

Nanofiltration membrane performance of layer-by-layer membranes with different polyelectrolyte concentrations

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ABSTRACT

Nanofiltration membranes produced with polyelectrolytes via the layer-by-layer technique are frequently researched, but misunderstood parameter is the polyelectrolyte concentration. Higher polyelectrolyte (PE) concentrations are known to produce thicker PE layers, but its effect on the membrane performance has only been studied in a limited fashion, leading to premature conclusions. In this work, two well-known strong polyelectrolytes, PDADMAC and PSS were used to prepare membranes using coating solutions with polyelectrolyte concentrations of 0.01, 0.1, 1.0, 2.5 and 5.0 wt% and two different salt concentrations in the coating solution of 0.05 and 1 M, as higher salt concentrations lead to thicker PE layers. The membrane performance of the prepared membranes is researched in terms of pure water permeability (PWP), molecular weight cut-off (MWCO) and the retention of different salts. In the first bilayer, membranes coated with a 0.05 M salt solution showed lower PWPs and MWCOs and higher salt retentions by increasing the PE concentration. After a certain number of coated bilayers, the MWCO and salt retentions reach a plateau for all PE concentrations; but the plateau value was obtained earlier by coating with a higher PE concentration. The membranes coated with the 1 M salt concentration had lower or comparable retention rates, except for MgCl_2 , than those coated with 0.05 M salt. The higher salt concentration resulted in more abundant PDADMAC in the membrane, which promotes the MgCl_2 retentions for all bilayers. In conclusion, we found that the polyelectrolyte concentration significantly alters the membrane performance, but after coating 7 bilayers, the same size exclusion plateaus are reached.

1. Introduction

The assembly of polyelectrolyte (PE) layers with the layer-by-layer (LbL) technique has provoked increasing interest in the preparation of nanofiltration (NF) membranes [1–3]. This LbL coating technique allows tailoring the membrane properties to suit several applications, such as removal of micropollutants and (partial) water desalination [4–6]. Commercially available NF membranes generally show a trade-off between high water permeability and high salt retention, thus compromising the quality or quantity of the purified stream. Nanofiltration membranes produced with the LbL technique can positively shift this trade-off, due to the production of nanometer scale layers [7,8]. To do so, knowing which parameters play a crucial role in the LbL coating process when producing LbL functionalized NF membranes is essential.

One of the most studied PE couples is PDADMAC/PSS

(polydiallyldimethylammonium chloride/ poly(sodium-4-styrene sulfonate)) [9–12]. Membranes coated with this PE couple possess relatively good permeabilities and selectivities compared to other PE couples [13]. Furthermore, this PE pair is recognized for its chemical and long-term stability also during aggressive cleaning protocols using sodium hypochlorite and alkaline solutions [14,15]. Due to these benefits, PDADMAC/PSS is a PE couple with high potential to be used for the purification of various streams [15,16]. Among all the parameters studied for the PDADMAC/PSS couple, the influence of the salt concentration in the coating solution is most frequently studied [9,17–25]. In contrast, the effect of the PE concentration on the membrane formation has received significantly less attention [17], especially when PE concentrations are higher. It is known that increasing the salt and the PE concentration thickens the active coating layer, thereby influencing the membrane filtration performance, although its impact differs

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significantly [19,26]. In addition most LbL research is conducted with relatively low PE concentrations (<0.1 wt%) [9,27–30]. In order to understand the influence of the PE concentration on filtration performance, systematic research is also necessary in this area.

Dubas et al. researched the effects of salt as well as PE concentration. Increasing the salt concentration (0–2 M) resulted in a 30-fold thickness increase, whereas by increasing the PE concentration (0–50 mM), the thickness increase was about 1.5-fold [19]. In addition, they found that at concentrations higher than 20 mM, the PE concentration does not further influence the layer thickness anymore [19].

Salt ions in the PE coating solution tremendously impact the formation of the layers, where a higher salt concentration results in thicker and simultaneously more open structures [19,22,31]. In the LbL process, the ionic linkages between the PC (polycation) and PA (polyanion) charge are referred to as intrinsic charge compensation. Introducing salt ions in the PE solution partially compensates the PE charges, called extrinsic charge compensation. Extrinsic charge compensation screens the charges of the PE, allowing for more PE adsorption [19,22,31]. In general, an increase in salt concentration magnifies the overall level of PE swelling and enhances the differences in swelling, where PDADMAC shows a higher swelling degree than PSS [13,32–34]. The swelling opens the PE structure, resulting in larger apparent pore sizes [13,32–34]. In addition, increasing the salt concentration increases the PE layer thickness and adsorption [19]; this generally enhances the membrane resistance [9].

The effect and underlying mechanisms of the PE concentration on the layer formation remain ambiguous. Several reports indicate an increase in layer thickness when using higher PE concentrations [19,26,35–37]; however, the membrane performance, while varying the PE concentration, remains relatively constant [13,17].

The limited influence of PE concentration on the membrane performance is surprising. The thickness increase with increasing PE concentration results from a higher PE mass adsorption due to more PE chain interactions with the underlying surface [38]. More PE adsorption thus automatically results in fewer binding sites per PE chain. The thicker layers thus automatically indicate more free charges (extrinsic charge compensation), as the charges compensation of the preceding layer happens with fewer binding sites. More extrinsic charge compensation typically results in thicker layers, commonly leading to lower water permeabilities. However, as said before, this was not observed in recent performance studies [13,17].

DuChanois et al. investigated the NF membrane performances by applying two bilayers of the frequently used PEs, PDADMAC and PSS [17]. They used five PE concentrations between $0.40 \cdot 10^{-3}$ –0.25 wt% for PDADMAC and $0.59 \cdot 10^{-3}$ –0.37 wt% for PSS (0.032, 0.16, 0.80, 4.0 and 20 mM based on molar mass). The difference in water permeability and glucose retention by adjusting the PE concentration is slim (maximum 1.25 times), except for the membranes coated at the lowest concentration due to incomplete coating.

Additionally, Menne et al. researched the behavior of hollow fiber supports coated with one bilayer of PDADMAC/PSS at different polyelectrolyte concentrations of 0.1, 1.0, 1.5 and 2.5 wt%. They observed no significant difference in pure water permeability and MgSO_4 retention [13]. The absence of difference is attributed to an adsorption limit where maximum surface coverage is reached at PDADMAC concentrations around 0.1 wt% [13,39]. Although there is a maximum PE adsorption, this maximum also depends on other factors, such as the charge density and porosity of the support surface.

The limited influence of the PE concentration on membrane performance is surprising because the layer thickness increases with the PE concentration. So far, the literature has only investigated the influence of low PE concentrations [17] or a low number of BLs [13]. To understand the impact of the polyelectrolyte concentration, 7 BLs are therefore coated with the PE pair PDADMAC/PSS using various polyelectrolyte (0.01, 0.1, 1.0, 2.5 and 5.0 wt%) and salt concentrations (0.05 M and 1 M). 7 BLs were supplied because a 7 BL coating is

sufficient to reach the salt retention plateau, even with diluted PE and salt concentrations [7].

2. Experimental

2.1. Chemicals

Poly(diallyldimethylammonium chloride) (PDADMAC, $M_w = 200$ –350 kDa, 20 wt% in water) was obtained from Sigma-Aldrich (the Netherlands). In addition, poly(sodium 4-styrene sulfonate) (PSS, $M_w = 500$ –700 kDa, 20.4 wt% in water) from Tosoh Organic Chemical Co. LTD (Japan) was used. Magnesium sulfate heptahydrate, magnesium chloride hexahydrate and ethanol absolute (>99.9 % purity) were obtained from VWR Chemicals (Belgium). Sodium sulfate decahydrate was obtained from Acros Organics (Belgium) and sodium chloride was obtained from Nouryon (Sanal®P, pharmaceutical grade) (the Netherlands). Polyethylene glycols (PEGs) with molecular weights of 200, 400, 600, 1000, 2000 and 4000 g/mol were obtained from Sigma-Aldrich (the Netherlands). All chemicals were used as received.

2.2. Nanofiltration membrane preparation

Hollow fiber tight ultrafiltration inside-out HFS membranes (molecular weight cut-off (MWCO) 10 kDa) kindly provided by Pentair X-Flow (the Netherlands) were used as membrane support. The support consisted of polyether sulfone hollow fibers with an inner diameter of 0.8 mm and was modified to get negatively charged groups on the inner surface; in the experiments lengths of 30 cm were used [35]. As a pre-treatment, the hollow fiber supports were submerged overnight in an ethanol/water mixture to remove preservatives and other excipients and were subsequently rinsed with ultrapure water.

The polyelectrolyte layers were coated by first immersing the fibers in the polyelectrolyte solution for 30 min with a manual refreshment every 5 min, starting with the PDADMAC (polycation) solution. Aside from the PE, the coating solution contained NaCl and ultrapure water. Afterward, the fibers were rinsed 3 times for 10 min in freshly prepared NaCl solutions with concentrations equivalent to the coating to remove loosely and unbound PEs. After that, the fibers were immersed in a PSS (oppositely charged) solution followed by 3 rinsing cycles as described above to end up with 1 BL. This process was repeated 6 times, forming an LbL-coated membrane with 7 BLs. After each BL coating, 6 fibers were taken for evaluation purposes. The membranes were coated with a coating solution with a PE concentration of 0.01, 0.1, 1.0, 2.5 and 5.0 wt % with the addition of 0.05 or 1.0 M NaCl.

2.3. Membrane performance

The membranes were characterized by pure water permeability (PWP), molecular weight cut-off (MWCO) and salt retentions using single salt solutions of 5 mM MgSO_4 , Na_2SO_4 , MgCl_2 or NaCl. From each coating step, 6 different membranes were evaluated. These membranes were fixed with chromatographic connectors (Inacom Instruments), making it possible to measure 18 membranes at the same time. The membranes were measured in crossflow operation with a trans-membrane pressure of 3 bar, controlled with a pressure regulator (Swagelok). To minimize the contribution of concentration polarization on the membrane performance the flow is driven with a diaphragm pump (KNF) with a nominal flow of 6 L/min at atmospheric pressure. 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 5 min and a minimum weight of 10 g. For the calculation of the pure water permeability, the permeate volume was weighed. Additionally, for the calculation of the retention, the conductivity of the permeate was measured with a Pocket Pro Cond_{LR} device. The pure water permeability $L_{p,0}$ ($\text{L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$) was calculated via Eq. (1).

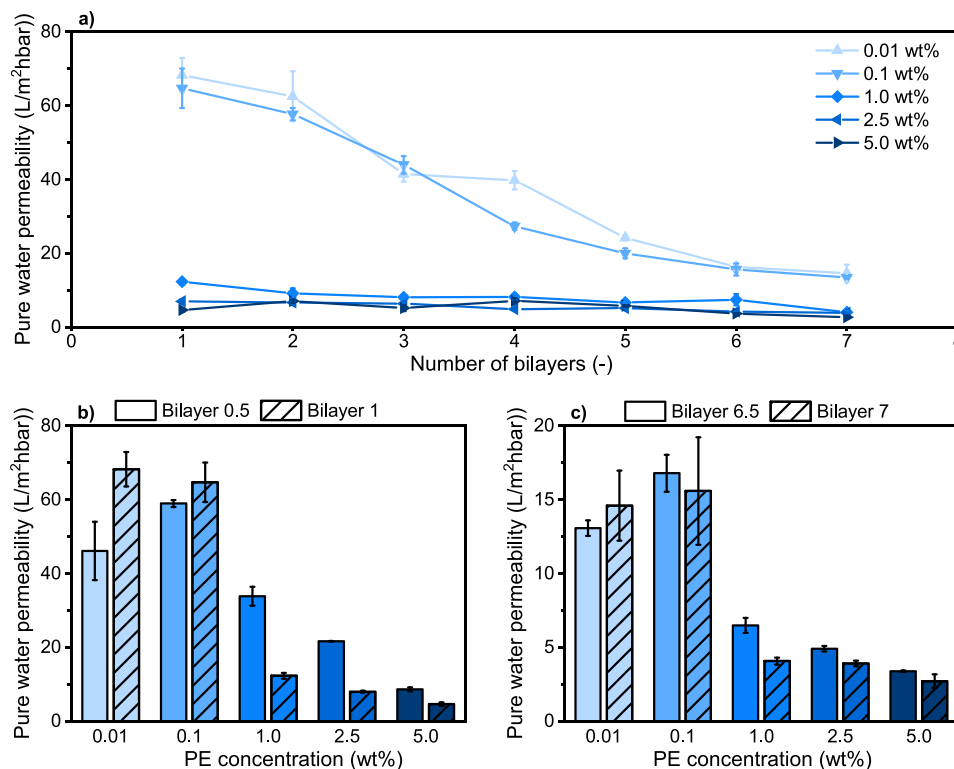


Fig. 1. Pure water permeability of PDADMAC/PSS coated membranes with varying PE concentrations of 0.01, 0.1, 1.0, 2.5 and 5.0 wt% (NaCl coating concentration of 0.05 M) for a) bilayers 1–7, b) bilayer 0.5 and 1 c) bilayer 6.5 and 7.

$$L_{p,o} = \frac{V_p}{A \cdot t \cdot \Delta P} \quad (1)$$

With V_p (L) the permeate volume, t (h) the permeation time and A (m²) the membrane area for filtration and ΔP (bar) the effective pressure. The observed salt and PEG retention R_{obs} (%) was calculated via Eq. (2).

$$R_{obs} = \left(1 - \frac{C_p}{C_f}\right) \cdot 100\% \quad (2)$$

Where R_{obs} (%) is the observed retention and C_p and C_f (mol/L) are the permeate and feed concentration, respectively. The salt concentrations were calculated via the conductivity using correlations obtained by Rosemount analytical [43].

The MWCO was determined by measuring the lowest M_w of PEG at which 90 % retention was observed. The concentration of each PEG in the feed solution was 1 g/L. The PEG concentration in the permeate and retentate samples was analyzed with Gel Permeation Chromatography (GPC) (Shimadzu LC-2050C 3D series) and a size exclusion column (Shodex OHpak SB-802.5 HQ 8 × 300 mm² column 200 Å, 6 μm). The flow rate was 1 mL/min and the eluent was ultrapure water.

3. Results and discussion

3.1. Influence of polyelectrolyte concentration

3.1.1. Pure water permeability

Fig. 1a shows the pure water permeability (PWP) of all membranes with PSS-terminated layers (BL 1–7) coated with 0.05 M NaCl and varying PE concentrations of 0.01, 0.1, 1.0, 2.5 and 5.0 wt%. To elucidate the impact of the terminating layer, Fig. 1b and c show both PDADMAC and PSS terminated membranes (odd-even effects) for BL 0.5/1 and BL 6.5/7, respectively.

Fig. 1a clearly shows a significant difference in the PWP for the various PE concentrations. In general, the PWP decreases with

increasing PE concentration, with the most significant jump visible between 0.1 and 1.0 wt%. The viscosity of the PE solutions increases with increasing PE concentrations, where a clear difference was observed between the 0.1 and 1.0 wt% solution. Higher viscosities will promote the adsorption of layers in the layer-dominated regime. Additionally, all produced membranes show a decline in PWP with increasing BLs, indicating additional PE adsorption with every BL [8]. More PE adsorption results in a thicker or denser selective layer and, thus higher resistance to permeation.

The difference in PWP between the PE concentrations is striking and has not been observed before. However, it is a logical trend caused by increased PE thickness and adsorption for increasing PE concentrations, as seen in multiple other studies [17,25,30,31]. The higher PE adsorption results from more PE chains interacting with the underlying surface [33]. More PE adsorption for a given salt concentration results in a higher permeation resistance.

Our analysis and previous studies differ due to other production conditions and procedures. Menne et al. [12] produced membranes coated with similar PE concentrations (up to 2.5 wt%) as the PE concentrations used in this study but did not find any significant difference in PWP. We attributed this to the PE coating procedure that differs from our work, as Menne et al. [12] flushed the lumen of the fibers for 3 min with the PE solution before the fibers were statically coated. The flushing was done to ensure that the lumen was entirely filled with the PE solution; however, this could force the PE to move on/through the support membrane, similar to dynamic coating [3,37]. The majority of PE adsorption happens within a few minutes; hence these 3 min of flushing can be crucial for layer formation, forcing the PEs more towards pore blocking of the surface pores located on the inner layer of the hollow fiber membrane resulting in a decreased water flux [38]. The sealing increases the adsorbed amount of PE, similar to increasing the PE concentration; hence the adsorption limit is reached at lower PE concentrations, and no effect is visible of the PE concentration at these conditions. DuChanois et al. [15] produced membranes with relatively

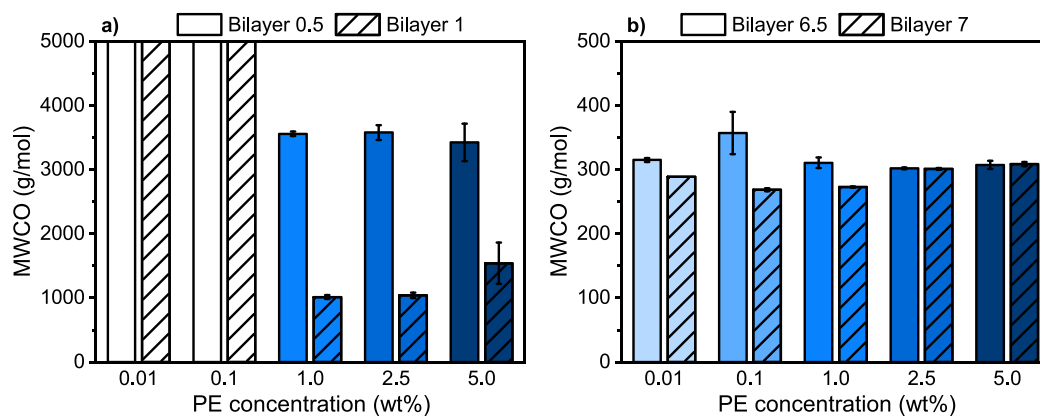


Fig. 2. MWCO of PDADMAC/PSS coated membranes with varying PE concentrations of 0.01, 0.1, 1.0, 2.5 and 5.0 wt% (NaCl coating concentration of 0.05 M) for a) bilayer 0.5 and 1 b) bilayer 6.5 and 7. Note: membranes with MWCOs higher than 5000 are represented in white bars.

low PE concentrations (below 0.4 wt%), while in our research, the most significant differences are at higher concentrations (between 0.1 and 1.0 wt%). Moreover, 0.5 M of salt is used in the coating solution, which is a ten-fold higher than the concentrations used here. The impact of salt during coating in combination with different PE concentrations cannot be neglected and will be discussed later.

Fig. 1b and c show striking differences between membranes terminated with PDADMAC or PSS. These so-called odd-even effects result from the location of the adsorbed PE layer and the swelling degree of PEs [8]. The PE layer can be adsorbed inside the pores or on top of the membrane support, resulting in different trends in the PWP [8]. For PDADMAC/PSS coated membranes, a pore-dominated regime shows

higher PWPs with PSS as the terminating layer, while a layer-dominated regime shows higher PWPs with PDADMAC terminated layer [8,39]. For 0.01 and partially 0.1 wt%, PSS-terminated membranes have a higher PWP than PDADMAC-terminated membranes, indicating adsorption inside the pores of the support. The other three concentrations show the opposite trend, indicating a layer-dominated regime, adsorption on top of the support. The difference between 0.1 and 1.0 wt%, indicates a transition point between the layer and pore dominated regime, after which the odd-even effects are reduced.

3.1.2. MWCO

Fig. 2 shows the MWCO data of membranes coated with 0.5/1 BL and

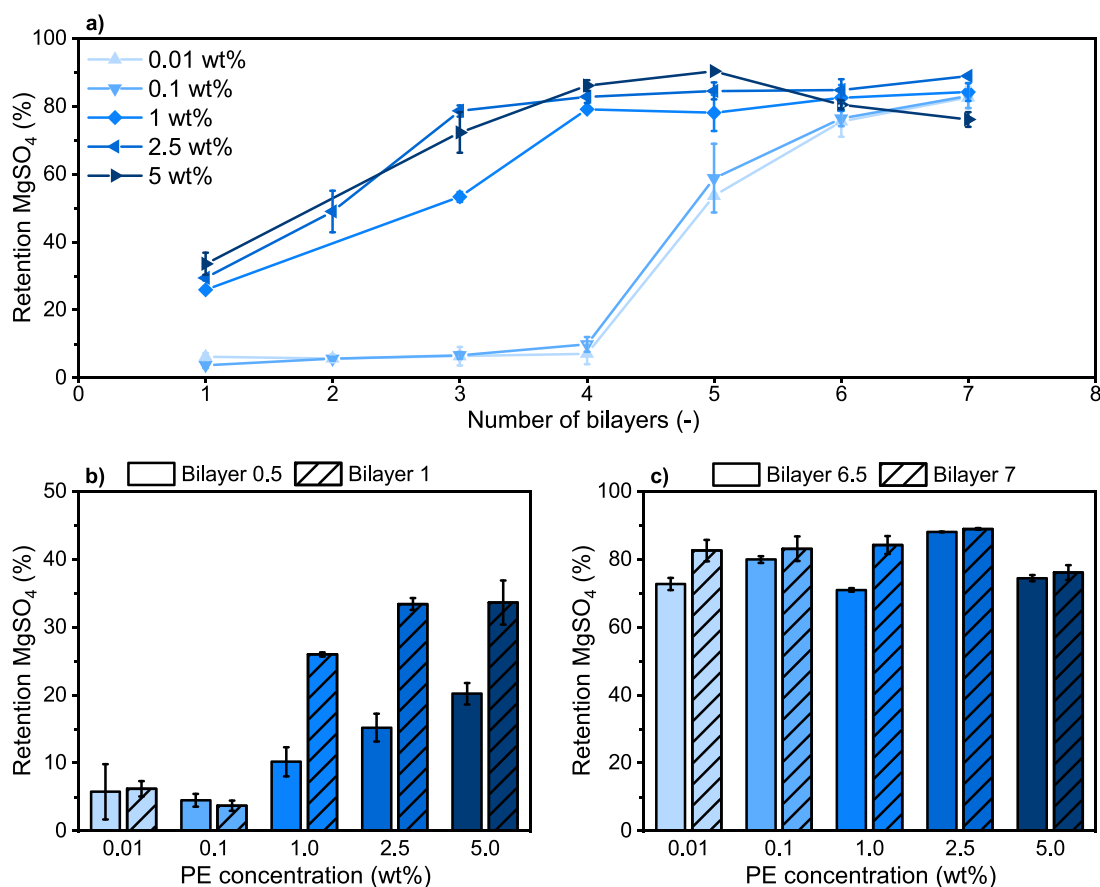


Fig. 3. MgSO_4 retention of PDADMAC/PSS coated membranes with varying PE concentrations of 0.01, 0.1, 1.0, 2.5 and 5.0 wt% (NaCl coating concentration of 0.05 M) for a) bilayer 1–7, b) bilayer 0.5 and 1 c) bilayer 6.5 and 7.

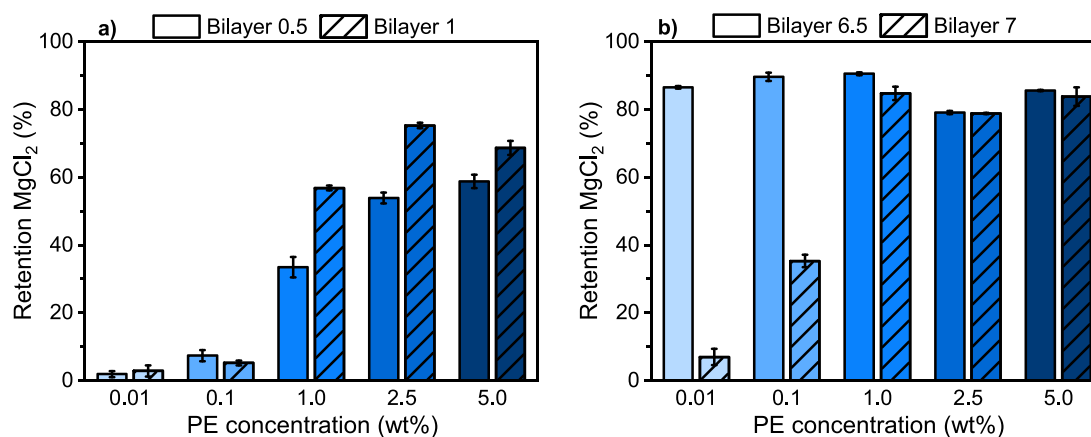


Fig. 4. MgCl_2 retention of PDADMAC/PSS coated membranes with varying PE concentrations of 0.01, 0.1, 1.0, 2.5 and 5.0 wt% (NaCl coating concentration of 0.05 M) for a) bilayer 0.5 and b) bilayer 6.5 and 7.

6.5/7 BL. The MWCO data of membranes coated with different PE concentrations significantly differ from each other. Huge differences were found in MWCO for 0.5 and 1 BL, but only minor differences in MWCO were found for membranes coated with 6.5 and 7 BLs.

For the first two layers (BL 0.5 and 1; Fig. 2a), there is a jump between the concentrations below 0.1 wt% and above 1 wt%. The MWCO of the membranes coated with 0.01 and 0.1 wt% could not be determined, as these values transcend the molecular weights investigated, indicating that the MWCO is higher than 5000 g/mol. The pristine support is known to have an MWCO of 10,000 g/mol [40]. These membranes have layers coated in the pore-dominated regime; hence it is expected that NF size exclusion is not reached with a single BL.

The membranes coated with one BL using the higher PE concentrations (1.0, 2.5, 5.0 wt%) show MWCO values in the open NF range. These relatively low MWCOs originate from the PE layers directly coated in the layer-dominated regime, as shown by the PWP (Fig. 1b). The additional PE adsorption, due to the higher PE concentration, results in a higher membrane resistance due to the formation of a coating that completely closes the membrane pores. Additionally, membranes coated with 0.5 BLs have a significantly higher MWCO and less closed structure than the 1 BL coated membrane, which can be caused by both the different PE characteristics (swelling degree and hydrophilicity) or the additional PE adsorption. Both effects are known to influence the size exclusion characteristics of LbL membranes [8,27]. However, from the MWCO and PWP of BL 0.5 and BL 1, it cannot be concluded which effects are accountable for the drop in MWCO value.

The differences in the MWCOs between the odd and even coating vanishes when coating with different PE concentrations at higher BLs, as shown for BL 6.5 and 7 in Fig. 2b. All membranes have MWCOs between 260 and 360 g/mol, and there are little differences between PDADMAC and PSS terminated membranes. The MWCOs for membranes coated with PDADMAC/PSS layers have a plateau for different coating conditions [7,13,32]. The MWCO is intrinsically limited and is only influenced by size exclusion effects (no charge effects). The pore size of the produced membranes determines the size exclusion of the membranes, resulting from the tightly knit PE network connected via intrinsic linkages.

The layer thickness increases upon PE adsorption [13,22], this directly increases the membrane resistance and decreases the initial pore size as shown for BL 1. The subsequently constructed bilayers, especially at higher PE concentration are mainly contributing to the mass flow resistance, the water flux. Miller and Bruening found by ellipsometry measurements, after forming 4 BLs out of a 0.4 wt% PE solutions in 0.5 M NaCl, a fourfold increase in swelling for the PDADMAC terminated bilayer when compared with the PSS terminated bilayer [35]. After applying 9 bilayers this difference in swelling behavior between the

different layers was canceled out and the swelling was independent of the terminated layer. This is in agreement with our own findings when coating with higher concentrated PE solutions. The bilayers become less prone to odd-even swelling phenomena and are therefore become almost constant in MWCO and flux. For the membranes coated with low PE concentration solutions, more coating layers are needed to end up with a coating layer independent MWCO. After 6.5 BLs the MWCO for the neutral PEG molecules becomes layer independent (Fig. 2b) while the retention that is based on the charge density of the layer, Donnan exclusion, still proceeds due to the increasing number of over-compensated charges on the PE backbone caused by intermolecular linkages.

3.1.3. MgSO_4 retention

Fig. 3 shows the MgSO_4 retention of the PDADMAC/PSS coated hollow fiber membranes with a salt concentration of 0.05 M. Fig. 3a shows the effect of the number of bilayers, where Fig. 3b and c focus on the difference between PDADMAC and PSS terminated membranes.

When the number of deposited bilayers increases, the membranes show an increase in MgSO_4 retention, after which it starts plateauing. The initial increase and subsequent plateau is seen for all PE concentrations and follows the MWCO plateau. Interestingly, increasing the PE concentration decreases the necessary bilayers to reach the plateau value. At 5.0 wt% after 5 BLs a small decrease is visible in the MgSO_4 retention. This is caused by practical limitations of the 5.0 wt% coating solution that has a high viscosity, which promotes coagulation of the polyelectrolytes and is therefore more difficult to control ending up in a somewhat heterogenous coating.

The decrease in necessary layers with an increasing PE concentration is a direct result of an increase in PE adsorption, visualized in the first two layers applied (Fig. 3b): at low PE wt%, the low adsorption of the PE results in a lower membrane resistance and a more open structure, resulting in low size exclusion characteristics as seen in the low MgSO_4 retention and the high MWCO. At high PE wt% (≥ 1.0 wt%), the higher PE adsorption results directly in a layer-dominated regime, resulting in higher initial MgSO_4 retentions of $\sim 30\%$. For BL 6.5 and 7 (Fig. 3c), the MgSO_4 retention is independent of the PE concentrations, which agrees with the MWCOs (Fig. 2b).

3.1.4. MgCl_2 retention

The MgCl_2 retention is measured to assess the charge exclusion properties of the different membranes. Charge exclusion effects are more prevalent for membranes in which the sign of the charge is equal to that of the multivalent ion [41]. Following this, positively charged membranes have a high MgCl_2 retention. Fig. 4 shows the MgCl_2 retention for membranes coated with the different PE concentrations for 0.5/1 BL and

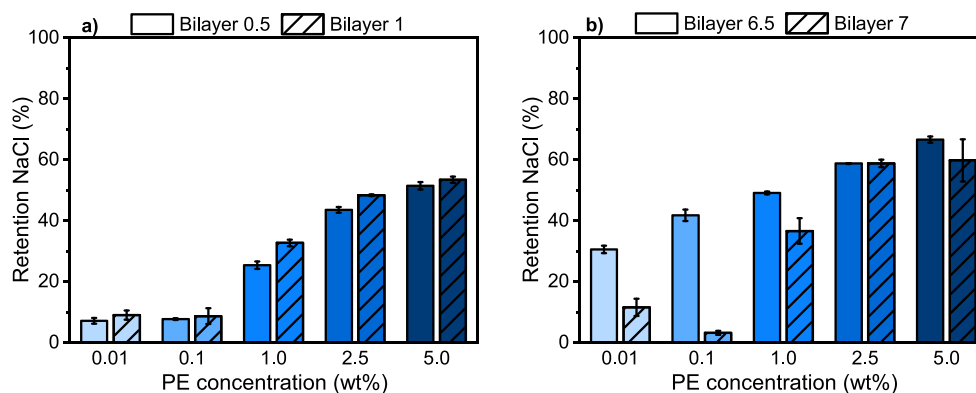


Fig. 5. NaCl retention of PDADMAC/PSS coated membranes with varying PE concentrations of 0.01, 0.1, 1.0, 2.5 and 5.0 wt% (NaCl coating concentration of 0.05 M) for a) bilayer 0.5 and b) bilayer 6.5 and 7.

6.5/7 BLs.

Fig. 4a shows the rise in the MgCl_2 retention with an increasing PE concentration due to increased size and charge exclusion. The differences between 0.5 and 1 BL show that 1 BL has higher MgCl_2 retentions than 0.5 BL for the PE concentrations of 1.0, 2.5 and 5.0 wt%. These higher retentions are counterintuitive, as a 1 BL membrane has a negatively charged PSS-terminating layer compared to the positively charged PDADMAC-terminated membrane coated with 0.5 BLs. Salt retention is determined by both size as well as charge exclusion. Thus although the charge exclusion is lower for the membranes coated with 1 BL as they are less positively charged compared to BL 0.5. Since the size exclusion is higher, the retention still increases. This is a result of the layers being directly coated in the layer-dominated regime, which results in a denser membrane for PSS terminated membranes as shown before by the MWCO values in Fig. 2a. Thus, when coating with 0.5 or 1 BL, the size exclusion mechanism is more dominant than the opposing forces of the charge exclusion.

The MgCl_2 retention is significantly higher than the MgSO_4 retention for the membranes coated with 1.0, 2.5, 5.0 wt%, ~ 70 and ~ 30 %, respectively. This difference in retentions results from charge exclusion effects due to a highly positively charged membrane surface. This effect was already found by Emonds and Kamp, where high PE concentrations (>10 wt%) caused accumulation of PDADMAC in the coating, which strengthened the influence of charge exclusion [42,43]. The so-obtained highly positive surface promotes the rejection of bivalent Mg^{2+} ions from the MgCl_2 salt.

The balance between size and charge exclusion also explains the odd-even effects shown in Fig. 4b. For the lower PE concentrations, 0.01 and 0.1 wt%, the influence of the terminating layer is evident, which is not visible for the membranes coated with the higher PE concentrations, 1.0,

2.5 and 5.0 wt%. At PE concentration ≤ 0.1 wt% high MgCl_2 retentions are measured for the PDADMAC-terminated membranes and low MgCl_2 retentions for the PSS-terminated. These apparent odd-even effects have been observed before and indicate distinct layers [44,45].

For membranes coated with PE concentrations ≥ 1.0 wt%, these odd-even effects are no longer visible due to the formation of an overall positive surface, irrespective of the terminating layer [42,43]. The diffusion rate of PDADMAC is higher than PSS, causing easier penetration in the already formed coating layer resulting in an overall positive coating after several coating steps. Resulting in a structure composed of a zone with an excess extrinsically charge compensated PDADMAC, with on top a stoichiometric complex of PDADMAC/PSS [22,46].

To visualize the impact of the charge exclusion, the Na_2SO_4 retention was measured and presented in the supporting information (SI Fig. S1). The presented Na_2SO_4 retention illustrates that the SO_4^{2-} anions determine the retention behavior. The increasing positive surface charge induced by applying more coating steps or by coating with a higher PE concentration results in a decrease in retention, which is opposite compared to the MgCl_2 retention. In general, when charge interactions play a role in the retention behavior, the retention of bi- and multivalent ions with opposite charges is lower compared to monovalent ions or ions with an equal signed charge [9,32,47].

3.1.5. NaCl retention

Finally, the retention capacity of the double monovalent salt NaCl is researched (see Fig. 5); here, an increase in PE concentration increases the NaCl retention. NaCl is notoriously difficult to remove with NF membranes because it consists of two small monovalent ions. However, as seen in Fig. 5a, the NaCl retention of the membranes coated with 0.5 and 1 BL reaches up to 50 %. The retention even increases to 70 % when

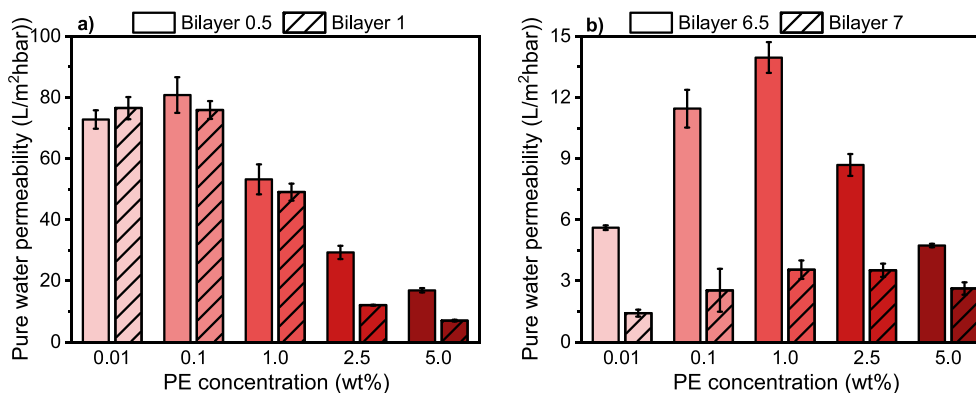


Fig. 6. Pure water permeability of PDADMAC/PSS coated membranes with varying PE concentrations of 0.01, 0.1, 1.0, 2.5 and 5.0 wt% (NaCl coating concentration of 1 M) for a) bilayer 0.5 and b) bilayer 6.5 and 7.

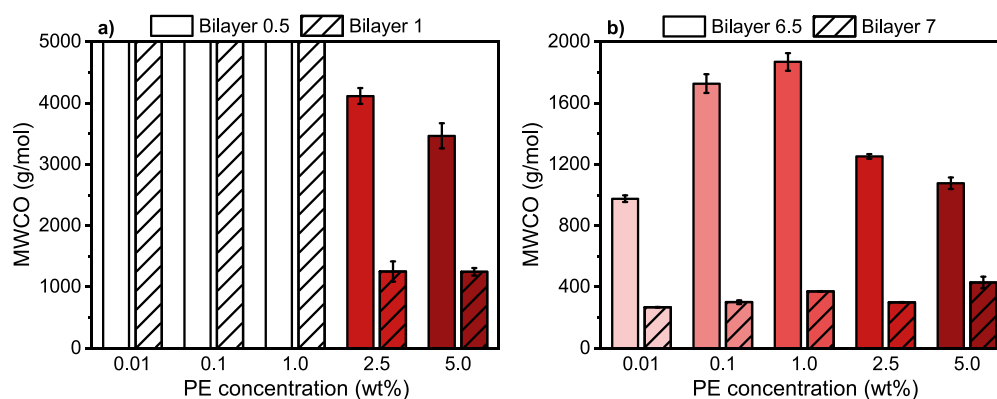


Fig. 7. MWCO of PDADMAC/PSS coated membranes with varying PE concentrations of 0.01, 0.1, 1.0, 2.5 and 5.0 wt% (NaCl coating concentration of 1 M) for a) bilayer 0.5 and 1 b) bilayer 6.5 and 7. Note: membranes with MWCOs higher than 5000 are represented in white bars.

coating 6.5 or 7 BLs (Fig. 5b).

The NaCl retention increases with increasing PE concentration, as these membranes are more positively charged. The impact of the positively charged membrane is already indicated by the MgCl_2 retention, which shows the same trend as the NaCl retention (see Fig. 4). However, with NaCl both ions are monovalent, but due to the difference in charge density between Na^+ and Cl^- (24 and $8\text{C}/\text{mm}^3$ for Na^+ and Cl^- respectively, as calculated using the Shannon-Prewitt ionic radius) [48]. Therefore, increasing the PE concentration results in higher NaCl retentions due to the build-up of positive charge. This impact of the membrane charge on the NaCl retention was observed before for different PE couples [45,49]. The benefit of a positive membrane for removing NaCl is again shown when comparing the last PDADMAC and PSS terminated layers for the lower PE concentrations. The positively charged PDADMAC terminated membrane has a higher retention than the PSS terminated membrane.

3.2. Influence of salt concentration

This section researches the interplay between the PE and salt concentrations in the coating solution on the final membrane performance. The performance of the membranes prepared with a 0.05 and 1.0 M salt solution was compared in terms of PWP, MWCO and salt retention analog to the procedure as described above for the 0.05 M NaCl solutions.

3.2.1. Pure water permeability

First, the PWP of PDADMAC and PSS terminated membranes for a salt concentration of 1 M during coating is given in Fig. 6a and b for BL 0.5/1 and BL 6.5/7, respectively.

Fig. 6a shows that for BL 0.5 and BL 1, increasing the PE concentration again results in a decline in PWP, as was observed before for the membranes coated with 0.05 M. The similarity between 0.05 M and 1 M indicates that an increase in PE concentration increases the membrane resistance, irrespective of the salt concentration. For all PE concentrations, the membranes coated with a salt concentration of 1 M experience more charge compensation by the ions in the solution, resulting in a thicker but more open coating than the 0.05 M coated membranes. The more open coating layer is more prone to swelling of the PE, resulting in higher PWP values.

There are apparent odd-even effects for BL 6.5 and 7; see Fig. 6b, a significantly higher permeability is measured for membranes with PDADMAC-terminated layers than PSS-terminated layers. This higher permeability stems from a relatively more open structure with PDADMAC-terminated layers due to the higher swelling tendency of PDADMAC compared to PSS. These trends are generally visible for membranes coated with high salt concentrations such as 1 M [9].

Moreover, for BL 6.5, and to a lesser extent for BL 7, the highest PWP

is obtained at 1.0 wt%, hence this is the membrane with the lowest membrane resistance. This is hypothesized to be caused by a combination of the influence of PE and salt concentration. The membrane resistance is both dependent on the membrane thickness as well as on the packing density of the PE layers. An increase in both PE and salt concentrations results in thicker layers [19]. In addition the PDADMAC swelling is more pronounced at higher salt concentrations, resulting in a more loose packing density of the PE layers which is reflected in the higher permeabilities [7,34]. The membranes that are formed with higher PE concentrations are thus thicker, but also have a greater PDADMAC excess which, is especially the case when the PDADMAC is the terminating layer, the 6.5 BL, resulting in a more severe swelling. The PWP trade-off between layer thickness and layer density has an optimum permeability for the PDADMAC/PSS couple when a coating solution is used that contains 1.0 wt% PE in a 1 M NaCl.

Additionally, when comparing the PWPs of BL 7 membranes, the PWP values are lower for the membranes coated with the 1 M salt solution compared to 0.05 M. The lower PWPs result from thicker PE layers because the polymer chains coil more and more PE adsorbs [18,33].

3.2.2. MWCO and salt retention

Fig. 7 shows the MWCO of PDADMAC and PSS terminated membranes for a salt concentration of 1 M during coating for BL 0.5/1 and BL 6.5/7, respectively.

Again, the first two layers demonstrate very high MWCOs, similar to the membranes coated with the 0.05 M salt coating solution (Fig. 2a). Only the MWCO of the membranes coated with 1.0 wt% differ between the different salt concentrations because here, the jump in openness of the membrane is most significant. All the membranes with the different PE concentrations have a more open structure coated with 1 M of salt concentration compared to 0.05 M, as seen by the difference in PWP (Figs. 1b and 6a). However, the membranes coated with a PE concentration of 1.0 wt% are the only membranes that go from a PWP of ~ 10 inside the NF region to $\sim 50\text{ L}/(\text{m}^2\text{hbar})$, significantly higher than normal NF permeabilities [50].

Fig. 7b shows the MWCOs of BL 6.5 and 7, where the MWCOs of BL 6.5 are significantly higher than for BL 7. Additionally, the membranes coated with 6.5 BLs and 1 M of NaCl in the coating solution differ significantly from the MWCOs coated with 0.05 M (Fig. 2). An increase in MWCO for a high salt concentration is caused by severe PDADMAC swelling, as seen before for the PWP of BL 6.5 in Fig. 6b.

Additionally, several salt retentions are obtained for the PDADMAC/PSS membranes coated at 1 M with different PE concentrations. The MgSO_4 and MgCl_2 retentions of BL 0.5 and 1 are given in the supporting information (Fig. S2). These retentions are very low ($<25\%$ for MgSO_4 and $<50\%$ for MgCl_2). In all cases, the retention is lower with 1 M compared to 0.05 M of salt concentration in the coating solution. The

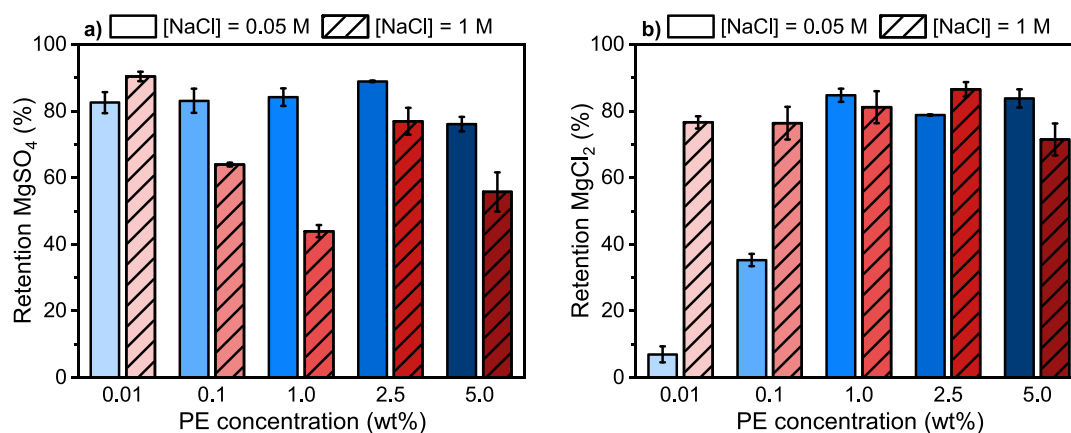


Fig. 8. PDADMAC/PSS coated membranes (NaCl coating concentration of 0.05 M and 1 M) with 7 BLs and varying PE concentrations of 0.01, 0.1, 1.0, 2.5 and 5.0 wt % for a) MgSO₄ retention b) MgCl₂ retention.

overall low retentions for the 1 M coated membranes are a direct result of the openness of the coating layer due to extrinsic charge compensation from the NaCl ions and swelling of the PEs.

The MgSO₄ and MgCl₂ retention of PDADMAC/PSS membranes coated with 7 bilayers is given for both salt concentrations in Fig. 8a and b. Here some striking differences are visible. The membranes coated with a 0.05 M salt concentration show a nearly constant MgSO₄ retention but significant differences in the MgCl₂ retention. The opposite effect is seen for the membranes coated with a 1 M salt solution.

As discussed before for the membranes coated with 0.05 M (see Figs. 3 and 4), an intrinsic limit of size exclusion results in a MgSO₄ retention plateau value. Additionally, increasing the PE concentration results in a more positively charged membrane, due to an increasing surplus of PDADMAC. This results in similar MgSO₄ retentions but increasing MgCl₂ retentions for increasing PE concentrations.

However, for 1 M, there is a difference in MgSO₄ retention, but not in the MgCl₂ retention. Hence the size exclusion differs, but the charge exclusion is similar. An increase both in PE and salt concentration result in thicker membranes [19]. Additionally, PDADMAC swells more at higher salt concentrations, resulting in more open layers [7,34]. The membranes with a higher PE concentration are thus thicker, but also have more PDADMAC excess, hence more swelling. These intertwining trends result in the lowest MgSO₄ retention at 1.0 wt% due to the highest amount of extrinsic linkages (this is also found by the highest PWP; hence the highest swelling). Additionally, coating at 1 M results in high MgCl₂ retentions due to an increased PDADMAC interdiffusion, resulting in a more positive coating layer for all PE concentrations.

4. Conclusions

This work assesses the influence of the polyelectrolyte concentration and the salt concentration of the coating solution on the filtration performance of LbL-coated nanofiltration membranes. The prepared membranes show that increasing the polyelectrolyte concentration increases the amount of polyelectrolyte adsorption. This resulted in lower pure water permeabilities due to a higher coating thickness. Still, within the concentration range investigated did not result in lower molecular weight cut-off values or higher MgSO₄ retentions. The number of layers necessary to reach a plateau value in MWCOs and MgSO₄ retentions decreases with an increasing polyelectrolyte concentration. Moreover, extra PE adsorption indicates fewer intrinsic linkages between the individual layers induced by more extrinsic charge compensation, leading to more especially PDADMAC interdiffusion in the previously applied bilayers. The higher diffusivity of PDADMAC compared to PSS resulted in highly positively charged membranes, resulting in higher MgCl₂ and NaCl retentions being measured.

In addition, the influence of the salt concentration in the coating solution in combination with the PE concentration is explored. An increased salt concentration in the coating solution, 0.05 to 1 M, induces a higher level of extrinsic charge compensation, leading to increased PDADMAC swelling and a more open and thicker layer. This results in higher pure water permeabilities for the BL 0.5, 1 and 6.5, the latter being the PDADMAC-terminated coating layer. Contrary, the membranes coated with 7 BLs, PSS-terminated and prepared out of 1 M salt solution show less swelling. Therefore, the thicker layers obtained provide a lower pure water permeability than those coated with PE solutions using a 0.05 M salt solution. Additionally, due to more restricted swelling of the 0.05 M coated membranes, all prepared membranes showed higher salt retentions except for the MgCl₂ retention. Therefore, for obtaining a high MgCl₂ retention, a more positive membrane coating caused by a PDADMAC excess is necessary, which can be obtained by employing a high salt concentration, 1 M, in the coating solution.

Overall, increasing the polyelectrolyte concentration and the salt concentration significantly affects the charge exclusion principles by an increase in the membrane surface charge, resulting in high MgCl₂ and NaCl retentions. However, the size exclusion principles are not altered, resulting in the same plateau values for the neutral MWCO values.

CRediT authorship contribution statement

Daniëlle Scheepers: Conceptualization, Data curation, Formal analysis, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Zandrie Borneman:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Kitty Nijmeijer:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.desal.2023.117246>.

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