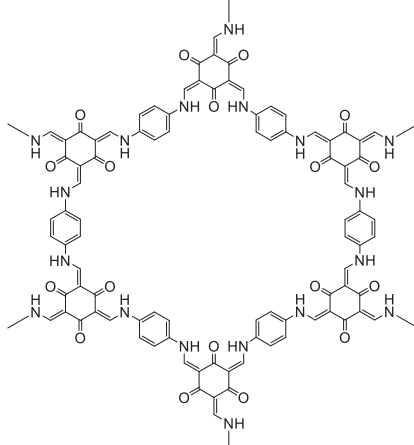
4.8.3. 1,3,5-tris(bromomethyl)-benzene-based membranes

Other polyamine TFC NF membranes were prepared based on 1,3,5-tris(bromomethyl)-benzene (TBMB) and either p-phenylenediamine (PPD, see Table 7) or MPD. UH030, a 30 kDa PES UF membrane (Microdyn-Nadir), was used as support [82]. Both in-situ as well as ex-situ pH stability tests were performed to evaluate the pH stability of the prepared membranes. The ex-situ tests featured storage of the membranes in either a 0.1 mol·L⁻¹ HNO₃ or a 0.1 mol·L⁻¹ NaOH solution at room temperature during approximately 60 days with intermittent membrane characterization, whereas in-situ tests featured nanofiltration of a 0.1 mol·L⁻¹ NaOH solution during 6 h followed by nanofiltration of a 0.1 mol·L⁻¹ HNO₃ solution during 6 h with intermittent membrane characterization. (PPD/TBMB)/PES and (MPD/TBMB)/PES membranes with pure water permeances of 0.28 L·m⁻²·h⁻¹·bar⁻¹ and 1.3 L·m⁻²·h⁻¹·bar⁻¹, MgCl₂ retentions of 68% and 67%, and a claimed MWCO of around 800 Da and 570 Da, respectively, were produced [82]. Both membranes were claimed to show excellent stability in the acid and alkaline solutions based on the ex-situ and the in-situ exposure tests. Based on the pH stability results for other polyamine membranes (see Section 4.8.1), this is indeed expected. However, a strong gradual increase in permeance (by a factor 5) and an initial increase in MgCl₂ retention (of almost 30%) for ex-situ exposure of (PPD/TBMB)/PES to 0.1 mol·L⁻¹ HNO₃ were observed. These were attributed to membrane cleaning by the solution, removing low molecular polymers and/or unreacted monomers. However, it is unlikely that this would be the only explanation for the observed phenomena, especially for the exposure of the membrane to the acid solution. Adsorption of protons present in the acid solution to form a quaternary ammonium group and a positively charged membrane, leading to higher hydrophilicity and potentially swelling of the membrane would be a more likely explanation. The observed increase in retention upon exposure of the membrane to the acid solution is probably caused by the increase in membrane flux, shifting the water transport mechanism from a diffusion - to a convection-dominated regime. The observed increase in permeance of (PPD/TBMB)/PES is in line with observed permeance increase for the (PEI/CC)/PES membrane produced by Lee et al. [24], as described in Section 4.8.1, albeit that the increase observed for (PPD/TBMB)/PES was considerably higher and did not level-off completely. At the same time in-situ exposure of this membrane to the 0.1 mol·L⁻¹ HNO₃ solution for (PPD/TBMB)/PES for 6 h resulted in a reduced MWCO and higher NaCl, MgSO₄, Na₂SO₄, and MgCl₂ retentions. This lower MWCO and these higher retentions can be (at least partly) caused by operation at a higher flux due to the increased permeance and constant characterization pressure (of 10 bar) used, shifting the water transport from a diffusion - to a convection dominated regime as mentioned earlier. The performance of this membrane for ex-situ exposure to a 0.1 mol·L⁻¹ NaOH solution led to stable MgCl₂ retention and a lower permeance increase than for the acid solution. For the polyamine (PEI/CC)/PES membrane prepared by Lee et al. [24] and for one of the samples of the (DETA/CC)/PES membrane [78] the ex-situ exposure to the 0.1 mol·L⁻¹ NaOH solution also led to a slight initial increase in permeance as mentioned in Section 4.8.1. FTIR and SEM analyses confirmed the pH stability of the (PPD/TBMB)/PES membrane, while contact angle measurements showed unchanged values for the pristine membrane and the membrane exposed to the alkaline solution and a lower value for the membrane exposed to the acid solution [78]. The latter is in line with the higher permeance of this membrane after exposure to the acid solution and was probably caused by the formation of the quaternary positively charged nitrogen regions under acid conditions.

For (MPD/TBMB)/PES stable permeance was obtained during the ex-situ experiments for 60 days with a strong (approximately 20%) initial

Table 7

Examples of covalent organic frameworks and other ring structures as thin film composite nanofiltration layers.

Amine	Molecular structure second monomer	Molecular structure polyamine
		
		

increase in MgSO_4 retention using a $0.1 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 solution, whereas the retention was stable and the permeance gradually increased by approximately 50% during ex-situ exposure to the $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution [82].

4.8.4. 1,3,5-triformylphloroglucinol-based membranes

Polyamine membranes having an in-situ formed covalent organic framework as separating layer were prepared from 1,3,5-triformylphloroglucinol (TFPG) and PPD on a flat sheet 60 kDa PSf support (Vonttron Technology Co.) [83] and on a hollow fiber 70 kDa PSf support (Solvay) [59]. The resulting structure of the COF separation layer can be found in Table 7.

Interfacial polymerization conditions used for the flat-sheet (PPD/TFPG)/PSf membrane evaluated for chemical stability in a $2 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution ($\text{pH} = 14.3$) and a $2 \text{ mol}\cdot\text{L}^{-1}$ HCl ($\text{pH} = -0.3$) solution for 7 days included the use of a 0.04 %w aqueous solution of PPD, a 0.05 % w TFPG solution in hexane, and a reaction time of 10 s at $T = 30^\circ\text{C}$. Although the MWCO of the membrane was not determined, a pore diameter for the COF layer membrane of 2.3 nm with narrow pore size distribution was estimated [83] based on Brunauer–Emmett–Teller (BET) measurements using crystalline PPD/TFPG COF particles produced especially for these analyses. If this pore diameter would indeed be valid for the produced membrane, the membrane would qualify as an open NF membrane or tight UF membrane with a pore size comparable to that for NTR-7450 [25]. The flat sheet (PPD/TFPG)/PSf membrane showed a relatively low IEP of 3.5, a high pure water permeance of approximately $33 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and a Congo Red retention close to 100% at $P = 2$ bar and $T = 25^\circ\text{C}$. The permeance and retention were hardly influenced by the exposure to the acid or alkaline solution. Only after exposure to the $2 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution a higher pure water permeance (of $40 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) was observed [83], which may be a

first indication of membrane instability at these extreme alkaline conditions. The use of a higher PPD concentration during the IP process of 2.0 %w at otherwise unchanged conditions apart from thermally treating the membrane at $T = 60^\circ\text{C}$ for 5 min resulted in a (PPD/TFPG)/PSf membrane with a higher pure water permeance ($50 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) and 99.5% Congo Red retention. This membrane showed a similar stability behavior for exposure to a $2 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution ($\text{pH} = 14.3$) and a $2 \text{ mol}\cdot\text{L}^{-1}$ HCl ($\text{pH} = -0.3$) solution for 7 days as the membrane prepared using the 0.04 %w aqueous solution. After both low and high pH exposure the retention hardly changed, whereas the permeance was unaffected after exposure to low pH and increased to almost $60 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ upon exposure to the alkaline solution [84].

Interfacial polymerization conditions used for the preparation of a hollow-fiber (PPD/TFPG)/PSf membrane evaluated for chemical stability in a $0.01 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution ($\text{pH} = 12$) for 120 h included the use of a 0.020 %w aqueous solution of PPD, a 0.0010 %w TFPG solution in hexane, a reaction time of 15 s, and a curing time of 3 min at $T = 80^\circ\text{C}$ [59]. This (PPD/TFPG)/PSf membrane showed a retention order of $\text{R Na}_2\text{SO}_4 > \text{R MgSO}_4 > \text{R MgCl}_2 > \text{R NaCl}$, using a single salt solution of $2000 \text{ mg}\cdot\text{L}^{-1}$ at $P = 5$ bar and room temperature. The MWCO or pore size of the membrane was not specified. The membrane was not completely stable, but the permeance increase from 8.5 to $9.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and the Na_2SO_4 retention reduction from 95.8% to 93.0% after 120 h of ex-situ exposure were limited [59], and much smaller than the change observed for a (Pip/TMC)/PSf polyamine hollow-fiber membrane (see Section 4.1).

A (PPD-Mel/TFPG)/PSf flat sheet membrane, prepared from an aqueous solution consisting of 0.04 %w PPD and 0.3 %w Mel, a 0.05 %w TFPG solution in hexane, and a reaction time of 10 s at $T = 30^\circ\text{C}$, was estimated to have multiple pore diameters of 1.9 nm, 2.4 nm and 3.4 nm based on BET measurements. The introduction of the Mel also seemed to

Table 8
Stability of polyamine membranes at extreme pH conditions.

Membrane type and name	Acid stability	Alkaline stability
Polyamine (PEI/CC)/PES	Stable during ex-situ immersion in a 0.1 mol·L ⁻¹ HNO ₃ solution for 900 h at room temperature, after an initial change in permeance [24] Stable during ex-situ exposure to a 3 %w HCl solution at T = 25 °C during 1800 h [80] Not fully stable during ex-situ exposure to a 3 %w HCl solution at T = 50 °C during 72 h [80] Stable during ex-situ immersion in a 0.1 mol·L ⁻¹ HNO ₃ solution for 35 days at room temperature [79] Stable during in-situ nanofiltration using a 0.1 mol·L ⁻¹ HNO ₃ solution for 12 h at room temperature [79]	Stable during ex-situ immersion in a 0.1 mol·L ⁻¹ NaOH solution for 900 h at room temperature, after an initial change in permeance [24]
Polyamine (PEI/CC)/PSf	Stable during ex-situ immersion in a 0.1 mol·L ⁻¹ HNO ₃ solution for 720 h at ambient temperature [63]	Stable during ex-situ immersion in a 0.1 mol·L ⁻¹ NaOH solution for 720 h at ambient temperature [63]
Polyamine (DETA/CC)/PES	Stable during ex-situ immersion in a 0.1 mol·L ⁻¹ HNO ₃ solution at room temperature for 1200 h exposure [78]	Stable during ex-situ immersion in a 0.1 mol·L ⁻¹ NaOH solution at room temperature for 1200 h exposure [78]
Polyamine (DETA/CC)/PVDF	Unstable during ex-situ immersion in a 5.0 mol·L ⁻¹ HCl solution probably at room temperature for 5 days exposure [81]	Probably unstable during ex-situ immersion in a 5.0 mol·L ⁻¹ NaOH solution probably at room temperature for 5 days exposure [81]
Polyamine (PEHA/CC)/PVDF	Possibly not fully stable during ex-situ immersion in a 0.1 mol·L ⁻¹ HNO ₃ solution probably at room temperature for 30 days exposure [62]	Possibly unstable during ex-situ immersion in a 0.1 mol·L ⁻¹ NaOH solution probably at room temperature for 30 days exposure [62]
Polyamine (PPD/TBMB)/PES	Probably stable during ex-situ immersion in a 0.1 mol·L ⁻¹ HNO ₃ solution at room temperature for 60 days exposure [82]	Probably stable during ex-situ immersion in a 0.1 mol·L ⁻¹ NaOH solution at room temperature for 60 days exposure after an initial permeance increase [82]
Polyamine (MPD/TBMB)/PES	Stable during ex-situ immersion in a 0.1 mol·L ⁻¹ HNO ₃ solution at room temperature for 60 days exposure after an initial permeance increase [82]	Probably stable during ex-situ immersion in a 0.1 mol·L ⁻¹ NaOH solution at room temperature for 60 days exposure after an initial permeance increase [82]
Polyamine (PPD/TFPG)/PSf	Stable during ex-situ immersion in a 2 mol·L ⁻¹ HCl solution at room temperature for 7 days exposure [83]	Probably stable during ex-situ immersion in a 2 mol·L ⁻¹ NaOH solution at room temperature for 7 days exposure [83]
Polyamine (PPD-Mel)/TFPG/PSf	Probably not completely stable during ex-situ immersion in a 2 mol·L ⁻¹ HCl solution at room temperature for 7 days exposure [83,84]	Not completely stable during ex-situ immersion in a 0.01 mol·L ⁻¹ NaOH solution at room temperature for 120 h exposure [59] Possibly not completely stable during ex-situ immersion in a 2 mol·L ⁻¹ NaOH solution at room temperature for 7 days exposure [83,84]

increase the IEP to slightly in excess of 4, which resulted from the increased amount of amine groups in the separation layer, and to reduce the crystallinity of the COF [83]. For this membrane ex-situ exposure measurements to a 2 mol·L⁻¹ NaOH solution (pH = 14.3) or a 2 mol·L⁻¹ HCl solution for 7 days indicate a slight reduction in Congo Red retention (worse for the alkaline solution) and an increase in permeance (worse for the alkaline solution as well), starting at around 97% and approximately 50 L·m⁻²·h⁻¹·bar⁻¹, respectively [83].

4.8.5. Summarizing the pH stability of developed polyamine membranes

Stable performance of the CC-based, TBMB-based, and TFPG-based polyamine membranes would be expected for treating solutions with extreme pH based on the top layer structure of polyamine membranes and their limited sensitivity to hydrolysis. For several of the recently developed membranes, such as (PEI/CC)/PES and (DETA/CC)/PES, this has indeed been proven for acid and alkaline solutions with a pH = 1 or pH = 13, respectively. However, for some of the prepared polyamine membranes this has not been proven beyond reasonable doubt. In some of the cases the potential chemical instability may be caused by the extremely high acidity or alkaline concentration (≥ 2.0 mol·L⁻¹, leading to a pH ≤ -0.3 for the acidic solution and a pH ≥ 14.3 for the alkaline solution), whereas in other cases the relatively high temperature (T = 50 °C) may be the cause. Nevertheless, based on the experimental results it is evident that the polyamine membranes are clearly more stable than their polyamide equivalents.

Observations regarding the acid and alkaline stability of the polyamine membranes have been summarized in Table 8.

4.9. Performance characteristics of newly developed NF membranes based on interfacial polymerization

In the previous sections the focus has been on the acid and alkaline stability of NF membranes produced via IP. In general, the polyamine-

based and polyurea-based IP NF membranes appear to have good acid and alkaline stability, whereas polysulfonamide-based IP NF membranes show good acid stability. Other polymeric NF membranes prepared via IP, such as poly(aryl cyanurate), polyesteramide, poly(amide-sulfonamide) and especially polyamide NF membranes, traditionally used for NF applications in the pH = 2 – 11 range, are significantly less pH stable (see Tables 4, 5 and 8 and the previous sections). However, the chemical stability alone is not sufficient for application of the developed membranes in industrial applications. Especially the membrane flux (which is related to membrane permeance, the osmotic pressure difference between the retentate and the permeate, and the concentrate and permeate viscosity) and the separation characteristics of the membrane (such as the retention of organic or inorganic salts and neutral components) strongly affect the applicability of the membrane. Available performance results based on reported membrane characterization prior to the exposure of the developed IP NF membranes to solutions with a pH outside the pH = 2 – 11 range are listed in Table 9. Unfortunately, experimental conditions used for the membrane characterization of the individual IP-based NF membranes were not always identical. Consequently, a direct comparison between the separation characteristics of the different developed membranes is not always possible. Nevertheless, as can be seen from the reported results, tight polyamine and polyurea NF membranes with a MWCO below 500 Da and good chemical stability outside of the pH = 2 – 11 range have been prepared (see Table 9). However, the high permeance obtained for less chemically stable tight (low MWCO) polyamide membranes has not been matched so far, although the use of the IP procedure produced thin film composite layers for tight polyamine membranes as well, resulting in permeances as high as 1 – 3 L·m⁻²·h⁻¹·bar⁻¹. Furthermore, substantial differences in IEP between polyamine and polyamide membranes have been found, usually making the polyamine membranes less negatively or more positively charged than the polyamide membranes, depending on the pH of the solution to which the membrane is exposed. This obviously leads to

Table 9

Characteristics of membranes produced via interfacial polymerization (Superscripts in the Table identify the conditions used for the determination of permeance and/or retention, see below the Table).

Membrane group	Membrane type	MWCO (Da)	Permeance at neutral pH (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	R Na ₂ SO ₄ (%)	R MgSO ₄ (%)	R NaCl (%)	R MgCl ₂ (%)	IEP	Ref.	
Polyamide	(Pip/TMC)/PES	–	1.5 ^l	–	72 ^l	–	–	3.3	[53]	
	(Pip/TMC)/PAN	230	7.0	–	–	40 ^m	–	4.2	[55]	
	(Pip/TMC)/PSf	–	7.1	97.6 ^a	95.0 ^a	54.2 ^a	–	5.0	[56]	
	(Pip/TMC)/PSf	–	5.6 ⁿ	–	92.5 ⁿ	48.9 ⁿ	–	4.0	[44]	
	(Pip/TMC)/PSf	340	8.0	98.3 ^c	–	34 ^c	38 ^c	3.9	[57]	
	(Pip/TMC)/PSf	–	2.4 ^o	–	> 99	–	–	–	[58]	
	(Pip/TMC)/PSf	–	5.6	92 ^b	≈ 90 ^b	≈ 30 ^b	≈ 58 ^b	–	[59]	
	(Pip/TMC)/PTFE	765	8–10	98.1 ^d	93.7 ^d	49.0 ^d	38.1 ^d	–	[60]	
	(MPD/TMC)/PE	< 100	1.7	99.9	99.9	99.6 ^e	99.8 ^e	–	[27]	
	(MPD/TMC)/PE after DMSO treatment	240	14.5	99.9	99.9	85.1 ^e	99.1 ^e	–	[27]	
	(MPD/TMC)/PVDF	–	3.6	–	47 ^f	–	–	–	[62]	
	after Tris surface modification									
	(TPT/TMC)/PSf	–	8.7	–	98.6 ^a	97 ^a	40.5 ^a	–	3.5	[56]
	(PEL/TMC)/PES	–	1.5 ^l	–	68 ^l	–	–	–	7.7	[61]
	(PEL/TMC)/PES	–	7.5 ^g	–	20 ^g	55 ^g	81 ^g	7.5	[24]	
	(PEL/TMC)/PSf	–	0.1	–	33 ^p	92.8 ^p	48.8 ^p	95.1 ^p	9.9	[63]
	(PEI-Mel/TMC)/PES	–	1.7 ^l	–	64 ^l	–	–	–	10.2	[61]
	(Pip-Mel/TMC)/PSf	–	6.1 ⁿ	–	95.5 ⁿ	24.7 ⁿ	–	–	3.5	[44]
	(Pip/TMC/HGPN-SiO ₂)/PSf	454	14	95.1 ^c	93.4 ^c	28 ^c	29 ^c	3.4	[57]	
	Polyesteramide	(MPD-BHPF/TMC)/PSf	–	2.7 ^h	–	–	95.1 ^h	–	–	[64]
	Poly(amide-sulfonamide)	(Pip/BDSC-TMC)/PES	–	2.2 ^l	–	68 ^l	–	–	3.2	[53]
(MPD/BDSC-TMC)/PES		–	1.8 ^l	–	70 ^l	–	–	4.3	[53]	
Poly(amide-ester-sulfonamide)	(Pip-SMeIF-SA/TMC)/PSf	–	12	–	96 ⁿ	20.6 ⁿ	–	4.0	[44]	
Polysulfonamide	(Pip/BDSC)/PES	–	2.6 ^l	–	47 ^l	–	–	3.1	[53]	
	(MPD/BDSC)/PES	–	1.5 ^l	–	33 ^l	–	–	4.2	[53]	
	(PEL/BDSC)/PVDF	–	3.2	–	–	–	–	–	[65]	
	(PEL-Pip/BDSC)/PVDF	–	4.4	–	–	–	–	–	[65]	
	(PEI-MPD/BDSC)/PVDF	–	4.2	–	–	–	–	–	[65]	
	(PAH/BDSC)/PES	720	6.8	55.2 ^q	89.2 ^q	56.8 ^q	92.4 ^q	8.5	[69]	
	(NENP-1-PAH/BDSC)/PES	620	15	54.3 ^q	90.2 ^q	58.2 ^q	93.3 ^q	9.2	[70]	
	(DETA/NTSC)/PSf	1500	0.73 ^e	92 ^e	≈ 77 ^e	≈ 58 ^e	≈ 48 ^e	4.3	[71]	
	(DETA/NTSC)/SPEEK/PSf	800	1.7 ^e	99.7 ^e	≈ 97 ^e	≈ 88 ^e	≈ 78 ^e	4.1	[71]	
	(Pip/TCSP)/PES spinning assisted multilayer IP	–	3.0 ⁱ	99.8 ⁱ	99.4 ⁱ	85.5 ⁱ	–	–	3.1	[39]
	(Pip/TCSP)/PES traditional IP	–	1.5 ⁱ	98.3 ⁱ	92.9 ⁱ	–	–	–	–	[39]
	Poly(aryl cyanurate)	(THPE/CC)/PES	400	1.8	97.1 ^g	92.8 ^g	51.3 ^g	32.1 ^g	–	[74]
	Polyurea	(PEI _{0.4} -Pip _{0.1} /PDI _{0.2})/PES	200	0.5	–	≈ 98 ^j	–	–	≈ 5	[77]
		(PEI _{0.4} -Pip _{0.1} /TDI _{0.2})/PES	200	1.0	–	≈ 97 ^j	–	–	–	[77]
	Polyamine	(PEL/CC)/PES	500	3.0	–	45 ^g	55–65 ^g	90 ^g	7.5	[24]
(PEL/CC)/PES		–	13.7	9.4 ^e	18.1 ^e	47.8 ^e	92.1 ^e	≈ 8	[79]	
(PEL/CC)/PSf		–	0.05	28.7 ^p	90.5 ^p	43 ^p	94.4 ^p	9.8	[63]	
(PEL/CC)/PSf		≈ 1000	2.5	50 ^k	–	–	94.8 ^k	–	[80]	
(DETA/CC)/PES		200	1.5	78	–	85.2	–	7.7	[78]	
(DETA/CC)/PVDF		≈ 350	0.7	–	85.7	–	–	–	[81]	
(PEHA/CC)/PVDF after Tris surface modification		–	8.0	–	90 ^f	–	–	–	[62]	
(PPD/TBMB)/PES		800	0.28	≈ 80 ^p	68 ^p	≈ 15 ^p	≈ 25 ^p	–	[82]	
(MPD/TBMB)/PES		570	1.3	54 ^p	67 ^p	20 ^p	43 ^p	–	[82]	
(PPD/TFPG)/PSf		–	8.5	95.8 ^b	92.3 ^b	38 ^b	72 ^b	–	[59]	
(PPD/TFPG)/PSf		–	33	–	–	–	–	3.5	[83]	
(PPD-Mel/TFPG)/PSf		–	≈ 50	–	–	–	–	4.1	[83]	

^a for 2 g·L⁻¹ single salt solution at P = 6.9 bar and T = 25 °C

^b for 2000 ppm single salt solution at P = 5 bar and room temperature

^c for 1000 ppm single salt solution at P = 4 bar and T = 25 °C

^d for 1.0 g·L⁻¹ single salt solution at P = 4 bar and T = 25 °C

^e for 1.0 g·L⁻¹ single salt solution at P = 10 bar and T = 25 °C

^f for 2000 ppm single salt solution at P = 6 bar

^g for 2.0 g·L⁻¹ single salt solution at P = 10 bar and room temperature

^h for 2000 ppm single salt solution at P = 20 bar and T = 25 °C

ⁱ for 2.0 g·L⁻¹ single salt solution at P = 10 bar and T = 25 °C

^j for 2000 ppm single salt solution at P = 20 bar and room temperature

^k for 2.0 g·L⁻¹ single salt solution at P = 10 bar

^l for 0.5 g·L⁻¹ MgSO₄ solution at P = 5 bar

^m for 2.0 g·L⁻¹

ⁿ for 2000 ppm single salt at P = 5 bar

^o for 2000 ppm single salt solution at P = 15.5 bar and T = 25 °C

^p for 1.0 g·L⁻¹ single salt solution at P = 10 bar and ambient temperature

^q for 1.0 g·L⁻¹ single salt solution at P = 5 bar and room temperature

differences in salt retention characteristics, where the polyamide membranes often retain polyvalent anions best, whereas the polyamine membranes show relatively high retention for polyvalent cations at (close to) neutral pH conditions (see Table 9). As can be seen in Table 9, within the polyamide and polyamine membrane groups the membrane charge can be influenced by the selection of e.g. different (ly sized) amines used during the membrane preparation or by the crosslinking degree that is used. However, it is evident that although polyamide NF membranes are more chemically stable than polyamide NF membranes, the first class of membranes does not always form a suitable alternative for extreme pH applications where polyamide NF membrane characteristics are needed. For polyurea membranes the same applies, especially since the permeance of the developed membranes is still significantly lower than that for the polyamide NF membranes. The newly developed polysulfonamide membranes, which show good chemical stability at low pH, also have an attractive membrane permeance but seem to be more open than the tight polyamide NF membranes. This can clearly have a disadvantage when the use of tight NF membranes is required for proper separation characteristics. Further optimization of the IP procedure for the preparation of chemically stable NF membranes with even thinner, more porous and/or less tortuous thin film composite layers aiming for better performance characteristics is therefore still needed.

5. Acid and alkaline stability of membranes based on an interfacial initiation of homo-polymerization

5.1. Poly(epoxyether) membranes

A poly(epoxyether) TFC NF membrane based on homo-polymerization of epoxide monomers was prepared on top of a cross-linked polyimide (PI) support, which was produced based on phase inversion [75]. EPON™ 1031, tetraphenolethane tetraglycidylether (EPON) was used as epoxy monomer, while N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHD) was used as initiator. The initiator was reported to not have been built into the top layer. The homo-polymerization was therefore categorized as “Interfacial Initiation of Polymerization (IPP)” [75] but is also referred to as anionic polymerization [85]. The EPON concentration was varied between 0.5 %w/v and 3.5 %w/v in toluene, which resulted in membranes with a water permeance between approximately $8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and below $0.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, and a Rose Bengal (RB, MW = $1017 \text{ g}\cdot\text{mol}^{-1}$) retention between approximately 60% and 90%. The prepared membranes were categorized as tight UF. The optimum EPON concentration of 1.5 %w/v resulted in a water permeance of approximately $2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and 90% Rose Bengal (RB) retention. Furthermore, top layers became increasingly thicker when higher EPON concentrations were used [75].

Possibly, NF membranes could be produced based on a mix of EPON and bisphenol-A-diglycidyl ether (BADGE), a smaller monomer than EPON [75]. The (EPON-BADGE)/PI membrane produced from 0.75 % w/v EPON and 0.75 %w/v BADGE in toluene at 2 h reaction time showed 95% RB retention at a permeance of $0.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ [75]. It should be noted that the RB used is a sodium salt at the pH used for membrane characterization, and is therefore retained not only by size exclusion, but by Donnan exclusion and possibly di-electric exclusion as well. This implies that for a neutral compound with the same molecular weight a lower retention could have been obtained, leading to a MWCO

of the membrane in excess of 1000 Da and consequently defining the membrane as a UF membrane.

The IEP for (EPON-BADGE)/PI and EPON/PI produced based on 1 h reaction time was approximately IEP = 3.5. The tight UF EPON/PI membrane was reported to be stable after 48 h exposure to an acid (pH = 1) solution, even though the permeance seemed to reduce by approximately 50% and the morphology of the membrane surface changed as determined via scanning electron microscopy (SEM) [75]. The membrane was not stable after 48 h exposure to an alkaline (pH = 13) solution. This was ascribed to the hydrolysis of the amide bonds formed after crosslinking the PI support.

(EPON-BADGE)/PI was not stable after 48 h exposure to an acid (pH = 1) solution as indicated by the strongly reduced Rose Bengal retention and the strongly increased permeance (more than a factor 8). Although the authors hypothesized that the ether bonds should be stable, the observed chemical instability of (EPON-BADGE)/PI was ascribed to the higher cleavage susceptibility of an ether bond adjacent to an aromatic ring [75]. The better stability of the EPON/PI membrane compared to the (EPON-BADGE)/PI membrane was ascribed to the fact that EPON is a tetrafunctional ether, whereas BADGE is only a bifunctional ether with less linkers to the polymeric matrix [75]. These membranes have not yet been evaluated for long-term acid stability but based on the obtained results acid stability cannot be guaranteed for EPON/PI nor for (EPON-BADGE)/PI as also hypothesized by the authors [75]. Hydrolysis of poly (epoxyether) polymers by acid and alkaline solutions is also reported for high-performance organic coatings [86], where the ether group is mentioned as sensitive group for hydrolysis. Further improvements in the performance of poly(epoxyether) TFC NF membrane, especially related to water permeance, were realized by optimizing the initiator concentration and type, and by changing solvent annealing procedures of the support during the IP reaction [87].

These newly developed polyepoxyether ultrafiltration or very open nanofiltration membranes based on interfacial initiation of interfacial polymerization show a water permeance below $2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, while salt retentions have not been reported (see Table 10). This water permeance is relatively low compared to traditional polyamide membranes and commercially available chemically stable membranes (see Tables 1, 2 and 9). These newly developed membranes therefore do not only need to be improved for chemical stability, but for performance as well.

6. Acid and alkaline stability of membranes based on single or multiple coating steps

6.1. Sulfonated polyether ether ketone membranes

Sulfonated polyether ether ketone (SPEEK) top layers were spin-coated on top of a PES flat sheet UP020 (Microdyn-Nadir) UF membrane with a MWCO = 20 kDa [88]. The SPEEK used during the spin-coating had a sulfonation degree of 80% (SD = 0.80). The resulting membrane permeance and MWCO depended on the curing time - temperature combination used. Membranes with a relatively strong variation in NF layer thickness were obtained, resulting in a relatively strong variation in permeance for the membranes prepared under the same conditions. This was reported to be inherent to the use of a spin-coating process [88]. The most optimal membrane had a permeance of $4.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ with a MWCO of 500 Da (at neutral pH) and an IEP < 2.

Table 10

Membrane characteristics of membranes produced via interfacial initiation of homo-polymerization.

Membrane group	Membrane type	MWCO (Da)	Permeance at neutral pH ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	R	R	R	R	IEP	Ref.
				Na_2SO_4 (%)	MgSO_4 (%)	NaCl (%)	MgCl_2 (%)		
Poly(epoxyether)	(EPON-BADGE)/PI	–	0.5 – 1.0	–	–	–	–	3.5	[75]
	EPON/PI	–	2	–	–	–	–	3.5	[75]

This membrane was therefore relatively open compared to commercially available membranes such as Desal-5DK and NF-270 [24] with chemical stability in the pH = 2 – 11 range, and MPF-34 [24,43], a pH stable membrane in the pH = 0 – 14 range. The MWCO of the membrane was comparable to or slightly higher than NP030 [24,30]. The optimal SPEEK/PES membrane had approximately the same permeance as Desal-5DK and a lower permeance than NF-270. NP030 and MPF-34 both have a lower permeance than the optimal SPEEK/PES membrane [24,30,88]. The prepared SPEEK/PES membranes were subsequently immersed (ex-situ) in NaOH or HNO₃ solutions with a pH = 13 for 24 days, pH = 1 for 7 days, pH = 14 for 7 days and pH = 0 for 10 days, and characterized at P = 10 bar for pure water permeance, MWCO and NaCl retention in between these periods to determine the pH stability. The prepared SPEEK/PES nanofiltration membranes showed proper chemical stability over the entire pH range evaluated [88].

A SPEEK on PSf (SPEEK/PSf) membrane was prepared via dip coating using SPEEK with an SD = 0.69 dissolved in methanol at 0.5 %w [71]. The SPEEK/PSf membrane with an IEP < 2 and a MWCO = 2200 Da (consequently a relatively open UF membrane) was not stable upon immersion in an 8 %w H₂SO₄ solution at 25 °C, as indicated by a reduction in retention (from approximately 95% to 75%) and an increase in water flux (from almost 43 to 70 L·m⁻²·h⁻¹) from characterization tests prior to and after the immersion of the membrane in the low pH solution using a 1.0 g·L⁻¹ Na₂SO₄ solution at P = 10 bar and T = 25 °C. Strange enough, the membrane was far less stable than a membrane prepared from IP using DETA and NTSC on SPEEK/PSf (see Section 4.5.2). Reasons for this different acid resistance behavior between these membranes were not provided by the authors [71]. The poor acid stability of the SPEEK/PSf membrane also seems to contradict the results obtained by Dalwani et al. [88] for a SPEEK/PES NF membrane with a MWCO = 500 Da, which appeared to be stable in a pH range from 0 – 14, as described in earlier in this section. One of the reasons for this difference could be the more open structure of the less stable SPEEK/PSf membrane.

6.2. Poly(alkanolamine ether) membranes

A branched PEI crosslinked nanofiltration layer on top of a relatively open PES UF membrane NP010 (Nadir) was produced via dip-coating [89]. Polyethylene glycol diglycidyl ether (PEGDGE) was used as crosslinker. Different PEI and PEGDGE concentrations in water were used for the dip-coating process. The zeta potential of the membrane obtained depended on the PEI/PEGDGE ratio and the concentration used during the coating process. A membrane prepared from a 7.5% polymer concentration and a 2:1 PEGDGE : PEI ratio was expected to have the highest charge effects based on zeta potential measurements. Based on salt retention results it was concluded that at neutral pH this membrane was positively charged. For 30 days storage in a HCl solution (pH = 1.8), the (PEI/PEGDGE)/PES membrane, containing ether, amine and alcohol groups [90] showed a stable water permeance of 0.68 L·m⁻²·h⁻¹·bar⁻¹ (at P = 30 bar) during intermittent characterization tests using a hydrochloric acid solution containing 500 ppm MgCl₂. Chloride permeation through the membrane initially gradually increased by several percentages (absolute) but leveled-off with time [89]. These results show that the membrane is stable in this HCl solution at pH = 1.8, at least for 30 days.

6.3. Polyamine membranes

PEI – 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMBP) based polyamine nanofiltration membranes were produced on a PES UF support with a MWCO between 30 and 40 kDa (Hangzhou Water Treatment Technology Center) by coating the hydrophilized support using a BCMBP in ethanol solution [91]. After drying at T = 30 °C for 2 min, the surface was coated with an aqueous PEI solution. The prepared (PEI/BCMBP)/PES nanofiltration membrane based on 0.6% PEI and 0.02%

BCMBP solutions, using a reaction temperature of T = 80 °C and a reaction time of 10 min, had a molecular weight cut-off of MWCO = 650 Da, a pure water permeance of 10 L·m⁻²·h⁻¹·bar⁻¹ at P = 2 bar, and magnesium chloride and sodium sulfate retentions of 95.6% and 20.2%, respectively for 500 ppm single salt solutions. The membrane appeared to be relatively stable for 24 h at T = 25 °C during nanofiltration of 500 ppm metal salt (either FeCl₃, CuCl₂ or ZnCl₂) solutions at pH = 1.5 (adapted via the addition of a HCl solution), as indicated by a stable flux and stable Fe³⁺, Cu²⁺ and Zn²⁺ retentions. Only the latter retention seemed to reduce by a few percent (absolute) but stayed in excess of 90%. The acid stability performance of this polyamine membrane produced via reactive coating is in line with the results reported for (PEI/CC)/PES membranes produced by IP [24,80] (see Section 4.8.1). The (PEI/BCMBP)/PES membrane was not completely stable during continuous nanofiltration of lignin lye (500 ppm lignin in a 4 %w/v NaOH solution) at pH = 14 and T = 25 °C. A significant reduction in lignin retention (of approximately 5%) and in permeance (20 – 30%) were observed during 12 h [92].

6.4. Poly(alkanolamine isocyanurate) membranes

Poly(alkanolamine isocyanurate) membranes were prepared using a triglycidyl isocyanurate (TGIC) solution in ethanol, an aqueous PEI (MW = 70,000 Da) solution and a 30 – 50 kDa PES UF support (Huzhou Research Institute) [92]. Solution concentrations were varied between 0.02 – 0.12 %w and 0.2 – 1.2 %w for TGIC and PEI, respectively. 0.2 %w SDS was added to the TGIC solution to hydrophilize the PES membrane. After the addition of the TGIC solution, the solvent was evaporated through drying at 30 °C. Furthermore, the reaction temperature and reaction time were varied between 50 – 100 °C and 5 – 30 min, respectively. The optimum (PEI/TGIC)/PES membrane based on solutions consisting of 0.02 %w TGIC and 0.8 %w PEI, using a reaction temperature and time of 80 °C and 10 min, respectively had a MWCO = 923 Da. This membrane showed good chemical stability during 180 h nanofiltration of a 4 %w/v NaOH (pH = 14) solution containing 500 ppm lignin, as indicated by a constant lignin retention (in excess of 95%) and flux (22 L·m⁻²·h⁻¹) at P = 2 bar and T = 25 °C [92]. The poly(alkanolamine isocyanurate) (PEI/TGIC)/PES membrane was more stable than the polyamine (PEI/BCMBP)/PES membrane. This increased stability at pH = 14 was ascribed to the presence of the triazine group [92]. The (PEI/TGIC)/PES membrane appeared to be stable in a HCl solution (pH = 1.5) containing FeCl₃ as well, as indicated by the constant flux (22 L·m⁻²·h⁻¹) and iron chloride retention (close to 100%) for 12 h of continuous nanofiltration [92].

6.5. Boron nitride membranes

Functionalized boron nitride (BN) membranes were prepared via dynamic coating (dead-end filtration) of boron nitride nanosheets on a hydrophilic nylon microfiltration membrane (Merck Millipore) [93]. The MWCO of the membrane, determined via diffusion dialysis, indicated that the prepared membrane was in the NF range. Storage of the membrane in a 0.5 mol·L⁻¹ NaOH solution, a 0.5 mol·L⁻¹ H₂SO₄ solution and a 0.5 mol·L⁻¹ HNO₃ solution (pH ≈ 0.3) for 24 h each (most likely at room temperature) did not seem to affect the acetone permeance in water and the toluene permeance in ethanol as obtained during diffusion dialysis experiments [93]. Nanofiltration experiments applying a pressure difference between the retentate and permeate were not reported [93]. Good acid and alkaline stability for a freestanding BN membrane up to T = 90 °C was reported for an unsupported BN membrane as determined through conductivity tests prior to and after exposure of the membrane to a 1 mol·L⁻¹ KOH solution or a 1 mol·L⁻¹ HCl solution for 1 week [94]. The BN membrane, prepared via filtration of a BN nanosheet solution over a 0.02 μm pore size Anodisc membrane filter (Whatman) and subsequently peeling off the produced BN membrane, showed an IEP ≈ 3. It must be noted that it was not determined whether the

membrane produced had characteristics in the nanofiltration range, nor were experiments using a pressure difference over the membrane performed [94].

6.6. Freestanding graphene oxide-based membranes

Imidazolium (Im)/graphene oxide (GO) freestanding hybrid membranes were prepared from monolayer exfoliated GO sheets of 4 – 14 μm (lateral size) [95]. Different imidazolium halides, 1-butyl-3-methylimidazolium chloride ([BuMIm]Cl), 1-benzyl-3-methylimidazolium chloride ([BeMIm]Cl), 1-vinyl-3-ethylimidazolium bromide ([VEIm]Br), and 1-allyl-3-vinylimidazolium chloride ([AVIm]Cl), were used in an attempt to stabilize the GO-based membrane sheets in aqueous solutions. The produced membranes were marked as BuMIm/GO, BeMIm/GO, VEIm/GO and AVIm/GO, respectively. To prepare the membrane a GO solution, an imidazolium solution containing one of the imidazolium halides mentioned earlier and deionized water were mixed. Subsequently, the pH was adjusted to pH = 12 through the addition of a NaOH solution and filtered over a cellulose acetate microfiltration membrane with a pore size of 0.45 μm (dynamic coating). Freestanding Im/GO membranes were obtained by manually peeling off the filtered layer [95]. The areal loading was 2 $\text{g}\cdot\text{m}^{-2}$ and the imidazolium content was approximately 1 $\text{mol}\cdot\text{kg}^{-1}$ for all prepared membranes. Im-free GO membranes were prepared as well for performance comparison with the Im/GO hybrid membranes. FT-IR analysis indicated strong $\pi - \pi$ (between the GO and the aromatic group within the imidazolium) and $\pi - \text{ion}$ (between the GO and the cation within the imidazolium) interactions for the Im/GO hybrid membranes. Water swelling of the Im/GO hybrid membranes was found to be limited and much lower than the virgin GO membrane. In nanofiltration permeation tests AVIm/GO appeared to have superior permeance (around 1.6 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) over the other three hybrid membranes (having permeances below 0.7 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), however, VEIm/GO showed the highest Na_2SO_4 retention (80%) of the four hybrid membranes with a NaCl retention of approximately 20% during membrane characterization experiments using 1 $\text{g}\cdot\text{L}^{-1}$ single salt solutions [92]. All membranes retained sucrose completely [95], indicating a low MWCO. Immersion of the virgin GO membrane in a pH = 1 HCl solution, deionized water or a pH = 13 NaOH solution resulted in complete disintegration of the virgin GO membrane after 7 days of gently shaking. The Im/GO membranes all stayed intact in the solutions even after more than 14 days of vigorous stirring. The d-spacing for the hybrid membranes after immersion in the acid HCl solution was similar to that for immersion in deionized water, whereas immersion in the alkaline NaOH solution resulted in an increased d-spacing. The increased d-spacing was explained by electrostatic repulsion due to deprotonation of the carboxylic and phenolic groups [95]. Consequently, the hybrid membranes appear to be stable in the pH = 1 acid solution, whereas conformational changes are observed upon immersion in a pH = 13 alkaline solution based on d-spacing measurements. A nanofiltration performance evaluation comparing results prior to and following immersion in the acid and alkaline solutions was not reported.

Inorganic anion/GO hybrid membranes using an inorganic anion [96] instead of the imidazolium anion [95] were prepared as well [96]. The membranes were produced via casting GO laminates on a PVDF support, drying overnight at $T = 60\text{ }^\circ\text{C}$ and subsequently peeling the membrane from the PVDF support to obtain freestanding GO based membranes. Hybrid inorganic anion/GO membranes were produced from several inorganic anions (Ca^{2+} , Mg^{2+} , Ba^{2+} and K^+), however, only Ca^{2+} /GO and reduced Ca^{2+} /GO (reduction with HI followed by a thermal treatment leading to a decreased amount of epoxy or hydroxyl functional groups on the GO nanosheets) membranes were immersed in 0.5 $\text{mol}\cdot\text{L}^{-1}$ KOH, NaOH, HCl, HNO_3 or H_2SO_4 solutions for 7 days. The virgin GO membrane, used as reference, did not show any integrity at all in these solutions. The Ca^{2+} /GO and reduced Ca^{2+} /GO membranes maintained their original shape in these solutions [96]. The effect of

immersion in these solution on filtration performance was not studied.

6.7. Hybrid organic/inorganic membranes

Hybrid membranes based on polyvinyl alcohol (PVA) and amino-propyl triethoxysilane (APTES) on a 50 kDa Psf support (MEY Membrane Technology Co., China) were prepared via brush coating [97]. The (APTES/PVA)/Psf membrane, prepared based on a 1:1 APTES:PVA ratio and an APTES concentration of 1.0 %w/v in the coating solution, showed good chemical stability for subsequent immersion in a 5 %w/v H_2SO_4 solution and in a 5 %w/v HCl solution for 30 days each. Immersion was probably done at room temperature although this was not mentioned explicitly [97]. The stability of the membrane was evaluated based on intermittent characterization using a 2000 ppm Na_2SO_4 solution at 20 bar pressure and room temperature. During immersion of the same membrane sample in a 20 %w/v H_3PO_4 solution and subsequently in a 15 %w/v H_2SO_4 solution for 30 days each, an increase in membrane flux of some 10% per solution was observed, however, the sulfate retention was stable for all solutions. The membrane is therefore considered to be reasonably, but possibly not completely, stable in acid solutions. Immersion of the membrane (another sample) in a 4 %w/v NaOH (1.0 $\text{mol}\cdot\text{L}^{-1}$) solution for 30 days showed a gradual linear reduction in sulfate retention of approximately 1.5% (absolute). Consequently, even though the reduction is small, and the sulfate retention is still high (97%) after exposure to the alkaline solution, the membrane seems to be reasonably, but not completely stable at high pH.

3-Mercaptopropyltriethoxysilane (MPTES) and PVA were also used to prepare hybrid membranes [98]. The obtained gel was brush-coated onto a 50 kDa Psf support (MEY Membrane Technology Co.) and crosslinked after drying using formaldehyde. The thiol groups of the obtained membranes were oxidized into sulfonic acid groups by immersing the membranes into a hydrogen peroxide solution. The thus obtained (SMPTES/PVA)/Psf membrane and its unoxidized (MPTES/PVA)/Psf membrane, both based on a 1 %w PVA and a 0.6 %w MPTES solution, were evaluated for their acid stability in a 5 %w/v H_2SO_4 solution and in a 15 %w/v H_2SO_4 solution at room temperature for 30 days. (MPTES/PVA)/Psf appeared to be stable for 30 days of immersion in both solutions as indicated by its unchanged Na_2SO_4 retention and a minor increase in permeance from intermittent characterization experiments using a 2000 ppm Na_2SO_4 solution at $P = 20$ bar. (SMPTES/PVA)/Psf appeared to be slightly less stable than (MPTES/PVA)/Psf with a slight reduction in Na_2SO_4 retention and an increase in water permeance, especially for immersion in the solution with the high H_2SO_4 concentration, where the retention reduced from 98.0% to 96.0% and the flux increased from 43.3 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to 48.3 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. Immersion of the (SMPTES/PVA)/Psf membrane in a 4 %w/v NaOH solution resulted in a steep initial increase in the water permeance and reduction in the Na_2SO_4 retention after 7 days, followed by only minor changes during the next 23 days. However, Na_2SO_4 retention stayed in excess of 95% after 30 days of immersion in this alkaline solution [98].

6.8. Performance characteristics of newly developed NF membranes based on single or multiple coating steps

Out of the group of newly developed membranes prepared via a single or multiple coating steps only the sulfonated polyether ether ketone, polyamine and poly(alkanolamine isocyanurate) membranes show a sufficiently high permeance (see Table 11), comparable to the permeances obtained for commercially applied NF membranes (see Tables 1 and 2). Given the proper chemical stability for these newly developed NF membranes, these membranes show potential for commercial application. However, these three membranes do have relatively high molecular weight cut-off (MWCO > 500 Da), which limits their use to applications where relatively open nanofiltration membranes can be used. Furthermore, the SPEEK/PES membrane is especially suitable for applications targeting retention of multivalent anions, whereas the

Table 11
Membrane characteristics of membranes produced via single or multiple coating steps.

Membrane group	Membrane type	MWCO (Da)	Permeance at neutral pH (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	R Na ₂ SO ₄ (%)	R MgSO ₄ (%)	R NaCl (%)	R MgCl ₂ (%)	IEP	Ref.
Sulfonated polyether ether ketone	SPEEK/PES	500	4.5	95 ^e	–	65 ^e	–	≪ 2	[88]
Poly(alkanolamine ether)	(PEI/PEDGE)/PES	> 500	0.68 ^a	52 ^a	85 ^a	75 ^a	95 ^a	–	[89]
Polyamine	(PEI/BCMBP)/PES	650	10	20.5 ^b	–	–	95.6 ^b	≈ 6	[91]
Poly(alkanolamine isocyanurate)	(PEI/TGIC)/PES	923	11	–	–	–	95 ^b	8.8	[92]
Boron nitride	BN	–	–	–	–	–	–	≈ 3	[94]
Graphene oxide	AVIm/GO	< 342	≈ 1.6	55 ^c	–	10 ^c	15 ^c	–	[95]
	VEIm/GO	< 342	≈ 0.6	80 ^c	–	20 ^c	23 ^c	–	[95]
	BeMIm/GO	< 342	≈ 0.6	70 ^c	–	15 ^c	20 ^c	–	[95]
	BuMIm/GO	< 342	≈ 0.7	65 ^c	–	15 ^c	18 ^c	–	[95]
Hybrid organic/inorganic	(APTES/PVA)/PSf	–	0.7 ^d	98.5 ^d	97.9 ^d	53.6 ^d	48.1 ^d	–	[97]
	(MPTES/PVE)/PSf	–	0.55 ^d	97.2 ^d	–	–	–	–	[98]
	(SMPTES/PVE)/PSf	–	2.2 ^d	98 ^d	97.2 ^d	50.6 ^d	48 ^d	–	[98]

^a for 500 ppm salt in hydrochloric acid (pH = 1.8) solution at P = 30 bar

^b for 500 ppm single salt solution at P = 2 bar and room temperature

^c for 1.0 g·L⁻¹ single salt solution at P = 4 bar

^d for 2000 ppm single salt solution at P = 20 bar and room temperature

^e for 2.0 g·L⁻¹ single salt solution at P = 10 bar and room temperature

newly developed polyamine and poly(alkanolamine isocyanurate) membranes are more suitable for applications requiring high multivalent cation retentions.

7. Acid and alkaline stability of membranes based on layer-by-layer (LBL) coating

The preparation of NF membranes via layer-by-layer coating has received a lot of interest in recent years, amongst others because the prepared membranes can have very thin separating layers, consequently have the potential for high membrane permeance, and layer-by-layer coating is a simple and versatile method [99,100]. Since the stability of the membrane over a broad pH range is considered to be important for practical application, most studies deal with strong polyelectrolytes such as poly(diallyldimethylammoniumchloride) (PDADMAC) and poly(styrenesulfonate) (PSS), since these maintain their anionic or cationic nature over a broad pH range [49,50,99,101–103]. Several studies also evaluate polyelectrolyte combinations consisting of one or more weaker polyelectrolytes and compare their pH stability performance with the PDADMAC/PSS based membranes. These weaker polyelectrolytes investigated include poly(allylamine hydrochloride) (PAH), PAH functionalized with guanidine groups (PAH-Gu) and sodium poly(acrylate) (PAA) [49,99]. It is known that the conditions used during the coating process largely determine the membrane performance and stability. The parameters that can be tuned during the coating process include the polyelectrolyte and inorganic salt concentration of the coating solution, the number of coating steps, and the coating method (e.g. dynamic coating or dip coating) [99]. The next sections describe the polyelectrolyte membranes prepared and their stability at extreme pH conditions.

7.1. Membranes based on strong polyelectrolytes

Several studies report the preparation and pH stability evaluation of layer-by-layer coated polyelectrolyte multilayer (PEM) membranes using the strong polyelectrolytes PDADMAC and PSS [49,50,99,101–103]. In these studies, different membrane supports, number of polyelectrolyte layers, coating conditions and techniques, acid and alkaline solutions and experimental conditions were used.

NF membranes consisting of 3, 5 or 7 PDADMAC/PSS bi-layers coated on a Pentair X-Flow UFCLE PES UF membrane ((PDADMAC/PSS)_x/PES with x = 3, 5 or 7) were prepared by dynamic coating (via dead-end filtration) at unspecified pressure and temperature, using a coating solution containing either 0.05, 0.5 or 1 mol·L⁻¹ NaCl and an

unspecified polyelectrolyte concentration at neutral pH [102]. The membrane top layer facing the solution to be treated always consisted of negatively charged PSS. The membranes based on a coating solution containing 0.5 mol·L⁻¹ NaCl were evaluated for performance and pH stability during short term (1 h) crossflow experiments. Model solutions consisting of 45 g·L⁻¹ Fe²⁺, 90·10⁻³ g·L⁻¹ Sc³⁺, and either 0.1 mol·L⁻¹ HCl (pH = 0.1), 0.3 mol·L⁻¹ HCl (pH = 0.5) or 1.0 mol·L⁻¹ HCl (pH = 1.0), or a 1:5 volume based diluted TiO₂ pigment production waste stream (with a pH adjusted to pH = 1.5) were used [102]. For all bi-layer membranes stable scandium (Sc³⁺) and iron (Fe²⁺) retentions were obtained at pH = 1.5. The use of a higher (1 mol·L⁻¹) NaCl concentration in the coating solution for the preparation of the 3 bi-layer membrane (PDADMAC/PSS)₃/PES had a negative effect on the Sc³⁺ retention stability, whereas for the use of a lower (0.05 mol·L⁻¹) NaCl concentration stable performance was obtained. Stability results for higher bi-layer number membranes based on varied coating solution NaCl concentrations were not reported. None of the bi-layer membranes prepared from the coating solution containing 0.5 mol·L⁻¹ NaCl could be considered stable during membrane filtration experiments using the model solutions having a pH of pH = 0.1, pH = 0.5 or pH = 1.0, as indicated by reduced Sc³⁺ retentions obtained after only 1 h of exposure to the model solutions [102]. Additionally, 3 and 5 bi-layer membranes prepared from on a coating solution containing 1.0 mol·L⁻¹ NaCl were evaluated under even more acidic conditions using solutions consisting of 0.5·10⁻³ mol·L⁻¹ MgSO₄ and either 1.0, 2.0 or 3.0 mol·L⁻¹ HCl. In this case the 3 bi-layer membrane was unstable as well, whereas the 5 bi-layer membrane showed significantly better stability [102]. Unfortunately, the exposure time to these acid solutions was not reported but based on the other experiments reported the exposure time was probably relatively short. The results show that the number of bi-layers coated, the salt concentration of the coating solution and the pH of the solution to which the membrane is exposed have a clear impact on the pH stability of the (PDADMAC/PSS)_x/PES membrane during short term exposure.

Four and eight bi-layer PDADMAC/PSS NF membranes on a single fiber 100 kDa PES or 10 kDa sPES UF support, prepared through dynamic coating (dead-end filtration) at P = 3 bar using 1.0 g·L⁻¹ polyelectrolyte and 0.5 mol·L⁻¹ NaCl solutions, were exposed to 15 %w phosphoric acid (pH = 0.7) solutions [101]. Again, the top layer of the membrane facing the solution consisted of the negatively charged PSS in all cases. The membranes were tested in a crossflow cell for 24 h [101]. Prior and subsequent membrane characterization experiments using a 0.5 mol·L⁻¹ MgSO₄ solution were used to verify the membrane stability. Probably room temperature was used during the experiments although this was not specified. Relatively stable membrane performance could

be obtained for all membranes with an acceptable membrane flux at pressures below 10 bar. Mg^{2+} retentions during characterization experiments at $P = 5$ bar appeared to be relatively low for all membranes evaluated at a relatively stable level of approximately 40% for the eight bi-layer (PDADMAC/PSS)₈/PES NF membrane and approximately 60% for the other three NF membranes, (PDADMAC/PSS)₄/PES, (PDADMAC/PSS)₄/sPES and (PDADMAC/PSS)₈/sPES. It should be noted that the $MgSO_4$ concentration (and therefore the ionic strength) of the solution used for characterization was high, which may be (part of) the reason for the relatively low retentions. Furthermore, it seems that the change in the number of bi-layers did not have an adverse effect on the pH stability. For a (PDADMAC/PSS)₄/PES membrane module consisting of 10 hollow-fibers changes in the membrane flux and the Mg^{2+} retention after nanofiltration of the phosphoric acid solution were obtained. The increased flux and the reduced retention were ascribed to membrane swelling, but the reasons for the difference in behavior between the four bi-layer single hollow-fiber membrane and the module consisting of 10 hollow-fibers were not provided and are not clear.

The effect of the number of coated polyelectrolyte bi-layers on the performance and pH stability of the membrane was evaluated more extensively for similar NF membranes prepared via dynamic layer-by-layer coating at unspecified pressure and temperature, using 1.0 g·L⁻¹ polyelectrolyte in 0.5 mol·L⁻¹ NaCl solutions [50]. Prepared membranes featured subsequently coated PDADMAC and PSS layers on either UFCLC, a hollow-fiber polyethersulfone (PES) UF support with a MWCO = 100 kDa, or on HFS, a sulfonated polyethersulfone (sPES) hollow-fiber UF membrane with a MWCO = 10 kDa (both Pentair X-Flow) [49,50,104]. The number of bi-layer coatings varied from 4 to 9 on a single hollow-fiber, and the final layer coated consisted of PSS (a negatively charged layer) in all cases. Single hollow fiber ((PDADMAC/PSS)_x/sPES) and ((PDADMAC/PSS)_x/PES) NF membranes were evaluated for the recovery of phosphoric acid from a solution containing 10 % w phosphoric acid and 2 g·L⁻¹ Al³⁺ (added as aluminum hydroxide) at pH = 0.7 and T = 20 °C. Based on experiments that lasted (only) 1 h all bi-layer membranes showed quite stable performance at this low pH. The use of 6 bi-layers appeared to be optimal regarding low phosphoric acid retention, high Al³⁺ - phosphoric acid separation selectivity and limiting of the number of bi-layers. The membrane based on the PES support had a higher Al³⁺ retention than the NF membrane based on the sPES support and was therefore preferred. For a 6 bi-layer PDADMAC/PSS on PES membrane ((PDADMAC/PSS)₆/PES) with 20 hollow fibers per module a pure water permeance of 21 L·m⁻²·h⁻¹·bar⁻¹ was reported. During batch concentration to a concentration factor of CF = 4, an Al³⁺ retention of 93–96% was reported in combination with a phosphate retention between 10 and 20%, which increased with increasing concentration factor. During this batch concentration, the membrane permeance reduced from 3.8 L·m⁻²·h⁻¹·bar⁻¹ to 3.1 L·m⁻²·h⁻¹·bar⁻¹, probably at least partly due to the increasing osmotic pressure differences between the concentrate and permeate. ((PDADMAC/PSS)₆/PES) showed a 16 times higher permeance, a slightly lower Al³⁺ retention and a significantly lower phosphorous retention than the commercially pH stable A-3012 membrane (see Section 3). After the batch concentration the pure water permeance reduced to 17.3 L·m⁻²·h⁻¹·bar⁻¹. A specific reason for this reduction could not be validated but might be due to the rearrangement of the layers during treatment of the phosphoric acid solution [50]. Nevertheless, the batch concentration experiment provides a clear indication that the membrane is stable for at least multiple hours.

The phosphoric acid retention for (PDADMAC/PSS)₆/sPES, prepared via dynamic coating at 3 bar using a 0.1 g·L⁻¹ polyelectrolyte and 0.05 mol·L⁻¹ NaCl coating solution, was higher than for (PDADMAC/PSS)₆/sPES prepared using a 1.0 g·L⁻¹ polyelectrolyte and 0.5 mol·L⁻¹ NaCl coating solution [49]. In contrast, the Al³⁺ retention was lower for a lower polyelectrolyte - NaCl concentration combination for this membrane based on experiments performed at $P = 5$ bar and $T = 20$ °C. The optimized (PDADMAC/PSS)₆/sPES membrane prepared using a 1.0 g·L⁻¹

polyelectrolyte – 0.5 mol·L⁻¹ NaCl concentration showed a substantially lower pure water permeance (6.1 L·m⁻²·h⁻¹·bar⁻¹) than (PDADMAC/PSS)₆/PES [49,50]. This relatively low pure water permeance probably resulted, at least partly, from the substantially lower pure water permeance of the sPES support compared to that of the PES support (80 L·m⁻²·h⁻¹·bar⁻¹ vs 1100 L·m⁻²·h⁻¹·bar⁻¹ [49,50,104]). The optimized (PDADMAC/PSS)₆/sPES membrane did show much higher permeance than A-3012 at lower phosphoric acid and cation impurity retentions during batch concentration of sewage sludge ash leachate, containing phosphoric acid, sulfuric acid and multiple monovalent - and multivalent cationic impurities, at pH = 1, $P = 9$ bar and $T = 20$ °C [49]. The exposure time of the membranes to the low pH solution was limited and long-term stability differences between the membranes were not investigated.

The effect of the membrane surface charge on the performance and the pH stability was evaluated by coating hollow-fiber polyether sulfone (PES) ultrafiltration (UF) membranes with a MWCO = 10 kDa with 8 or 8.5 bi-layers, leading to a negatively charged and positively charged top layer, respectively [99]. Membranes were prepared via dip-coating using coating solutions consisting of 0.1 g·L⁻¹ polyelectrolyte and 0.05 mol·L⁻¹ NaCl at a pH = 6.0 [99]. The membranes were immersed in either different strong acid (HNO₃) solutions (pH = 1 for 1600 h followed by pH = 0 for 340 h) or strong alkaline (NaOH) solutions (pH = 13 for 1600 h followed by pH = 14 for 340 h) to validate their long-term pH stability [99]. Based on membrane characterization experiments using pure water and different salt solutions, the (PDADMAC/PSS)/PES membranes appeared to exhibit good stability for low as well as for high pH conditions. The prepared (PDADMAC/PSS)/PES membranes, characterized at ambient temperature and 5 bar pressure, were shown to be typical NF membranes. After exposure to the 1 mol·L⁻¹ NaOH solution or the 1 mol·L⁻¹ HNO₃ solution, the (PDADMAC/PSS)/PES membrane with a negatively charged top layer retained its low molecular weight cut-off (MWCO = 279 Da) and showed high and virtually unchanged permeance (10.7 L·m⁻²·h⁻¹·bar⁻¹) and magnesium sulfate retention (95.5%). The (PDADMAC/PSS)/PES membrane type with a positively charged top layer showed stable performance under the same conditions as well, albeit that this membrane showed slightly lower MWCO and pure water permeance, and slightly higher $MgSO_4$ retention than its negatively charged top layer counterpart [99].

A clear disadvantage of the prepared PEM membranes described is the relatively low maximum pressure allowed for the polymeric hollow-fiber UF supports, which limits the applicability of these membranes to low pressures (below $P = 10$ bar), whereas spiral wound alternatives would be more suitable for higher pressure operation. Additional developments for these membranes for high pressure applications are therefore needed.

(PDADMAC/PSS)₃/Ceramic, a 3 bi-layer PDADMAC/PSS membrane on a ceramic monolith support (Metawater, Japan), with a MWCO = 240 Da and a $MgSO_4$ retention of 88%, was prepared by dynamic coating at constant flux (30 L·m⁻²·h⁻¹) using a solution consisting of 1 g·L⁻¹ polyelectrolyte and 0.1 mol·L⁻¹ NaCl. The membrane was shown to be stable during immersion in a 0.1 mol·L⁻¹ (pH = 13) NaOH solution for approximately 70 h, followed by immersion in a 1.0 mol·L⁻¹ (pH = 14) NaOH solution for approximately another 90 h [103]. This was indicated by its slightly increasing water permeance from 11 to 13 L·m⁻²·h⁻¹·bar⁻¹ after the first 25 h of exposure to pH = 13, followed by a constant water permeance during the remainder of the exposure time to the NaOH solutions, as determined from intermittent characterization testing using pure water at $P = 3.5$ bar. Immersion in a 0.01 mol·L⁻¹ HCl (pH = 2) solution for approximately 55 h showed an initial increase in the pure water permeance from 15 to 18 L·m⁻²·h⁻¹·bar⁻¹ during the first few hours, followed by a more gradual increase in the permeance to 21 L·m⁻²·h⁻¹·bar⁻¹ for the subsequent period at pH = 2. Subsequent immersion in a 0.1 mol·L⁻¹ HCl (pH = 1) solution for approximately 90 h resulted in a constant pure water permeance of 23 L·m⁻²·h⁻¹·bar⁻¹, while further immersion in a 1.0 mol·L⁻¹ HCl (pH = 0) solution for

approximately 20 h resulted in a reduction of the pure water permeance from 22 to 18 L·m⁻²·h⁻¹·bar⁻¹. Despite the observed changes in permeance, and especially the increase at pH = 2, the membrane appears to be stable at these low pH levels, at least at pH = 1 and higher [103]. The membrane seems to be stable at lower pH as well, however, due to the relatively short time and the limited permeance results during this period this is less clear. Unfortunately, results regarding solute retentions for the exposure to extreme pH conditions have not been reported.

Although in most studies the exposure time of (PDADMAC/PSS)-based membranes to extreme pH conditions is quite limited, several studies indicate the potential of these membranes for long term exposure to extreme pH conditions [99,103]. Based on the short-term exposure studies, initial indications for membrane optimization regarding the polyelectrolyte and salt concentration during the coating, the support selection, the type of layer-by-layer coating used and the number of (bi-) layers coated have been obtained. However, there is still a need for creating better insights and more optimal preparation procedures for these types of membranes, especially when exposure to extreme pH is targeted.

7.2. Membranes based on a strong and a weak polyelectrolyte

NF membranes prepared based on dynamic layer-by-layer coating at P = 3 bar using the strong anionic polyelectrolyte PSS and either PAH or PAH-Gu, both weak cationic polyelectrolytes, form examples of PEM membranes based on a combination of strong and weak polyelectrolytes [49]. The prepared (PAH-Gu/PSS)₆/sPES and (PAH/PSS)₆/sPES membranes consisted of 6 bi-layers on a sPES support. In contrast to (PDADMAC/PSS)₆/sPES (see Section 7.1), the (PAH-Gu/PSS)₆/sPES and (PAH/PSS)₆/sPES membranes optimized for the recovery of phosphoric acid from a solution containing 10 %w phosphoric acid and 2 g·L⁻¹ Al³⁺ at pH = 0.7 and T = 20 °C were prepared using a coating solution with relatively low (0.1 g·L⁻¹) polyelectrolyte and NaCl (0.05 mol·L⁻¹) concentrations [49]. For (PAH-Gu/PSS)₆/sPES and (PAH/PSS)₆/sPES pure water permeances of 5.4 L·m⁻²·h⁻¹·bar⁻¹ and 2.1 L·m⁻²·h⁻¹·bar⁻¹, respectively, were reported [49]. The optimized (PAH-Gu/PSS)₆/sPES membrane showed substantially lower permeance and slightly higher phosphorous retention than the optimized (PDADMAC/PSS)₆/sPES membrane (see Section 7.1) during batch concentration of sewage sludge ash leachate, containing phosphoric acid, sulfuric acid and multiple monovalent - and multivalent cationic impurities, at pH = 1, P = 9 bar and T = 20 °C. The latter membrane showed lower Fe³⁺ and Mg²⁺ retentions. (PAH/PSS)₆/sPES results were not reported because of the low membrane flux. The longer-term stability of these membranes was not assessed by the authors [49].

Other NF membranes based on a strong and a weak polyelectrolyte were prepared via layer-by-layer dip-coating using either PAH and PSS or PDADMAC and PAA on a hollow-fiber polyether sulfone (PES) ultrafiltration (UF) membrane with a MWCO = 10 kDa as support [99]. The negatively charged supports were coated with either 8 or 8.5 bi-layers, leading to a negatively charged and positively charged top layer, respectively. The prepared NF membranes were immersed in different strong acid solutions (pH = 1 for 1600 h followed by pH = 0 for 340 h) and strong alkaline solutions (pH = 13 for 1600 h followed by pH = 14 for 340 h) for almost 2000 h. Based on membrane lab-scale characterization experiments using pure water and different salt solutions, the (PAH/PSS)/PES membranes with negatively and positively charged top layers appeared to exhibit good stability for low pH conditions, whereas the (PDADMAC/PAA)/PES membranes composed of the weak anion PAA were unstable at pH = 1. This low stability is caused by the relatively low pH of the solution in relation to the apparent pK_a of PAA, leading to a relatively low dissociation degree of PAA [105] and consequently strongly reduced ionic interactions between PDADMAC and PAA. The (PAH/PSS)/PES membrane with a negatively charged top layer retained its low MWCO (249 Da) after exposure to the 1 mol·L⁻¹

HNO₃ solution [99], since both polyelectrolytes are strongly dissociated at the pH applied. The membrane also showed high and virtually unchanged permeance (9.7 L·m⁻²·h⁻¹·bar⁻¹) and magnesium sulfate retention (97.5%). The same membrane type but with a positively charged top layer showed an even slightly lower MWCO and pure water permeance, and a slightly higher MgSO₄ retention than its negatively charged top layer counterpart. (PAH/PSS)/PES and (PDADMAC/PAA)/PES membranes were unstable in the alkaline solutions, irrespective of their top layer charge. According to the authors the poor stability of (PAH/PSS)/PES in high pH solutions could potentially be caused by the pH used during the preparation process (pH = 6) [99], leading to less stable layers as shown by Alonso et al. [106], which could be remediated during exposure of the membrane to low pH, but not during exposure of the membrane to high pH. The preparation procedure may have affected the stability of the membrane as mentioned by the authors, however, PAH will become deprotonated at pH > 10 leading to reduced ionic interaction with PSS and the reduced ionic interactions between the polyelectrolytes at high pH is a more likely explanation of the observed instability of the (PAH/PSS)/PES membrane in high pH alkaline solutions.

7.3. Membranes based on weak polyelectrolytes

NF membranes based on two weak polyelectrolytes, PAH and PAA, were prepared via a similar procedure as the (PDADMAC/PSS)/PES, (PAH/PSS)/PES and (PDADMAC/PAA)/PES membranes see Sections 7.1 and 7.2). The prepared (PAH/PAA)/PES membranes with 8 or 8.5 bi-layers showed strong instability at pH = 13 and pH = 1 [99], and were consequently significantly more instable than the NF membranes based on a combination of strong cationic and anionic polyelectrolytes (see Section 7.1) prepared and evaluated according to the same conditions. The poor stability of the (PAH/PAA)/PES membranes at these extreme pH conditions is in line with the production of relatively thick polyelectrolyte bilayers, indicating relatively low ionic interaction strengths between the polyelectrolytes, when coating solutions with either low (pH = 2.5) or high (pH = 9) pH for both polyelectrolyte solutions were used [107]. Furthermore, molecular modelling also showed strongly reduced ionic interactions between these polyelectrolytes at low or high pH [105], making these polyelectrolytes unsuitable for the preparation of membranes that need to be stable at extreme pH conditions.

7.4. Summarizing the pH stability of developed polyelectrolyte membranes

Observations regarding the acid and alkaline stability of the LBL membranes have been summarized in Table 12.

It is evident that nanofiltration membranes based on layer-by-layer coated polyelectrolyte membranes have a clear potential for pH stability, especially when strong polyelectrolytes are used. This has been proven for (PDADMAC/PSS)/PES membranes for immersion in alkaline as well as in acid solutions. Long-term acid stability has also been proven for layer-by-layer coated PEM membranes based on a weak polyelectrolyte cation (PAH) and a strong polyelectrolyte anion (PSS). Possibly the stability for this (PAH/PSS)-based membrane type can be extended to alkaline conditions as well when the preparation procedure would be optimized. However, this has not been proven for weak polyelectrolyte cation/strong polyelectrolyte anion-based membranes and is less likely based on ionic interaction considerations.

7.5. Performance characteristics of newly developed NF membranes based on layer-by-layer coating

The newly developed NF membranes prepared via layer-by-layer coating using a combination of strong polyelectrolytes or a combination of a strong and a weak polyelectrolyte show permeances similar to commercially applied NF membranes (see Tables 1, 2 and 13). Furthermore, these membranes can be categorized as tight NF

Table 12
Summary of LBL membrane stability for extreme pH conditions.

Membrane name	Acid stability	Alkaline stability
(PDADMAC/PSS)/PES (with different bi-layer numbers and preparation methods)	Stable in a 0.1 mol·L ⁻¹ HNO ₃ solution for 1600 h and after subsequent immersion in a 1 mol·L ⁻¹ HNO ₃ solution for 340 h [99] Stable during batch concentration of a 10% phosphoric acid and 2 g·L ⁻¹ aluminum phosphate solution at pH = 0.7 [50] Relatively stable for separation of Mg ²⁺ from a 15 %w phosphoric acid solution during 24 h [101] Stable during 1 h for separation of scandium (Sc ³⁺) from Fe ²⁺ in a HCl solution at pH = 1.5. For pH = 1.0 or lower the membrane was not stable [102] Practically stable for unspecified but probably short exposure time in solutions consisting of 0.5·10 ⁻³ mol·L ⁻¹ MgSO ₄ and either 1.0, 2.0 or 3.0 mol·L ⁻¹ HCl [102]	Stable in a 0.1 mol·L ⁻¹ NaOH solution for 1600 h and after subsequent immersion in a 1 mol·L ⁻¹ NaOH solution for 340 h [99]
(PDADMAC/PSS)/sPES (with different bi-layer numbers and preparation methods)	Stable during batch concentration of a 10% phosphoric acid and 2 g·L ⁻¹ aluminum phosphate solution at pH = 0.7 [49] Stable during batch concentration of sewage sludge ash leachate, containing phosphoric acid, sulfuric acid and multiple monovalent - and multivalent cationic impurities, at pH = 1.15 [49] Relatively stable for separation of Mg ²⁺ from a 15 %w phosphoric acid solution during 24 h [101]	
(PDADMAC/PSS) ₃ /Ceramic	Probably stable in a 0.01 mol·L ⁻¹ HCl (pH = 2) solution for approximately 55 h, followed by immersion in a 0.1 mol·L ⁻¹ HCl (pH = 1) solution for approximately 90 h and immersion in a 1.0 mol·L ⁻¹ HCl (pH = 0) solution for another approximately 20 h [103]	Stable in a 0.1 mol·L ⁻¹ (pH = 13) NaOH solution for approximately 70 h followed by immersion in a 1.0 mol·L ⁻¹ (pH = 14) NaOH solution for approximately another 90 h [103]
(PAH/PSS)/PES (with different bi-layer numbers)	Stable in a 0.1 mol·L ⁻¹ HNO ₃ solution for 1600 h and after subsequent immersion in a 1 mol·L ⁻¹ HNO ₃ solution for 340 h [99]	Not stable in a 0.1 mol·L ⁻¹ NaOH solution [99]
(PAH/PSS) ₆ /sPES	Stable during batch concentration of a 10% phosphoric acid and 2 g·L ⁻¹ aluminum phosphate solution at pH = 0.7 [49]	
(PAH-Gu/PSS) ₆ /sPES	Stable during batch concentration of a 10% phosphoric acid and 2 g·L ⁻¹ aluminum phosphate solution at pH = 0.7 [49] Stable during batch concentration of sewage sludge ash leachate, containing phosphoric acid, sulfuric acid and multiple monovalent - and multivalent cationic impurities, at pH = 1 [49]	
(PDADMAC/PAA)/PES (with different bi-layer numbers)	Not stable in a 0.1 mol·L ⁻¹ HNO ₃ solution [99]	Not stable in a 0.1 mol·L ⁻¹ NaOH solution [99]
(PAH/PAA)/PES (with different bi-layer numbers)	Not stable in a 0.1 mol·L ⁻¹ HNO ₃ solution [99]	Not stable in a 0.1 mol·L ⁻¹ NaOH solution [99]

membranes based on their low MWCO. Another advantage of the layer-by-layer coating preparation step is the possibility to tune the charge of the membrane by either finalizing the coating procedure using a solution containing a polyanion or a solution containing a polycation. This provides the opportunity to prepare membranes suitable for preferentially retaining multivalent anions or multivalent cations (see Table 13). Given the seemingly good chemical stability of especially NF membranes based on LBL coating using strong polyelectrolytes, these newly developed membranes have a high potential for further development and commercial introduction for application at harsh pH conditions. One of the disadvantages of these types of membranes is the limited stability at high ionic strength (high salt concentration conditions) during application [113] and the limited pressure range of the hollow fiber supports used thus far.

8. Acid and alkaline stability of membranes based on phase inversion

8.1. Asymmetric sulfonated nitro-polyphenylsulfone membranes

Phase inversion was used to prepare asymmetric sulfonated nitro-polyphenylsulfone (SPPS_y-NO₂, where y is the ion exchange capacity in meq·g⁻¹) membranes [108]. Membranes had different ion exchange capacities (IEC), ranging from 0 to 2.2 meq·g⁻¹ and were prepared using either demineralized water, a 0.1 mol·L⁻¹ HCl solution or a 1 mol·L⁻¹ NaCl solution as non-solvent [108]. SPPS_{1.2}-NO₂ membranes with an IEC = 1.2 meq·g⁻¹ and prepared using demineralized water or a NaCl solution as non-solvent were exposed to a 0.1 mol·L⁻¹ HCl solution (pH = 1) for 7 days and characterized before exposure, after 3 days of

exposure and after 7 days of exposure. Both membranes showed an unchanged Na₂SO₄ retention (80% and 78% for the membrane prepared using demineralized water and the 1 mol·L⁻¹ NaCl solution, respectively) and permeance (0.24 L·m⁻²·h⁻¹·bar⁻¹ and 3.1 L·m⁻²·h⁻¹·bar⁻¹ for the membrane prepared using demineralized water and the 1 mol·L⁻¹ NaCl solution, respectively), indicating good stability at low pH conditions for the exposure time used.

8.2. Crosslinked PVDF membranes

Phase inversion was also used to prepare PVDF membranes [81,109]. These membranes were either crosslinked using *para*-xylenediamine (XDA) or 1,6-hexanediamine (HAD). The pH stability of the membranes was evaluated by immersing the prepared membranes in either a 5 mol·L⁻¹ HCl solution or a 5 mol·L⁻¹ NaOH solution for 125 h and 5 days for the XDA crosslinked PVDF membrane [109] and the HDA crosslinked membrane [81], respectively. PVDF_{XDA} membranes showed a high Rose Bengal retention (around 99%) and a water permeance of approximately 0.55 L·m⁻²·h⁻¹·bar⁻¹ [109], while the PVDF_{HDA} membrane had the same RB retention but a higher water permeance of 1.9 L·m⁻²·h⁻¹·bar⁻¹ [81]. PVDF_{XDA} appeared to be stable in the acid solution based on an unchanged RB retention. However, the water permeance dropped considerably to below 0.3 L·m⁻²·h⁻¹·bar⁻¹ [109]. Exposure to the alkaline solution resulted in a small reduction in the RB retention of 2% (absolute) and an unchanged to slightly lower water permeance. It should be noted that the permeance values had a relatively high standard deviation, especially after exposure to the alkaline solution [109]. PVDF_{HDA} was stable in the acid solution as indicated by an unchanged permeance and retention. Exposure of this membrane to the alkaline

Table 13
Membrane characteristics of membranes produced via layer-by-layer coating.

Membrane group	Membrane type	MWCO (Da)	Permeance at neutral pH (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	R	R	R	R	IEP	Ref.
				Na ₂ SO ₄ (%)	MgSO ₄ (%)	NaCl (%)	MgCl ₂ (%)		
Strong polyelectrolytes	(PDADMAC/PSS) ₆ /PES	–	21	–	–	–	–	–	[50]
	(PDADMAC/PSS) ₆ /sPES	–	6.1	–	–	–	–	–	[49]
	(PDADMAC/PSS) ₈ /PES	279	10.7	> 99 ^a	95.5 ^a	38 ^a	23 ^a	–	[99]
	(PDADMAC/PSS) _{8.5} /PES	270	–	57 ^a	97 ^a	49 ^a	96 ^a	–	[99]
	(PDADMAC/PSS) ₃ /Ceramic	240	13	–	88 ^b	–	–	–	[103]
A strong / weak polyelectrolyte combination	(PAH/PSS) ₈ /PES	249	9.7	92 ^a	97.5 ^a	40 ^a	98 ^a	–	[99]
	(PAH/PSS) _{8.5} /PES	231	–	75 ^a	98 ^a	72 ^a	>99.5 ^a	–	[99]
	(PAH/PSS) ₆ /sPES	–	2.1	–	–	–	–	3.4	[49]
	(PAH-Gu/PSS) ₆ /sPES	–	5.4	–	–	–	–	4.7	[49]
	(PDADMAC/PAA) ₈ /PES	320	–	78 ^a	11 ^a	6 ^a	0 ^a	–	[99]
Weak polyelectrolytes	(PDADMAC/PAA) _{8.5} /PES	327	–	50 ^a	8 ^a	5 ^a	0 ^a	–	[99]
	(PAH/PAA) ₈ /PES	190	1.3	81 ^a	80 ^a	26 ^a	78 ^a	–	[99]
	(PAH/PAA) _{8.5} /PES	180	1.5	35	78 ^a	67 ^a	93 ^a	–	[99]

^a for 5 mmol·L⁻¹ salt solution

^b for 5 mmol·L⁻¹ salt solution and P = 3.5 bar

solution reduced the retention marginally, while the permeance increased strongly to approximately 3.0 L·m⁻²·h⁻¹·bar⁻¹ [81], indicating that the membrane was not fully stable at this extremely high pH.

8.3. Crosslinked poly(sulfone-co-ethernitrile) random copolymer with tertiary amine groups membrane

A crosslinked poly(sulfone-co-ethernitrile) random copolymer ultrafiltration (UF) membrane with tertiary amine groups and cyano groups was prepared based on non-solvent induced phase inversion using bisphenol A, 4,4'-dichloro biphenyl sulfone (DCBPS), 2,6-difluorocyanophenyl (2,6-DFBN) and N-(N,N-dimethylaminoethyl)-3,3-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (PPH-DMEA) as monomers [110]. 3-bromopropyltrimethylammonium bromide (BPTAB) was added to produce a partially di-quaternized random copolymer. Subsequently, the UF membrane was converted into a NF membrane through a 5 h crosslinking procedure, using a 0.25 %w/v solution of the p-xylylene dichloride (PXDC) crosslinker in isopropyl alcohol (IPA). This (PScEN)_{PXDC} membrane showed a MWCO = 880 Da, a pure water permeance of 4.1 L·m⁻²·h⁻¹·bar⁻¹, and NaCl, Na₂SO₄, MgCl₂, and CaCl₂ retentions of 87.2%, 70.7%, 98.2%, and 97.3% respectively, for 0.5 g·L⁻¹ single salt solutions, indicating a positively charged membrane, even though streaming potential measurements using a 10⁻² mol·L⁻¹ KCl solution indicated a IEC ≈ 5.5. The membrane appeared to be stable in a NaOH solution with pH = 12 at T = 25 °C for 30 days as indicated by stable permeance and MgCl₂ retention during intermittent characterization experiments [110].

8.4. Hybrid membranes

Flat sheet hybrid NF membranes were prepared [111] based on 20 % w PES, 1 %w polyvinyl pyrrolidone (PVP) and concentrations of hyperbranched PEI grafted on multiwall carbon nanotube (MWCNT) ranging from 0.2 to 0.8 %w, with a PEI:MWCNT weight-based ratio of 5 during the grafting of PEI on MWCNT. The MWCO and the pure water permeance of the membrane increased with an increasing PEI-MWCNT concentration. The PEI-MWCNT-PES membrane prepared using a PEI-MWCNT concentration of 0.6 %w, leading to a MWCO = 600 Da, an IEP = 10 and a pure water permeance of 7.6 L·m⁻²·h⁻¹·bar⁻¹, was successfully used for removal of arsenic (AsO₄³⁻) from heavy metal containing wastewater [111] at pH = 11.5 with a retention as high as 98.5%. Long term stability of the membrane under alkaline conditions was not reported.

9. Acid and alkaline stability of membranes based on grafting

Membranes (sPSt/PVDF) based on sulfonated polystyrene (sPSt) were produced via grafting of polystyrene (PSt) on PVDF supports prepared via phase inversion followed by sulfonation using chlorosulfonic acid [112]. The sulfonation procedure was performed after a single, double or triple grafting step [112]. Furthermore, part of the membranes prepared using a single grafting step followed by a sulfonation step were either subjected to an annealing step at T = 80 °C or subjected to a second grafting step. Characterization revealed that the pristine PVDF membrane was unstable when immersed in either a 1.0 mol·L⁻¹ NaOH solution or a 1.0 mol·L⁻¹ HCl solution at room temperature for a week, as indicated by a strongly increased permeance and strongly reduced Rose Bengal and NaCl retentions. In contrast, sPSt/PVDF based on three grafting steps prior to a sulfonation step appeared to be stable in the alkaline and the acid solution as indicated by an unchanged permeance, Rose Bengal retention and NaCl retention [112] during membrane characterization. This sPSt/PVDF membrane, with a claimed MWCO < 500 Da based on Rhodamine B retention (it should be noted that Rhodamine B contains charged groups and its retention is not only due to the pore radius only, but due to Donnan exclusion and/or di-electric exclusion as well), showed a water permeance of 2.4 L·m⁻²·h⁻¹·bar⁻¹ and Rose Bengal, NaCl and MgSO₄ retentions of 99.4%, 57.1% and 77.4%, respectively, in dead-end stirred cell filtration tests at pressures between P = 20 – 30 bar. The temperature used during these experiments was not revealed but was probably room temperature.

10. Progress in pH stable membrane development in relation to commercially available pH stable membranes

As outlined in the previous sections several developments during the last years have resulted in alternative pH stable membranes, especially for treating solutions with pH < 2. For some of the membranes that appear to be (practically) stable for acidic or alkaline solutions a direct general performance comparison with commercially available pH stable membranes is difficult. However, for several of these membranes, performance characteristics have been reported and have been discussed in earlier sections. For these membranes, and especially for the chemically stable membranes for which permeability and MWCO have been reported, this is easier. Fig. 11 shows these characteristics for (practically) acid solution stable NF membranes (for polyelectrolyte layer-based and imidazolium-graphene oxide-based NF membranes in Fig. 11a and for other polymeric membranes in Fig. 11b). On the basis of these results it is clear that currently only a limited amount of the recently prepared membranes appears to have the potential to outperform the

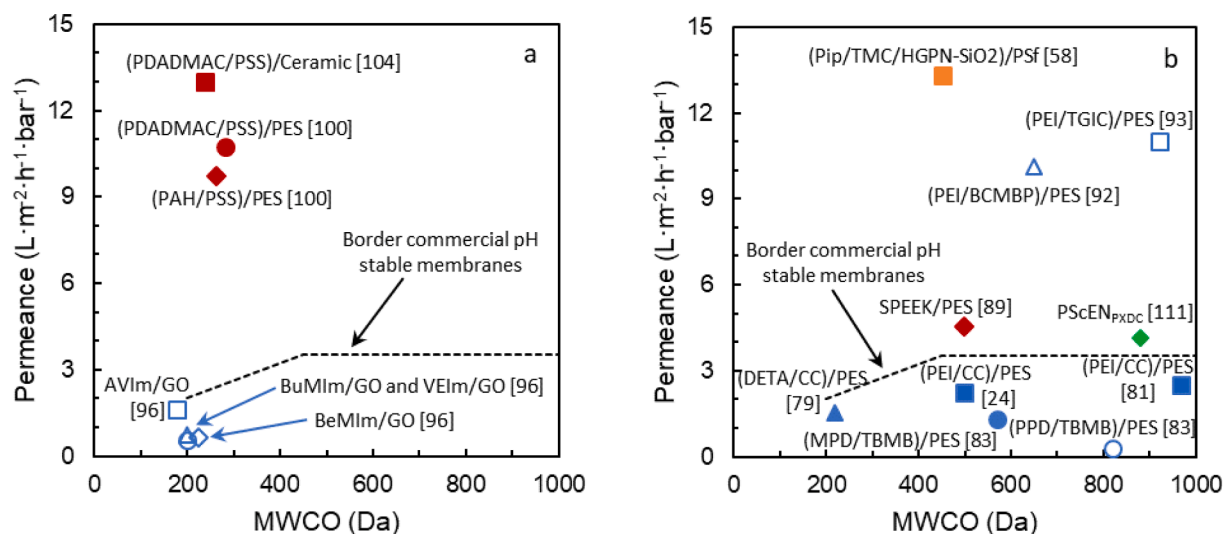


Fig. 11. Permeance and MWCO characteristics of developed (practically) acid stable NF membranes, a) for polyelectrolyte layer and imidazolium based graphene oxide based membranes and b) for other polymeric membranes, compared with characteristics of commercially available pH stable NF membranes, for which the maximum border is shown, see Table 2.

commercially available membranes for treating acid solutions with pH < 2. These membranes include polyelectrolyte membranes prepared via layer-by-layer coating, (PDADMAC/PSS)/PES, (PDADMAC/PSS)/Ceramic and (PAH/PSS)/PES (see Fig. 11a), which combine a relatively low MWCO (below 300 Da) with a high permeance. The low MCWO membranes would be especially suitable for the purification of solutions containing small inorganic acids (such as HCl and HNO₃) used e.g. in the food industry for cleaning in place (CIP) of manufacturing equipment [3] or in the concentration or sulfuric acid solutions [10]. Furthermore, several other polymeric membranes, mostly produced via (reactive) coating or interfacial polymerization, outperform the commercially available NF membranes for low pH conditions. However, these developed membranes are all relatively open with a MWCO > 450 Da (see Fig. 11b). These higher MWCO membranes are less attractive for treating spent CIP solutions or concentrating sulfuric acid solutions, but are of interest for the recovery and purification of phosphoric acid solutions or sulfuric acid solutions, where generally as low as possible phosphoric acid [49,50,101,102] or sulfuric acid [10] retention in combination with an as high as possible retention for metal ions is needed. Other acid stable membranes shown in Fig. 11 do not yet outperform current commercially available membranes. However, they may have potential for commercialization provided that their permeance can be increased and/or MWCO can be reduced, as discussed earlier, by e.g. production of thinner, more porous or less tortuous top layers, further crosslinking or a combination of these approaches.

As mentioned earlier especially layer-by-layer coating approaches using polyelectrolyte multi-layers seem to show strong potential for the development of commercially attractive chemically stable NF membranes for harsh pH conditions. One of the advantages is that these membranes can be tuned for either a high multivalent cation retention or a high multivalent anion retention by changing the charge of the top layer of the membrane facing the feed stream [99]. However, at present the use of these membranes during nanofiltration using a solution with a high salt concentration is still a challenge due to the limited stability of these membranes at these conditions [113]. Crosslinking of the positively and negatively charged polyelectrolyte layers may further improve the stability of these membranes during nanofiltration of solutions with a high ionic strength [114]. However, it is also evident that these crosslinks need to be stable under extreme pH conditions as well. Furthermore, these polyelectrolyte multi-layer membranes have so far mainly been prepared on hollow-fiber UF supports strongly limiting their use to low operating pressure. Application of these membrane

types outside the water production industry, such as in the chemical, food and mining industry, would require the development of spiral wound polyelectrolyte multilayer membranes or ceramic polyelectrolyte multilayer membranes capable of withstanding much higher pressures. The use of ceramic supports could have the disadvantage that these supports would be relatively expensive compared to polymeric supports, increasing the cost price of the membranes [115].

For other NF membranes such as polyamine membranes, often produced via IP, optimization of the IP preparation step can yield potentially improved commercially attractive acid stable NF membranes. However, these polyamine membranes are often more positively charged than the standard polyamide NF membranes, making them more suitable for retaining multivalent cations than multivalent anions. However, potentially the use of sulfonated aromatic multi-amines such as sulfonated PPD (1,4-phenylenediamine 2-sulfonic acid) in combination with e.g. cyanuric acid may result in sulfonated polyamine membranes. Due to the presence of the sulfonate groups these membrane types may well be less positively charge (possibly even negatively charged) than their non-sulfonated multi-amine-based alternatives and can as a consequence of the more negatively charged membrane surface be a suitable chemically stable alternative for polyamide NF membranes. However, to the best of my knowledge NF membranes on the basis of sulfonated aromatic polyamines have not been reported in open scientific literature.

Based on the reported results for the preparation of polyamine membranes (reactive) coating seems to be an interesting alternative for the commonly applied IP preparation method. This (reactive) coating procedure features coating of one of the reactants in e.g. ethanol on the support followed by (complete) drying and subsequent coating of the other reactant in water followed by reaction to produce the polyamine NF membrane. This preparation procedure even resulted in a stable polyamine NF membrane ((PEI/BCMBP)/PES) [91] with higher permeance than other PEI based polyamine NF membranes produced via IP, as can be seen from Fig. 11 b. For these membrane types further optimization of the IP procedure as well as of the (reactive) coating preparation may lead to tighter NF membranes with a high permeance and may thus yield commercially interesting acid stable membranes.

Only a limited number of the recently developed pH stable membranes can cope with extreme alkaline conditions (pH > 11). Specific reasons for the stronger focus on acid stability have not been mentioned in the reviewed publications but may be due to the strong attention for acid recycling in the mining industry. Studies featuring alkaline stability

are often related to dye separation, which requires the use of very open NF or tight UF membranes since low (divalent) salt retention is required. Since the focus of this review is on nanofiltration at extreme pH conditions, this may exclude new membrane developments for alkaline solutions in dye separation where tight ultrafiltration membranes are used.

The newly developed membranes stable at high pH include several polyamine membranes, polyelectrolyte NF membranes produced by layer-by-layer coating (only PDADMAC/PSS based membranes, e.g. [99]), a poly(alkanolamine isocyanurate) (PEI/TGIC)/PES membrane prepared by reactive coating and possibly PEI-MWCTN-PES, although for the latter membrane long term stability at alkaline conditions was not determined [111]. The low MWCO type membranes, such as the PDADMAC/PSS based membrane developed, could especially be suitable for the purification of alkaline CIP solutions in the food industry [3], steeping lye in viscose production [9], or NH_4OH solutions with organic contaminants, or for the separation of chlorides and sulfates from brines at high pH [4,43]. Slightly more open NF membranes (with a higher MWCO) could be very suitable for the removal of lignin from an NaOH solution [92], the removal of arsenic (AsO_4^{3-}) from heavy metal containing wastewater [111], heavy metal wastewater treatment in general [59], or for dye/salt separation from alkaline wastewater streams [59,83,84]. Obviously, these membranes, such as the poly(alkanolamine isocyanurate) (PEI/TGIC)/PES membrane [92], should have a sufficiently high permeance and the required retention characteristics as well to become attractive for commercial application. Potential (further) improvements of these membranes can be reached following the same research lines as suggested for acid stable membranes earlier in this section.

11. Conclusions

During recent years the development of nanofiltration membranes for treating acid solutions ($\text{pH} < 2$) or alkaline solutions ($\text{pH} > 11$) has received a lot of attention even though a structured general approach to develop or improve nanofiltration membranes for extreme pH conditions is lacking. Common commercially available polyamide membranes show a limited stability for these acid or alkaline solutions and currently available pH stable membranes are either relatively open (too high molecular weight cut-off) or have a relatively low permeance compared to the commercially available membranes with a limited pH stability. Recent membrane developments have mainly focused on acid stability, even though alkaline stability has been targeted in several studies as well. Specific reasons for this strong focus on acid stability have not been mentioned in the reviewed publications but may be due to the strong attention for acid recycling in the mining industry. Studies featuring alkaline stability are often related to dye separation, which requires the use of very open NF or tight UF membranes since low (divalent) salt retention is required. Since the focus of this review is on nanofiltration at extreme pH conditions, this may exclude new membrane developments for alkaline solutions in dye separation where tight ultrafiltration membranes are used.

Especially polyamine and polyurea NF membranes, often prepared via interfacial polymerization on an ultrafiltration support, polyelectrolyte multilayer based nanofiltration membranes, usually prepared via layer-by-layer coating on an ultrafiltration support, and poly(alkanolamine isocyanurate) membranes prepared via reactive coating outperform polyamide NF membranes regarding acid stability. Hybrid membranes based on polyvinylalcohol and ethoxysilanes also show potential for acid stability with only minor changes in performance after immersion in highly concentrated acids. Polysulfonamide membranes outperform polyamide membranes as well, however, these membranes show less acid stability than the polyamine membranes. The proper acid stability of polyamine membranes is mainly due to the reduced hydrolysis rate of the amine bond as compared to amide and sulfonamide bond hydrolysis. Furthermore, the stability of the polyelectrolyte-based

membranes is due to the strong ionic bonds between the subsequent anionic and cationic polyelectrolyte layers provided that these polyelectrolyte layers maintain their ionic form at the pH of the solution treated and the membranes are not exposed to too high ionic strength solutions. These membranes have so far mainly been prepared on hollow-fiber UF supports, strongly limiting their use to low operating pressure. Application of these membrane types outside the water production industry, such as in the chemical, food and mining industry, would require the development of spiral wound polyelectrolyte multilayer membranes capable of withstanding much higher pressures. Furthermore, application of these polyelectrolyte multilayer membranes for solutions with a high ionic strength, such as solutions containing high concentrations of salts, would require crosslinking of the anionic and cationic polyelectrolyte layers. Obviously, these crosslinks should be able to withstand extreme pH conditions as well to maintain the desired chemical stability under strong acid or alkaline conditions.

Polyelectrolyte multilayer membranes based on PDADMAC or PAH and PSS are not only more acid stable than traditional polyamide membranes, but show a significant permeance improvement at low MWCO (below 300 Da) over the current commercially available acid stable membranes as well. Another advantage of these membranes is the tunability of their surface charge, which allows direct control over the (divalent) anion and cation retention and consequently over the separation efficiency. A few other polymeric NF membranes also show a higher permeance than the commercially available acid stable NF membranes, but these newly developed membranes have a relatively high MWCO (in excess of 450 Da). Other membranes with a proper pH stability could only be of commercial interest provided that the top layer of these membranes can be further improved such that the permeance of the membranes increase and/or the MWCO decreases.

For the treatment of alkaline solutions only a limited number of newly developed membranes appear to be suitable. Polyelectrolyte-based nanofiltration membranes, especially those produced from PDADMAC and PSS, show potential for commercialization in this case, especially for applications where relatively tight nanofiltration membranes are needed. For limitations and further development of these membranes the same considerations apply as discussed for their application at extreme acidic condition. Poly(alkanolamine isocyanurate) membranes show high potential for application under strong alkaline conditions where more open NF membranes are needed such as for the separation of dyes and salts from waste streams. Polyamine membranes show potential for the treatment of alkaline solutions as well, provided that the membranes can be optimized further and that a higher membrane permeance at the same MWCO can be obtained. This optimization might be achieved through further optimization of the IP preparation procedure or via the use of a reactive coating procedure. The MWCO of the polyamine membrane can be varied relatively easily over the entire NF MWCO range by selecting the proper multi-amine size and cross-linking degree.

It should be noted that practically all studies reviewed used lab-scale membrane samples with a low membrane surface area. This means that most developed membranes suitable for extreme pH still need to be scaled up before they can be applied in real industrial membrane applications. Consequently, further development of pH stable membranes is still required.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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