Asymmetric layer-by-layer polyelectrolyte nanofiltration membranes with tunable retention

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Abstract
Nanofiltration (NF) membrane processes are attractive to remove multivalent ions. As ion retention in NF membranes is determined by both size and charge exclusion, negatively charged membranes are required to reject negatively charged ions. Layer-by-layer assembly of alternating polycation (PC) and polyanion layers on top of a support is a versatile method to produce membranes. Especially the polyelectrolyte (PE) couple polydiallyldimethylammonium chloride and poly(sodium-4-styrenesulfonate) (PDADMAC/PSS) is extensively investigated. This PE couple cannot form highly negatively charged membrane surfaces, due to interdiffusion and charge overcompensation of PDADMAC into the PSS layers, which limits the operational window to tailor membrane properties. We propose the use of asymmetric layer formation and show how combining two charge densities of one PC can produce negatively charged NF membranes. Starting from hollow fiber ultrafiltration supports coated with base layers of PDADMAC/PSS, they are coated with PDADMAC/PSS or poly(acrylamide-co-diallyldimethylammonium chloride), P(AM-co-DADMAC)/PSS layers. P(AM-co-DADMAC) has a charge density of only 32% compared to 100% for PDADMAC. The particular novel membranes coated with P(AM-co-DADMAC) have a highly negatively charged surface and high permeabilities (7–19 L/[m²hbar]), with high retentions for Na₂SO₄ of up to 95%. These values position the developed membranes in the top range compared to commercial and other layer-by-layer membranes.

KEYWORDS
charge density, layer-by-layer, nanofiltration, polyelectrolyte membrane, water purification

1 | INTRODUCTION
Nanofiltration (NF) membrane processes are attractive to remove multivalent ions from surface, ground, and industrial waters. Among others, multivalent ion removal is often required for water softening and food processing. Especially when the removal of negatively charged multivalent ions (e.g., sulfate, chromate, arsenate, and perchlorate) is required, it is key to have access to negatively charged membranes to obtain high retentions. As ion retention in NF membranes is determined by both size exclusion as well as charge exclusion, the introduction of
negative membrane charges increases the repulsion of negatively charged ions.5–12 Moreover, negatively charged NF membranes are also key to reduce fouling since several organic foulants are negatively charged (e.g., humic acid, sodium dodecylbenzene sulfonate).13–15

One of the upcoming methods to fabricate NF membranes is layer-by-layer (LbL) coating.16–18 Here, alternating layers of oppositely charged polyelectrolytes (PEs) are adsorbed on a porous support forming a PE multilayer NF membrane. A set of one positively charged PE, a polycation (PC), and one negatively charged PE, a polyanion (PA) layer is called one bilayer (BL). The advantage of LbL is the simplicity and versatility of the approach, while simultaneously having nanoscale control over several membrane properties, such as porosity, hydrophilicity, pore size, selectivity, charge density, and membrane thickness.19–22 Another strength of the LbL method is the wide variety of possibilities to tune the properties of these membranes by varying the PE layer chemistry and/or coating parameters. Among others, these parameters are the type of PEs, their charge densities, the number of BLs, the terminating layer, and the salt concentration of the coating solution.8,18,23–30

Obviously, the PE type and subsequent membrane charge (density) significantly influence the membrane performance as those determine the strength of charge exclusion. Charge exclusion results from a misbalance between anion and cation concentrations in the feed and permeate solution due to the charge of the membrane.31 This misbalance arises because the charge (e.g., negative) of a membrane restricts the permeation of co-ions (i.e., negatively charged ions) while it facilitates the transport of counter ions (i.e., positively charged ions). This results in a potential difference (i.e., Donnan potential) over the membrane. This potential difference determines both counter-ion and co-ion transport. Multivalent counter-ion results in lower retentions in comparison with monovalent counter-ions. Oppositely, multivalent co-ions result in higher retentions in comparison with monovalent co-ions.32

Moreover, the salt concentration (ionic strength) of the PE coating solution impacts the formation of the PE layers tremendously.8,18,23,29,30 Normally, the PC charges are ionically linked to the PA charges, called intrinsic charge compensation. By introducing salt ions in the PE solution, the PE charges will be partially compensated by the ions instead of, called extrinsic charge compensation. By introducing salt ions in the PE solution, the PE charges will be partially compensated by the ions instead of, called extrinsic charge compensation. More extrinsic charge compensation results in thicker, but simultaneously more open PE layers.24,27,28

One of the most frequently used PE couples for the partial desalination of water streams is the combination of polydiallyl dimethylammonium chloride (PDADMAC) and poly(sodium 4-styrene sulfonate) (PSS).8,33–36 The terminating layer of the membrane (PDADMAC or PSS) affects the membrane performance, in literature referred to as the odd-even effect.8,23,37,38 This odd-even effect is caused by the higher swelling degree of PDADMAC compared to PSS, which can be up to a four-fold more at high ionic strengths.38 The exact odd-even effect depends on whether the formation of the PE layers is in the pore or layer-dominated regime.8 In the pore-dominated regime, the PE layers are predominantly coated at the inside of the distinct physical pores of the support. In that case, PSS as terminating layer results in a higher flux than PDADMAC as terminating layer due to the higher swelling of PDADMAC narrowing the pores. In the layer dominating regime, the opposite is applicable and the higher swelling of PDADMAC results in a thicker but more open layer with a correspondingly higher water permeability compared to PSS as terminating layer.39

Although the terminating PE layer influences the membrane structure and performance, the PE layers do not necessarily form distinct separate layers.16,29,40 The PE layers can interdiffuse into each other, resulting in areas with mixed PDADMAC/PSS regions in the membrane.29,41,42 The diffusion mobility of PDADMAC is higher than that of PSS and PSS is relatively immobile.29 The higher PDADMAC diffusion can give rise to an excess of positive charges, also in the PSS layers. Consequently, in such cases, the PSS charges do not fully compensate for the excess of PDADMAC charges present at the membrane surface, and the PDADMAC/PSS build-up is not completely overcompensated.29,41 The result is a positively charged membrane, irrespective of the terminating layer with a decreased retention for the targeted negatively charged components.

To overcome this effect, asymmetric layer build-up can be applied to materialize the specific characteristics of the individual PEs. Asymmetric membranes are formed by applying different PE couples in one membrane.36,43,44 Several PE couples have already been researched, consisting of PDADMAC, PAH as PCs, and PAA, PSS as PAs.36,43,44 When combined in one membrane assembly, these PE couples form asymmetric membranes with a relatively open, more permeable base layer and a thin dense top layer, which determines the separation properties. These combinations result in lower permeabilities compared to membranes with an open base layer only, but significantly higher retentions.36,43,44

Ideally, a membrane has unchanged permeabilities, but higher retentions though. Therefore, contrary to what has been done before, here we develop an asymmetric membrane with an open base layer as well as an open terminating layer. This combines a high permeability due to the open structure of the layers with a high retention towards negative ions applying an open terminating layer that does determine the surface charge.
To do so, we use polyacrylamide-co-diallyl dimethylammonium chloride (P(AM-co-DADMAC)), a copolymer of PDADMAC, as PC. Where PDADMAC has a charge density of 100%, its copolymer P(AM-co-DADMAC) has a charge density of only 32% (percentage of charged monomer units to the total amount of monomer units present in the PE). It is hypothesized that this will decreases the amount of available positive charges at the membrane surface and with that, the permeation and retention behavior can be tuned. The use of an asymmetric layer build-up is necessary because membranes coated with solely P(AM-co-DADMAC)/PSS layers are limited in their layer build-up. After a few layers, further layer growth is not possible anymore, which is caused by the limited intrinsic charge compensation due to the lower charge density of P(AM-co-DADMAC). The total intrinsic charge compensation that can occur is lower for low charge density PEs due to fewer available adsorption sites. Therefore, complete charge reversal upon adsorption of the PE is more difficult and limits continuous adsorption of PE layers.

To circumvent the limited PE layer build-up while maintaining the possibility to tune the membrane charges, in this research, a new combination is made of PDADMAC/PSS and P(AM-co-DADMAC)/PSS layers in one single membrane. To guarantee high permeabilities, first, a series of PDADMAC/PSS layers are coated on a porous support to build an open LbL structure in the layer-dominated regime while simultaneously closing/narrowing the support pores. Additionally, two BLs of P(AM-co-DADMAC)/PSS are applied on this same LbL membrane to establish a negative membrane surface charge enhancing the effect of Donnan exclusion to increase the retention of negatively charged ions in the NF process.

2 | EXPERIMENTAL

2.1 | Chemicals

Two PCs were used and obtained from the Sigma-Aldrich (the Netherlands): poly(diallyldimethylammonium chloride) (PDADMAC, \( M_w = 150 \) kDa, charge density: 100%, 20 wt% in water) and poly(acrylamide-co-diallyldimethylammonium chloride) (P(AM-co-DADMAC), \( M_w = 250 \) kDa, 55 wt% of acrylamide, charge density: 32%, 10 wt% in water). As PA poly(sodium 4-styrene sulfonate) (PSS, \( M_w = 500-700 \) kDa, charge density: 100%, 20.4 wt% in water) from the Tosoh Organic Chemical Co. LTD (Japan) was used. The chemical structures of the PEs are depicted in Figure 1.

Polyethylene glycols with different molecular weights (\( M_w = 200, 300, 400, 600 \) g/mol) were obtained from the Sigma-Aldrich (the Netherlands). Magnesium sulfate heptahydrate (\( \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \)) (\( M_w = 246.47 \) g/mol), sodium sulfate anhydrous (\( \text{Na}_2\text{SO}_4 \)) (\( M_w = 142.04 \) g/mol), and calcium chloride dihydrate (\( \text{CaCl}_2 \cdot 2\text{H}_2\text{O} \)) (\( M_w = 147.01 \) g/mol) were obtained from the Sigma-Aldrich (the Netherlands). Sodium chloride (\( \text{NaCl} \)) (\( M_w = 58.44 \) g/mol) pharmaceutical grade (Sanal® P) was kindly supplied by AkzoNobel, currently known as Nouryon (the Netherlands). All chemicals were used as supplied. All solutions were prepared with ultrapure water PURELAB Option, Veolia Water Solutions & Technologies (the Netherlands).

2.2 | Membrane support

Hollow fiber tight ultrafiltration inside-out HFS 60 membranes with a molecular weight cut-off (MWCO) value of 10 kDa were kindly provided by Pentair X-Flow (the Netherlands) and used as support membrane for LbL deposition. The HFS 60 membranes have a length of 154 cm and an inner diameter of 0.8 mm. Before coating, the support was cut in lengths of 30 cm. The hollow fiber membrane support consists of polyethersulfone (PES) and the negatively charged sulfonated polyethersulfone (SPES). The SPES is predominantly present at the inside of the fibers.

2.3 | Membrane preparation

Before coating the PE layers, the hollow fiber membrane supports were submerged in an ethanol/water mixture overnight to remove impurities in the support. Because of the negatively charged nature of the inner side of the hollow fiber membrane support, the supports were coated on the inside. Also, because of the negative nature, first, a PC layer was applied. This was followed by a PA layer and this approach was repeated until the required number of bilayers was applied. During coating, the
membrane support was completely immersed in the PE solution with a manual refreshment every 5 min and a total immersion time of 30 min. Afterward, the membranes were immersed in an NaCl solution with equivalent ionic strength as in the PE solution. This was done for 10 min and repeated three times to remove any weakly bound PE present. The NF membranes were coated using 0.01 wt% PE in 0.05 or 0.5 M NaCl solutions at (pH = 5.8) and room temperature.

Firstly, one membrane set with an ionic strength of 0.05 M and one membrane set with an ionic strength of 0.5 M was coated solely using PDADMAC/PSS layers. This was done to determine the optimum number of PDADMAC/PSS base layers.

Next, for the formation and comparison of asymmetric membranes, four different membrane sets were produced. For an ionic strength of 0.05 M, two membrane sets were coated with seven bilayers with PDADMAC/PSS layers and terminated with either two PDADMAC/PSS or two P(AM-co-DADMAC)/PSS layers. Additionally, for an ionic strength of 0.5 M, two membrane sets with five bilayers of PDADMAC/PSS were coated and terminated with either two PDADMAC/PSS or two P(AM-co-DADMAC)/PSS layers. The compositions of these four different combinations are given in Table 1. After each subsequent PE layer coating, a sample of seven membranes was taken. One sample for surface charge characterization and six samples for the pure water permeability and retention measurements.

### Table 1

| [NaCl] (M) | Composition of base BLs | Composition of terminating BLs |
|------------|-------------------------|-------------------------------|
| 0.05       | (PDADMAC/PSS)$_7$      | (PDADMAC/PSS)$_2$            |
|            | (P(AM-co-DADMAC)/PSS)$_2$ |                               |
| 0.5        | (PDADMAC/PSS)$_5$      | (PDADMAC/PSS)$_2$            |
|            | (P(AM-co-DADMAC)/PSS)$_2$ |                               |

2.4 | Membrane charge

The surface charge of the membrane support and the LbL coated membranes was determined using an electrokinetic analyzer (SurPASS™ 3, Anton Paar, Austria). The zeta potential is derived from the streaming current generated by flowing an electrolyte solution along the membrane. The electrolyte solution consisted of 1 mM KCl solution. Two membrane samples were measured for 20 measurement cycles at room temperature at a constant pH of 5.8.

2.5 | Membrane performance

The performance of the prepared membrane sets was characterized by their pure water permeability, MWCO, and retention of 5 mM MgSO$_4$, CaCl$_2$, or Na$_2$SO$_4$. To ensure reproducibility, six different membranes were measured of every applied PE layer of the PDADMAC/PSS, and P(AM-co-DADMAC)/PSS membrane sets were measured. The membranes were fixed with the use of chromatographic connectors (Inacom Instruments, the Netherlands), such that 18 membranes could be measured simultaneously to determine the pure water permeability or retention.

After fixation, a crossflow through the membranes was employed with the use of a diaphragm pump (KNF, Switzerland), with a nominal flow of 6 L/min at atmospheric pressure. The applied transmembrane pressure was 3 bar and was controlled with a pressure regulator (Swagelok). This resulted in a crossflow velocity of 7.8 m/s and a minimum Reynolds number of 6000 through the membrane fibers. The permeate volume was collected for a minimum duration of 10 min and a minimum weight of 10 g. For the calculation of the pure water permeability, the permeate volume was weighed. The pure water permeability $L_{p,0}$ (L/[m$^2$ h bar]) was calculated via Equation (1).

$$L_{p,0} = \frac{V_p}{A \cdot t \cdot \Delta P}$$  \hspace{1cm} (1)

With $V_p$ (L) the permeate volume, $t$ (h) the permeation time, $A$ (m$^2$) the membrane area for filtration, and $\Delta P$ (bar) the effective pressure.

To determine the MWCO, the concentrations of uncharged PEGs of different molecular weights (200, 300, 400, and 600 g/mol) in feed and permeate streams were experimentally measured. Afterward, the corresponding observed retentions ($R_{obs}$ [%]) were calculated using Equation (2).

$$R_{obs} = \left(1 - \frac{C_p}{C_f} \right) \times 100\%$$  \hspace{1cm} (2)

where $C_p$ and $C_f$ (mol/L) are the permeate and feed concentration, respectively.

For the determination of the concentrations, feed and permeate samples were analyzed by gel permeation chromatography (GPC) (Agilent 1200/1260 Infinity GPC/SEC series, Polymer Standards Service column compartment, and data center [UDC 810 Interface]) with two size exclusion columns (Polymer Standards Service Suprema 8 × 300 mm$^2$ columns 1000 Å, 10 μm and 30 Å, 10 μm). The flow rate of the PEG sample
solutions was 1 ml/min, and the eluent was 50 mg/L NaN3 in Milli-Q water.44

The feed and permeate concentrations were obtained via GPC analysis as a function of the molecular weight of the PEGs. With these concentrations, the MWCO was defined as the corresponding PEG molecular weight for which the observed retention reaches 90%.

To determine the salt retentions of the LbL membranes, the conductivity of the permeate and feed for a specific salt solution was measured with a Pocket Pro CondLR device. These conductivities were subsequently used to calculate the corresponding concentrations using the correlations obtained by Rosemount analytical.46

3 | RESULTS AND DISCUSSION

3.1 | PDADMAC/PSS base layer membranes

For a fair comparison of the effect of asymmetric layers on the membrane performance, the native porous membrane support is first coated with a series of only PDADMAC/PSS layers to ensure that the physical pores of the UF support are covered and the membrane operates in the layer-dominated NF regime. Permeation then occurs through the PE layers with pores (i.e., void spaces, free volume) in the NF regime. The number of base layers required to guarantee the regime where pore size is independent of the addition of more layers is determined for two coating solutions with different ionic strengths (0.05 and 0.5 M) from the plateau value in the MgSO4 retention, as shown in Figure 2.

For a coating solution with an ionic strength of 0.05 M, the critical number of BLs to reach the MgSO4 retention plateau is seven whereas for an ionic strength of 0.5 M five BLs are sufficient to reach this retention plateau.

The lower number of BLs at higher ionic strength is caused by a change of the mechanism of charge compensation from intrinsic (at low ionic strength) to extrinsic (at high ionic strength) charge compensation.24,27,28 More extrinsic charge compensation results in a higher amount of PE adsorption and the formation of thicker PE layers. The thicker PE layers increase the resistance of the membrane, which results in increased retention.24,27,28

Plateau values for MgSO4 retentions for membranes coated with PDADMAC/PSS layers have been observed before for different coating conditions.23,47 This retention plateau is a result of the balance between a simultaneous increase of PE adsorption, an increase of PDADMAC/PSS interdiffusion, and related swelling behavior. Upon PE adsorption the layer thickness increases and this directly increases the membrane resistance.29,47 This can be seen from the increase in retention up to seven BLs for 0.05 M and five BLs for 0.5 M. Directly correlated to that is a continuous decrease in permeability as well, which can be seen in Figure S1.

Contrary to that, PDADMAC/PSS interdiffusion results in an enriched PDADMAC concentration throughout the thickness of all PE layers, due to the higher mobility of PDADMAC compared to PSS.29 The higher PDADMAC diffusivity can give rise to an excess of positive charges, also in the PSS layers. In such cases, for every BL deposition, the PSS charges do not fully compensate for the excess of PDADMAC charges present at the membrane surface.

The excess of PDADMAC results in higher membrane swelling because PDADMAC has a higher swelling degree than PSS at similar conditions.38 This membrane swelling results in more open structures, which would on its own, result in lower retentions.38

The balance of PE adsorption, interdiffusion, and swelling thus determines the overall retention and permeation behavior of the membrane. Within the range between 5 and 9 BLs, the balance between these opposing effects explains the plateau retention that is reached.

To compare membranes prepared at both ionic strengths, the number of BLs at which the plateau value is first reached is selected as starting point to compare the effect of the last two BLs on the performance. Despite the difference in the number of BLs, these two types of base membranes do have very similar MgSO4 retention

![FIGURE 2](https://example.com)
values and thus allow a fair comparison of the different membrane sets in terms of retention. All further membranes are thus prepared starting from a base membrane with either seven BLs of PDADMAC/PSS prepared at an ionic strength of 0.05 M NaCl or five BLs of PDADMAC/PSS applied at an ionic strength of 0.5 M.

### 3.2 Type of polycation terminating layer

#### 3.2.1 Pure water permeability

To investigate the effect of the type of terminating PC layer on the membrane performance, base membranes are subsequently coated with up to two additional BLs with either PDADMAC/PSS or P(AM-co-DADMAC)/PSS. Next, their pure water permeability is determined and shown in Figure 3.

The permeabilities of the PDADMAC/PSS, as well as the P(AM-co-DADMAC)/PSS coated membranes are lower at the higher ionic strength (Figure 3(A,B)). This is because the permeability of the base membrane (i.e., BLs = 0) is already significantly higher when coated at an NaCl concentration of 0.05 M compared to 0.5 M (~17 and 8 L/[m²·h·bar], respectively). Lower permeabilities for higher ionic strengths result from more PE adsorption due to extrinsic charge compensation, resulting in a higher membrane resistance. For an ionic strength of 0.05 M, small differences in behavior for the PDADMAC and the P(AM-co-DADMAC) coated membranes are visible. PDADMAC/PSS terminating layers show a permeability decrease and P(AM-co-DADMAC)/PSS terminating layers show a small permeability increase with an increasing amount of BLs.

At the lower ionic strength, odd-even effects are not visible for PDADMAC/PSS, which is uncommon for these layers, because swelling of PDADMAC is more severe than that of PSS usually resulting in more open, more permeable layers for PDADMAC terminated membranes. This absence of odd-even effects has been observed before, where the odd-even effects seem very limited after five BLs. A possible explanation for this is the suppression of swelling due to the low ionic strength and high charge density of PDADMAC and PSS. Generally, a high charge density results in a higher density of intrinsic linkages, which can become extrinsic linkages for high ionic strengths. Intrinsic linkages suppress the swelling of PEs, hence the permeability difference between PDADMAC and PSS terminated layers is very limited. This is visible as a continuous decrease upon addition of a next layer (increased resistance, due to PE adsorption) irrespective of the type of layer that is deposited.

For P(AM-co-DADMAC)/PSS terminated membranes coated at 0.05 M NaCl though, different behavior is observed. The water permeability slightly increases compared to that of the base membrane. This is attributed to the hydrophilicity of PSS as well as acrylamide, introduced by the P(AM-co-DADMAC) addition. Membranes terminated with PSS layers are known to be more hydrophilic, compared to PDADMAC. However, due to the higher swelling of PDADMAC, this effect is normally neglected. For the layer formation with P(AM-co-DADMAC), the swelling tendencies are less visible, hence the hydrophilicity of the membrane can have a bigger influence.

On the contrary, for the membranes coated at 0.5 M NaCl much more pronounced differences are observed. For PDADMAC/PSS terminated membranes the permeability changes depending on the terminating layer (odd-even effects), whereas for P(AM-co-DADMAC)/PSS terminated membranes a relatively constant permeability is observed. For the PDADMAC/PSS membrane coated at 0.5 M NaCl, the odd-even trend shows a higher permeability for PC terminating layers. This is caused by the higher swelling tendency of PDADMAC compared to PSS resulting in a more open structure when the membrane is PC terminated. This open structure results in a higher permeability for PC terminated layers compared to PA terminated membrane. This is generally observed for layer-dominated regimes as applicable in this work, especially when layers are coated at high ionic strengths such as 0.5 M.
Again, for the P(AM-co-DADMAC)/PSS membranes, the permeability does not decrease as a function of the number of layers deposited. This is attributed to the limited adsorption of P(AM-co-DADMAC), due to its low charge density and correspondingly lower number of charged sites for intrinsic charge compensation. The low intrinsic charge compensation results in open layers, which cannot significantly influence the permeability.

3.2.2 Molecular weight cut-off

The molecular weight cut-off (MWCO) gives information about the tendency of membranes to retain uncharged solutes. The MWCO is defined as the smallest molecular weight that is retained by a membrane for at least 90%. The experimentally determined MWCO values of the LbL membranes are given in Figure 4.

Clearly, the MWCO data follow similar behavior as the pure water permeability data. The MWCO data of the membranes coated at 0.05 M NaCl are slightly higher than those coated at 0.5 M, as is the case with the water permeability. An increase in MWCO is expected due to the natural trade-off between permeability and retention but is still very limited compared to the big difference in permeability between the membranes coated at 0.05 and 0.5 M NaCl (Figure 3). The small MWCO difference compared to the permeability is a result of the difference in membrane resistance and exclusion tendencies. In other words: although the permeability decreases for an increasing membrane thickness, and hence increasing resistance, this does not necessarily impact the size exclusion characteristics of the membranes as when layers with similar characteristics are applied, the retention remains unchanged. Therefore, although the thickness of the membranes coated with 0.05 or 0.5 M NaCl can be different, the MWCOs can be similar.

Also, where both the PDADMAC and the P(AM-co-DADMAC) membranes coated at the lower salt concentration show reasonably similar behavior, the PDADMAC and the P(AM-co-DADMAC) membranes coated at the higher concentration show a distinctively different behavior, with a clear odd-even effect for the membranes coated with PDADMAC/PSS and a constant value for the membranes containing the copolymer.

When terminated with a PDADMAC layer, the top layer of these membranes has a relatively open structure due to excessive swelling of PDADMAC, giving much higher MWCO values, even exceeding the molecular weight range investigated. Except for these membranes, all other membranes are in the NF regime and have an MWCO value between 250 and 350 Da.

3.2.3 Zeta potential

To investigate the effect of the terminating layer on the membrane surface charge, the apparent zeta potential of all membranes is determined and shown in Figure 5.

The apparent zeta potential is in general higher (e.g., more positive or less negative) at a higher ionic strength for all membranes (Figure 5A,B). This is because the apparent zeta potential of the base membrane (i.e., BLs = 0 in the graphs) is already significantly less negative for an NaCl concentration of 0.5 M compared to 0.05 M (≈ −7 and −38 mV, respectively). The formation of the overall less negatively charged membrane base at 0.5 M, is caused by the interdiffusion of PDADMAC into the PSS layers, which is more significant at higher ionic strengths. The interdiffusion gives rise to an excess of positive charges in the PE layers, which can be seen by the only slightly negative surface charge at BL = 0.29

All membranes show clear odd-even effects, but these are more pronounced for PDADMAC/PSS terminated membranes and less clear for P(AM-co-DADMAC)/PSS terminated membranes. Interestingly, the pure water permeability and MWCO do not show these odd-even effects for PDADMAC/PSS. The membrane permeability and MWCO depend on the PE build-up and the amount of
material deposited, but not the PE charge. The zeta potential, however, purely depends on the amount of PE charge. Clearly, PC (positive charge) terminated membranes are more positively charged, compared to PA (negative charge) terminated membranes.

Additionally, the odd-even effects are more severe for high charge density PEs, such as PDADMAC and PSS, compared to low charge density PEs, such as P(AM-co-DADMAC). The low charge density of P(AM-co-DADMAC) results in a less positive membrane charge compared to PDADMAC due to limited adsorption. Less/no odd-even effects can be useful in practical operations, since it is known that disassembly of PE layers at high ionic occurs first in the superficial layers and is later developed in the bulk of the layers. By suppressing odd-even effects, a longer constant operation of the membranes will be possible.

Although all membranes show odd-even effects, the PDADMAC/PSS membranes clearly show the dominance of the positive PDADMAC charges, whereas for the P(AM-co-DADMAC)/PSS membranes the negative charges of the PSS layer prevail. Although the zeta potential data may suggest that a base membrane coated with one BL of PDADMAC results in a negatively charged NF membrane, this goes at the expense of the permeability, which is higher for the membranes coated with the copolymer (Figure 4).

### 3.2.4 Salt retention

To investigate the effect of the terminating layer on the membrane performance, the retentions for MgSO\(_4\) of the PDADMAC/PSS as well as the P(AM-co-DADMAC)/PSS terminated membranes are presented in Figure 6.

The MgSO\(_4\) retention clearly follows the pure water permeability and MWCO data. Odd-even effects are only visible for PDADMAC/PSS membranes coated at 0.5 M whereas all other membranes show fairly constant and equally high retentions. PDADMAC terminated membranes coated at 0.5 M have retentions as low as ~25% and their MWCOs are well exceeding 600 g/mol. This is due to the excessive swelling of PDADMAC when assembled at higher ionic strengths compared to PSS, being up to four-fold more. Therefore, the NF pore size of these PDADMAC terminated membranes at 0.5 M is significantly bigger, resulting in lower MgSO\(_4\) retentions.
For both the 0.05 and 0.5 M P(AM-co-DADMAC)/PSS combinations the MgSO₄ retention is independent of the number of coating layers. Additional layers do not affect the retention based on size exclusion, due to the limited amount of P(AM-co-DADMAC) adsorption, as is confirmed by the constant pure water permeability and the MWCO results (Figures 3 and 4). Moreover, as Mg²⁺ and SO₄²⁻ have the same valency (divalent ions), charge exclusion is not affected by the terminating layer. The retention of the membranes for NaCl (both monovalent ions) is also not influenced by the terminating layer and has significantly lower retentions (Figure S2).

Especially challenging though is the retention of salts consisting of one monovalent and one multivalent ion such as Na₂SO₄ and CaCl₂. These retentions are presented in Figure 7.

Very clearly, the Na₂SO₄ retentions of the membranes coated with P(AM-co-DADMAC) always well exceed those of the membranes coated with PDADMAC. So these membranes combine a high pure water permeability with high retention for MgSO₄ as well as for Na₂SO₄. Moreover, these values are independent of the type of terminating layer (for the membranes coated at 0.5 M this applies from 1 BL on) and remain high over the full membrane composition range. The high Na₂SO₄ retention indicates a successful asymmetric layer build-up.

Oppositely, all PDADMAC/PSS membranes show strong odd-even effects in the Na₂SO₄ and CaCl₂ retentions. The Na₂SO₄ retention is highest for PSS terminated membranes and shows maximum retention of PDADMAC/PSS of ~90 for an ionic strength of 0.05 M. This indicates that the retention is caused by the negative membrane charges of the terminating PSS layer. For PDADMAC/PSS at 0.5 M, low Na₂SO₄ retentions and high CaCl₂ retentions are observed for all layers. This observation is in agreement with the results obtained by de Grooth et al. and is caused by an increasing interdiffusion of PDADMAC in the PSS layers. The interdiffusion of PDADMAC makes the PSS terminating membranes less negative, as observed before from the zeta potential results, making negative Donnan repulsion less strong resulting in lower retention values.

Moreover, the same odd-even effect is visible (higher Na₂SO₄ and CaCl₂ retention for PSS compared to PDADMAC terminated membranes). This is a result of the limited size exclusion of PDADMAC terminated membranes, as was seen before by the high pure water permeability and MWCO. Therefore, the CaCl₂ retention of PDADMAC terminated membranes can be lower (compared to PSS terminated membranes), while the charge exclusion is expected to be higher.

The retention behavior of the membranes as described above follows the apparent zeta potential data. The order in retention of the asymmetrically coated membranes (Na₂SO₄ < MgSO₄ < CaCl₂) clarifies that retention is predominantly determined by charge exclusion effects. If retentions would have been based on size, Mg²⁺ was better retained than Na⁺ due to size exclusion originating from steric hindrance. The high Na₂SO₄ retentions and subsequent lower CaCl₂ retentions compared proves that the use of P(AM-co-DADMAC) instead of PDADMAC results in higher retentions.

**Figure 7** Na₂SO₄ and CaCl₂ retention of PDADMAC/PSS (blue, open symbols) and P(AM-co-DADMAC)/PSS (red, closed symbols) terminating layers. Na₂SO₄ retention (A) an ionic strength of 0.05 M NaCl and seven base BLs of PDADMAC/PSS and (B) 0.5 M NaCl and five base BLs of PDADMAC/PSS. CaCl₂ retention (C) an ionic strength of 0.05 M NaCl and seven base BLs of PDADMAC/PSS and (D) 0.5 M NaCl and five base BLs of PDADMAC/PSS. Of PDADMAC/PSS (blue, open symbols) and P(AM-co-DADMAC)/PSS (red, closed symbols) terminating layers. The origin of the graphs represents the base case, 0.5 represents one additional polycation layer, 1 represents one BL, and so forth. Dotted lines are used as a guide for the eye [Color figure can be viewed at wileyonlinelibrary.com]
of PDADMAC successfully tunes the membrane surface charge.

3.3 | Performance benchmarking of the asymmetric membranes

Finally, the obtained performance results reported in this study are compared to the performance of other LbL NF membranes reported in literature and commercially available NF membranes (Figure 8).

The data in Figure 8 highlight that the developed asymmetric LbL NF membranes outperform many of the earlier reported LbL NF membranes and show very comparable performance as commercially available NF membranes. For NF applications it is not always necessary to fully retain all salts, as they will be used for specific waste streams or as a pretreatment step, but maintaining a high permeability is important as well.6,7 Moreover, the high Na_2SO_4 retentions are a clear indication that the produced membranes are negatively charged. This is key for the retention of negatively charged ions and the suppression of fouling of, often, negatively charged pollutants. Moreover, the high flexibility of LbL layer coating combined with its simplicity and environmental sustainability (water-based coating) shows the strong potential of this approach to produce asymmetric NF membranes with tunable retention behavior for large-scale industrial water treatment processes.

4 | CONCLUSION

Asymmetric NF membranes are produced by layer-by-layer assembly of PEs on a porous support and the membrane filtration performance was determined and related to the accompanying type and number of layers. Our work shows that asymmetric LbL coating provides a very versatile method to tailor membrane properties. For the first time, the combination of PDADMAC and P(AM-co-

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**Data point** | **Membrane composition** | **[Salt] (M)** | **Data point** | **Membrane composition** | **[Salt] (M)**
--- | --- | --- | --- | --- | ---
1 | (PAH/PAA)₀₈₅ | 0.05 | 10 | (PAH/PAA)₁₅ | 0.005
2 | (PAH/PAA)₀₈ | 0.05 | 11 | NF 270 | —
3 | (PDADMAC/PAA)₀₈ | 0.05 | 12 | (PDADMAC/PSS)₀₅ | 0.05
4 | (PDADMAC/PAA)₀₈₅ | 0.05 | 13 | (PAH/PSS)₀₈ | 0.05
5 | (PDADMAC/PSBMA/PSS)₀₃ | 0.2 | 14 | (PDADMAC/PSS)₀₂ | 0.2
6 | NF 9₀ |
7 | (PEI/PSS)₀₂ | 0.5 | 16 | (PDADMAC/PSS)₀₂ | 0.2
8 | (PAH/PSS)₀₂ | 0.5 | 17 | (PDADMAC/PSS)₀₂ | 0.2
9 | (PAH/PSS)₀₅ | 0.05 | 18 | CA3₀ | —

**FIGURE 8** Comparison between asymmetric LbL NF membranes (red diamonds) with other LbL NF membranes reported in literature (white diamonds) and commercial NF membranes (gray diamonds). Data points: 1–4, 9, 12, 13, 53, 54, 6, 55, 7, 14, 16, 17, 56, 8, 15, 57, 10, 58, 11, 59, 18. [Color figure can be viewed at wileyonlinelibrary.com]
DADMAC) layers in one membrane was used. This combination resulted in the successful production of negatively charged LbL membranes with both high permeabilities and high retentions for negatively charged ions, while simultaneously reducing odd-even effects. The prepared membranes have pure water permeabilities between 7 and 19 L/(m²hbar) and a negative surface charge resulting in retentions of Na₂SO₄ of up to 95%. These values position the developed membranes in the top range compared to commercial membranes and other LbL membranes reported in the literature.

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