Article

Multiple Approaches to the Buildup of Asymmetric Polyelectrolyte Multilayer Membranes for Efficient Water Purification

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ABSTRACT: The versatility of polyelectrolyte multilayer (PEM) coatings is very promising for their use as separation layers in nanofiltration applications. These membranes can for example be suited for the removal of micropollutants, such as medicines and pesticides, from water. The selectivity of PEM coatings can be further improved by so-called asymmetric coating. In this approach, the pores of the support membrane are filled with an open PEM layer to maintain a good water permeability, and subsequently a thin, dense layer is coated on top to determine the separation properties. Coating a dense top layer can be achieved in different ways. In this work, we systematically investigate the effectiveness of these different types of top layers. We show that coating a top layer at lower ionic strength than the bottom layer leads to a higher permeability and $MgSO_4$ retention, compared with the reference, bottom-type layer coated with the same total number of layers. Also, other salt retentions can be improved with this approach. However, micropollutant retentions are hardly affected. Coating a top layer with a polyelectrolyte pair that forms denser layers at equal ionic strength, in contrast, leads to a significant change in separation properties with much higher $MgSO_4$ and micropollutant retentions and improved water permeability compared with the reference layer. The concept of membrane optimization via asymmetric coating is thus most effective when using different polyelectrolyte pairs on top of each other. Moreover, we show that this approach allows us to selectively cross-link the top layer for further enhancement of the micropollutant retention, while water permeability is not much reduced. Asymmetric PEM coatings are therefore a promising method to optimize PEM membranes for micropollutant removal and other separation processes.

KEYWORDS: polyelectrolyte multilayers, membranes, nanofiltration, micropollutants, water purification

INTRODUCTION

Recently, the self-assembly of oppositely charged polyelectrolytes has shown itself a very powerful and versatile method to create membranes.[1] In this so-called layer-by-layer (LbL) assembly, a substrate is alternatively exposed to polycations and polyanions to build polyelectrolyte multilayers (PEMs).[2] These multilayers can be coated as a dense separation layer on top of a membrane support. The adsorption process during each LbL step is self-limited because of reversal of the surface charge. Therefore, single polyelectrolyte layers are very thin, down to 0.5 nm.[3,4] This provides the opportunity to coat ultrathin layers for nanofiltration and reverse osmosis applications, which will result in a high water permeability of the layer. The thickness of a single layer, as well as other multilayer properties such as density and charge, can be fine-tuned by many parameters, for example, the chosen polyelectrolytes and the ionic strength or pH of the coating solutions.[4,5] Therefore, PEMs provide many options to optimize membrane performance for specific separation processes.

However, as a PEM is coated on a porous support, a certain thickness of the multilayer is required to close all pores and avoid defects. This means that the main benefit of the PEM, making ultrathin and therefore highly permeable separation layers, is

annulled when the support is completely coated with a dense separation layer. Moreover, the multilayer will grow not only on the outer surface of the asymmetric support but also inside the pores, even if the molecular weight of the polyelectrolytes is larger than the molecular weight cutoff of the support membrane.[6] This is probably a result of the strong repulsion between the charged moieties of the polyelectrolyte, causing the latter to be very elongated in solution with a small effective diameter. Polyelectrolyte deposition in the support pores causes the actual pathway through the multilayer to be substantially longer than the thickness of the multilayer itself. This will lead to very low water permeabilities when closing the pores with a dense PEM. An open PEM will have a higher water permeability but consequently a lower rejection of small solutes.

This problem, of a minimal membrane thickness that defines the maximum permeability that can be reached without changing separation properties, is general in membrane
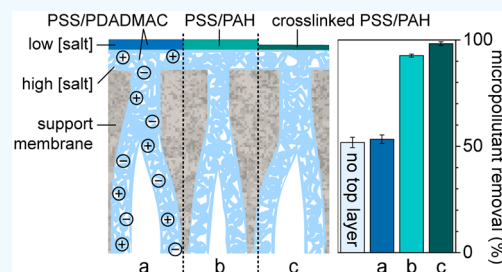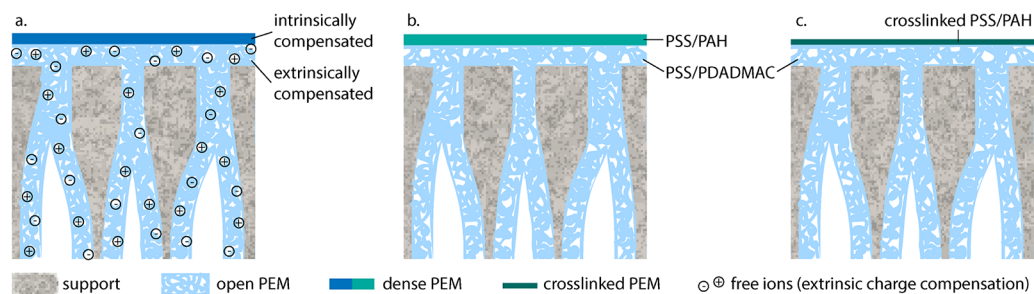
Figure 1. Schematic cross section of the surface of a porous support membrane, asymmetrically coated with open and dense polyelectrolyte multilayers: (a) by decreasing ionic strength during the coating process, (b) by coating different polyelectrolyte pairs, and (c) by coating different polyelectrolyte pairs and selectively cross-linking the top layer for further densification.

technology. For porous ultrafiltration membranes, a minimal membrane thickness is necessary to prevent the membrane from failing under pressure. This trade-off between mechanical strength and permeability was circumvented by applying asymmetry in such membranes. Asymmetric ultrafiltration membranes are thick enough to be mechanically stable, but very open, with a thin separation layer with very small pore size only at one or both of the membrane surfaces. This concept has been proven to be very useful in optimizing membrane processes as it leads to increased solvent permeability without compromising on solute retention. A similar principle was of crucial importance in the development of cost-effective reverse osmosis systems.[7]

To improve the performance of PEM membranes, it is possible to apply the very same concept by using an asymmetric PEM coating. In this approach, a relatively thick but open PEM is coated on the support for closing the pores, and on top of that a thin, dense multilayer is coated to perform the actual separation (Figure 1). This allows us to increase the density of the separation layer while hardly compromising pure water permeability, as we have shown before as a proof of concept.[8] The asymmetric PEM membranes we created showed exceptional performance with 98% micropollutant retention, very low salt retention (10−15%), and 5−10 times higher water permeability than commercial membranes with similar micropollutant removal capabilities. As a follow-up, in this paper we study in a systematic way which methods are most suitable to create a dense top layer and achieve such enhanced performance.

One possible way to tune the density of PEMs is by lowering the ionic strength during the coating process because salt plays a crucial role in polyelectrolyte adsorption. The entropic gain of the release of counterions is the main driving force in the formation of PEMs.[9,10] When more ions are already present in the solution, the entropic gain of counterions upon release is reduced. The result of this is that at higher ionic strengths fewer counterions are released, and thus more counterions remain bound to the polyelectrolyte. For a better clarification, Schlenoff et al. distinguished two types of charge compensation within the multilayer.[4,10] When the charges of the polyelectrolyte are balanced by the oppositely charged polyelectrolyte, this is called "intrinsic charge compensation". The other case, when the polyelectrolyte charges are balanced by counterions, is called "extrinsic charge compensation". In general, multilayers are thicker with increasing extrinsic charge compensation, having a more open structure and more mobile polymer chains.[10,11] For example, the thickness of a multilayer of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(styrene-

sulfonate) (PSS) increases with ionic strength, resulting in lower water permeability. However, at identical total layer thickness, the pure water permeability is lower for layers prepared at lower ionic strength.[6] Thus, at lower ionic strength, much denser PEM layers are formed, with rejections typical for the nanofiltration regime, and thus pore sizes below 2 nm. If one decreases the ionic strength during coating, an intrinsically charge-compensated top layer can be coated on top of an extrinsically charge-compensated layer, which presumably leads to a thin separation layer on top of the PEM (Figure 1a).

Another way to influence PEM density is the choice of polyelectrolyte pair. Krasemann et al. showed that it is possible to obtain denser membranes by using poly(allylamine hydrochloride) (PAH) instead of PDADMAC.[5] The higher density of PSS/PAH layers is probably a result of the higher charge density of the PAH polymer compared with PDADMAC, which leads to a higher number of interactions within the multilayer and thus a smaller effective pore size. Several experimental studies show a correlation between polyelectrolyte charge density and permeation rates of both neutral and charged compounds.[5,12,13] Krasemann et al. proposed that the high flexibility of PAH could be an additional factor in the small effective pore size of multilayers containing PAH.[5] The pore diameter of PSS/PAH membranes was estimated to be 0.34−0.52 nm, comparable to the estimated pore size of some commercial RO membranes (0.2−0.8 nm).[14] Therefore, a PSS/PAH layer could be a suitable dense layer on top of a PSS/PDADMAC layer (Figure 1b).

An additional advantage of coating two different polyelectrolyte pairs on top of each other is that it allows the selective cross-linking of the top layer. In the case of a dense PSS/PAH layer on top of an open PSS/PDADMAC layer, it is for instance possible to cross-link the primary amine groups of PAH with glutaraldehyde.[15] This leads to a further densification of the top layer[15,16] without affecting the PSS/PDADMAC layer that is used to fill the pores of the membrane support (Figure 1c). As a consequence, salt and micropollutant retention can be further improved while water permeability decreases as little as possible. Moreover, the cross-linked top layer will be more resistant toward harsh conditions, such as exposure to surfactants, extreme pH, high temperature, and high osmotic pressure.[15,17] A cross-linked PSS/PAH layer is also fairly resistant toward sodium hypochlorite treatments for membrane cleaning.[18] Because PSS/PDADMAC is by itself very stable and chlorine-resistant,[19] cross-linking of the PSS/PAH top layer contributes to the stability and lifetime of the entire membrane.

An important separation process that needs optimization is the removal of micropollutants from wastewater and surface water. Micropollutants are organic molecules with molecular

weights between 100 and 1000 Da that result from human activity. They involve for example plasticizers, pesticides, and pharmaceuticals, among which are hormones.[20−22] Concentrations of such contaminants in surface waters are increasing[20−25] while micropollutants have the potential to cause long-term harm to humans and the environment.[20] Because micropollutants are small and often uncharged, they are difficult to remove by conventional membranes, which are usually designed to remove larger molecules (ultrafiltration, nanofiltration) or charged species (nanofiltration, reverse osmosis). With the versatility of the PEM coating process, we have the possibility to design and optimize PEM membranes specifically for micropollutant removal.[8]

In this paper we investigate pure water permeability, salt retention, and micropollutant retention of asymmetric PEM membranes that are built via different strategies. We coated hollow fiber supports with several layers of PSS/PDADMAC at high ionic strength and subsequently monitored the effect of different top layers, depending on the polyelectrolyte pair or ionic strength. Finally, we also examined separation properties of a selectively cross-linked PSS/PAH top layer on a PSS/PDADMAC bottom layer.

■ EXPERIMENTAL SECTION

Chemicals. Poly(diallyldimethylammonium chloride) (PDADMAC, Figure 2a, 200−350 kDa, 20 wt % in water) and poly(styrene-
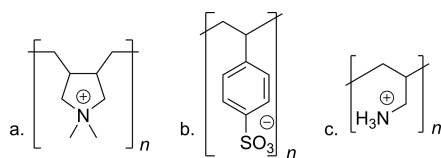

Figure 2. Polyelectrolytes used in this study: (a) poly(diallyldimethylammonium chloride), (b) poly(styrenesulfonate), and (c) poly(allylamine hydrochloride).

sulfonate) (PSS, Figure 2b, 200 kDa, 30 wt % in water) were obtained from Sigma-Aldrich. Poly(allylamine hydrochloride) (PAH, Figure 2c, 150 kDa, 40 wt % in water) was obtained from Nittobo Medical, Japan. Glutaraldehyde (25 wt % in water) was obtained from Alfa Aesar-Thermo Fisher. Sodium chloride was obtained from AkzoNobel, sodium sulfate from Merck, and sulfamethoxazole from Fluka. All other chemicals were obtained from Sigma-Aldrich.

Reflectometry. Optical reflectometry was performed as described by de Grooth et al.[26] Adsorption was calculated by using $dn/dc_{PSS} = 0.18$ mL/g, $dn/dc_{PDADMAC} = 0.18$ mL/g, and $dn/dc_{PAH} = 0.21$ mL/g[27] and the corresponding Q-factors of 30 for PSS and PDADMAC and 26 for PAH.

For switching to a different ionic strength, after eight layers the wafer and flow cell were extensively rinsed with a salt solution corresponding to the new ionic strength (5 or 50 mM NaCl). After stabilization of the signal, this signal was used as the new S_0 value to calculate adsorption of the subsequent layers.

Layer-by-Layer PEM Coating. Polyelectrolyte multilayers were coated on a porous hollow fiber support (tight positively charged ultrafiltration membranes, MWCO 10 kDa, inner diameter 0.7 mm, NX Filtration, The Netherlands). The fibers were first rinsed in NaCl solution before being completely immersed for 15 min in the first polyelectrolyte solution (PSS). After each polyelectrolyte coating step, the membranes were rinsed 3 × 5 min in three subsequent NaCl solutions. All polyelectrolyte solutions contained 0.1 g/L of polyelectrolyte and 5, 50, or 500 mM NaCl. The NaCl concentration of the rinsing solutions always corresponded to the salt concentration in the polyelectrolyte solutions. To produce asymmetric multilayers, after 13 layers the membranes were still rinsed twice in the corresponding

rinsing solutions and subsequently rinsed twice in the rinsing solutions of the subsequent set of coating solutions. Coating at the new conditions was then continued as before.

After each PSS coating step and rinsing twice, a set of four membranes was taken out of the coating process and immersed in 15 wt % glycerol solution for at least 4 h. The membranes were subsequently dried overnight, and single membranes were potted in 20 cm long modules for characterization (details can be found in Figure S1 and the accompanying text).

All membranes in Figure 4 were prepared in one batch (from the same batch of PSS/PDADMAC 13 layer membranes). The membranes in Figure 7 were prepared as a different batch, in slightly different conditions: the PAH solution was adjusted to pH 5.0, and the membranes were coated by a dip-coating machine. Also for the membranes in Figures S2b and S4, the PAH solution was adjusted to pH 5.0. Standard errors as depicted in the figures are standard errors within the given batch of membranes. Membranes prepared from different batches might have slightly different characteristics.

As a result of the complete immersion in the polyelectrolyte and rinsing solutions, both the inner and outer surfaces of the hollow fibers are coated with the PEM. However, because the membranes have a much smaller pore size at the inner surface, only at this surface a defect-free separation layer will be formed.

Cross-Linking. To (selectively) cross-link PSS/PAH layers, membranes were immersed in 7.5 mM glutaraldehyde solution for 1, 3, or 5 h and rinsed 3× in demineralized water before immersion in glycerol solution and subsequent drying.

Membrane Characterization. Membranes with a PSS/PDADMAC bottom layer were analyzed by using a crossflow setup equipped with an Ismatec ISM895 gear pump and a Micropump L19735 pump head. Salt and micropollutant retentions were determined at a crossflow velocity of 1.0 m/s at 2.0 bar. To measure pure water permeability, the crossflow setup was equipped with an additional dispensing pressure vessel (Amicon) and operated at a total pressure of 2.8−5.4 bar (depending on the number of polyelectrolyte layers) and a crossflow velocity of 0.5 m/s. For the cross-linked membranes and pure PSS/PAH membranes, a crossflow setup was operated by a rotary vane pump (BN71B4 pump motor, Bonfiglioli, Italy; IMTI 1.5M inverter, Electroil, Italy; PA411 pump head, Fluid-o-Tech, Italy). For permeability measurements it was operated at 3.8 bar and a crossflow velocity of 2.2 m/s and for salt and micropollutant retentions at 2.0 bar and 1.0 m/s. For PSS/PAH membranes (Figure S2), the same setup was operated at 3.7 bar and a crossflow velocity of 2.2 m/s for permeability measurements and for salt and micropollutant retentions at 1.7 bar and 5.6 m/s. Feed and permeate salt concentrations were measured with a WTV 3210 conductivity meter.

To measure micropollutant retentions, a cocktail was prepared containing 3 mg/L of each of the micropollutants (atenolol, atrazine, bezafibrate, bisphenol A, bromothymol blue, naproxen, phenolphthalein, and sulfamethoxazole) and adjusted to pH 5.8. Process conditions were the same as for the salt retentions. The separation process was allowed to stabilize o/n while leading permeate back into the feed to make sure that the permeation of micropollutants is not influenced by adsorption. Subsequently, around 2 mL of permeate was collected from each module, and a calibration range was prepared from the feed. All samples were separated by UHPLC (Dionex Ultimate 3000, water/acetonitrile, 0.1% phosphoric acid) over a Thermo Scientific Acclaim RSLC 120 C18 column (2.2 μm, 2.1 × 100 mm), and micropollutant concentrations were determined via UV/vis detection at 225 nm and bromothymol blue at 430 nm.

Scanning Electron Microscopy. Membranes were incubated overnight in demineralized water and then incubated for 1 h in subsequently 25% isopropanol, 50% isopropanol, 75% isopropanol, 100% isopropanol, 25% n-hexane in isopropanol, 50% n-hexane in isopropanol, 75% n-hexane in isopropanol, and 100% n-hexane (percentages in vol %). The membranes were then dried under ambient conditions.

The membranes were prepared for cross-section imaging by freezing them in liquid nitrogen and breaking them. Membrane pieces were then glued on a sample holder with conductive silver paint and dried in a
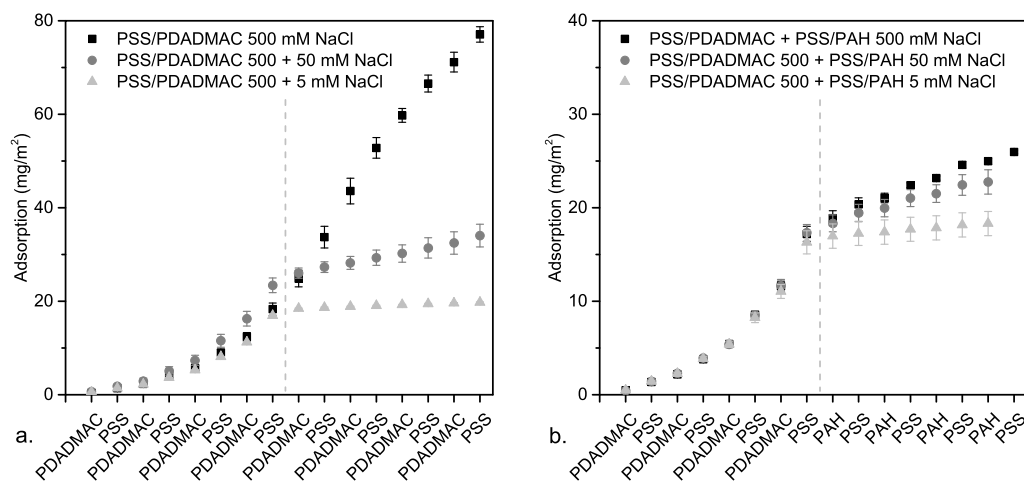
Figure 3. Optical reflectometry of asymmetric PEM buildup, with a PSS/PDADMAC bottom layer coated at 500 mM NaCl and different top layers. (a) PSS/PDADMAC top layers coated at different ionic strengths; (b) PSS/PAH top layers coated at different ionic strengths. By moving to lower ionic strength, or from PSS/PDADMAC to PSS/PAH, significantly less polyelectrolyte is adsorbed, which indicates the formation of thin and possibly dense layers. Error bars: standard error, n = 3.
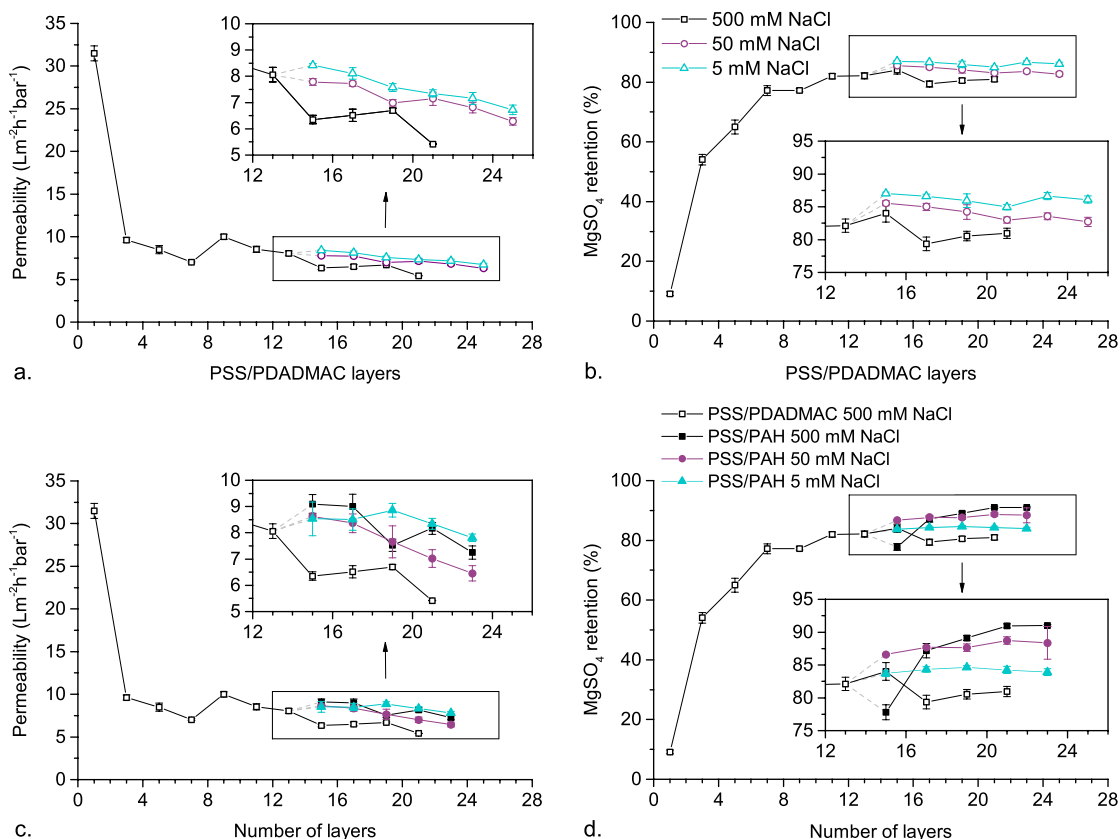

Figure 4. Permeability and MgSO$_4$ retention of PSS-terminated asymmetric multilayers as a function of the total number of layers. The first 13 monolayers are coated with PSS/PDADMAC at 500 mM NaCl, until the pores are closed, as is visible by stabilizing MgSO$_4$ retentions. Coating is continued at 500, 50, and 5 mM NaCl with PSS/PDADMAC (a, b) or PSS/PAH (c, d). Compared with the reference PSS/PDADMAC top layer coated at 500 mM NaCl, all asymmetric layers show an eventually higher permeability and higher MgSO$_4$ retention. Error bars: standard error, n = 4.

vacuum oven at 30 °C. The samples were sputter-coated with 5 nm platinum–palladium and then imaged in a JEOL JSM-7610F field emission scanning electron microscope.

■ RESULTS AND DISCUSSION

Asymmetric PEM Buildup on a Model Surface. The adsorption of polyelectrolytes during PEM buildup can be followed in real time by optical reflectometry. For this purpose we use a flat model surface, a plasma-treated silicon wafer with a thin silicon oxide layer, as a substrate. Figure 3 shows the reflectometry results of coating eight monolayers PSS/PDADMAC at 500 mM NaCl and subsequently eight monolayers of PSS/PDADMAC or PSS/PAH at 500, 50, or 5 mM NaCl. We chose to work with these salt concentrations
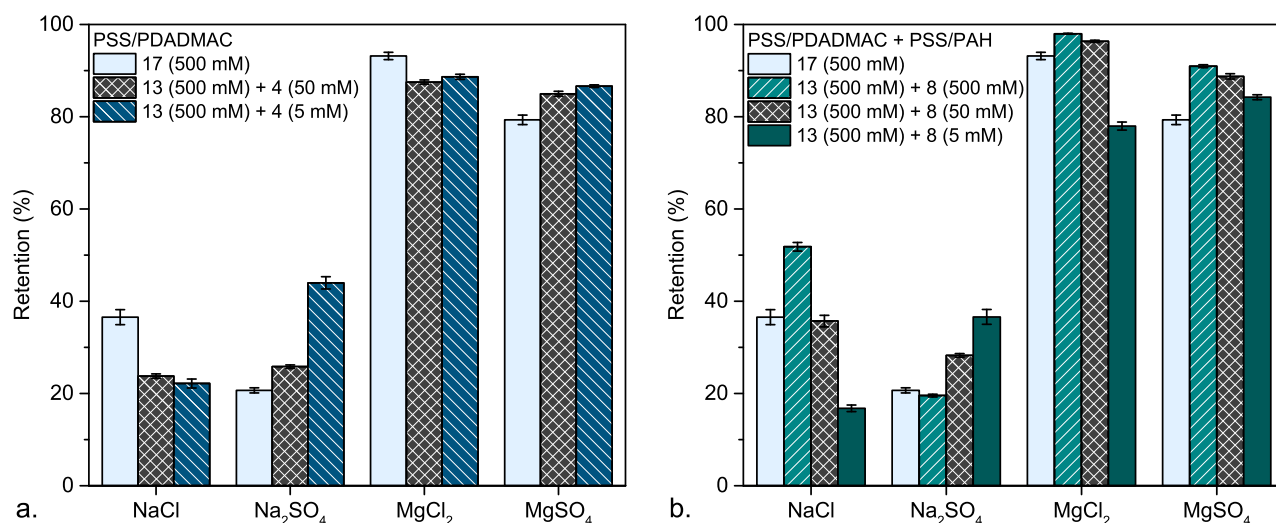
Figure 5. Salt retention properties of asymmetric PEM membranes with different top layers on 13 monolayers of PSS/PDADMAC coated at 500 mM NaCl, in comparison with PSS/PDADMAC multilayers fully coated at 500 mM NaCl. (a) PSS/PDADMAC top layers coated at different ionic strengths. (b) PSS/PAH top layers coated at different ionic strengths. Top layers coated at high ionic strength show typical charge separation (Donnan exclusion) patterns, whereas top layers coated at low ionic strength show an increase in retention with increasing ion size and valency. Error bars: standard error, $n = 4$.

because they were used before working on PSS/PDADMAC multilayers and were found to show significant differences in layer growth and properties,[6] as a result of different balances between intrinsic and extrinsic charge compensation.

The first eight layers show exponential growth as is typical for PSS/PDADMAC coated at high ionic strength.[6] The adsorption of polyelectrolyte material decreases when we lower the ionic strength or switch to PSS/PAH, which leads to a linear growth regime as described before for these coating conditions.[6,28] For the PSS/PDACMAC top layer coated at 5 mM NaCl, 20 times less material is adsorbed onto the bottom layer than for the control layer coated at 500 mM NaCl. For the PSS/PAH top layer coated at 5 mM NaCl, even 26 times less material is adsorbed than for the control PSS/PDADMAC layer. The difference in thickness between these different top layers is expected to be even larger than these numbers because the layers coated at high ionic strength are expected to be more open, i.e., swollen, than the ones coated at low ionic strength.[4] This shows that besides being beneficial for the membrane properties, asymmetric coating is also efficient because pore closure can be achieved in fewer steps compared with coating of the dense layer only. The most important conclusion, however, is that the PSS/PDADMAC bottom layer does not interfere with the adsorption of a thin top layer in these experiments. This demonstrates that asymmetric adsorption is feasible and could be performed on membrane supports as well.

Permeability and MgSO₄ Retention. We coated positively charged poly(ether sulfone) hollow fiber membranes to investigate the permeation and separation properties of the asymmetric PEM layers. The hollow fiber membranes were coated with 13 monolayers of PSS/PDADMAC at 500 mM NaCl and subsequently with several layers of the different polyelectrolyte pairs at different ionic strengths. Layer buildup was followed by monitoring the pure water permeability and magnesium sulfate retention for each odd number of layers, which are the ones terminated by a PSS layer (Figure 4). PEMs with a negatively charged surface are of more interest than the positively charged ones because they are less prone to fouling,[29]

and in the case of PSS/PDADMAC they show better separation properties.[6]

Coating the supports with the PSS/PDADMAC bottom layer at 500 mM NaCl leads to a quick initial decrease of the permeability, while the MgSO₄ retention increases. After nine layers, however, the permeability increases again, which is probably caused by positive charge accumulation in the multilayer. PDADMAC is well-known for its large degree of overcompensation and interpenetration during multilayer buildup, such that PSS after several layers cannot completely compensate for the positive charge deep in the multilayer.[30,31] The resulting excess of PDADMAC in the layer could explain the increase in permeability after several layers because it leads to a more open structure compared with layers that are completely neutralized with PSS[6] as of swelling due to repulsion between the excess positive charges. Upon further coating, the permeability decreases again as thickness is increasing.

After 13 layers, the MgSO₄ retention does not further increase, which indicates that the support pores are now fully closed by the PEM. Therefore, we continued the adsorption of the different top layers at this point. However, regarding the MgSO₄ retention that hardly increases after seven layers, for an optimal coating process it might be very well possible to coat the top layer on only seven layers of PSS/PDADMAC. Remaining defects will then be closed by the top layer.

For the PSS/PDADMAC top layers coated at 50 or 5 mM NaCl, the permeability decreases more slowly than for the reference layer that was further coated at 500 mM NaCl. This is expected as these layers consist of less material (see Figure 3) and are therefore likely to be thinner. At the same time, the higher MgSO₄ retention indicates that these layers are denser. These results immediately show that the concept of asymmetric PEMs can lead to higher permeability and selectivity at the same time.

When applying a top layer of PSS/PAH, the permeabilities are slightly higher than for PSS/PDADMAC top layers and not very dependent on ionic strength. Again, also the MgSO₄ retention is improved in comparison with the PSS/PDADMAC bottom layer, which can be explained by the higher density of PSS/PAH.
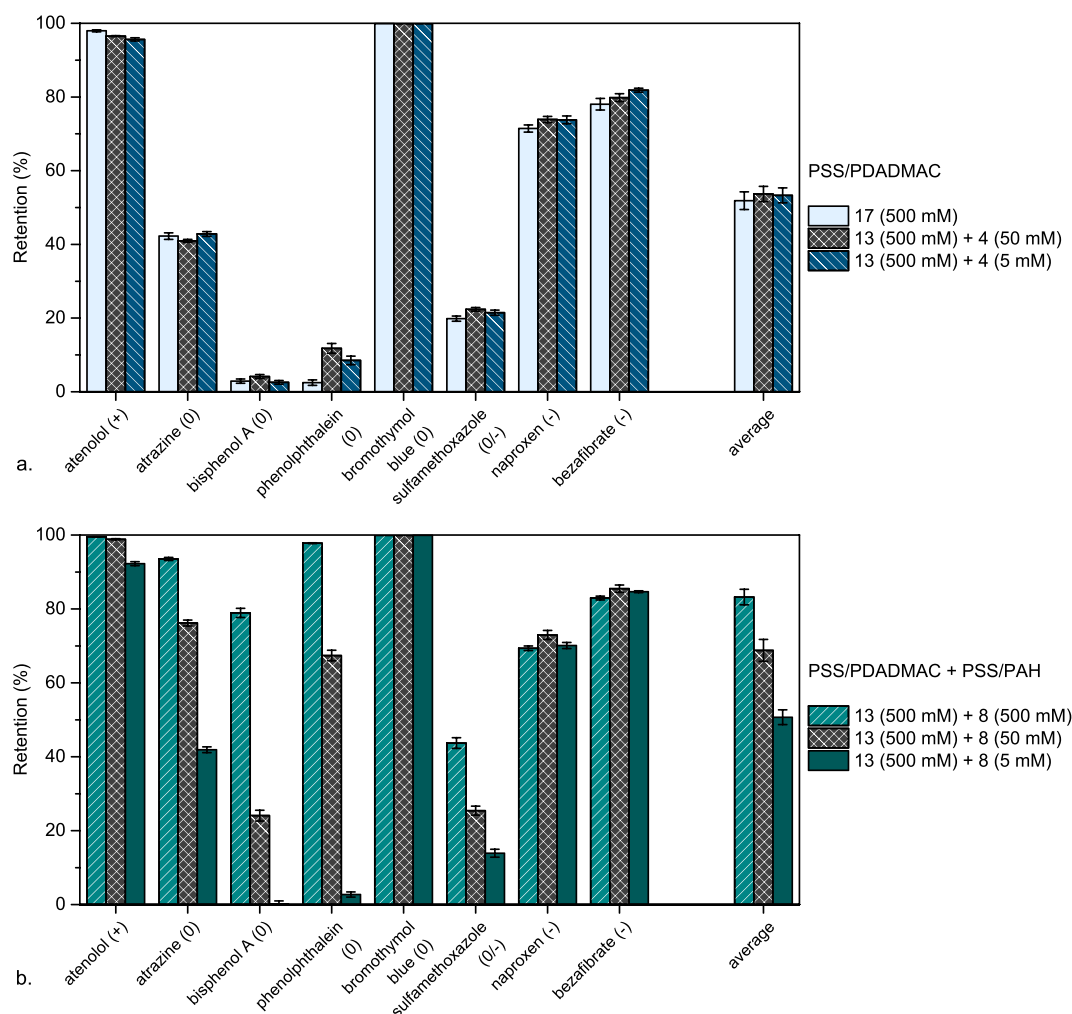
Figure 6. Micropollutant retention of PEM membranes with different top layers on 13 monolayers of PSS/PDADMAC coated at 500 mM NaCl: (a) PSS/PDADMAC top layers; (b) PSS/PAH top layers. Micropollutants from left to right: atenolol (MW 267), atrazine (MW 216), bisphenol A (MW 228), phenolphthalein (MW 318), bromothymol blue (MW 624), sulfamethoxazole (MW 253), naproxen (MW 229), and bezafibrate (MW 361). Only by coating a PSS/PAH top layer at 50 or 500 mM NaCl, a significant improvement in micropollutant retention is obtained. Error bars: standard error, $n = 4$.

The highest $MgSO_4$ retentions, over 90%, are reached when the top layer is coated at 500 mM NaCl. This might be a result of the large degree of extrinsic charge compensation, leading to high excess charge in the multilayer and thus stronger repulsion of charged species. This effect is known as Donnan exclusion. Another possible explanation is that at low ionic strength the small amount of adsorbed polyelectrolyte moves into the very open and mobile surface of the extrinsically compensated PSS/PDADMAC bottom layer before being immobilized by electrostatic interactions, rather than forming a layer on top of it. Such mixing of the top and bottom layer would reduce the density of the top layer.

To summarize, these first results show that permeability and retention can be increased at the same time by introducing asymmetry in the separation layer. Therefore, we continue by monitoring how this asymmetry affects the retentions of different kinds of solutes.

Mono- and Divalent Salt Retention. The separation properties of the different top layers were further explored by monitoring the retention of different salts. This was done for the top layers consisting of four and eight monolayers for the PSS/PDADMAC and PSS/PAH top layers, respectively (Figure 5).

The results show that the separation properties are largely determined by charge. All multilayers contain an excess of positive charge, as the retentions for the divalent positively charged Mg^{2+} ions are higher than for the monovalent Na^+ ions. This is expected because of the charge overcompensation by PDADMAC.[30,31] Also in PSS/PAH an excess positive charge is commonly present in the internal layer, even if the multilayer is terminated with PSS.[32] Furthermore, the top layers coated at high ionic strength show typical charge separation properties as the retentions for the divalent negatively charged SO_4^{2-} ions are slightly lower than for the monovalent Cl^- ions, meaning that more negatively charged species are more easily traveling through the positively charged multilayers even if they are larger. Ion separation properties are thus determined by Donnan exclusion and not by layer density. When coating the top layer at lower ionic strength, in contrast, the retentions of the bulky SO_4^{2-} ions are becoming higher than the Cl^- retentions, especially in the case of PSS/PAH coated at 5 mM NaCl. This could be caused not only by influences of size exclusion mechanisms but also by dielectric exclusion. Coating at lower ionic strength leads to a lower density of excess charge,[30] which

is expected to decrease the hydration of the layer, leading to a higher density and lower dielectric constant.

For all salts, there is at least one top layer available that improves retention in comparison with the reference PSS/PDADMAC top layer coated at 500 mM NaCl. The highest NaCl, MgCl$_2$, and MgSO$_4$ retentions are reached with the PSS/PAH top layer coated at 500 mM NaCl. This is probably the combined result of the higher density of PSS/PAH and high excess positive charge in the layer because it is coated at high ionic strength. For Na$_2$SO$_4$, retentions go up for top layers coated at lower ionic strength, likely because of a lower density in excess positive charge, such that SO$_4^{2-}$ ions are not dragged into the layer as strongly. Additionally, this lower charge density might increase SO$_4^{2-}$ retention via size and dielectric exclusion as mentioned above.

So although our asymmetric membranes with dense top layers are designed for the optimization of size exclusion processes, positive effects are seen in ion retention as a result of asymmetric layer buildup, even though the separation mechanism for these ions is mainly charge based and not size based. Asymmetric layers can therefore be used to improve ion retentions along with the water permeability of the membrane.

Micropollutant Retention. We can learn much more about size exclusion of the different top layers by monitoring the retentions of a micropollutant cocktail. Our cocktail contains different charged and neutral molecules with a molecular weight range between 200 and 700 Da (Table S1); most of them are actual pharmaceuticals, and other compounds that can be found in waste or surface water. The neutral micropollutants allow us to look at size separation without charge exclusion involved and thus give us a better idea of the density, or effective pore size, of the different separation layers.

The PSS/PDADMAC membranes coated at 500 mM NaCl show highly variable micropollutant retentions (Figure 6a). Retentions of the charged species are reasonable, in agreement with the high magnesium retentions, especially the positively charged atenolol is retained well. Bromothymol blue is retained completely likely because it is much larger than all the other micropollutants. However, the other neutral micropollutants show low, some even negligible retentions. Apparently, the effective pore size of the PSS/PDADMAC multilayer is not sufficient to retain molecules with a molecular weight in the range 200−400 Da. Similar results are found when a top layer is applied at 50 or 5 mM NaCl. The average micropollutant retention, just above 50%, does not change significantly, even though a higher density of the top layer and thus better separation properties were expected. Therefore, these results suggest once more that the thin top layer mixes with the highly mobile PSS/PDADMAC bottom layer, such that the properties of the top layer disappear.

A similar approach with PSS/PAH for the bottom and top layers instead of PSS/PDADMAC might be a solution to this problem because PSS/PAH is known to form well-defined layers with little polyelectrolyte mobility.[33] Reflectometry measurements support this low mobility as the layers are growing linearly (Figure 3b and Figure S2a); during adsorption, interpenetration of the layers must therefore be limited. However, when symmetric PSS/PAH membranes coated at 500 mM NaCl are compared with asymmetric ones with a top layer coated at 5 mM NaCl, similar effects are obtained as for the PSS/PDADMAC membranes (Figure S2b). While the water permeability increases with 30%, the average micropollutant retention is not significantly different for the asymmetric PSS/PAH

membrane compared with the symmetric one. Taken together with the higher permeability and the reflectometry results of both asymmetric PSS/PDADMAC and asymmetric PSS/PAH multilayers, it seems that the strategy of decreasing ionic strength does not lead to a denser top layer, but only to a thinner layer. Apparently, the density of the top layer is affected by the bottom layer. Although the PSS/PAH bottom layer is much less mobile than a PSS/PDADMAC bottom layer, it seems that still some mixing of the top and bottom layer takes place, either by adsorbed polyelectrolyte moving into the open bottom layer or by counterions from the bottom layer moving into the top layer. Consequently, the density of the small amount of material in the top layer decreases, such that the top layer hardly contributes to the overall separation properties.

In contrast to the minimal changes that can be made by coating a top layer at low ionic strength without changing polyelectrolyte pairs, a top layer of PSS/PAH on PSS/PDADMAC can significantly improve micropollutant retentions as shown in Figure 6b. However, this is only the case when the PSS/PAH layer is coated at sufficiently high ionic strength. When the top layer is coated at 5 mM NaCl, the micropollutant retentions are equal to those of the PSS/PDADMAC bottom layer (51% on average), indicating that interpenetration between the top and bottom layer is still a problem when the top layer is very thin. As a consequence, the best micropollutant retentions are obtained for the PSS/PAH top layer coated at 500 mM NaCl. This top layer leads to a tremendous increase of the micropollutant retention, in particular the retention of neutral micropollutants, to 83% on average. This shows that the separation properties of PSS/PAH multilayers (Figure S2b) can be successfully applied on top of a PSS/PDADMAC layer. We imaged this layer by scanning electron microscopy (SEM). Although the asymmetry in the layer cannot be visualized via this method, the images confirm the presence of a dense, defect-free PEM of around 100 nm in thickness (Figure S3).

The permeability of these membranes (8.2 ± 0.2 L m^{-2} h^{-1} bar^{-1}) is higher than for the ones coated with PSS/PDADMAC at 500 mM NaCl only (5.42 ± 0.01 L m^{-2} h^{-1} bar^{-1}, Figure 4). This is probably a result of the total thickness of the layer. PSS/PDADMAC layers are thicker than PSS/PAH layers, which is reflected by the larger adsorption of material per layer (Figure 3) and also observed via SEM (Figure S3). As a result, the permeability decreases faster with the number of layers. Here, this effect apparently overrules the effect of the larger density of PSS/PAH.[5]

Thus, decreasing the ionic strength during the coating process turns out to have no influence on micropollutant retention. However, a large improvement can be made by coating a high density polyelectrolyte pair as a top layer. We argue that polyelectrolytes from the top layer could penetrate into the open bottom layer during the coating process or that counterions from the extrinsically compensated bottom layer could move into the top layer, such that the intrinsic charge compensated properties of the top layer largely disappear. This problem can be circumvented by using a different polyelectrolyte pair for the top layer, with a higher density at the same ionic strength. Assuming that mixing only takes place at the surface of the bottom layer, this would still lead to the formation of a denser top layer if enough material of the denser polyelectrolyte pair is adsorbed. Another possibility is that less mixing takes place when coating the top layer at high ionic strength, because more material is adsorbed.
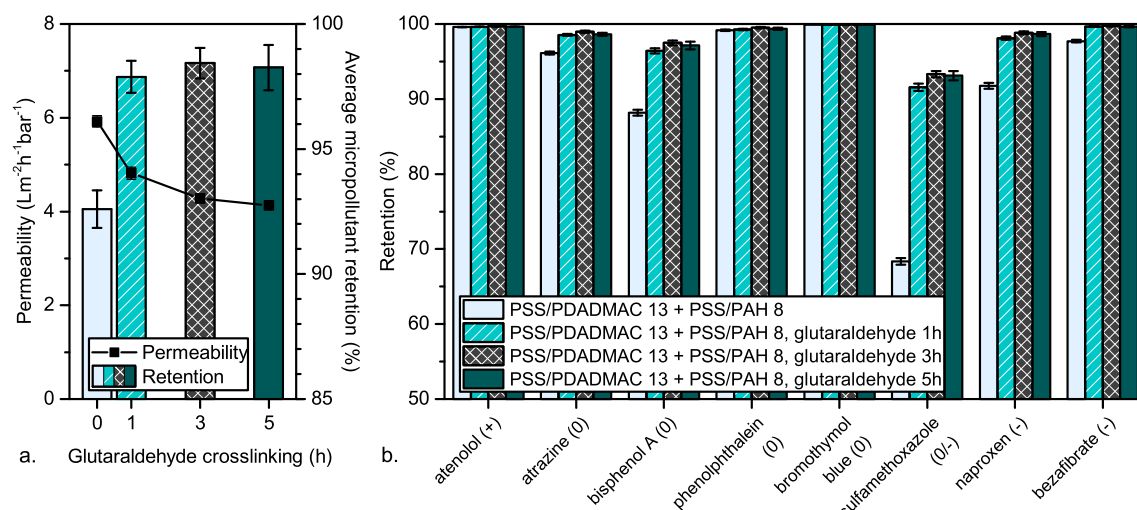
Figure 7. Pure water permeability and micropollutant retention of PSS/PDADMAC + PSS/PAH membranes, coated at 500 mM NaCl and cross-linked in 7.5 mM glutaraldehyde. (a) Pure water permeability and average micropollutant retention. (b) Micropollutant retention for separate micropollutants. From left to right: atenolol (MW 267), atrazine (MW 216), bisphenol A (MW 228), phenolphthalein (MW 318), bromothymol blue (MW 624), sulfamethoxazole (MW 253), naproxen (MW 229), and bezafibrate (MW 361). While the water permeability decreases only 20−30% upon cross-linking, the permeation of micropollutants is reduced with 70%. Error bars: standard error, $n = 4$.

Cross-Linking of the PSS/PAH Top Layer. Selective cross-linking of the PSS/PAH layer coated at 500 mM NaCl is expected to lead to an even denser top layer and therefore further enhanced micropollutant retentions, without affecting the permeability of the bottom layer. Therefore, new PSS/PDADMAC + PSS/PAH membranes were produced as before and incubated in 7.5 mM glutaraldehyde for 0, 1, 3, or 5 h. The characteristics of these membranes are shown in Figure 7. The new un-cross-linked membranes turn out to be slightly denser than the previous set, having a higher micropollutant retention (93% on average) and a lower pure water permeability than before (5.9 ± 0.1 L m^{-2} h^{-1} bar^{-1}) due to a slightly different preparation procedure. The pure water permeability, however, is still higher compared with membranes coated with 21 layers PSS/PDADMAC (5.42 ± 0.01 L m^{-2} h^{-1} bar^{-1}, Figure 4). The permeability decreases with cross-linking time, but not dramatically, as it stays above 4 L m^{-2} h^{-1} bar^{-1}. Our results (Figure S4) and other studies have shown that layers completely consisting of PSS/PAH decrease 40−90% in permeability upon glutaraldehyde cross-linking.[17,18] For our membranes, pure water permeability decreases only 20−30% after cross-linking. We argue that this is a result of the PSS/PDADMAC bottom layer that is not cross-linked by glutaraldehyde such that the major part of the PEM layer stays very open and permeable.

As expected, cross-linking increases salt retentions (Figure S5) and micropollutant retentions (Figure 7) of the asymmetric layer, showing that the PSS/PAH separation layer indeed becomes denser. After only 1 h of cross-linking, all micropollutant retentions are already above 90%, and upon longer incubation in glutaraldehyde hardly any further increase can be obtained. On average, the non-cross-linked membranes retain micropollutants for 93%, while 98% is retained after 1 h of cross-linking. This single hour of cross-linking is thus enough to reach 70% lower total passage of micropollutants, while the pure water permeability is decreased by only 20%. Moreover, we expect the cross-linked membranes to be more resistant toward harsh conditions such as extreme pH, high osmotic pressure, and exposure to surfactants.[15,17] Thus, although the membranes presented in this work do not show better separation properties

than the asymmetric membranes we previously reported,[8] we expect that these cross-linked membranes are much more chemically stable, which is a large advantage in certain applications.

In comparison with membranes coated purely with PSS/PDADMAC at high ionic strength (52% average micropollutant retention, Figure 6a), the application of the 1 h cross-linked PSS/PAH top layer even leads to a 96% decrease in total micropollutant passage, with only 13% loss of water permeability for membranes with the same number of layers in total. These results emphasize the tremendous improvement in selectivity that can be made by the application of an asymmetric PEM coating, instead of a regular PEM coating.

■ CONCLUSION

We explored the efficiency of asymmetric PSS/PDADMAC and PSS/PAH multilayer membranes for nanofiltration applications. The asymmetric PEM coating concept involves coating a thin and dense polyelectrolyte multilayer on top of an open multilayer that closes the support pores, such that the separation properties are improved while only slightly compromising on water permeability. Indeed, we showed that asymmetric layers can improve salt and micropollutant retention. Even the permeability of the membranes is slightly improved compared with fully open layers because of the smaller increment in thickness when coating dense layers. However, these differences are small when coating a top multilayer at low ionic strength on a bottom multilayer coated at high ionic strength, probably because the top layer is mixing into the bottom layer. In contrast, a vast improvement in micropollutant retention is obtained when coating PSS/PAH on top of PSS/PDADMAC at high ionic strength. Moreover, this approach allows for selective cross-linking of the top layer with glutaraldehyde, which further improves micropollutant retention while water permeability is only slightly compromised. We therefore conclude that asymmetric coating, especially with two different polyelectrolyte pairs, has a lot of potential for the development of efficient PEM membranes for different applications, such as micropollutant removal and desalination.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.9b01038.

> Micropollutant details, module fabrication details, asymmetric PSS/PAH layer data, PEM membrane SEM images, permeability of cross-linked PSS/PAH membranes, and salt retention of cross-linked asymmetric membranes (PDF)

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■ ABBREVIATIONS

PEM, polyelectrolyte multilayer; LbL, layer-by-layer; PSS, poly(styrenesulfonate); PDADMAC, poly(diallyldimethylammonium chloride); PAH, poly(allylamine hydrochloride); UHPLC, ultrahigh performance liquid chromatography, SEM, scanning electron microscopy.

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