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Multifunctional polyelectrolyte multilayers as nanofiltration membranes and as sacrificial layers for easy membrane cleaning

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ABSTRACT

This manuscript investigates the modification of an ultra-filtration (UF) membrane support with polyelectrolyte multilayers (PEMs) consisting of the weak polyelectrolytes poly(allyl amine) hydrochloride (PAH) and poly(acrylic acid) (PAA). These prepared polyelectrolyte multilayer membranes have a dual function: They act as nanofiltration (NF) membranes and as sacrificial layers to allow easy cleaning of the membranes. In order to optimize the conditions for PEM coating and removal, adsorption and desorption of these layers on a model surface (silica) was first studied via optical reflectometry. Subsequently, a charged UF membrane support was coated with a PEM and after each deposited layer, a clear increase in membrane resistance against pure water permeation and a switch of the zeta potential were observed. Moreover these polyelectrolyte multilayer membranes, exhibited rejection of solutes in a range typical for NF membranes. Monovalent ions (NaCl) were hardly rejected (<24%), while rejections of >60% were observed for a neutral organic molecule sulfamethoxazole (SMX) and for the divalent ion SO_3^{2-}. The rejection mechanism of these membranes seems to be dominated by size-exclusion. To investigate the role of these PEMs as sacrificial layers for the cleaning of fouled membranes, the prepared polyelectrolyte multilayers were fouled with silica nano particles. Subsequent removal of the coating using a rinse and a low pressure backwash with pH 3, 3 M $NaNO_3$ allowed for a drop in membrane resistance from $1.7 \cdot 10^{14} \, m^{-1}$ (fouled membrane) to $9.9 \cdot 10^{12} \, m^{-1}$ (clean membrane), which is nearly equal to that of the pristine membrane ($9.7 \cdot 10^{12} \, m^{-1}$). Recoating of the support membrane with the same PEMs resulted in a resistance equal to the resistance of the original polyelectrolyte multilayer membrane. Interestingly, less layers were needed to obtain complete foulant removal from the membrane surface, than was the case for the model surface. The possibility for backwashing allows for an even more successful use of the sacrificial layer approach in membrane technology than on model surfaces. Moreover, these PEMs can be used to provide a dual function, as NF membranes and as a Sacrificial coating to allow easy membrane cleaning.

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1. Introduction

Fouling of surfaces and interfaces is a well-known and often studied problem in colloid and interface science. Irrespective of the anti-fouling strategies employed, all surfaces will eventually become fouled under adverse conditions [1]. Fouling is an especially crucial issue in membrane technology [2]. Separation processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are used widely for numerous commercial applications in various fields such as water and wastewater treatment, desalination, the food industry, biotechnology and others [3]. However, fouling is an inherent problem

for all of these membrane processes, causing fluxes to decline and thus leading to a decrease in productivity and/or an increase in energy demand. While the removal of foulants can be performed using various cleaning techniques, cleaning is often found to be incomplete (irreversible fouling) and cleaning can damage the membrane itself. In both cases, the membrane will need to be replaced, which increases the operational cost of the process. Over the years much research has been devoted to develop methods to make the cleaning easier, such as the use of surfactants [4], superhydrophobic coatings with self-cleaning properties [5], nanobubbles [1] and antifouling layers such as polymer brushes [6]. A very different approach to cleaning was proposed a few years ago and was denoted as the "sacrificial layer" approach [7,8]. This sacrificial layer approach involves the precoating of a surface with a nanometer thick polymer layer that upon fouling can be des-

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orbed/sacrificed from the surface along with any attached foulants. Sacrificing the layer is based on a simple trigger i.e. a change in pH, salt concentration or by the addition of a surfactant. The cleaned surface can subsequently be recoated with a new polymer layer to use it again. As this polymer layer inhibits the contact between foulant and the interface, the success of the approach should be independent of the type of foulant. Additionally when polymers are coated on an interface, it results in a change in the surface properties of the interface. The sacrificial layer coating could thus have additional benefits such as antifouling or anti adhesive properties. We strongly believe that the sacrificial layer approach is also ideally suited for membrane applications. Especially as for membranes, the sacrificial layer coating could not only be used for easy cleaning, but could even function as the active separation layer. A schematic representation of this concept on membranes is illustrated in Fig. 1.

To modify the surface of the materials to provide them with the desired properties, a simple and versatile approach is the use of polyelectrolyte layer-by-layer assembly (LbL) [9,10]. This approach involves alternatingly dipping of a substrate in a polycation solution and a polyanion solution, typically with an intermediate rinsing step with solvent to remove loosely bound electrolytes from the surface. This LbL approach allows to prepare polyelectrolyte multilayers (PEMs) of just a few nanometers in thickness on an interface. The possibility to use a wide range of water soluble polyelectrolytes, its easy application, and the ability to apply it on surfaces of any shape and size are the key strengths of this technique. Since its discovery [10], this technique has been proposed for many applications, including drug delivery, solar sensors, lenses, cell engineering, fuel cells, and membrane processes [11]. For membrane processes the PEMs are always coated onto a membrane support, and have been employed for the preparation of both gas [12] and liquid separating membranes [13]. The key strength of the PEM membranes is the large variety of membrane properties that can be achieved by building in a LbL fashion. As such PEM membranes with a wide variety of properties have been produced for use as reverse osmosis membranes [14], nanofiltration membranes [14–18], solvent resistant nanofiltration (SRNF) membranes [19], forward osmosis membranes [20], low fouling membranes [21–26], antiseptic/antibacterial membranes [22,26–28], stimuli responsive membranes [8,29–32] and ion selective membranes [33–36]. Selection of the right combination of polyelectrolytes can also make the membrane sensitive to a certain trigger (such as a change in pH or salt concentration) that leads to a controlled destruction of these PEMs when required [7,37–39]. The above shows that PEMs hold much promise for membrane technology, especially in combination with its use as sacrificial layers. For the polymers to be used as sacrificial layers we need to tune the interaction between the polymers.

The use of one or more polymers bearing weak acid/base functionality affords the possibility of controlling the average charge per repeat unit and thus the extent of interaction between charged polymers [38]. Bruening and co-workers [8] have successfully used a PEMs as both a sacrificial layer and as the separating layer of an NF membrane. However, they chose to use the combination of poly(styrene sulfonate) (PSS) and PAH to create their PEM based NF membranes, a combination of polyelectrolytes that is known to give extremely stable layers. They could only remove or sacrifice their multilayer by physical means, e.g. backwashing at high pressure. To make the sacrificial layer concept work it is key to have a system that is easy to apply, but also easy to remove. For our sacrificial layer approach, we propose to use a system of weak poly electrolytes of which the charge can be easily controlled by the pH [7]. For this study a model system of weak polyelectrolytes PAH and PAA was selected (Fig. 2). In the PAH/PAA system (pKa 9.3 and 5.4 respectively), the dissociation of PAH increases under acidic conditions while the dissociation of PAA increases under basic conditions. Both these sensitivities could be used as triggers to induce PEM desorption.

In this work, we prepare a PEM membrane, where the PEM functions as a selective NF separation layer and as a sacrificial layer for easy membrane cleaning. Initially the growth of PAA/PAH multilayers on model surfaces is studied by optical fixed angle reflectometry under various amounts of added poly electrolyte to determine the optimal growth conditions for the PEMs. Subsequently different triggers were applied to sacrifice these layers, with and without foulants. This allowed us to understand the buildup and removal of the multilayer systems at different conditions, something that cannot be precisely monitored on the membrane itself. Then tight hollow fiber UF membranes were coated with PEMs under identical coating conditions. The membranes were characterized after deposition of each subsequent layer in terms of membrane resistance to pure water permeation and change in zeta potential of membranes. Furthermore, rejection of different solutes was studied to investigate the performance of
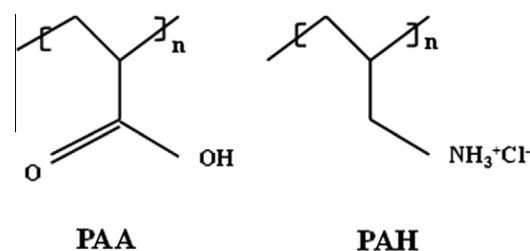

Fig. 2. Polyelectrolytes used for this study PAA poly(acrylic acid) and PAH poly(allyl amine) hydrochloride.
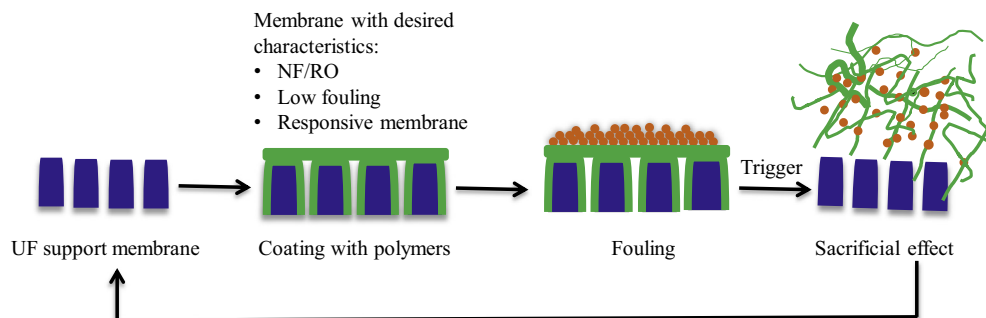

Fig. 1. Schematic representation of the application of a thin polymer film onto a UF support membrane and its subsequent use as a "sacrificial layer" to remove fouling. For membranes the sacrificial layer could act double as the effective separating layer to create NF, RO membranes, and/or to create low-fouling and responsive membranes.

the layer as a nanofiltration membrane. Then membranes ware subjected to foul with Ludox and when the membranes became fouled, membranes were cleaned with a trigger to release the sacrificial layer, indeed leading to full removal of all foulants. The membrane could then be recoated in a simple manner.

2. Materials and methods

2.1. Materials

Polyelectrolytes used in this study were poly(allyl amine) hydrochloride (PAH; M_w = 15,000 g mol^{-1}) and poly(acrylic acid) (PAA; M_w = 15,000 g mol^{-1}). Silica particles (Ludox SM, radius approximately 9 nm) were used as a model fouling agent. Sodium nitrate (NaNO$_3$) was used as a background electrolyte in all solutions. All chemicals were obtained from Sigma–Aldrich (The Netherlands) and were used as received without any further purification. Polyelectrolyte solutions always contained 0.1 g l^{-1} of polymer at a pH of 6, but with various amounts of background electrolyte (5 mM, 50 mM or 500 mM NaNO$_3$). Deionized water (Milli Q, 18.2 MΩ cm) was used to rinse the membranes and to prepare polyelectrolyte and feed solutions. All solutions were used within eight days after preparation.

2.2. Reflectometry studies of PEMs

The adsorption and desorption of PEMs and model foulants (silica particles) onto a silica surface was monitored with fixed-angle optical reflectometry. In reflectometry, measurements are performed under well-defined hydrodynamic conditions using a stagnation point flow cell [40]. It is a sensitive tool to study the alternating adsorption of different polyelectrolytes on flat, reflective surfaces [41]. The reflectometer is equipped with a He-Ne laser (monochromatic light, λ = 632.8 nm) with linearly polarized light. When this monochromatic light hits the wafer around the Brewster angle (71°), it is reflected toward a detector, where the reflected light is split into its parallel (R_p) and perpendicular (R_s) polarized components. The ratio between these two components (R_p/R_s) is defined as the signal S (–) and the change in this ratio (Δs) is directly proportional to the amount of mass adsorbed on the wafer, according to Eq. (1):

$$\Gamma = Q(\Delta S/S_0) \tag{1}$$

where Γ is the amount of mass adsorbed on the silicon wafer (mg m^{-2}), and where Q is a sensitivity factor, which depends on the angle of incidence of the laser (θ), the refractive indices (n), the thicknesses (d) of the layers on the silicon wafer in nanometer, and the refractive index increment (dn/dc) of the adsorbate. To calculate the Q-factor an optical model was used based upon values as used in our previous study [7]. The Q-factor thus obtained to calculate the actual mass adsorption is 30 mg m^{-2} for all of our experiments. S_0 is the starting output signal of the bare silicon wafer immersed in solvent (–). All experiments were performed on a silicon wafer with a 85 nm SiO$_2$ top layer. Before the experiment the silicon surface was cleaned by O$_2$ plasma treatment.

2.3. LbL coating of membranes

Polyelectrolyte layers were deposited on hollow fiber dense ultrafiltration membranes prepared from poly(ether sulfone) with a sulfonated poly(ether sulfone) separation layer. These so-called Hollow Fiber membranes intended for colloidal silica removal were kindly supplied by Pentair X-Flow The Netherlands and have a molecular weight cut-off of 10,000 Da. PEMs were coated on membranes via a dip coating method. For this purpose, fibers were cut

into specific lengths (to make bundles) and kept in 15 wt.% ethanol in water overnight to wet the fibers. After wetting, fibers were rinsed with deionized water three times followed by three times rinsing in the chosen background electrolyte solution (5, 50 or 500 mM NaNO$_3$). For coating, the fibers were completely immersed in 0.1 g l^{-1} polycation solution with the same background electrolyte solution, for 30 min, followed by rinsing three times with the used background electrolyte solution. The rinsing step removes any loosely bound or excess polyelectrolyte from the membrane surface. In the same fashion, the polyanion (PAA) layer was adsorbed to give a single bilayer of PAH and PAA. The dipping procedure was then repeated to give the desired number of layers. By dipping the membranes in the coating solution, PE deposition is not only limited to the inner surface of the membrane but also whole the porous structure can be coated. In theory this approach of also coating the inner structure could lead to problems when backflushing, as the polymer released from the inner structure would need to be flushed through the membrane top layer. While we did not observe such problems in our experiments, we still believe that for the real application dynamic coating from the inner side of the hollow fiber is the preferred option. After each coating step a membrane sample was taken for analysis. Membranes coated with the desired number of layers were immersed in a glycerol/water (15 wt.%/85 wt.%) solution for at least 4 h, followed by a drying step under ambient conditions for at least 8 h. For filtration experiments, PEM coated membrane fibers were potted in a module with a fiber length of approximately 10 cm.

2.4. Membrane characterization

For each prepared membrane, the pure water flux was measured at 20 °C with demineralized water in a dead-end mode at a trans-membrane pressure of 2.5 bar. From the obtained clear water flux the membrane resistance was calculated using Eq. (2):

$$R = \frac{\Delta p}{\mu \times J} \tag{2}$$

where R is membrane resistance in m^{-1}, J the membrane flux in m s^{-1}, μ the dynamic viscosity of the feed in Pa s and P the trans-membrane pressure in Pa. The membrane resistance was measured for two separate coating conditions (5 mM and 50 mM), each measurement was performed in triplet.

The membrane performance was investigated by performing retention experiments on salts (NaCl and Na$_2$SO$_4$) and on a small organic pollutant, sulfamethoxazole (SMX) M_w = 253.28 g mol^{-1} with neutral charge. These retention experiments were carried out in a cross-flow mode with a cross flow velocity of 4 m s^{-1} in order to limit the effect of concentration polarization. The trans-membrane pressure during filtration was 2 bar. This corresponds to a Reynolds number of approximately 3500, and is well in the turbulent regime. The salt concentration was measured with a WTW cond 3210 conductivity meter, while the concentration of the organic molecule was measured using a Dionex Ultimate 3000 U-HPLC system equipped with a RS variable wavelength detector. For the organic molecule, the permeate sample was collected after a minimum of 24 h to ensure steady state rejections. The retention was based on the one minus ratio between the permeate and concentrate concentrations.

The zeta potential measurements were performed with an electrokinetic analyzer SurPASS system (Anton Paar, Graz Austria). The zeta potential was calculated by measuring the streaming current versus the pressure in a 5 mM KCl solution at room temperature using Eq. (3):

$$\zeta = \frac{dI}{dp} \frac{\eta}{\varepsilon\varepsilon_0} \frac{L_s}{A_s} \tag{3}$$

where ζ is the zeta potential (V), I is the streaming current (A), P is the pressure (Pa), η is the dynamic viscosity of the electrolyte solution (Pa s), ε is the dielectric constant of the electrolyte, ε_0 is the vacuum permittivity (F m^{-1}), and A_s is the cross section of the streaming channel (m^2).

2.5. Membrane fouling, cleaning and regeneration

To test the suitability of the PEM as a sacrificial layer, the coated membrane was rinsed with a trigger (pH 3, 3 M) solution for 20 min in a cross flow mode with 2 bar pressure. Removal of the coating was investigated by comparing the resistance before and after rinsing. For experiments with a fouled membrane, a feed solution containing Ludox particles (300 mg l^{-1}) was filtered in dead end mode for 20 h at a pressure of 2.5 bar. Subsequently, the membrane resistance was determined again. After the membrane fouling, the membrane was rinsed with the trigger solution to see if the resistance could be restored to that of the pristine membrane. The rinsing was performed for approximately 20 min in a cross flow mode. In a subsequent experiment the membrane was also cleaned with the trigger solution in a back flush mode for about 30 min. After these cleaning steps, the PEM coating was regenerated with fresh polyelectrolyte solutions in a cross flow mode.

3. Results and discussion

Our results and discussion section is split into three major parts. In the first part, the adsorption and desorption of PAH and PAA multilayers on model surfaces is studied, with and without fouling agents, to determine the optimal coating and cleaning conditions. The second part encompasses the growth of PEM layers on the membrane surface, and describes the performance of the created membranes. In the third and final part we test the PEM as a sacrificial layer for easy membrane cleaning. We stress that the abbreviation PEM refers to Polyelectrolyte Multilayer and not to another common term Polymer Electrolyte Membrane.

3.1. Layer by layer coating and layer removal on model surfaces

3.1.1. Polyelectrolyte multilayer growth

The preparation of a polyelectrolyte multilayer on a silica surface was measured over time using optical fixed-angle reflectometry. This technique enables the real time continuous monitoring of the adsorbed amount of polymer (in mg m^{-2}) during exposure to various solutions. Fig. 3(a) shows typical reflectometry data with step by step growth of a PAA and PAH PEMs on a silica surface. The measurement starts by exposure of the silica surface to a solvent solution (pH 6, 50 mM NaNO$_3$) and provides the measurement baseline (S_0). Then switching to a solution containing the weak cationic polymer PAH (denoted with +, 0.1 g l^{-1}, pH 6, 50 mM NaNO$_3$) leads to a small adsorption to the negatively charged silica. Subsequent exposure to the weak negative polymer PAA (denoted with a −, 0.1 g l^{-1}, pH 6, 50 mM NaNO$_3$) leads to an increased adsorbed amount, with the negative PAA adsorbing to the positive PAH. Continued switching between PAH and PAA exposure leads to a stepwise building of the multilayer. In our system, the pH was kept constant at 6 because at this pH both polyelectrolytes have a similar degree of dissociation and will adsorb in roughly similar amounts [42].

In Fig. 3(b), we show the plateau adsorbed amounts as a function of the adsorbed number of layers. The experiments were done for three different ionic strengths: 5 mM, 50 mM and 500 mM. It is well established that PEM growth and the properties of the resulting layer depend on the ionic strength of the deposition solution and its pH [42–44]. In our work, we thus regard the ionic strength as a control parameter to optimize membrane performance and sacrificial layer properties. Indeed, we find large differences in growth behavior for different ionic strengths. At low ionic strength (5 mM), PEMs grow linearly as compared to 50 mM where the layer growth is exponential. Linear growth of PEMs is associated with a low mobility of chains in the layer, while exponential growth is due to the presence of highly mobile chains [45]. However, at the fairly high ionic strength of 500 mM we can see a distinctly different growth feature of these layers. Initially the growth rate is higher than at 5 mM and 50 mM but after a certain number of steps the growth stops. During PAH injection, quite some polymer adsorbs, but this is then followed by desorption with the introduction of the next polymer (PAA). At this high salt concentration, it seems that PAA is able to complex with PAH, but then desorbs as a (quasi) soluble complex. These effects were also observed for other PEM systems [39].

These initial experiments would indicate that the optimal membrane coating conditions would be around 50 mM NaNO$_3$. At this ionic strength the growth is exponential, resulting in much thicker films in a smaller number of coating steps than is the case with linearly grown LbL thin films (at 5 mM NaNO$_3$). Higher ionic strengths, however, lead to unstable PEMs. Still, the ionic strength could also affect the eventual membrane performance [46] and possibly the performance as sacrificial layer. As such both 5 and 50 mM NaNO$_3$ are studied in coming sections.

3.1.2. Study of triggers for sacrificing PEMs

For the sacrificial layer approach to be successful, it is key to have a good trigger mechanism to completely desorb the layer. PEMs, depending on the used polyelectrolytes, can be erased by
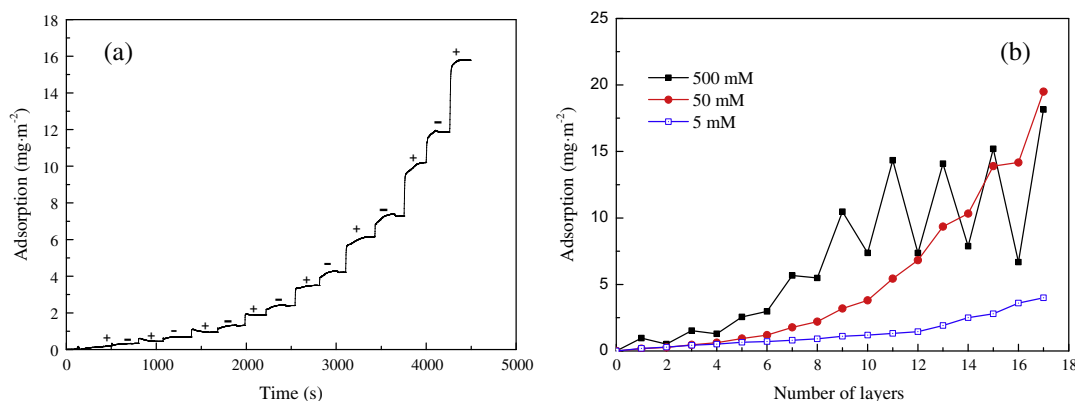

Fig. 3. (a) A typical refelectometry graph showing step by step growth of PEMs from PAH (+) and PAA (−) at 0.1 g l^{-1} in 50 mM NaNO$_3$ and at pH 6. (b) Effect of salt concentration on the growth of PEMs monitored with reflectometry; subsequent adsorption of PAH (+) and PAA (−) at 0.1 g l^{-1} in 5 mM, 50 mM and 500 mM NaNO$_3$.

applying external stimuli such as a change in pH [7,45,47] or an increase in ionic strength [38,39]. However, the stimuli that will completely remove the fouled PEMs from the membrane surface should not damage the polymeric membrane surface. In previous work [7], PAH/PAA multilayers were desorbed by switching to a pH of 1, a trigger unsuitable for membranes. Here we propose to apply, for the first time, the combination of low pH and high ionic strength to desorb polyelectrolyte multilayers. For this study we did not go below pH 3 because lower pH might damage the polymer membrane surface. Simultaneously we increased the salt concentration from 0.05 M to 3 M, with the results shown in Fig. 4. As a reference, we also applied high ionic strength solutions at pH 6. Only the combination of pH 3 and 3 M of NaNO$_3$ resulted in the complete layer removal desired for our application. From these experiments it follows that it is indeed the combination of low pH and high ionic strength that leads to the complete removal of the layer. At low pH, PAA becomes significantly uncharged, the high ionic strength then further weakens the ionic interactions leading to disintegration of the layer.

3.1.3. Effect of layer mass on the performance as sacrificial layer

In Fig. 5(a) we show a reflectometry experiment to study PAH/PAA multilayers as a sacrificial layer for easy cleaning. By subsequent adsorption of PAH and PAA we built up the PEMs, ending in this case with a (cationic) PAH layer. Subsequently, we applied a solution containing our model fouling agent, Ludox silica parti-

cles (0.1 g l^{-1} Ludox, pH 6, 50 mM NaNO$_3$), which are spherical silica particles approximately 9 nm in radius, on top of the PAH layer. As can be seen, these particles lead to a large increase in the adsorbed amount. However, when rinsed with a pH 3, 3 M solution the adsorbed PEMs, along with the fouling agent, are desorbed from the silicon wafer surface again, demonstrating the potential of these PEMs as a sacrificial coating. We applied this trigger for a different number of layers having fouling agent adsorbed on top and after applying the trigger solution we investigated the remaining layer mass. Fig. 5(b) shows the effect of the number of PAH and PAA layers on the residual adsorbed amount, for two different coating conditions, 5 mM NaNO$_3$ and 50 mM NaNO$_3$. At both coating conditions the residual adsorption decreases with an increasing number of layers. For polyelectrolyte layers built at low salt concentration, 5.5 bilayers (PAH/PAA) are sufficient to obtain complete desorption.

Here the role of the number of layers (layer mass) on the performance as a sacrificial layer is important to consider because the polyelectrolytes that are released into the solution upon destruction of the layers are expected to act as so-called anti-redeposition agents. By adsorbing to the released fouling agents they act to prevent possible re-adsorption of the fouling agents on the surface [7]. However other than layer mass, we can also see the role of the layer structure on the sacrificial layer performance. For an ionic strength of 50 mM the residual adsorbed amount decreases with increasing layer mass but complete desorption is never obtained. A very small amount (0.1 mg m^{-2}) is left on the surface. We hypothesize that this is because of the high mobility of the polymer chains in this layer, connected to the exponential growth regime at this ionic strength. Such mobility would allow some of the highly charged silica particles to penetrate into the layer and to reach the interface. Still, the remaining adsorbed amount is very low. Our results indicate that both the 5 and the 50 mM grown PAA/PAH PEMs have the potential to function as a sacrificial layer coating on membranes.

3.2. Formation and properties of a polyelectrolyte multilayer membrane

After optimizing the coating and release conditions for PEMs with reflectometry, negatively charged UF membranes were coated with PAH/PAA multilayers via a dip coating method. Change in water permeance (l m^{-2} h^{-1} bar^{-1}) through the membrane after deposition of the layer is one of the ways to see if the PEMs are being deposited. Reduction in permeability with every deposited layer (mass) corresponds to an increase in the membrane hydraulic resistance (Eq. (1)). To confirm the deposition of PEMs on mem-
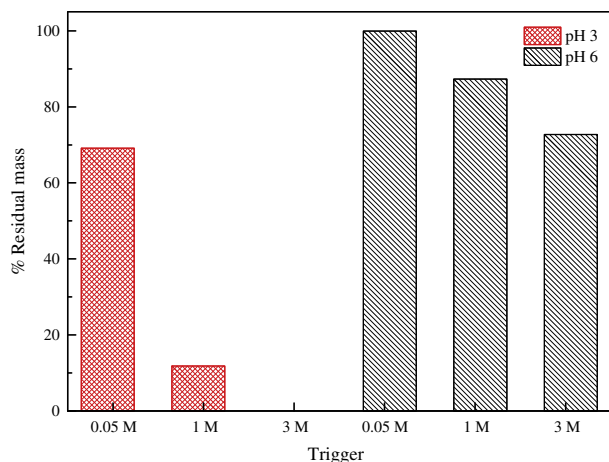

Fig. 4. Effect of different triggers on layer mass removal. The investigated layer was (PAH/PAA)$_5$ prepared at 50 mM, pH 6.
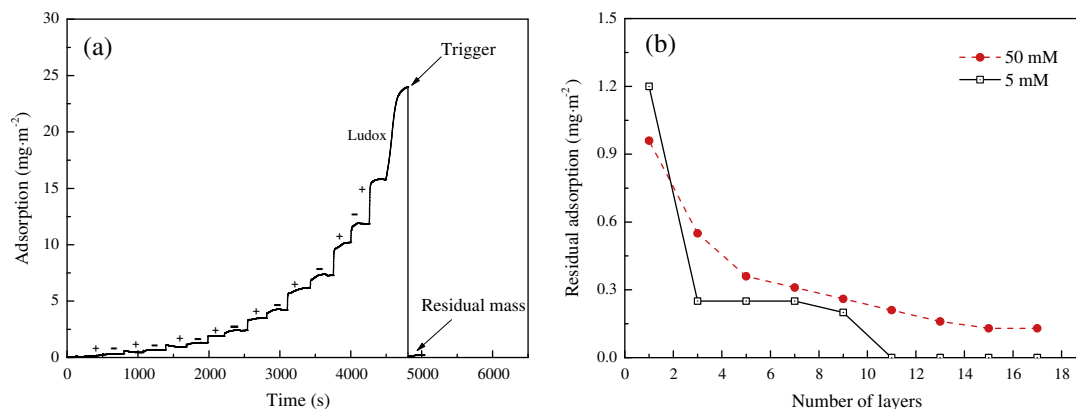

Fig. 5. (a) Adsorption and desorption of PAH, PAA and Ludox particles (0.1 g l^{-1}, pH 6, 5 mM NaNO$_3$) on model surfaces as studied with reflectometry. (b) The residual adsorption of Ludox particles after desorption of the sacrificial PEMs as a function of the number of layers.
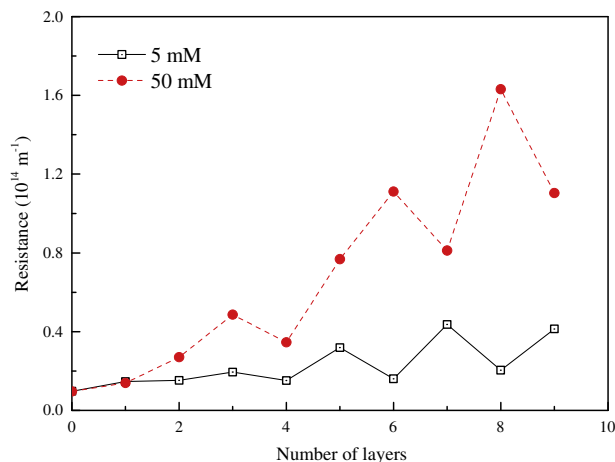
Fig. 6. Membrane resistance against pure water permeation for PEMs coated on a UF membrane support as a function of the number of deposited layers. All data are for a polyelectrolyte concentration of 0.1 g l^{-1}, pH 6, and at a salt concentration of either 5 mM or 50 mM; as indicated.

branes the hydraulic resistance of the membrane was measured after every deposited layer. In Fig. 6 we show the effect of coating the HFS membranes at different ionic strengths on the membrane resistance. Here we can observe increase in resistance with each increment in PEM. Based upon the results of the reflectometry data we coated the membranes under two salt concentrations 5 mM and 50 mM. A significant effect of the ionic strength on the membrane resistance can be observed. At higher ionic strength of the coating solution, the membrane resistance per bilayer increases much stronger than the resistance at the lower ionic strength. This is completely in line with the reflectometry data in Fig. 3(b). At higher ionic strengths, thicker layers are formed on the membrane due to increased extrinsic charge compensation within the multi-layers. These thicker layers result a higher membrane resistance [46]. Here we also observe a zig–zag behavior which is related to the odd–even effect. Other than coating conditions, the properties of the total PEM are also dependent on the terminating-layer. The changes with respect to the different terminating layers are often referred to as odd–even effects. One well established odd–even effect is that the hydration of a PEM depends on the final layer being either the polycation or the polyanion. As shown by de Gro-oth et al. [46] the observed odd–even effect in resistance can give information on the structure of the layer. If the PEM is predomi-

nately coated inside of the pores (pore dominated regime), swell-ing of the PEM layer will narrow the pore and lead to a clear increase in resistance. However, if the PEM forms a dense layer on top of the membrane (layer dominated regime), an increase in hydration (swelling) will actually lead to a more permeable layer and thus a lower resistance.

For the membrane formed at 5 mM, we always observed an increase in the resistance upon PAH adsorption and a decrease in the resistance upon adsorption of PAA. This would indicate that this membrane is always in the pore dominated regime. However for 50 mM, much thicker PEM layers are formed. Here we observed a clear transition (at layer 5) from PAH giving the highest resis-tance, to PAA giving the highest resistance. This would indicate a transition from the pore dominated regime to the layer dominated regime, as also observed by de Grooth et al. [46] for PDADMAC/PSS multilayers. For potential use as a sacrificial layer, it is likely to be beneficial to be in the layer dominated regime, as it would prevent any potential fouling agents from entering the membrane pores. Based on our reflectometry data (Fig. 3a), we know that we have about 1.7 mg/m^2 of polymer after 5 coating steps. With a typical PEM hydration of 50%, this would correspond to a layer thickness of roughly 3 nm. For our dense UF membranes, a layer of such a thickness could indeed fully fill its pores, with subsequent coating being only possible on top of the membrane.

To test the stability and compressibility of our PEM membranes, we measured the resistance of a 10 layer PEM (deposited at 50 mM NaNO$_3$, pH 6) at multiple pressures (5, 10, 15, 20, 25 and 30 bar). We did not find any significant changes in resistance even at the highest pressures, and from that conclude that the layers are stable and not compressible at this range of pressures.

The zeta potential of the surface of the membranes was investigated after each coating step (Fig. 7a). As expected, charge reversal of the negatively charged membrane was observed after coating with a positively charged PAH (layer 1). Subsequently, after each additional layer the charge shifts from positive to negative and back. These results are exactly what was expected for the formation of a PEM on the membrane and is another clear indication of a success-fully applied coating. As we also want to desorb these PEMs made from weak polyelectrolytes by changing the pH, we also investigated the effect of the surrounding pH after coating on the zeta potential of the 14th layer (Fig. 7(b)). As expected, for the set of weak polyelec-trolytes, also the zeta potential of the layer depends strongly on the solution pH. At a pH of 2–3 the zeta potential becomes 0, indicat-ing that the final PAA layer is becoming uncharged.

In Fig. 8 we show the rejection performance of PAA/PAH polyelec-trolyte multilayer membranes prepared under two coating condi-
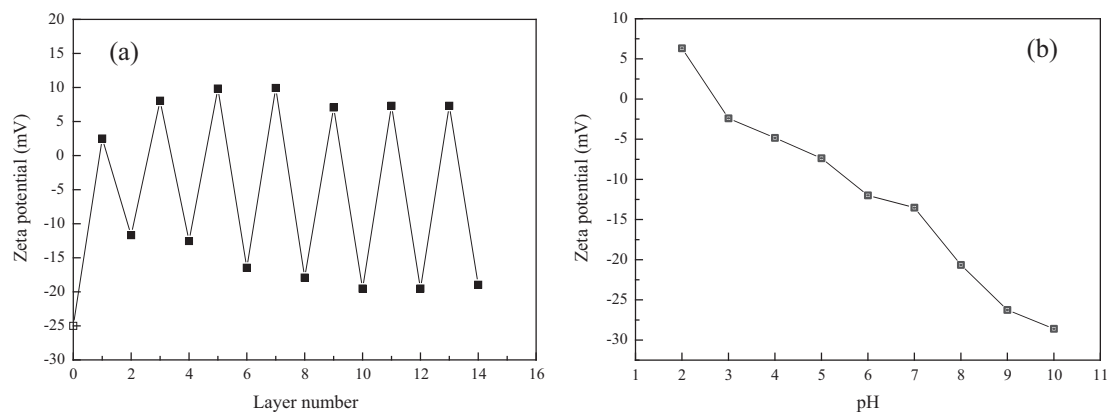

Fig. 7. (a) The membrane zeta potential as measured after every deposited layer. The membrane was coated with 0.1 g l^{-1} PAH and PAA at pH 6, 50 mM NaNO$_3$, the experiment was performed at pH 6, 5 mM KCl. (b) Zeta potential as a function of the surrounding pH for a PEM of (PAH/PAA)$_7$, prepared at 50 mM NaNO$_3$, pH 6, experiment performed at 5 mM KCl.
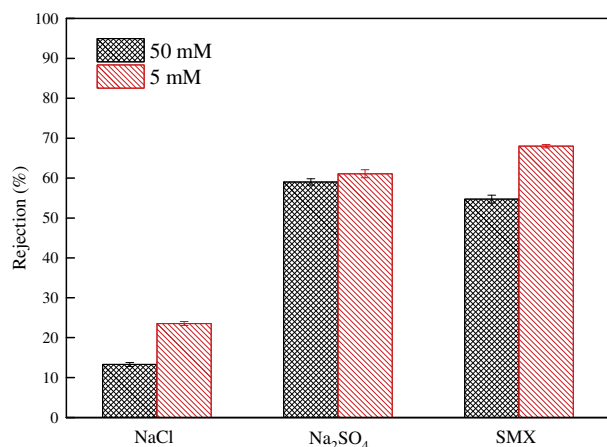
Fig. 8. Solute rejection by (PAH/PAA)$_4$PAH polyelectrolyte multilayer membranes prepared under different coating conditions, as indicated.

Fig. 9. Measured membrane resistance to pure water permeation after the following steps (I) a clean UF support membrane; (II) UF membrane coated with PEMs; (III) PEMs fouling with Ludox particles; (IV) rinsing of fouled PEMs with cleaning solution for 20 min; (V) backwashing of fouled PEMs with cleaning solution at 2 bar pressure for 30 min; (VI) regeneration of PEMs on cleaned UF membrane support.

tions, 5 mM and 50 mM of NaNO$_3$. The membranes were coated with 9 layers (4.5 bi-layers). The membrane thus has a small positive zeta potential (Fig. 7a) as the final layer is the cationic PAH. We investigated the rejection of monovalent ions (NaCl), a divalent ion (Na$_2$SO$_4$) ion and an uncharged small organic molecule, the pharmaceutically active compound SMX (Mw = 253.28 Da). We observe that monovalent ions can relatively easily pass the prepared membranes, while the divalent ion and SMX show a much higher rejection. The prepared membranes thus perform as typical nanofiltration membranes, allowing the passage of monovalent ions, while rejecting divalent ions and small organics. The rejection performance for the membranes prepared under different coating conditions are quite similar. Still, the rejection of the membranes prepared at 5 mM is somewhat higher for all solutes. Polyelectrolyte multilayers prepared at lower ionic strength are known to have lower hydrations [45], leading to thinner and less open layers that can provide better retention behavior [46]. The rejection of the solutes by NF membranes is typically described by taking size, charge, valence and dielectric exclusion into account [48]. For a positively charged membrane a lower retention would be expected for Na$_2$SO$_4$ compared to NaCl when charge exlusion (Donnan) would be prevalent. As this is not the case here, we believe the rejection mechanism is mostly governed by size exclusion. Still, other separation mechanisms can play a role as well.

3.3. The polyelectrolyte multilayer as a sacrificial layer for easy membrane cleaning

In the previous section, we clearly demonstrated that one can prepare PAH/PAA polyelectrolyte multilayer membranes with the typical characteristics of a NF membrane. Here we will investigate the possibility to use the same PEM coating as a sacrificial layer for easy cleaning of fouled membranes. Initially it was investigated whether the coating was fully removable by rinsing a coated membrane ((PAH/PAA)$_3$PAH, prepared at 50 mM NaNO$_3$) with the chosen trigger solution (pH 3, 3 M NaNO$_3$) in a cross flow mode at very low pressure (2 bar) for a short duration of time (20 min). After this rinsing step the membrane resistance reached exactly the level of an uncoated UF membrane confirming the complete removal of the PEM from the membrane surface.

We subsequently investigated if the removal of our sacrificial coating could indeed be used to remove foulants from the membrane. In Fig. 9 we show the membrane resistance against pure water permeation for several steps, including PEM coating, membrane fouling by silica particles, membrane cleaning by sacrificing
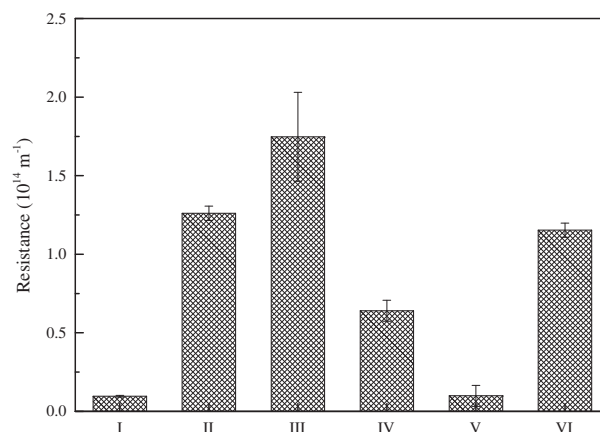
the PEM coating and subsequent re-coating. Here we applied the same rinsing step for PEM removal, but only rinsing could not completely remove the fouled PEM and an additional backwashing step with the same cleaning solution was incorporated. Backwashing with the cleaning solution for 30 min resulted in a decrease in the membrane resistance up to one that is nearly identical to the resistance of the uncoated membrane. If we compare these results with our reflectometry data (Fig. 5(b)), we find that for the same number of coated layers (7), rinsing our model surface with a trigger solution did not result in the complete removal of all foulants. On the membrane, the application of shear forces aid to completely remove the PEM along with any attached foulants. Interestingly, the sacrificial layer approach is thus found to work better on the membrane interface than on the model surfaces due to the added possibility of backwashing. After backwashing a PEM re-coating was performed. As the hollow fibers were already potted in a module, the recoating was performed in a cross flow mode. After coating with the same number of layers the original PEM layer resistance is obtained again.

4. Conclusions

In this manuscript we demonstrate the preparation of a PAA/PAH multilayer that, when coated on a UF membrane support, doubles as a nanofiltration membrane and a sacrificial layer to allow easy cleaning of the membrane. The optimal conditions for layer coating and layer removal were first studied on model surfaces using optical reflectometry. When coating with a background electrolyte concentration of 5 mM NaNO$_3$, a typical linear growth regime is observed for the PAA/PAH multilayers. At a higher ionic strength of 50 mM, thicker layers are formed per coating step and a typical exponential growth regime is observed. However, at an even higher ionic strength (500 mM), stable layers could not be coated. Complete desorption of the formed PEM layers could be achieved by combining a high ionic strength (3 M NaNO$_3$), with a low pH of 3. However, in combination with model fouling agents (small silica particles) a relatively large amount of polyelectrolyte layers (>10) is needed to obtain complete or near complete fouling removal.

Upon coating of the PAA/PAH multilayers on a charged UF support membrane, a clear increase in the membrane resistance against pure water permeation is observed. Coating at 50 mM NaNO$_3$ leads to a much stronger increase in resistance compared to coating at 5 mM, in line with the reflectometry experiments

that showed much thicker layers to form at higher ionic strength. Another proof of successful LbL coating of the membrane support comes from zeta-potential measurements, which demonstrate a clear switching between a positive and a negative zeta-potential after coating of the respective negative and positive polyelectrolytes. The formed polyelectrolyte multilayer membranes, were found to reject solutes in a way typical for nanofiltration membranes: Monovalent ions (NaCl) are hardly rejected, while for a neutral organic molecule such as SMX and for the divalent ion SO_4^{2-} rejections of around 60% were achieved. The basis for separation is expected to be size exclusion, as the investigated membrane was positively charged and still rejected both the negatively charged SO_4^{2-} and an uncharged small organic molecule.

Finally, the prepared polyelectrolyte multilayer membrane was fouled with silica nanoparticles. Subsequent release of the coating using a rinse and a backwash with pH 3, 3 M NaNO$_3$ resulted in almost all recovery of the membrane resistance nearly equal to that of the pristine membrane. The support membrane could then easily be recoated to give the resistance typical for the polyelectrolyte multilayer membrane. This is the first clear evidence that in membrane technology a PEMs can be used to provide a double function, as a nanofiltration membrane and as a sacrificial coating to allow easy membrane cleaning. Interestingly, less layers were needed to obtain complete foulant removal from the membrane, than was the case for the model surface. The possibility for backwashing and the resulting shear forces allow for an even more successful use of the sacrificial layer approach.

Acknowledgments

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