On the long-term pH stability of polyelectrolyte multilayer nanofiltration membranes

M.G. Elshof, W.M. de Vos, J. de Grooth, N.E. Benes [*]

Membrane Science and Technology Cluster, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500, Enschede AE, the Netherlands

A B S T R A C T

Long-term pH stability is critical for nanofiltration membranes in many applications, e.g. dairy and mining industry. We present a systematic study on the long-term pH stability of four different polyelectrolyte multilayer (PEM) nanofiltration membranes. The stability was assessed by comparing their performance before and after exposure to up to 1 M HNO_3 (~pH 0) and 1 M NaOH (~pH 14), in terms of pure water permeance (PWP), salt retention, and molecular weight cut-off (MWCO).

Poly(diallyldimethylammonium chloride) (PDADMAC)/poly(styrenesulfonate) (PSS) nanofiltration membranes show excellent stability under extreme acidic and basic conditions for more than 2 months (10.7 L $m^{-2}h^{-1}bar^{-1}$ PWP, 95.5% $MgSO_4$ retention, 279 g mol^{-1} MWCO), attributed to the use of strong polyelectrolytes, of which the charge is unaffected by pH. Poly(allylamine hydrochloride) (PAH)/PSS membranes show stable performance when exposed to extreme acidic conditions (9.7 L $m^{-2}h^{-1}bar^{-1}$ PWP, 97.5% $MgSO_4$ retention, 249 g mol^{-1} MWCO). Under these conditions, PAH remains charged and therefore a stable multilayer is maintained. PDADMAC/poly(acrylic acid) (PAA) and PAH/PAA membranes are not stable at extreme pH conditions.

These results highlight that PEM nanofiltration membranes, especially PDADMAC/PSS membranes, have tremendous potential for use at extreme pH conditions. Compared to most commercially available membranes they have superior long-term stability and very relevant performance.

1. Introduction

Nanofiltration (NF) membranes are used in a wide range of applications, such as water treatment, in the food industry, biotechnology and in the textile industry [1,2]. Over the past years, NF membranes prepared by Layer-by-Layer (LbL) coating of polyelectrolytes has received great attention. The resulting polyelectrolyte multilayer (PEM) NF membranes have many advantages over other membranes stemming from their high permeance, selectivity, tunability and ease of fabrication [1,3,4]. Moreover, the LbL approach to produce PEM NF membranes is quite sustainable, as no organic solvents are required, and they can easily be applied on any membrane geometry [3].

PEM membranes are prepared by alternatingly dip coating of polycations and polyanions onto a porous support. The charged polymers adsorb onto the oppositely charged surface, leading to the formation of a subsequent new thin layer [5] that becomes the membranes active separation layer. The formation of multilayers is mainly driven by the release of counter ions, leading to an entropic gain [6–8]. Though, other effects such as electrostatic effects, van der Waals forces, hydrogen bonding or hydrophobic interactions may also have an influence [9]. A great advantage of PEMs is that their properties can be finely tuned by varying a number of parameters, such as ionic strength, types of polyelectrolyte, pH and number of layers [6,10]. In this way, good control over the PEM material properties and thus over the final membrane properties can be achieved.

Over the years, substantial research has been performed on PEM NF membranes and their potential has been shown in applications such as micropollutant removal, water softening and solvent resistant nanofiltration [11–13]. Compared to conventional NF membranes, e.g. polyamide membranes prepared via interfacial polymerization, these membranes show excellent stability. De Grooth et al. showed that by careful selection of the polyelectrolytes, PEM hollow fiber nanofiltration membranes can be fabricated with high physical stability, i.e. resistance to sequential backwash cycles [14]. Likewise, a high chemical stability

was found against cleaning with hypochlorite [14], for which polyamide thin film composite membranes are not stable [15]. The high chemical stability of PEM based membranes is seen as a substantial advantage but has not been tested to its full extend.

The above illustrates that PEM NF membranes provide good alternatives to conventional NF membranes. Therefore, they may also offer solutions to other current challenges, especially in regards to membrane stability. One of these challenges is the search for pH stable NF membranes. These membranes are critical for applications that involve very low (<2) or very high (>12.5) pH environments, e.g. for the recovery of acids used in the metal and mining industries [16,17], the reuse of caustic cleaning solutions in the dairy industry [18] and in the treatment of effluents generated by the textile industry [19]. Unfortunately, only a limited number of commercial membranes are available. The traditional polyamide membranes undergo hydrolysis when exposed to these extreme pH conditions [20], while alternatives often have drawbacks such as only being resistant to acidic conditions, being expensive or having a high MWCO value [21].

Recent research has mainly focused on the preparation of pH stable membranes by choosing new monomers in the interfacial polymerization process [22,23], or by developing and tuning polymers for use in the phase inversion process [24]. NF membranes prepared by LbL coating of PEs could, however, offer an easy and sustainable alternative for use under extreme pH conditions.

While there are studies that assess the PEMs at mild pH conditions [25–28], there are only a limited number of studies that evaluate the performance of PEMs under extreme pH conditions. The majority of studies that assess the (extreme) pH stability of PEMs, typically only consider cross-linked layers or layers with additives such as nanoparticles or graphene. Nguyen et al. found that multilayers prepared by allyl-functionalized polyelectrolytes, have enhanced stability under harsh conditions (10 days exposure to pH 1 or 14), which was attributed to the thiol-ene crosslinking [29]. Similar results were found for composite hollow fiber membranes composed of multilayers of carboxymethyl cellulose and polyethyleneimine crosslinked with glutaraldehyde on a polypropylene substrate (48 h exposure to 0.5 M sulfuric acid and sodium hydroxide) [30]. In another study, researchers showed that by incorporating graphene oxide nanosheets into PEMs the stability of these membranes in sodium hypochlorite, sodium hydroxide and hydrochloric acid (4 h exposure) was improved [31].

Though, all these studies do not consider the performance of nanofiltration membranes composed of pure PEMs. However, Ahmadiianimini et al. [32] did evaluate the potential of PEMs as sacrificial layers. They showed that depending on whether the polyelectrolytes are strong or weak, layers could be removed by a treatment with either sodium hydroxide, hydrochloric acid, Triton X-100 surfactant or a combination of them. While it was shown that certain polyelectrolyte pairs, e.g. PDADMAC/PSS, were unaffected by pH exposure and therefore have potential for use under extreme pH conditions, multilayer stability was not the aim of that research and therefore was not studied over the long-term. Later studies further confirmed the stability of PDADMAC/PSS NF membranes in acidic solutions [33,34] and in alkaline solutions [35]. These studies also only assessed the short-term stability of these membranes. Since membranes are required to perform for months and even up to years in a stable, reproducible fashion under extreme pH conditions, membrane long-term stability is key. For this a multilayer would require both physical and chemical stability.

To the best of our knowledge, the long-term pH stability of different PEM NF membranes (without post treatment) and their potential for use under extreme pH conditions has not yet been systematically evaluated. In this study four different systems were evaluated (Fig. 1), representing combinations of both strong polyelectrolytes, e.g. charged over the full pH regime, and weak polyelectrolytes whose charge is dependent on the pH. The membranes were exposed to 0.1 M nitric acid (~pH 1) and sodium hydroxide solutions (~pH 13), and their performance was evaluated over time, for more than 2 months. The stable membranes were then exposed to solutions of 1 M nitric acid and 1 M sodium hydroxide for 2 weeks and assessed as well.

2. Experimental

2.1. Materials

Ethylene glycol (EG, anhydrous 99.8%), diethyleneglycol (DEG, Reagentplus 99%), glycerol (86–89% (T)), poly(acrylic acid) (PAA, M_w ~250,000, 35 wt %), poly(diallyldimethylammoniumchloride) (PDADMAC, M_w 200,000–350,000, 20 wt %), polyethyleneglycol 400, 600, 1500 (PEG), poly(sodium 4-styrenesulfonate) (PSS, Mw ~200,000, 30 wt %), sodium chloride (NaCl, ACS reagent, ≥99%, anhydrous, Redi-Dri™, free-flowing), sodium hydroxide (NaOH, puriss p.a., ACS reagent Ph. Eur., K ≤ 0.02%, ≥98%, pellets) and sodium sulfate (Na_2SO_4, ACS reagent, ≥99%, anhydrous, granular, free-flowing, Redi-Dri™) were
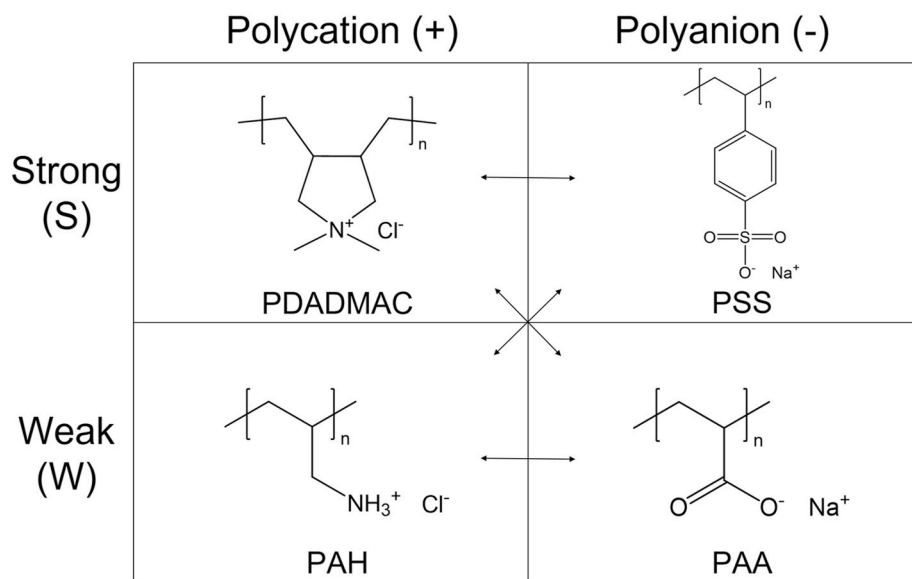

Fig. 1. Overview of used polyelectrolytes. The following combinations were studied: PDADMAC/PSS (S/S), PDADMAC/PAA (S/W), PAH/PSS (W/S) and PAH/PAA (W/W).

obtained from Sigma Aldrich. Magnesium chloride hexahydrate ($MgCl_2$, ACS reagent. Ph.Eur.) was purchased from VWR Chemicals. Magnesium sulfate heptahydrate ($MgSO_4$, ACS reagent. Ph.Eur.), nitric acid (HNO_3, 1 mol/L, Titripur®), ethanol (EtOH, EMSURE® ACS, ISO, Reag. Ph Eur.), PEG 1500 and PEG 2000 were supplied by Merck kGaA. PEG 200 was obtained from Fluka. Poly(allylamine hydrochloride) (PAH, M_w 150,000, 40 wt %) was received from Nittobo Medical Co. All chemicals were used without further purification.

Ultrafiltration (UF) hollow fiber membranes based on modified poly ether sulfone (PES) were kindly provided by NX Filtration (Enschede, the Netherlands).

2.2. Membrane fabrication

Polyelectrolyte multilayers (PEM) were coated on the UF PES hollow fibers. Untreated, these fibers have a permeance of 189 L $m^{-2}h^{-1}bar^{-1}$, a MWCO of 10 kDa, an inner diameter of 0.7 mm and a negatively charged separation skin.

The UF membranes were pretreated to remove residual conservation solution and to ensure pore wetting by overnight immersion in 10 wt% ethanol in water, followed by 3 rinsing cycles of 15 min each in fresh Milli-Q water.

The Layer-by-Layer dipcoating of polyelectrolytes was carried out manually. Fibers were bundled and coated in 1 L graduated cylinders by full immersion into the different solutions. Membranes were firstly exposed to a polycation solution (0.1 g L^{-1}, 0.05 M NaCl, pH 6.0) for 15 min. Thereafter three rinsing steps of 5 min in three separate graduate cylinders containing 0.05 M NaCl followed. Then, the membranes were immersed in a polyanion solution (0.1 g L^{-1} 0.05 M NaCl, pH 6.0) for 15 min, followed by another three rinsing steps in 0.05 M NaCl. This sequence was repeated until the desired number of bilayers was obtained.

It is well established that the exact conditions (pH, salinity) under which the PEMs are applied, will influence the separation properties. The conditions selected here for these membranes are known to lead to good quality separation layers [12,36].

Four different polyelectrolyte systems were studied: PDADMAC/PSS, PAH/PSS, PDADMAC/PAA and PAH/PAA. These commonly used polyelectrolyte systems were carefully chosen, consisting of two weak and two strong polyelectrolytes, such that all possible pairs; strong/strong, weak/strong, strong/weak and weak/weak could be made. The strong polyelectrolytes maintain their charge over the full pH regime, while the weak polyelectrolytes will lose charge above or below their pK_a. The difference in performance as a result of specific polyelectrolyte combinations can be studied in detail. For all pairs, the membranes were coated with 8 and 8.5 bilayers, so the effect of terminating polyelectrolyte could be studied as well.

After coating, PEM membranes were stored for 4 h in a 15 wt % glycerol in water mixture and then dried overnight in a fume hood.

2.3. Module preparation

Membrane modules were prepared by potting single PEM coated membrane fibers in a 6 mm diameter PE tubing. (A more detailed description of the potting procedure can be found in Ref. [37], supporting information). The final effective length of the fiber is approximately 167 mm and the inner diameter 0.7 mm, resulting in a total membrane area of $3.7 \cdot 10^{-4}$ m^2 per module. A photograph of the module can be found in Supplementary Fig. S1.

2.4. Membrane performance

The performance of the membranes was evaluated, in terms of pure water permeance, salt retention and molecular weight cut-off. For each data point, an average of six different membrane samples was taken. Error bars represent the 95% confidence interval.

For all permeation experiments, an in-house build cross-flow setup operated by a rotary vane pump (BN71B4 pump motor, Bonfiglioli, Italy; IMTI 1.5 M inverter, Electroil, Italy; PA411 pump head, Fluid-o-Tech, Italy) was used. A schematic overview and detailed description of the setup can be found in the Supplementary Information, Fig. S2. The membrane modules were inserted in the cross-flow setup by Festo connections. Measurements were performed at an average pressure of 5 bar over each module and a cross-flow velocity of 1.1 m s^{-1}, corresponding to a Reynolds number of approximately 863 (laminar flow regime).

2.4.1. Pure water permeance
The pure water permeance (PWP) was measured with demineralized water in cross-flow mode at room temperature. Permeance was calculated using Equation (1). In this formula P is the permeance ($L \cdot m^{-2}h^{-1}bar^{-1}$), Q the volumetric flow ($L \cdot h^{-1}$), A the membrane area (m^2) and ΔP the applied pressure difference (bar).

$$P = \frac{Q}{A \times \Delta P} \tag{1}$$

2.4.2. Salt retention
Single salt retention measurements were performed in cross-flow mode using 5 mM solutions of $MgSO_4$, $MgCl_2$, Na_2SO_4 and NaCl. Salt concentration was measured with a conductivity meter (WTW cond 3310). The retention (R) was calculated based on the ratio between conductivity in feed and permeate samples (Equation (2)).

$$R = \frac{c_f - c_p}{c_f} \times 100\% \tag{2}$$

Where c_f is the feed concentration ($mg \cdot L^{-1}$) and c_p the permeate concentration ($mg \cdot L^{-1}$).

2.4.3. Molecular weight cut-off
The molecular weight cut-off of the membranes was evaluated by permeating a feed mixture of EG, DEG and PEGs with mean molecular weights of 62, 106, 200, 400, 600, 1000, 1500 and 2000 g mol^{-1} at a concentration of 1g L^{-1} each. Feed and permeate was analyzed by gel permeation chromatography (GPC, Agilent 1200/1260 Infinity GPC/SEC series, Polymer Standards Service data center and column compartment) over two Polymer Standards Service Suprema 8 × 300 mm columns in series (1000 Å, 10 μM; 30 Å, 10 μm). Milli Q water with 50 mg L^{-1} NaN_3 was used as eluent at a flowrate of 1 mL min^{-1}. The compositions were determined by comparison to a calibration curve that was obtained with PEG standards. Refractive index detection was used to determine the concentrations of feed and permeate. Subsequently, PEG retention was calculated using Equation (2). Finally, the molecular weight cut-off is determined, as the smallest molecular weight that is retained for 90% or more.

2.5. pH stability tests

Long-term stability of these membranes was evaluated by ex-situ exposure to 0.1 M HNO_3 (~pH 1) and 0.1 M NaOH (~pH 13). At set time intervals the samples were taken out of the solutions, rinsed with Milli-Q water and hereafter the performance of the samples was evaluated via PWP and $MgSO_4$ retention. After more than 2 months exposure, the MWCO was measured and compared to the initial value.

The best polyelectrolyte pairs, in other words those that were stable after exposure to 0.1 M HNO_3 or NaOH, were tested for even more extreme conditions and exposed to 1 M HNO_3 (~pH 0) and 1 M NaOH (~pH 14) for 2 weeks. PWP, $MgSO_4$ retention and MWCO were again determined.

For these measurements, each data point represents an average of three different membrane samples. Error bars depict the 95% confidence interval.

3. Results & discussion

This section is divided into two different parts. The first part deals with the performance of the four different PEM membranes in terms of PWP, salt retention and MWCO prior to exposure to extreme pH. In the second part we show how the performance of the membranes evolves when they are exposed to different extreme pH conditions.

3.1. Performance PEM NF membranes

3.1.1. Pure water permeance

The pure water permeance results for the four different types of polyelectrolyte multilayer membranes are shown in Fig. 2.

All polyelectrolyte multilayers were successfully coated on the UF hollow fibers, evident from the reduction in permeance from 189 ± 8 L $m^{-2}h^{-1}bar^{-1}$ for an uncoated fiber to $1{-}13$ L $m^{-2}h^{-1}bar^{-1}$ for the coated membranes.

The pure water permeance varies from system to system as we expected based on previous studies [12,38,39]. PDADMAC/PSS and PAH/PSS membranes show the highest permeances (12.1 ± 0.6 and 12.8 ± 0.8 L $m^{-2}h^{-1}bar^{-1}$ respectively for $(-)$ terminated). The lowest permeance of 1.3 ± 0.06 L $m^{-2}h^{-1}bar^{-1}$ was observed for PAH/PAA multilayer membranes, in agreement with the fact that at pH 6 dense layers are formed [12,40]. This is the result of a high ionic cross-link density for PAH/PAA. Compared to PDADMAC and PSS, PAH and PAA bear more charge per C atom, i.e. they have a higher charge density [41]. Membranes prepared with PDADMAC and PAA show a slightly higher permeance of around 2.7 ± 0.2 L $m^{-2}h^{-1}bar^{-1}$, as a result of a more open layer originating from a lower ionic cross-link density [39].

Besides a permeance variation dependent on the types of polyelectrolytes, a difference in permeance is also observed depending on which PE terminates the layer. For PDADMAC/PSS and PAH/PSS a higher permeance is observed for the polyanion terminated layers, while the opposite is true for PDADMAC/PAA and PAH/PAA. These shifts in permeance are typical for PEMs and is known as the so-called odd-even effect [36,42,43], where the charge of the final layer influences the swelling of the entire multilayer and thereby also the water permeance of PEM membranes.

3.1.2. Salt retention

Fig. 3 shows the retention of four different salts by the studied PEM membranes. Salts composed of both multivalent and monovalent ions were studied, in order to gain insights into the separation mechanisms.

In general, of the four systems, PAH/PSS has the highest retention for all salts, followed by PDADMAC/PSS and PAH/PAA. Membranes prepared with PDADMAC/PAA have a considerably lower retention.
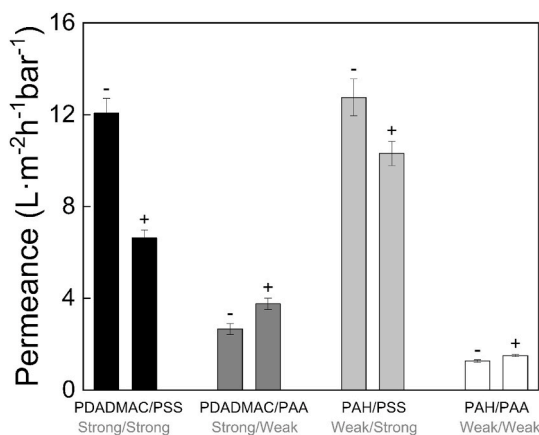
Fig. 2. Pure water permeance of four different polyelectrolyte multilayer membranes. Terminated with polyanion $(-)$ or polycation $(+)$ respectively.

In Fig. 3A the salt retentions are shown for PDADMAC/PSS. These PEM membranes are known for a separation mechanism dominated by Donnan exclusion [36], and that is also the case here. Retention decreases from $MgCl_2$ to $MgSO_4$ to Na_2SO_4 when terminated with a positive layer, and increases when terminated with a negative layer.

PDADMAC/PAA membranes have the lowest salt retention as can be seen in Fig. 3B. Compared to other polyelectrolyte systems such as PAH/PAA, this system is known to have a lower ionic crosslink density, that might lead to the lower retention [39]. It is also possible that defects are present in the layer giving rise to the low salt retention.

The highest salt retentions are obtained with PAH/PSS as is shown in Fig. 3C. Especially for $MgCl_2$ and $MgSO_4$ very high retention are obtained, up to 99%. It is known that PAH/PSS multilayers have a significant excess of positive charge in the bulk of the PEM [44]. Therefore, divalent positive ions are retained best and the effect of terminating layer is small, that is also observed in our results.

PAH/PAA membranes show average retention for all salts (Fig. 3D). For the positive terminated layers, a similar "Donnan exclusion" trend is observed as for PDADMAC/PSS, yet in this case the retention is much lower, perhaps due to a lower excess charge. Therefore separation is probably based on a combination of Donnan and size exclusion. The negative terminated layers show a different trend, with a higher retention for $MgCl_2$ than for NaCl. This indicates that retention is probably the result of dielectric and size exclusion.

3.1.3. Molecular weight-cut off

The salt retention gives an indication of the performance of the PEM membranes, specifically about their ability to retain small and charged species. Another important parameter is the MWCO, that gives information about how well the membranes are able to separate uncharged species based on size. The results for the MWCO of the PEM membranes, described as the smallest molecular weight that is retained for 90% or more by the membrane, are shown in Fig. 4.

Nanofiltration membranes have a MWCO smaller than 1000 g mol^{-1}. All four types of PEM membranes have a MWCO smaller than 350 g mol^{-1} and therefore we can conclude that the prepared membranes fall well within the nanofiltration regime.

Besides high water permeances and high salt retentions, PDADMAC/PSS and PAH/PSS membranes have low MWCO values of 283 ± 4 and 264 ± 7 g mol^{-1} respectively (for $(-)$ terminating layer), meaning that they are also able to retain small uncharged molecules. A slightly higher MWCO is observed for polyanion terminated layers, that might be the result of a more open layer, as also observed from the higher permeances for these negatively terminated layers (Fig. 2), but this could also be due to differences in flux during the assessment of the differently charged fibers.

PDADMAC/PAA membranes have a MWCO similar to the other three systems (316 ± 10 g mol^{-1} for $(-)$ terminating layer). Therefore we can rule out the presence of defects in the layer. The observed low salt retention, together with this MWCO, shows that the separation mechanism is primarily based on size exclusion and not on charge.

PAH/PAA membranes show the lowest MWCO of 185 ± 14 g mol^{-1}. Combined with the lowest permeance of 1.3 ± 0.06 L $m^{-2}h^{-1}bar^{-1}$, it indicates that these membranes have the most dense layer of all four types studied. The formation of dense PAH/PAA layers is consistent with earlier work and a result of the high charge density of the used polyelectrolytes [12,40,41].

Overall it can be concluded, that when looking at pure water permeance, salt retention and MWCO, we have successfully prepared four different PEM nanofiltration membranes. PAH/PSS and PDADMAC/PSS are the better performing membranes in terms of permeance and retention, while PAH/PAA forms the densest separation layer in terms of MWCO.

It must be highlighted that the goal of this research is not to make the best performing membranes. These first results will serve as a reference point for the rest of this research concerning the long-term pH stability
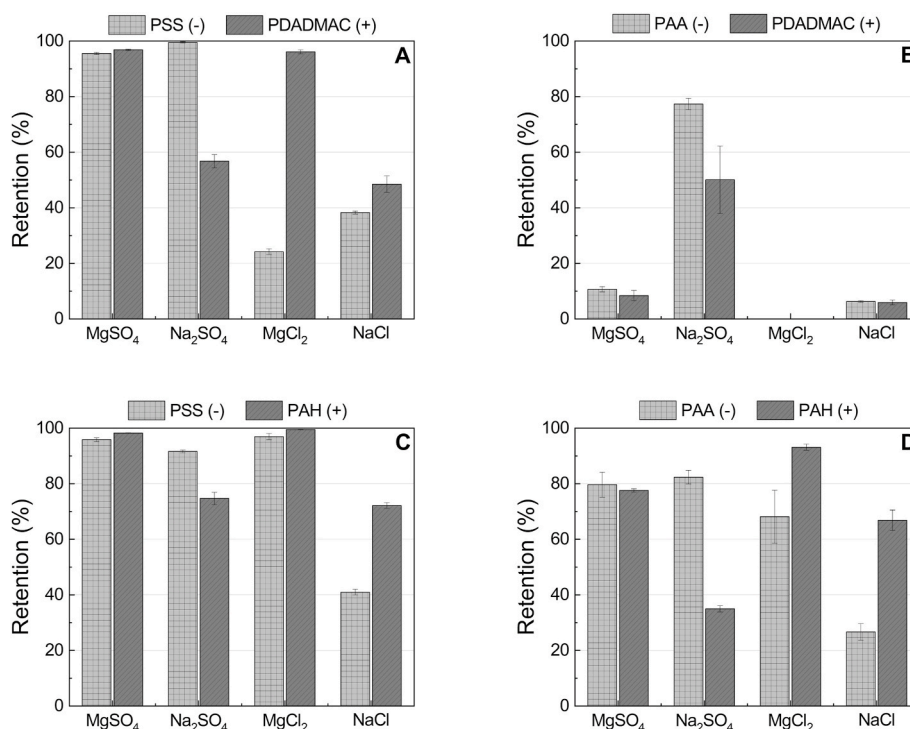
Fig. 3. Retention (y-axis) for four different salts (x-axis) for four different PE pairs: (A) PDADMAC/PSS, (B) PDADMAC/PAA, (C) PAH/PSS, (D) PAH/PAA.
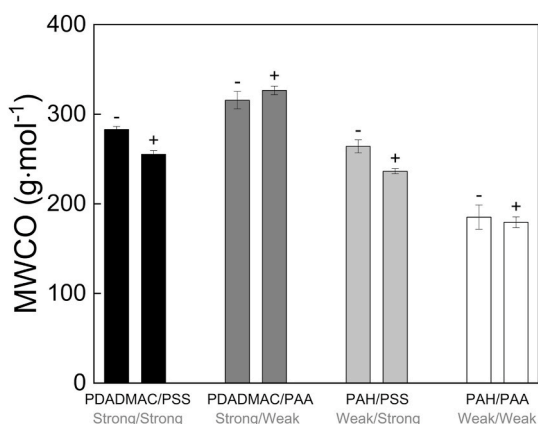

Fig. 4. Molecular weight cut-off of four different PEM nanofiltration membranes. Terminated with polyanion (−) or polycation (+) respectively.

of these membranes.

3.2. Long-term pH stability

After the performance of the four PEM membranes was established, they were exposed to extreme pH conditions, to test their long-term stability. Both the pure water permeance and $MgSO_4$ retention are evaluated over time. The outcome for exposure to 0.1 M nitric acid is shown in Fig. 5.

Fig. 5A indicates that the performance of the PDADMAC/PAA membranes is stable over the full time period. For the polycation terminated membranes, performance is unaffected, while for the polyanion terminated layer, a drop in pure water permeance (~24%) is observed. In the latter, apparently the layer becomes less swollen (odd-even effect smaller), leading to a slight densification and modification in performance. Overall, we can consider these membranes to be stable, with a final performance of 8.8 ± 0.6 L $m^{-2}h^{-1}bar^{-1}$ and $96.0 \pm 0.2\%$

$MgSO_4$ retention. Since both PDADMAC and PSS are strong polyelectrolytes, they maintain their charge over the full pH range. For this reason their electrostatic interactions remain stable when exposed to acidic conditions and so does the performance.

In Fig. 5B, the behavior of PDADMAC/PAA PEM membranes is shown. In the first hundred hours an increase in permeance is observed, however afterwards the permeance drops again and reaches a stable level similar to the starting value. The retention behavior is unexpected, since it has a sharp increase in the beginning and then stabilizes at around 40%, a value much higher than the initial retention of just a few percent.

PAA is a weak polyelectrolyte and becomes uncharged at low pH, that is expected to result in an unstable layer. However, research by Alonso et al. shows that even at pH 3, i.e. below the pK_a of PAA (4.5), PDADMAC/PAA can still assemble into stable multilayers. On the contrary, at higher pH (pH 6 and 10), it is shown that the resulting layers are less stable; after each PDADMAC step, the layer is getting thinner. While we coated our membranes at pH 6, it is possible that an unstable layer is formed. As a result of exposure to acidic environments, rearrangement of the PDADMAC/PAA multilayer starts, finally leading to a more stable layer at low pH. This may explain the observed trend in the performance.

PAH/PSS membranes behave much like the PDADMAC/PSS membranes (Fig. 5C). A slight decrease in permeance is observed over time (~20%), accompanied with an increase in retention, leading to a final permeance of 9.7 ± 0.5 L $m^{-2}h^{-1}bar^{-1}$ and $97.5 \pm 1.2\%$ $MgSO_4$ retention. These membranes can be labeled as stable performing membranes as they do not decompose under these conditions. PAH is a charged polyelectrolyte at low pH values and therefore in this system, when combined with the strong polyelectrolyte PSS, a stable multilayer is created that is unaffected by the low pH of 0.1 M nitric acid.

Fig. 5D shows an immediate loss in performance for PAH/PAA NF membranes when exposed to nitric acid. The permeance for polyanion terminated layers increases from 1.3 ± 0.2 to 17.6 ± 9.3 L $m^{-2}h^{-1}bar^{-1}$ and the retention decreases from 78.1 ± 15.3 to $17.6 \pm 9.3\%$ in the first 24 h. The polycation terminated membranes show the same behavior with a permeance increase from 1.5 ± 0.1 to 29.2 ± 17.5 and retention
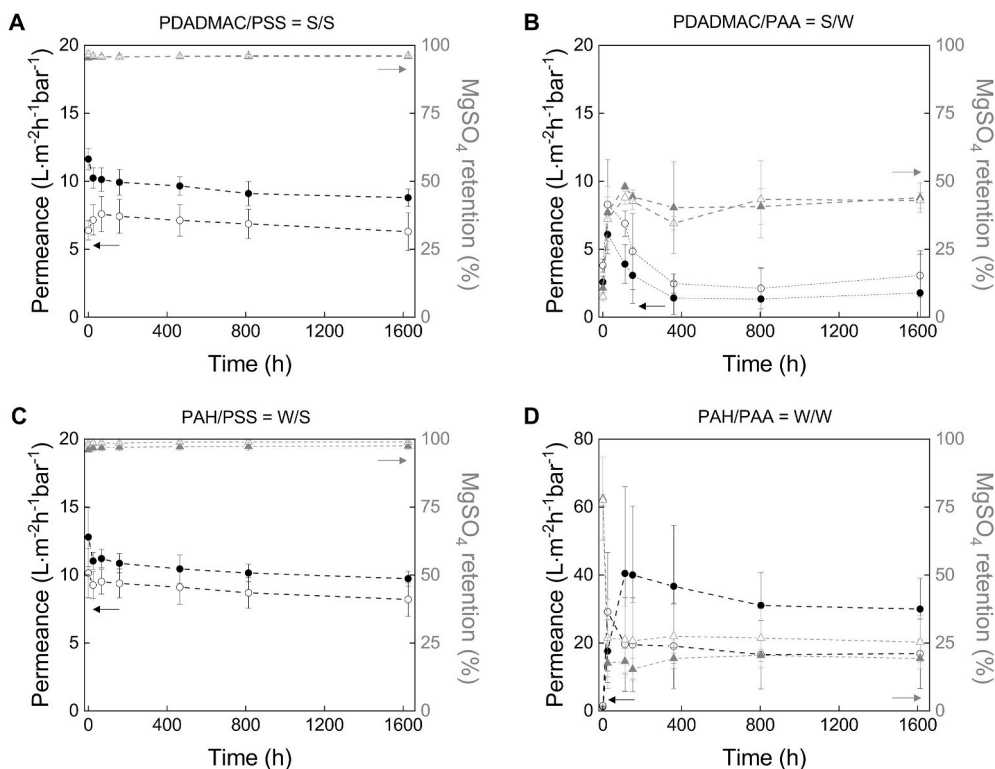
Fig. 5. Long-term pH stability tests; performance over time when exposed ex-situ to 0.1 M HNO₃. Closed symbols represent polyanion (−) terminated layers, open symbols represent polycation (+) terminated layers. (A) PDADMAC/PSS, (B) PDADMAC/PAA, (C) PAH/PSS, (D) PAH/PAA.

decrease from 77.6 ± 0.8 to $26.8 \pm 14.3\%$. PAH and PAA are both weak polyelectrolytes so their charge is sensitive to pH. Under these conditions, PAA is not dissociated anymore and becomes uncharged, resulting in breakdown of the multilayer. This is consistent with earlier research by Jurin et al. showing that a layer of PAH/PAA partially desorbs at pH 2 [28].
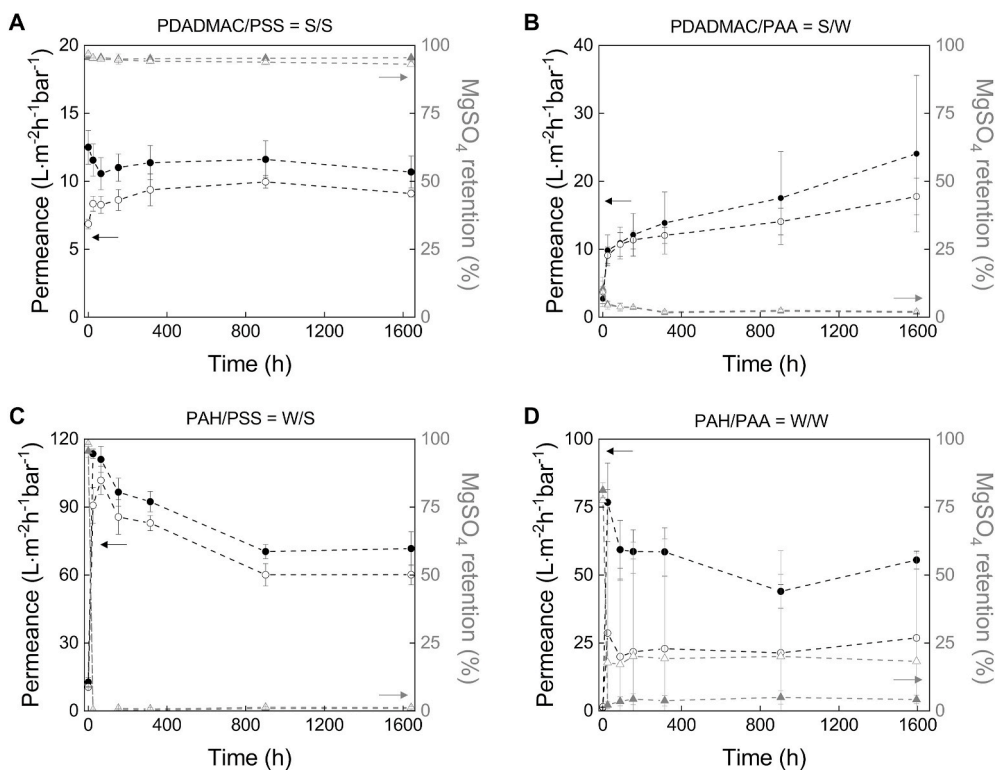

Fig. 6. Long-term pH stability tests; performance over time when exposed to 0.1 M NaOH. Closed symbols represent polyanion (−) terminated layers, open symbols represent polycation (+) terminated layers. (A) PDADMAC/PSS, (B) PDADMAC/PAA, (C) PAH/PSS, (D) PAH/PAA.

In short, we can conclude that under extreme acidic conditions, PDADMAC/PSS and PAH/PSS have a stable performance. The polyelectrolytes are all charged under these conditions and the multilayers stay intact. The type of terminating polyelectrolyte does not have a significant effect on the stability of the membranes.

Next, the stability of the PEM membranes in 0.1 M sodium hydroxide was evaluated. Under these conditions only a limited amount of commercially available membranes are stable and most of them have certain limitations [21]. Therefore, new membranes for use under alkaline applications are of high interest.

Fig. 6 shows the performance of the four PEM NF membranes after they were exposed ex-situ to 0.1 M NaOH. PDADMAC/PSS membranes (Fig. 6A) show a similar behavior as in acidic conditions; i.e. their performance is stable over the full exposure time (10.7 ± 1.2 L m^{-2}h^{-1}bar^{-1}, 95.5 ± 0.1% MgSO$_4$ retention). A small change in permeance and retention is observed over time, which can be attributed to small rearrangements of the multilayers and possibly fouling, but no unexpected or unstable behavior occurs. The strong polyelectrolytes, PDADMAC and PSS, remain fully charged under these alkaline conditions. Therefore they maintain their electrostatic interactions and stable membrane behavior is observed.

Initially we expected a similar behavior for the PDADMAC/PAA membranes, because PAA, a polyacid, should be more charged at higher pH conditions. This would result in two charged polyelectrolytes under the exposed conditions and therefore the electrostatic interactions within the layer would be maintained. However, over time an increase in permeance is observed, combined with a decrease in retention and thus the performance of the PDADMAC/PAA layers is lost (Fig. 6B).

Since pH only affects the charge of weak polyelectrolytes, PAA is the determining factor in this case. Alonso et al. found that in contrast to what is expected, at high pH, almost no assembly of PDADMAC/PAA is observed [45]. They attribute this to the high hydration of PAA at these conditions, which makes the interaction with the more hydrophobic PDADMAC thermodynamically less favorable. These findings corroborate the behavior observed for our PDADMAC/PAA membranes at high pH. The polarity mismatch between the highly polar hydrated PAA and the hydrophobic regions of PDADMAC causes a repulsion that overcomes the electrostatic attractive interactions and consequently results in decomposition of the layer. For this reason no stable pH performance under alkaline conditions is observed.

Both PAH/PSS and PAH/PAA membranes show an immediate loss in performance, evident by the increase in permeance and decrease in retention as can be seen in Fig. 6C and D. Since, PAH, a weak polyelectrolyte, loses its charge at high pH, this behavior is a result of that.

Table 1 summarizes the MWCO of the membranes before and after exposure to 0.1 M HNO$_3$ and NaOH. The results support the findings of pure water permeance and MgSO$_4$ retention trends. After acidic exposure, PDADMAC/PSS and PAH/PSS maintain their MWCO. In the case of alkaline exposure, the only stable performance is observed for PDADMAC/PSS membranes. Although the terminating layer has a great influence on a number of parameters, it is not important for the pH stability.

Under acidic conditions, the MWCO of the PDADMAC/PAA membranes seemed to be unaffected. However, when we performed similar MWCO measurements after 473 h exposure (see Supplementary Table S1), we found a value of >2000 g mol^{-1} for PDADMAC/PAA membranes, meaning that the membranes degraded after prolonged exposure to acidic conditions. Considering PWP, salt retention and MWCO, it seems that these membranes show performance loss after exposure to 0.1 M HNO$_3$, but over time performance is recovered indicated by the increased salt retention and low MWCO. It is not clear if this new improved performance is coming from a new layer, pore collapse, or other causes.

Finally, the membranes that were stable after 1600 h (2 months) exposure to 0.1 M solutions, were exposed to 1 M HNO$_3$ or NaOH (pH ~0 and ~14 respectively) to investigate if they also remained stable under these even more extreme conditions. Fig. 7 and Fig. 8 show the pure water permeance and MgSO$_4$ retention of these four membranes over time up to 340 h. The final performance after 2 months exposure is used as reference point at time zero under 1 M conditions.

Fig. 7 shows the results for PDADMAC/PSS and PAH/PSS membranes after exposure to 1 M nitric acid conditions. In general a (small) decrease in permeance of the membranes can be observed, that can be a result of fouling that is often observed in NF membranes [32,46]. Above all, the results in Fig. 7A and B shows that even under these extreme pH conditions the membranes remain stable.

PDADMAC/PSS membranes were also tested under 1 M NaOH conditions, as were PDADMAC/PAA membranes because they were not fully degraded after 2 months exposure to lower concentrations (Fig. 8). The excellent stability of PDADMAC/PSS membranes is evident from the stable performance over the full exposure time (Fig. 8A). The performance of PDADMAC/PAA membranes seems to stabilize compared to the first two months at an increased permeance and a low salt retention with respect to the initial values.

To further analyze the membrane performance after 1 M exposure, also here MWCO measurements were performed and compared to the initial values. The results are summarized in Table 2.

It is clear that the stability of PDADMAC/PSS and PAH/PSS membranes under 1 M pH conditions is also confirmed by the MWCO data as no significant differences can be found. The performance of PDADMAC/PAA membranes, however, is completely lost and so the degradation observed after 0.1 M exposure, was further developed.

From the long-term pH stability measurements, we can conclude that PDADMAC/PSS NF membranes are stable under extreme pH conditions, both acidic and alkaline. Next to that, PAH/PSS NF membranes are useful under extreme acidic conditions for long-term filtration. PDADMAC/PAA and PAH/PAA are not stable under the exposed pH conditions.

The PDADMAC/PSS NF membranes provide a combination of excellent performance and long-term stability over the full pH range (0-14). Compared to commercially available alternatives they provide a lower MWCO and higher permeance, e.g. when compared to Nadir NP030 or Inopor® nano membranes. In addition, as compared to membranes that are stable only in the extreme acidic or alkaline regime, such as AMS A3014 or B4022 and GE Duracid membranes, these PEM NF membranes also provide an enhanced stability [21].

4. Conclusions

This systematic study into the long-term pH stability of PEM NF membranes showcases the potential of these membranes for use under extreme pH conditions. Four different polyelectrolyte systems were studied and exposed ex-situ to 0.1 M HNO$_3$ and 0.1 M NaOH solutions after which their performance was evaluated over time. Depending on the chosen combination of strong and weak polyelectrolytes, membrane

Table 1
MWCO after ~1600 h pH exposure (0.1 M).

Membranes		MWCO (g mol^{-1})		
		Before	After	
			0.1 M HNO$_3$	0.1 M NaOH
PDADMAC/PSS	–	283 ± 4	274 ± 2	279 ± 3
	+	255 ± 4	259 ± 7	270 ± 2
PDADMAC/PAA	–	316 ± 10	262 ± 63[a]	1339 ± 671
	+	327 ± 5	322 ± 228[a]	783 ± 263
PAH/PSS	–	264 ± 7	249 ± 4	>2000
	+	236 ± 3	233 ± 1	>2000
PAH/PAA	–	185 ± 14	>2000	>2000
	+	179 ± 6	>2000	>2000

[a] Contradicting with results found after 473 h testing, see Supplementary Table S1.

Fig. 7. Performance after exposure to 1 M HNO₃. Closed symbols represent polyanion (−) terminated layers, open symbols represent polycation (+) terminated layers. (A) PDADMAC/PSS, (B) PAH/PSS.
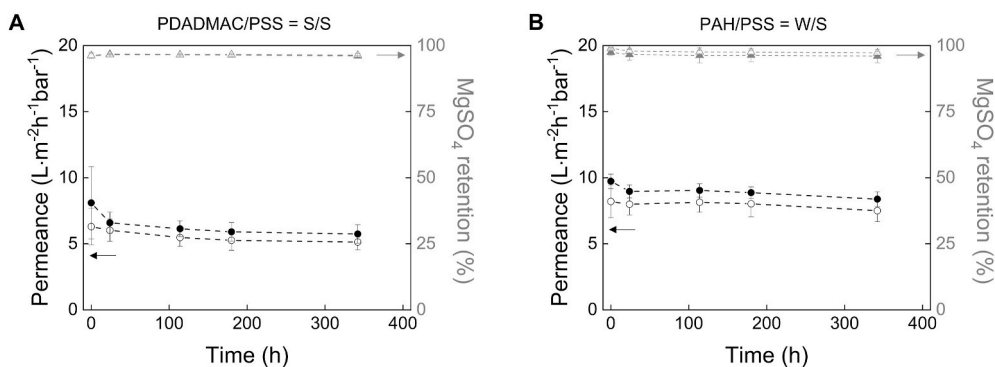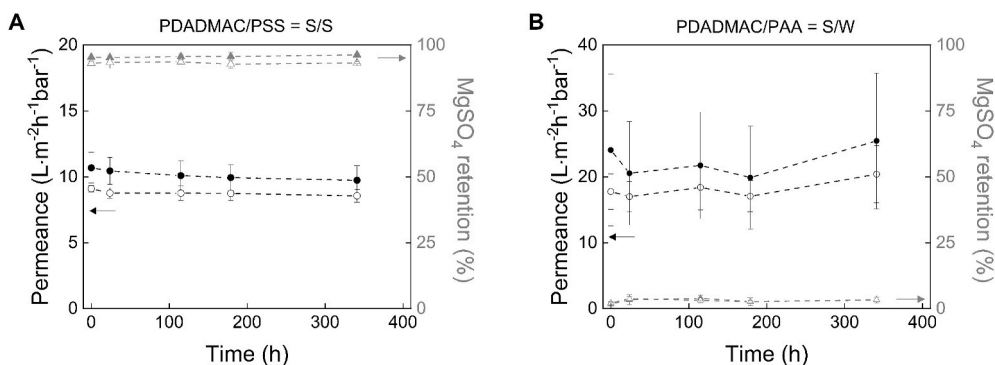

Fig. 8. Performance after exposure to 1 M NaOH. Closed symbols represent polyanion (−) terminated layers, open symbols represent polycation (+) terminated layers. (A) PDADMAC/PSS, (B) PDADMAC/PAA.

Table 2
MWCO after 340 h pH exposure (1 M).

Membranes		MWCO (g mol^{-1})		
		Before	After	
			1 M HNO₃	1 M NaOH
PDADMAC/PSS	−	283 ± 4	281 ± 1	279 ± 2
	+	255 ± 4	270 ± 5	270 ± 2
PDADMAC/PAA	−	316 ± 10		>2000
	+	327 ± 5		>2000
PAH/PSS	−	264 ± 7	233 ± 3	
	+	236 ± 3	227 ± 2	

performance and stability varies, which can be attributed to the strength of the electrostatic interactions between polyelectrolytes under exposure conditions.

Overall, it can be concluded that PDADMAC/PSS PEM NF membranes (both strong PEs) show excellent behavior under both extreme pH conditions. After more than 2 months exposure, their performance was still stable, i.e. a pure water permeance of 10.7 L m^{-2}h^{-1}bar^{-1}, 95.5% MgSO₄ retention and a MWCO of 279 g mol^{-1}. Next to this, PAH/PSS PEM NF membranes are stable under extreme acidic conditions (9.7 L m^{-2}h^{-1}bar^{-1} PWP, 97.5% MgSO₄ retention, 249 g mol^{-1} MWCO). Both membranes also show stable performance when exposed to much more extreme pH conditions (1 M HNO₃ and/or NaOH).

These findings implicate a great potential for use of PEM NF membranes, and specifically PDADMAC/PSS, in application areas with extreme pH conditions, e.g. dairy, mining and textile industries. These PEM membranes outperform most commercially available membranes in terms of long-term stability and show very relevant performance. This study highlights that with the appropriate selection, based on the well-studied interactions between polyelectrolyte pairs, pH stable PEM nanofiltration membranes can be made without the need for any (chemical) post-treatment steps.

Credit author statement

M.G. Elshof: Conceptualization, Validation, Investigation, Visualization, Writing – Original Draft, project administration. W.M. de Vos: Conceptualization, Supervision, Writing – Review & Editing. J. de Grooth: Conceptualization, Supervision, Writing – Review & Editing. N. E. Benes: Supervision, Writing – Review & Editing, Funding acquisition.

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.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2020.118532.

References

[1] M. Paul, S.D. Jons, Chemistry and fabrication of polymeric nanofiltration membranes: a review, Polymer (Guildf) 103 (2016) 417–456, https://doi.org/10.1016/j.polymer.2016.07.085.

[2] N. García Doménech, F. Purcell-Milton, Y.K. Gun'ko, Recent progress and future prospects in development of advanced materials for nanofiltration, Mater. Today Commun. 23 (2020) 100888, https://doi.org/10.1016/j.mtcomm.2019.100888.

[3] N. Joseph, P. Ahmadiannamini, R. Hoogenboom, I.F.J. Vankelecom, Layer-by-layer preparation of polyelectrolyte multilayer membranes for separation, Polym. Chem. 5 (2014) 1817–1831, https://doi.org/10.1039/c3py01262j.

[4] L.Y. Ng, A.W. Mohammad, C.Y. Ng, A review on nanofiltration membrane fabrication and modification using polyelectrolytes: effective ways to develop membrane selective barriers and rejection capability, Adv. Colloid Interface Sci. 197–198 (2013) 85–107, https://doi.org/10.1016/j.cis.2013.04.004.

[5] G. Decher, Fuzzy nanoassemblies: toward layered polymeric multicomposites, Science 277 (1997) 1232–1237, https://doi.org/10.1126/science.277.5330.1232.

[6] S.T. Dubas, J.B. Schlenoff, Factors controlling the growth of polyelectrolyte multilayers, Macromolecules 32 (1999) 8153–8160, https://doi.org/10.1021/ma981927a.

[7] J. Fu, J.B. Schlenoff, Driving forces for oppositely charged polyion association in aqueous solutions: enthalpic, entropic, but not electrostatic, J. Am. Chem. Soc. 138 (2016) 980–990, https://doi.org/10.1021/jacs.5b11878.

[8] S. Lindhoud, W. Norde, M.A.C. Stuart, Reversibility and relaxation behavior of polyelectrolyte complex micelle formation, J. Phys. Chem. B 113 (2009) 5431–5439, https://doi.org/10.1021/jp809489f.

[9] J. van der Gucht, E. Spruijt, M. Lemmers, M.A. Cohen Stuart, Polyelectrolyte complexes: bulk phases and colloidal systems, J. Colloid Interface Sci. 361 (2011) 407–422, https://doi.org/10.1016/j.jcis.2011.05.080.

[10] K. Ariga, J.P. Hill, Q. Ji, Layer-by-layer assembly as a versatile bottom-up nanofabrication technique for exploratory research and realistic application, Phys. Chem. Chem. Phys. 9 (2007) 2319–2340, https://doi.org/10.1039/b700410a.

[11] S. Ilyas, N. Joseph, A. Szymczyk, A. Volodin, K. Nijmeijer, W.M. de Vos, I.F. J. Vankelecom, Weak polyelectrolyte multilayers as tunable membranes for solvent resistant nanofiltration, J. Membr. Sci. 514 (2016) 322–331, https://doi.org/10.1016/j.memsci.2016.04.073.

[12] E. te Brinke, D.M. Reurink, I. Achterhuis, J. de Groot, W.M. de Vos, Asymmetric polyelectrolyte multilayer membranes with ultrathin separation layers for highly efficient micropollutant removal, Appl. Mater. Today 18 (2020), https://doi.org/10.1016/j.apmt.2019.100471.

[13] L. Ouyang, R. Malaisamy, M.L. Bruening, Multilayer polyelectrolyte films as nanofiltration membranes for separating monovalent and divalent cations, J. Membr. Sci. 310 (2008) 76–84, https://doi.org/10.1016/j.memsci.2007.10.031.

[14] J. de Groot, B. Haakmeester, C. Wever, J. Potreck, W.M. de Vos, K. Nijmeijer, Long term physical and chemical stability of polyelectrolyte multilayer membranes, J. Membr. Sci. 489 (2015) 153–159, https://doi.org/10.1016/J.MEMSCI.2015.04.031.

[15] Y.-N. Kwon, J.O. Leckie, Hypochlorite degradation of crosslinked polyamide membranes II. Changes in hydrogen bonding behavior and performance, J. Membr. Sci. 282 (2006) 456–464, https://doi.org/10.1016/j.memsci.2006.06.004.

[16] S. Platt, M. Nyström, A. Bottino, G. Capannelli, Stability of NF membranes under extreme acidic conditions, J. Membr. Sci. 239 (2004) 91–103, https://doi.org/10.1016/j.memsci.2003.09.030.

[17] B.C. Ricci, C.D. Ferreira, A.O. Aguiar, M.C.S. Amaral, Integration of nanofiltration and reverse osmosis for metal separation and sulfuric acid recovery from gold mining effluent, Sep. Purif. Technol. 154 (2015) 11–21, https://doi.org/10.1016/J.SEPPUR.2015.08.040.

[18] P. Fernández, F.A. Riera, R. Álvarez, S. Álvarez, Nanofiltration regeneration of contaminated single-phase detergents used in the dairy industry, J. Food Eng. 97 (2010) 319–328, https://doi.org/10.1016/j.jfoodeng.2009.10.023.

[19] A. Bes-Piá, M.I. Iborra-Clar, A. Iborra-Clar, J.A. Mendoza-Roca, B. Cuartas-Uribe, M.I. Alcaina-Miranda, Nanofiltration of textile industry wastewater using a physicochemical process as a pre-treatment, Desalination 178 (2005) 343–349, https://doi.org/10.1016/J.DESAL.2004.11.044.

[20] A. Antony, R. Fudianto, S. Cox, G. Leslie, Assessing the oxidative degradation of polyamide reverse osmosis membrane-Accelerated ageing with hypochlorite exposure, J. Membr. Sci. 347 (2010) 159–164, https://doi.org/10.1016/j.memsci.2009.10.018.

[21] K.P. Lee, J. Zheng, G. Bargeman, A.J.B. Kemperman, N.E. Benes, pH stable thin film composite polyamine nanofiltration membranes by interfacial polymerisation, J. Membr. Sci. 478 (2015) 75–84, https://doi.org/10.1016/j.memsci.2014.12.045.

[22] K.P. Lee, G. Bargeman, R. de Rooij, A.J.B. Kemperman, N.E. Benes, Interfacial polymerization of cyanuric chloride and monomeric amines: pH resistant thin film composite polyamine nanofiltration membranes, J. Membr. Sci. 523 (2017) 487–496, https://doi.org/10.1016/j.memsci.2016.10.012.

[23] Z. Jiang, J. Miao, Y. He, X. Hong, K. Tu, X. Wang, S. Chen, H. Yang, L. Zhang, R. Zhang, A pH-stable positively charged composite nanofiltration membrane with excellent rejection performance, RSC Adv. 9 (2019) 37546–37555, https://doi.org/10.1039/c9ra06528h.

[24] C. Van Goethem, M. Mertens, I.F.J. Vankelecom, Crosslinked PVDF membranes for aqueous and extreme pH nanofiltration, J. Membr. Sci. 572 (2019) 489–495, https://doi.org/10.1016/j.memsci.2018.11.036.

[25] J.J. Harris, M.L. Bruening, Electrochemical and in situ ellipsometric investigation of the permeability and stability of layered polyelectrolyte films, Langmuir 16 (2000) 2006–2013, https://doi.org/10.1021/la990620h.

[26] J.M. Silva, S.G. Caridade, R.R. Costa, N.M. Alves, T. Groth, C. Picart, R.L. Reis, J. F. Mano, PH responsiveness of multilayered films and membranes made of polysaccharides, Langmuir 31 (2015) 11318–11328, https://doi.org/10.1021/acs.langmuir.5b02478.

[27] V.V. Lulevich, O.I. Vinogradova, Effect of pH and salt on the stiffness of polyelectrolyte multilayer microcapsules, Langmuir 20 (2004) 2874–2878, https://doi.org/10.1021/la049934h.

[28] F. Jurin, C. Buron, C. Magnenet, M. Quinart, S. Lakard, C. Filiâtre, B. Lakard, Predictive tools for selection of appropriate polyelectrolyte multilayer film for the functionalization of organic membranes, Colloid Surf. A Physicochem. Eng. Asp. 486 (2015) 153–160, https://doi.org/10.1016/j.colsurfa.2015.09.043.

[29] T.T.T. Nguyen, S. Belbekhouche, P. Dubot, B. Carbonnier, D. Grande, From the functionalization of polyelectrolytes to the development of a versatile approach to the synthesis of polyelectrolyte multilayer films with enhanced stability, J. Mater. Chem. A 5 (2017) 24472–24483, https://doi.org/10.1039/c7ta06855g.

[30] Q. Chen, P. Yu, W. Huang, S. Yu, M. Liu, C. Gao, High-flux composite hollow fiber nanofiltration membranes fabricated through layer-by-layer deposition of oppositely charged crosslinked polyelectrolytes for dye removal, J. Membr. Sci. 492 (2015) 312–321, https://doi.org/10.1016/j.memsci.2015.05.068.

[31] L. Wang, N. Wang, H. Yang, Q. An, T. Zeng, S. Ji, Enhanced pH and oxidant resistance of polyelectrolyte multilayers via the confinement effect of lamellar graphene oxide nanosheets, Sep. Purif. Technol. 193 (2018) 274–282, https://doi.org/10.1016/J.SEPPUR.2017.10.061.

[32] P. Ahmadiannamini, M.L. Bruening, V.V. Tarabara, Sacrificial polyelectrolyte multilayer coatings as an approach to membrane fouling control: disassembly and regeneration mechanisms, J. Membr. Sci. 491 (2015) 149–158, https://doi.org/10.1016/J.MEMSCI.2015.04.041.

[33] K. Remmen, R. Schäfer, S. Hedwig, T. Wintgens, M. Wessling, M. Lenz, Layer-by-layer membrane modification allows scandium recovery by nanofiltration, Environ. Sci. Water Res. Technol. 5 (2019) 1683–1688, https://doi.org/10.1039/c9ew00509a.

[34] L. Paltrinieri, K. Remmen, B. Müller, L. Chu, J. Köser, T. Wintgens, M. Wessling, L. C.P.M. de Smet, E.J.R. Sudhölter, Improved phosphoric acid recovery from sewage sludge ash using layer-by-layer modified membranes, J. Membr. Sci. 587 (2019), https://doi.org/10.1016/j.memsci.2019.06.002.

[35] D. Menne, C. Üzüm, A. Koppelmann, J.E. Wong, C. van Foeken, F. Borre, L. Dähne, T. Laakso, A. Pihlajamäki, M. Wessling, Regenerable polymer/ceramic hybrid nanofiltration membrane based on polyelectrolyte assembly by layer-by-layer technique, J. Membr. Sci. 520 (2016) 924–932, https://doi.org/10.1016/j.memsci.2016.08.048.

[36] J. de Groot, R. Oborný, J. Potreck, K. Nijmeijer, W.M. de Vos, The role of ionic strength and odd-even effects on the properties of polyelectrolyte multilayer nanofiltration membranes, J. Membr. Sci. 475 (2015) 311–319, https://doi.org/10.1016/j.memsci.2014.10.044.

[37] E. te Brinke, I. Achterhuis, D.M. Reurink, J. de Groot, W.M. de Vos, Multiple approaches to the buildup of asymmetric polyelectrolyte multilayer membranes for efficient water purification, ACS Appl. Polym. Mater. 2 (2020) 715–724, https://doi.org/10.1021/acsapm.9b01038.

[38] R. Malaisamy, M.L. Bruening, High-flux nanofiltration membranes prepared by adsorption of multilayer polyelectrolyte membranes on polymeric supports, Langmuir 21 (2005) 10587–10592, https://doi.org/10.1021/la051669s.

[39] S.U. Hong, R. Malaisamy, M.L. Bruening, Optimization of flux and selectivity in Cl-/SO42- separations with multilayer polyelectrolyte membranes, J. Membr. Sci. 283 (2006) 366–372, https://doi.org/10.1016/j.memsci.2006.07.007.

[40] S. Ilyas, S.M. Abtahi, N. Akkilic, H.D.W. Roesink, W.M. de Vos, Weak polyelectrolyte multilayers as tunable separation layers for micro-pollutant removal by hollow fiber nanofiltration membranes, J. Membr. Sci. 537 (2017) 220–228, https://doi.org/10.1016/j.memsci.2017.05.027.

[41] L. Krasemann, B. Tieke, Selective ion transport across self-assembled alternating multilayers of cationic and anionic polyelectrolytes, Langmuir 16 (2000) 287–290, https://doi.org/10.1021/la991240z.

[42] R.A. Ghostine, M.Z. Markarian, J.B. Schlenoff, Asymmetric growth in polyelectrolyte multilayers, J. Am. Chem. Soc. 135 (2013) 7636–7646, https://doi.org/10.1021/ja401318m.

[43] J.E. Wong, F. Rehfeldt, P. Hänni, M. Tanaka, R. V Klitzing, Swelling behavior of polyelectrolyte multilayers in saturated water vapor, Macromolecules 37 (2004) 7285–7289, https://doi.org/10.1021/ma0351930.

[44] T. Rijnaarts, D.M. Reurink, F. Radmanesh, W.M. de Vos, K. Nijmeijer, Layer-by-layer coatings on ion exchange membranes: effect of multilayer charge and hydration on monovalent ion selectivities, J. Membr. Sci. 570–571 (2019) 513–521, https://doi.org/10.1016/j.memsci.2018.10.074.

[45] T. Alonso, J. Irigoyen, J.J. Iturri, I.L. Larena, S.E. Moya, Study of the multilayer assembly and complex formation of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(acrylic acid) (PAA) as a function of pH, Soft Matter 9 (2013) 1920–1928, https://doi.org/10.1039/c2sm26884a.

[46] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review: recent advances and future prospects, Desalination 356 (2015) 226–254, https://doi.org/10.1016/j.desal.2014.10.043.