Weak polyelectrolyte multilayers as tunable separation layers for micro-pollutant removal by hollow fiber nanofiltration membranes

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ABSTRACT

The presence of micro-pollutants in wastewater and in drinking water and its sources, is posing both environmental and health concerns. This work describes the development of weak polyelectrolyte multilayer (PEM) based hollow fiber nanofiltration (NF) membranes to remove micro-pollutants from aqueous sources. The charge density of weak polyelectrolytes (PEs) can be controlled by the pH of the coating solution, providing an additional parameter to tune the performance of the prepared membranes. In this study, PEMs of weak PEs poly (allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) were coated in a layer by layer (LbL) fashion on top of an ultrafiltration support to obtain PEM based NF membranes. Before coating the membranes, the role of the pH during coating on the buildup of multilayers was studied on model surfaces via reflectometry. Detailed investigations were then carried out on the membrane performance, by studying the pure water permeability, salt retention (NaCl, CaCl$_2$ and Na$_2$SO$_4$) and the retention of micro-pollutants of varying size (~200–400 g mol^{-1}), charge and hydrophilicity. Variation of the coating pH provided a large degree of control over the separation performance of the weak PEM based membranes. The rejection was found to be dominated by size exclusion together with Donnan exclusion. A PEM membrane prepared at pH 6 showed a high micro-pollutant retention (60–80%) while showing only low ion retentions. Such a membrane would be well suited to reduce the problem of micro-pollutants, without significant alteration of the ionic composition of the feed.

1. Introduction

Over the past few decades, the occurrence of micro-pollutants in aquatic environments around the world has become a serious environmental concern, and is posing a new challenge to the scientific community. Micro-pollutants, also termed emerging contaminants (ECs), are low molecular weight compounds (M$_w$ between 100 and 1000 Da) and cover a broad range of synthetic chemicals (i.e. pesticides, pharmaceuticals, personal and household care products, cosmetics, and industrial chemicals), which are essential to modern human society [1]. Currently more than a million synthetic chemicals are registered in Europe [2], many of which will find their way into the environment at some stage in their life cycle. The presence of micro-pollutants in the surface and the ground water in many countries around the globe has been reported by several studies [3–14]. Generally, these micro-pollutants are only present in very low concentrations (from few ng l^{-1} to several µg l^{-1}), but their continuous and unregulated build-up in the environment do affect surface and ground

water quality which can potentially impact aquatic life, but also drinking water supplies and human health [15].

Conventional wastewater treatment plants based upon an activated sludge process are considered to be a hot spot for the release of micro-pollutants into the environment [16,17], as these wastewater treatment facilities were never designed for micro-pollutant removal. However, applying advanced treatment methods such as oxidation (UV–H$_2$O$_2$, O$_3$–H$_2$O$_2$), adsorption and membrane processes as a polishing step, just before discharging the treated effluent of wastewater plants, could significantly reduce the micro-pollutant load into the water bodies. Though the capital and operational cost of advanced treatment methods can be high due to increased energy demands or due to the consumption of chemicals, upcoming more stringent regulations are expected to make these techniques much more common place. An additional complication, is that due to their diverse nature (chemical structure, solubility, charge and hydrophobicity/hydrophilicity) a single advanced treatment method might not be suitable for removing all types of micro-pollutants. However by employing a combination of these

techniques full removal could be achieved, although for this purpose the advanced techniques need to be flexible, simple and as cheap as possible. For these reasons, membrane based treatment methods, especially nanofiltration (NF) and reverse osmosis (RO), are becoming a much more common technology in water-treatment facilities [18]. Membrane based processes show great potential for the removal of micro-pollutants with several advantages such as easy scale-up and high product quality, but also some disadvantages such as cost and fouling [19]. Among membrane based methods, RO has already proven to be successful for micro-pollutant removal, however the high energy demand of RO and the associated costs are a limiting factor. Moreover, RO treatment not only removes all micro-pollutants, but also all ions, and these ions need to be added again later in the process to be able to use the water for consumption or irrigation purposes.

Due to their low operating pressures, NF membranes are considered as a cheaper and more promising alternative to RO membranes to remove small organic contaminants (micro-pollutants) from water [20,21]. Some of the commercially available NF membranes are already reported to achieve partial or near complete removal of micro-pollutants from water and wastewater [22–30]. In water production, NF is sometimes already applied as a combinatory process to remove components such as di-valent ions, natural organic matter, dyes, metals, and viruses in just a single step [16,31].

NF membranes, just like RO membranes, have an asymmetric structure with a thin and dense selective top layer on a very open and permeable membrane support. However, the membrane geometry is another important aspect for membrane separation processes, especially in terms of fouling. Nearly all commercially available NF membranes are flat sheet, used together with a spacer in a spiral wound module, which offers limited hydraulic and chemical cleaning possibilities making these membranes much more prone to fouling. For this reason, an expensive pretreatment step is often needed, before NF treatment. In contrast, the hollow fiber (HF) geometry allows for a larger membrane surface area per m^3 of membrane module, as compared to a spiral wound geometry. Moreover, hollow fiber membranes are also better equipped to withstand fouling due to the lack of spacers and additional fouling interface, while they can also be cleaned much better by physical cleaning, for example allowing backwashing at higher pressures. By using hollow fiber membranes, one might thus be able to leave out the expensive pre-treatment step needed for spiral wound modules. Unfortunately, most of the commercially available hollow fiber membranes are designed for ultrafiltration (UF) and microfiltration (for removal of bacteria and viruses). So far Pentair X-Flow is the only producer of polymeric NF hollow fiber membranes (HFW 1000) with molecular weight cutoff (MWCO) of 1000 Da, a membrane that was never designed to remove micro-pollutants of small size.

A promising and easy way to prepare hollow fiber NF membranes with a lower MWCO is the surface modification of existing UF membranes. Several studies have shown that the assembly of polyelectrolyte multilayers on a porous support is an easy and suitable method to make NF membranes for the separation or removal of ions [32–44] sugars [45], and dyes [46]. Moreover, the used polyelectrolytes (PEs) are water soluble and can increase the hydrophilicity of the resulting membranes, leading to a lower fouling tendency [47]. However, all of these studies utilized flat sheet membrane supports to prepare PEM based NF membranes. Recently, LbL assembly of PEMs on hollow fiber UF membrane supports has been developed in order to produce hollow fiber NF membranes [48–50]. Moreover, this versatile method allows one to prepare hollow fiber NF membranes with desired functionalities for some particular applications (Fig. 1). De Grooth et al. [51] developed hollow fiber NF membranes using multilayers of zwitterions for the removal of charged (both positive and negative) micro-pollutants from water. In our previous study we developed PEM based NF membranes with a responsive outer layer that can be sacrificed (removed) to quickly and thoroughly clean the membrane surface [52].
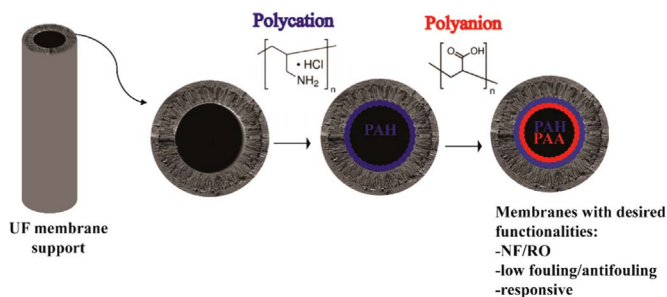

Fig. 1. Graphical representation of LbL deposition of PEMs on hollow fiber UF membrane support to make hollow fiber NF membranes with desired functionalities.

PEM membranes are highly versatile, as the layer properties (molecular structure inside and charge on the outside of layers) can be controlled by the choice of polyelectrolyte, the number of deposition steps and the ionic strength of the coating solution [53], which tunes the separation behavior of membranes for different solutes. Compared to strong PEs the use of weak PEs is advantageous, as their ionization degree PEs is determined by the pH of the coating solution, providing an additional control parameter over the charge density of PEs and the resulting thickness and properties of the deposited PEMs [54–57]. Therefore, two weak PEs (both the polyanion and the polycation) can be useful as the pH during coating can be used to tune the membrane performance [34]. Recently we have shown how the pH can be used to tune the separation properties of weak PEMs based membranes for solvent resistant nanofiltration (SRNF) [58], truly allowing one to optimize the membrane for specific applications. An additional benefit of weak PEM based membranes is the possibility to easily and thoroughly clean the membranes by utilizing a sacrificial layer approach [52,59].

In this work, we describe the preparation of weak PEM based hollow fiber NF membranes by LbL assembly of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) on an UF membrane support. Three pH combinations were used to prepare PEM based NF membranes (PAH/PAA: 6.0/6.0, 6.0/3.5, 3.5/3.5). The effect of the coating conditions on the growth and composition of the PEM layers was studied by preparing and characterizing them on model surfaces. Subsequently, the PEMs were coated on an UF membrane support under identical coating conditions to make NF membranes with a hollow fiber geometry. The newly formed multilayered NF membranes were carefully characterized for their water permeability and solute rejection (salt and micro-pollutant) performance. The results on multilayers properties obtained from model surfaces were the basis to explain the observed membrane performance. We show that the retention behavior of weak PEM based membranes towards salts and micro-pollutants can be tailored by varying the coating solution's pH, leading, for example, to a membrane with a high micro-pollutant retention that does not strongly affect the ionic composition of the feed.

2. Experimental

2.1. Chemicals

Polyelectrolytes used for this study were poly(allyl amine) hydro-chloride (PAH) $M_w = 17,500$ g mol^{-1} and poly(acrylic acid) (PAA) $M_w = 15,000$ g mol^{-1}. Sodium nitrate (NaNO$_3$) was used as a background electrolyte. Polyelectrolyte solutions always contained 0.1 g l^{-1} of polymer. Polyelectrolyte and feed solutions were prepared using de-ionized (DI) water (Milli Q, 18.2 MΩ cm). The pH was adjusted using hydrochloric acid (HCl) and sodium hydroxide (NaOH). All coating solutions were used within eight days after preparation. NaCl, CaCl$_2$ and Na$_2$SO$_4$ were used to study the retention performance of membranes. The molecular structures and properties of micro-pollutants used for the rejection experiments are given in Fig. 2. All chemicals
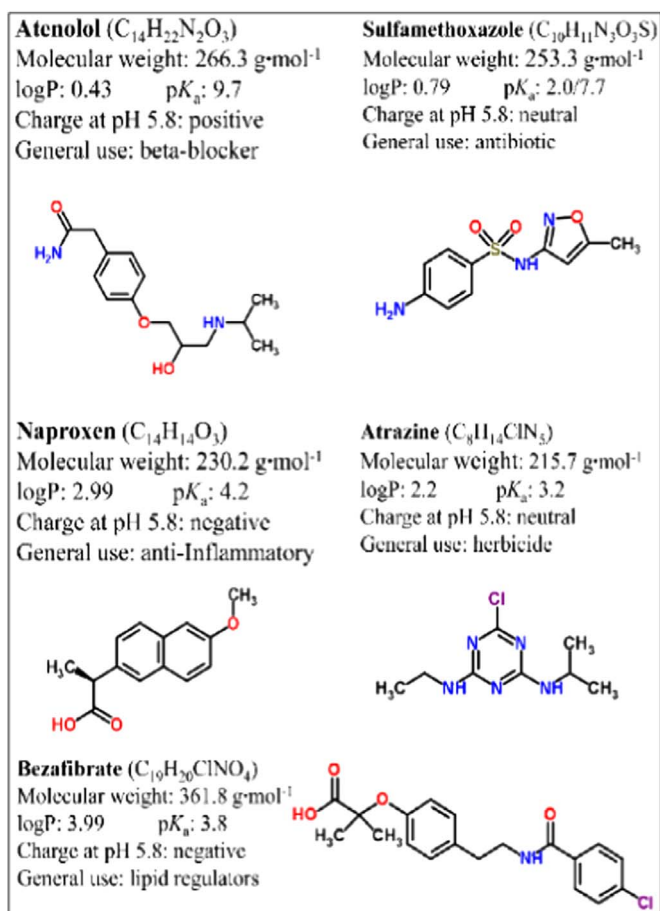
Fig. 2. Physico-chemical properties and chemical structures of micro-pollutants used for this work. Chemicalize.org by ChemAxon was used to estimate some properties (http://www.chemicalize.org) [60].

were of analytical grade and were supplied by Sigma-Aldrich (The Netherlands).

2.2. Reflectometry

To monitor the alternating adsorption of PEs onto a model surface (a silicon wafer with a silica surface), fixed-angle optical reflectometry equipped with a He-Ne laser (monochromatic light, $\lambda = 632.8$ nm) was used. In reflectometry, using a stagnation point flow cell, the measurements can be performed under well-defined hydrodynamic conditions [61]. When the laser beam strikes the adsorbing substrate in the cell around the Brewster angle (71°), it reflects towards the detector and is split into its perpendicular (R_s) and parallel (R_p) components. The ratio of these two components (R_p/R_s) provides the reflectometric signal S. A change in signal (ΔS) is directly proportional to the quantity of material adsorbed on the substrate, according to Eq. (1):

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

Here Γ is the quantity of material which is adsorbed on silicon wafer (mg m^{-2}) Q is a sensitivity factor, that depends on many factors like the angle of incidence of the laser beam (θ), the thickness of the silicon layer (d), the refractive indices (n), and the refractive index increment (dn/dc) of the adsorbing material. All measurements were carried out on a clean silicon wafer surface (with a 70 nm SiO$_2$ top layer). The Q-factor was calculated using an optical method based on values from our previous work [52,62]. The Q-factor value thus obtained is 20 mg m^{-2} for PAH and 27 mg m^{-2} for PAA and is used to calculate the actual adsorbed mass of polymer. S_0 is the initial output signal of a clean silicon wafer immersed in solvent. Before starting the reflectometry

measurements the silicon surface was treated for 10 min by O$_2$ plasma (Femto-Diener electronic plasma cleaner, Germany, at 50% power). The excess of either PAH or PAA monomers, with regards to a 1:1 ratio, was calculated by dividing the adsorbed mass with the monomeric molecular weight of the respective polyelectrolyte, and subsequently subtracting the total weak anionic monomers from the weak cationic monomers. While we cannot be certain of the exact degree of dissociation of these monomers, an excess of one type of monomer provides information on the qualitative excess of charge present in and on the layer.

2.3. Water contact angle of multilayers

PEMs deposited on silicon wafers were characterized for their water contact angle using the OCA21 from Dataphysics Instruments GmbH, Germany. The procedure used for the deposition of multilayers is provided below. Before deposition of PEMs, pre-treatment of silicon wafers was carried out for 10 min by O$_2$ plasma (Femto-Diener electronic plasma cleaner, 50% power, Germany). After the plasma treatment silicon wafers were used within an hour. Before measuring the contact angle, the PEMs deposited under different pH conditions using the LbL technique were dried using a nitrogen gas stream. The contact angle of a sessile water drop of 2 μL on the PEMs terminated with PAH (+) and PAA (-) was measured using the OCA21 at five different locations for every coating at 20 °C in a static mode. The contact angle was measured 5 s after placing the water droplet although no substantial effect of time was observed.

2.4. Membrane modification using LbL coating

A commercially available hollow fiber UF membrane (Hollow Fiber Silica (HFS), with a MWCO of 10 kDa) was used as a support on which the polyelectrolyte multilayers were coated. This UF support was kindly provided by Pentair X-Flow, The Netherlands. This UF support has a separation skin layer of sulfonated poly(ether sulfone) towards the lumen side and is designed to remove colloidal silica from water. This membrane support was coated with PEMs using dip coating as reported elsewhere [52]. To wet the fibers and remove impurities, the hollow fibers were kept overnight in 15 wt% ethanol in water. Rinsing of the fibers was performed three times with DI water with the background electrolyte solution (50 mM NaNO$_3$). Next the fibers were dipped in solution of polycation (PAH) with 0.1 g l^{-1} polymer concentration and same background electrolyte concentration for about 30 min, followed by three times rinsing in background electrolyte solution. We used three combinations of pH for PAH/PAA and resulting membranes are [6.0/6.0], [6.0/3.5] and [3.5/3.5]. Here for example [6.0/6.0] represents multilayer membranes coated with PAH at pH 6.0 and the PAA at pH 6.0. Rinsing with 50 mM background electrolyte with the same pH as of the PE solution between every polyelectrolyte coating is performed to remove any loosely attached or extra PE from the surface of membrane and to avoid formation of complex in the bulk solution. The same coating steps were repeated with other PE to obtain the required number of layers. After each coating step the membranes were immersed in glycerol/water (15 wt%/85 wt%) solution for at least 4 h, and then dried for at least 8 h in air. Later the coated fibers were potted in modules. The effective length of the fibers in modules was approximately 10 cm.

2.5. Characterization of PEM based membranes

2.5.1. Filtration and rejection

The prepared membranes were first characterized for their pure water flux at 20 °C in a dead end mode. The applied trans-membrane pressure (TMP) was 1.8 bar. Normalization of the measured pure water flux gave the water permeability. The performance of prepared membranes was further checked by retention measurements on salt

ions (NaCl, CaCl$_2$ and Na$_2$SO$_4$) and 5 common micro-pollutants (covering medicinal compounds and herbicides). Retention measurements were performed by applying a cross flow velocity of 3.8 m s^{-1} (corresponding to a Reynolds number of approximately 3100). The applied cross-flow velocity and corresponding Reynolds number was choses such that the filtration process occurred at turbulent conditions, strongly reducing the effects of concentration polarization. The concentration of salts used for these filtration experiments was always 5 mM. A conductivity meter WTW cond 3210 was used to measure the salt concentration. Micro-pollutants used for this study included positive, negative and neutral molecules (at a pH of 5.8) and included both hydrophobic and hydrophilic molecules. Properties of these micro-pollutants are given in Fig. 2. The micro-pollutant molecular weight range is between 200 and 400 g mol^{-1}. Filtration of membranes with solutions containing all five micro-pollutants (concentration of 10 mg l^{-1}) was performed. Saturation of membranes with solutes and steady state rejection was ensured by taking the permeate samples after 24 h of filtration.

Eq. (2) was used to calculate the retention:

$$R\ (\%) = (1 - \frac{C_p}{C_f}) \times 100 \tag{2}$$

where C_p is the solute concentration of the permeate and C_f is the solute concentration of the feed (concentrate), respectively. For measurements two membranes of each type were used and each membrane was measured three times.

2.5.2. Analysis of micro-pollutants

The concentration of micro-pollutants in both the concentrate and permeate was determined by a U-HPLC Dionex Ultimate 3000 system equipped with an RS variable wavelength detector. Micro-pollutant separation was done on an Acclaim RSLC C18 2.2 μm column (Thermo Scientific) at 45 °C, while applying a gradient flow from 95 wt% H$_2$O + 5 wt% acetonitrile at pH 2–5 wt% H$_2$O + 95 wt% acetonitrile at 1 ml min^{-1}.

3. Results and discussion

We divided this section in three main parts. The first part entails the characterization of the PEMs on model surfaces via reflectometry and contact angle measurements in order to understand their composition and structure. The second part deals with the characterization of the prepared PEMs based membranes in terms of permeance and salt rejections. In the third part the NF performance of membranes (prepared under different pH conditions) regarding the retention of five micro-pollutants is given.

3.1. Properties of PEMs

3.1.1. Growth behavior and total charge on multilayers

The growth of weak PAH/PAA PEMs under three pH combinations (6.0/6.0, 6.0/3.5 and 3.5/3.5) was monitored on silicon wafers using optical fixed angle reflectometry (Fig. 3). A typical measurement starts when the silicon wafer is exposed to the solvent solution (with identical pH and salt concentration as the cationic polyelectrolyte) and this gives the baseline signal (S$_0$). Adsorption starts when the negatively charged silicon wafer is exposed to a solution containing the positively charged polyelectrolyte (PAH), leading an increase in the mass adsorbed. Further exposure to the negatively charged anionic polyelectrolyte PAA leads to another increase in adsorbed amount. Continuous switching between cationic and anionic polyelectrolytes results in stepwise growth of the PEMs as shown in Fig. 3.

Every time before switching between polyelectrolyte solutions, the cell was rinsed with a background electrolyte solution for at least 200 s to remove loosely adsorbed polymer chains. The used salt concentration
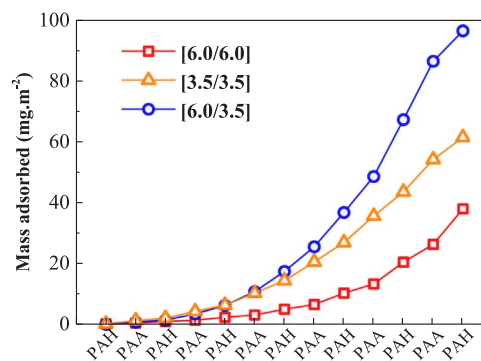

Fig. 3. Effect of pH of coating solutions on building of PAH/PAA multilayers on silicon wafer monitored via reflectometry (polyelectrolyte solution contained polymer concentration of 0.1 g l^{-1} with 50 mM NaNO$_3$). Straight lines are shown to depict the trend.

of 50 mM in the coating solutions was chosen based upon our previous work [52]. Fig. 3 shows multilayer growth at three different combinations of pH. The amount of material adsorbed during multilayers formations for the same number of bilayers shows substantial difference for all pH conditions. In Fig. 3, we observe exponential growth for polyelectrolyte multilayers prepared under the three different pH conditions. However, with the same number of bilayers the amount of mass adsorbed during multilayer formations is significantly different for the studied pH conditions (Fig. 3). The lowest adsorbed amount is found at pH [6.0/6.0], at the pH conditions [3.5/3.5] and especially [6.0/3.5] much more material is adsorbed.

Clearly, the growth behavior and in turn the structure of the multilayers is affected by the pH of the polyelectrolyte solutions. For this pair of weak PEs (PAH/PAA), the composition, the thickness and organization of the PEMs can be tuned by variation in the pH of each of the PE solutions [54,55,63]. The pH controls the degree of dissociation of the basic and acidic groups on the polymer chains and thus controls the charge density. PAH with pK$_a$ of 8–9 and PAA with pK$_a$ of 5.4 [63], are mostly charged (with nearly 80–90% ionized groups) at a pH combination of [6.0/6.0] and hence form thin layers, with a small quantity of material needed to compensate all charges from the previous deposited layer (most probably with high intrinsic charge compensation within the bulk of the multilayers). Thicker and more swollen multilayers are formed at [3.5/3.5] and [6.0/3.5] when PAA is only partially charged. Here the PE adopts a more coiled conformation while also more extrinsic charge compensation is found [64].

A monomeric excess of a particular polymer during PEM build-up can give an indication on the overall charge in multilayers. To get into insight of the overall charge in prepared multilayers, the excess of particular polymers after each adsorption was also calculated (see Fig. S1). We observed a zigzag behavior with the addition of each positive (PAH) or negative (PAA) layer. Here adsorption of PAH leads to a significant excess of cationic monomers, while after PAA addition layers we come to just a very small excess of negative polymer. This effect is strongest for pH conditions [6.0/3.5] and [3.5/3.5] where thicker layers are formed and weakest for the thin layers of pH [6.0/6.0] condition (Fig. 3). These observations are in line with zeta potential of these multilayers, where switching between the PEs reverses the charge of the surface of multilayers which shows that outside of the multilayers represents excess of that particular PE [52]. However, the excess of PAH is so large that it cannot just stem from an excess on the outside of the PEM. The expectation is that also the bulk of the PEM is somewhat positively charged after a PAH adsorption step. A similar effect was found for the cationic PDADMAC and the anionic PSS, with an excess of the cationic charge throughout the PEM layer after PDADMAC deposition. The observed excess of PAH, would be in line with the observed exponential growth regime, where PAH might diffuse into the whole multi-layer, leading to excess charge spread throughout the layer [65,66]. Indeed, the bulk of the PEMs can carry charges and may not
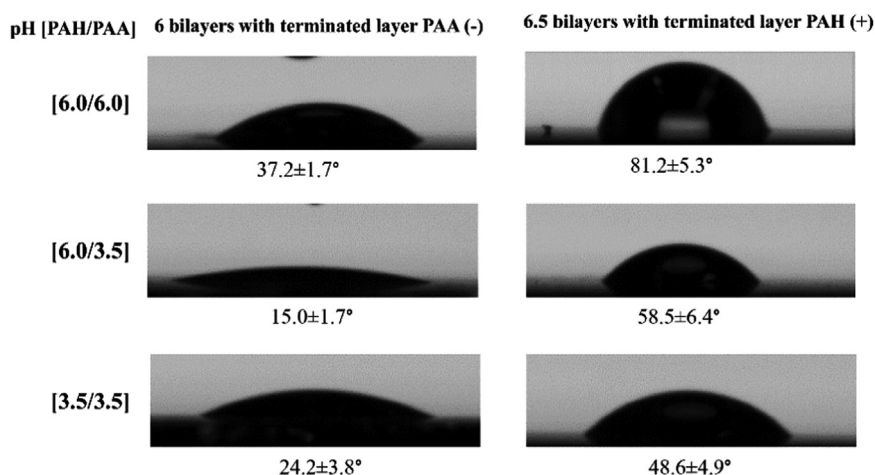
Fig. 4. Representative contact angle measurements of multilayers with different terminal layers (prepared at [6.0/6.0], [6.0/3.5] and [3.5/3.5] pH combinations with polymer concentration of 0.1 g l^{-1} and 50 mM NaNO$_3$).

be overall neutral [67,68]. The additional cationic charge would then also be expected to lead to stronger swelling after deposition of the cationic polymer.

3.1.2. Contact angle of multilayers

The wettability of multilayers prepared under the different pH combinations was investigated for PAH (+) and PAA (-) terminated layers by means of contact angle measurements. These measurements provide insight into the hydrophilicity of the multilayers which can be important for their eventual transport properties. Furthermore, it is common knowledge that membranes with higher a hydrophilicity tend to offer better resistance to fouling [47,69]. In Fig. 4 we present water contact angles measured on the multilayers prepared with the PAH/PAA with three pH combinations (6.0/6.0, 6.0/3.5 and 3.5/3.5) at 50 mM NaNO$_3$ and 0.1 g l^{-1} polymer. In all cases, results show a change in the layer hydrophilicity for differently terminated layers, with the positively (PAH) terminated layers having a higher contact angle than the negatively (PAA) terminated layers. When comparing three different multilayers, the [6.0/6.0] layers show relatively higher contact angles (37° and 81° for PAA and PAH terminated layer respectively) thus more hydrophobic layers, which was expected due to the high level of intrinsic charge compensation and dense structure of these layers (few free -NH$_2$ and -COOH groups) which is comparable to our previous observations [58]. The contact angles measured on [6.0/3.5] and [3.5/3.5] PEMs with a final layer of PAA (-) are 15° and 24° respectively, indicating these layers are more hydrophilic compared to multilayers terminated with PAH (+). These results further demonstrate that the segments of the final layer dominates the surface layers.

3.2. Membrane performance

3.2.1. Water permeability

A UF support was coated with PEMs (PAH/PAA) using the same coating conditions as applied for the silicon wafers. After every coating step, the membranes were characterized for their pure water permeability. The effect of coating the UF membrane support at different pH conditions on the water permeability is given in Fig. 5. For all pH conditions, the membrane permeability decreases with the number of coated layers. This is in agreement with the reflectometry data of multilayer growth and represents that the addition of material on the membrane surface decreases the pore size of membranes leading to a decline in the water permeability. This is in agreement with the reflectometry data of multilayer growth and represents that the addition of material on the membrane surface decreases the pore size of membranes leading to a decline in the water permeability. We observe a typical zig-zag behavior in the permeability of membranes
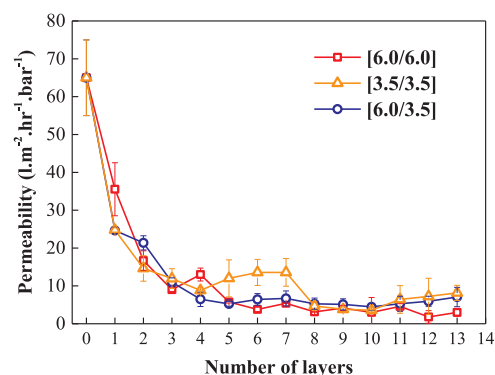

Fig. 5. Pure water permeability of membrane support versus the number of coated layers at three pH combinations for PAH/PAA [6.0/6.0], [6.0/3.5] and [3.5/3.5]. All coating solutions contained 0.1 g l^{-1} polymer and 50 mM NaNO$_3$.

prepared at pH condition [6.0/6.0] which is an indication of the odd-even effect [48,52]. Often, the degree of swelling of a whole PEM will depend on the final adsorbed layer. In our reflectometry investigation (Figs. 3 and S1), we already established a large excess of cationic monomer after PAH adsorption, which would be expected to lead to stronger swelling of the PEM. Initially, after PAH adsorption the permeability is lowest as the additional swelling of that layer closes of the pores. This is most clearly observed between layer 3 and 4 and indicates a pore dominated regime. However, after 5 deposited layers we see a flip in the odd-even effect, with PAH terminated layers having a higher permeability. With this we have entered the layer dominated regime where a PEM layer has formed on top of the support. A more swollen layer is now also a more open and thus permeable layer. After depositing 6 bilayers PAA is less permeable (1.8 ± 1.6 l m^{-2} h^{-1} bar^{-1}) because of its dense layer structure, while addition of a layer of PAH makes multilayers swell and more permeable (3.0 ± 0.5 l m^{-2} h^{-1} bar^{-1}). PAA terminated layers are thus expected to be denser and to show better solute retention behavior. We did not see a clear odd even effect for membranes [6.0/3.5] and [3.5/3.5]. An important observation to make is that the membranes prepared under [6.0/6.0] give the lowest permeability, while we know from reflectometry that these are also the thinnest layers. This must mean that layers prepared under [6.0/6.0] are significantly denser than the layers prepared under other pH conditions. This effect is most clear after 12 and 13 layers, where the water permeability of membranes coated with similar number of bilayers of PAH/PAA at pH condition [6.0/3.5] and [3.5/3.5] was almost two times higher than membranes prepared at pH conditions [6.0/6.0] i.e., 11.5 ± 0.8 l m^{-2} h^{-1} bar^{-1} and

$7.2 \pm 0.48 \, l \, m^{-2} \, h^{-1} \, bar^{-1}$ respectively. For LbL membranes solubility and diffusivity of solutes are mainly determined by hydration of layers and the affinity of the solute to the membranes [48]. More hydrated layers are swollen and more open with more volume between the polymer chains, allowing easier transport.

3.2.2. NF performance

Various salts (NaCl, CaCl₂ and Na₂SO₄) were utilized to check the rejection performance of the prepared membranes. The UF support used to prepare these membranes are unable to reject any salt ions, and therefore we are really studying the separation performance of the PEMs. During the filtration of the salt solutions no significant permeability changes were observed compared to the clean water permeabilities, demonstrating a stable performance. Retention of salts is a typical characterization of NF membranes which can also provide proof of successful deposition of PEMs on the support membrane. By studying the retention for a number of salts one can also achieve insight into of the main retention mechanism of the membranes [48]. To describe the solute rejection in NF-membranes usually size/steric hindrances, charge, dielectric exclusion, valence, and adsorption are taken into account [48,70–73].

In Fig. 6 the rejection performance of PAA/PAH PEM based membranes for monovalent (NaCl) and divalent ions (Na₂SO₄ and CaCl₂) is shown. The membranes were coated with 6 (-) and 6.5 (+) bilayers under 3 different pH combinations (6.0/6.0, 6.0/3.5 and 3.5/3.5) at an ionic strength of 50 mM. We observe that all of the prepared membranes reject a significant amount of the SO_4^{2-}, while the membranes hardly retain Na^+ and Ca^{2+} ions. The prepared PEMs based membranes thus perform as NF membranes, allowing passage to the monovalent ions, and rejecting bigger divalent ions. Still, the ionic rejection, especially for the PAA/PAH (6.0/6.0) membrane is rather low. This could be seen as competitive advantage to remove organic compounds without significantly affecting the ionic composition of the feed, something that we will come back to. We found membrane performance in terms of rejection quite similar for the different pH conditions used. For differently terminating layers (PAH or PAA) for [6.0/6.0] membranes show very small differences in terms of retention are observed, which indicates only a very small contribution of the membrane charge towards solute retention. However we do see some role of terminal layer charge for [6.0/3.5] and [3.5/3.5] membranes especially for SO_4^{2-} retention. If the rejection was dominated by Donnan exclusion then the order of retention would be $SO_4^{2-} > Na^+ > Ca^{2+}$ for negatively charged membranes and the inverse for positively charged membranes. These trends are clearly absent in our retention data. An alternative would be di-electric exclusion, which is especially powerful in retaining multivalent charged species. However, the low CaCl₂ retention for all membranes makes this statement very unlikely. For our dense PAA/PAH layers the retention mechanism seems to be based mainly on the size exclusion. When the ions are dissolved in water, the dynamic hydrated radius of ions is the good representation of their size in water [74], although size differences of the ions used here are not large and their order of size is: $SO_4^{2-} > Ca^{2+} > Cl^- > Na^+$. Indeed the larger SO_4^{2-} is the most rejected ion, independent of the charge of the membrane, something that we can only really explain on the basis of size exclusion as the dominating separation mechanism for these solutes. Still, other mechanisms are expected to play an additional role.

3.2.3. Micro-pollutant rejection

To examine the ability of prepared multilayered membranes to reject small organic molecules, the retention of a cocktail of five micropollutants was measured with membranes coated under different pH conditions for PAH/PAA [6.0/6.0, 6.0/3.5 and 3.5/3.5]. Filtration experiments for micro-pollutants were carried out for 24 h in order to exclude adsorption as a separation mechanism. It is important to mention that rejection of trace organic compounds by pressure driven membranes is a complex mixture of factors including electrostatic repulsion, steric hindrance, solute/membrane properties and solution effect [75], feed water composition and operating conditions [21]. Van der Bruggen et al. [30] shown that for organic pollutants removal by NF, the key parameters of solute and membrane that can influence the retention are hydrophobicity, molecular size and charge (pKₐ).

In Fig. 7, the micro-pollutant retention of the multilayered membranes, prepared under different pH conditions, are given. All of these membranes show between 40% and 80% retention for the micropollutants, significantly better than the ion retentions given in Fig. 6. Interestingly, the membrane with the lowest ion retentions, [6.0/6.0], has a superior micro-pollutant retention compared to the other membranes, [6.0/3.5] and [3.5/3.5], although the negatively charged Naproxen and Bezafibrate have a comparable rejection for all the three membranes. It seems that for [6.0/3.0] and [3.5/3.5] some Donnan exclusion plays a role leading to a preferred rejection of the negative micro-pollutants, while for [6.0/6.0] the high retention of all micropollutants, suggests that the retention of these [6.0/6.0] membranes is
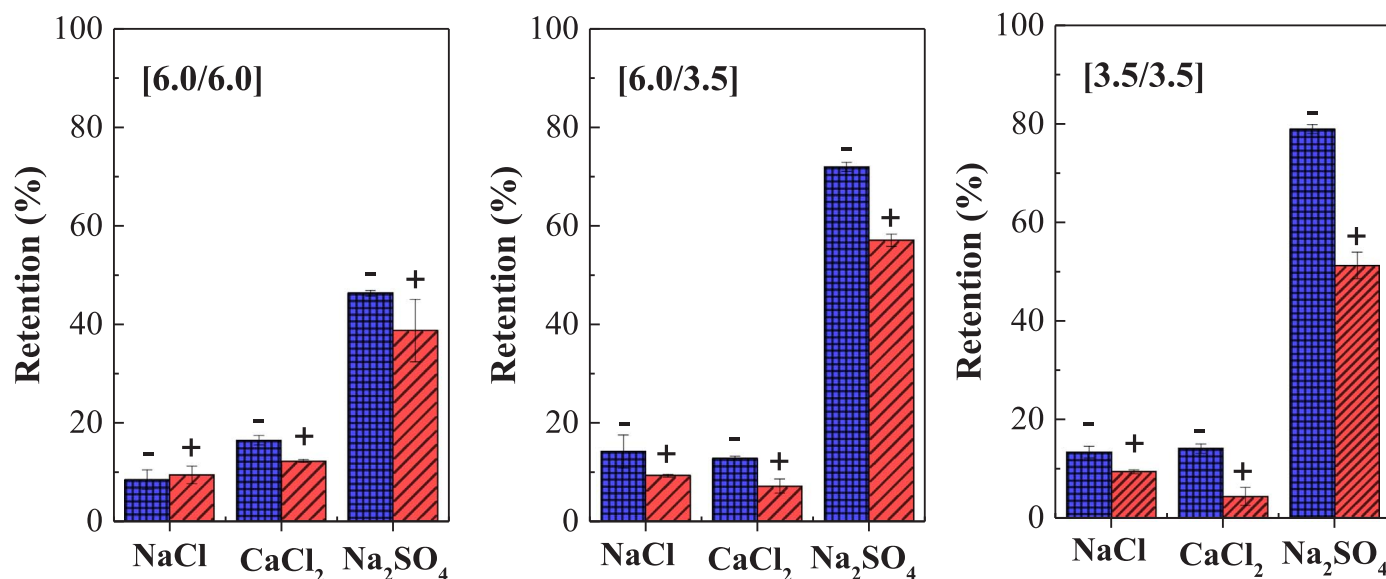

Fig. 6. Different ions retention of multilayered membranes with 6 (-) and 6.5 (+) bilayers of PAH/PAA prepared at [6.0/6.0], [6.0/3.5] and [3.5/3.5] pH combinations with 50 mM NaNO₃ and 0.1 g l⁻¹ polymer.
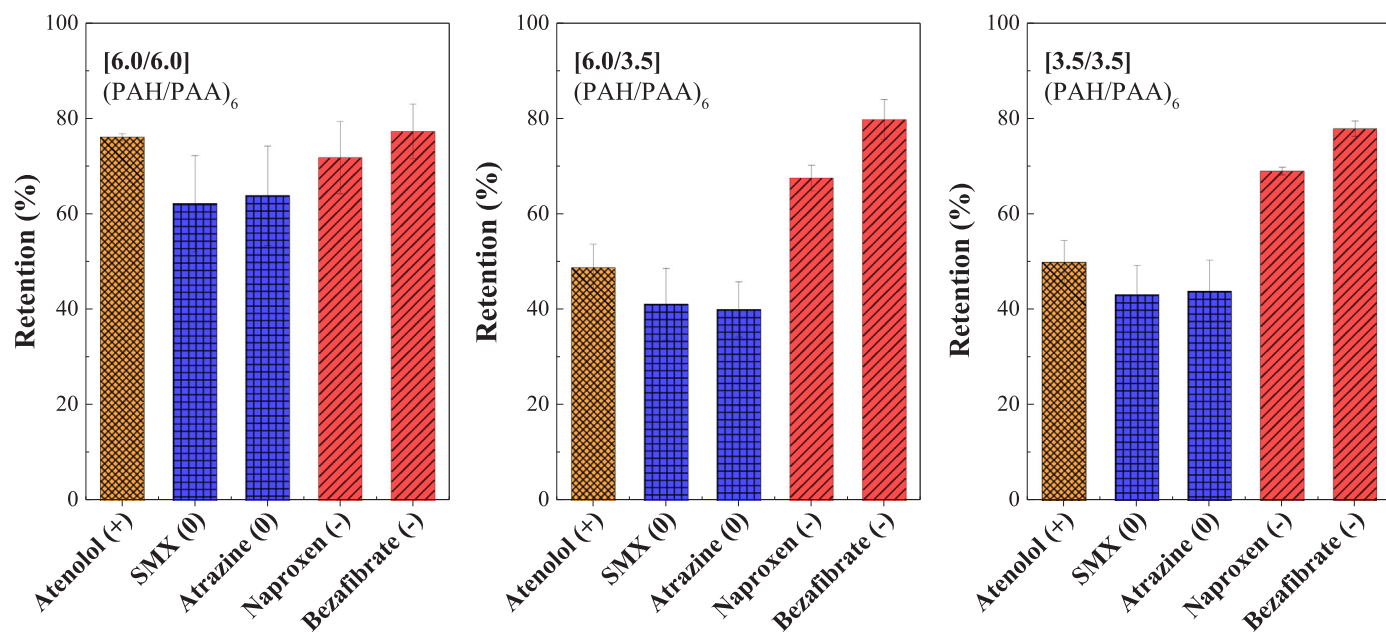
Fig. 7. Retention of different micro-pollutants at pH 5.8 by PEM membranes with 6 (-) bilayers of PAH/PAA (prepared with different combinations of pH [6.0/6.0], [6.0/3.5], and [3.5/3.5] and ionic strength of 50 mM with 0.1 g l^{-1} polymer). Conditions for filtration experiments were: pH 5.8, Re ≈ 3100, and a TMP of 1.8 bar.

based mainly on size or steric retention. As mentioned before in discussion of the water permeability, the membranes prepared at [6.0/6.0] are expected to be much denser in nature.

As there is just a relatively small difference in molecular size of the used compounds (range of 200–400 g mol^{-1}) it is difficult to observe a direct relation between molecular size (Fig. 8) and rejection of molecules, and we expect that rejection is combination of both size and charge. However other factors such as hydrophobicity may also contribute to the observed retention to some extent.

To describe the hydrophobicity of micro-pollutants, an often used indicator is logP which is the octanol/water partition coefficient. The logP values of micro-pollutants used in this study (Fig. 2) range from 0.49 (most hydrophilic) to 4.04 (most hydrophobic). In Fig. 9 the rejection is shown as a function of logP, however there is again no clear trend in rejection of micro-pollutant with the degree of hydrophobicity. One thing that is clear from results is that retention of ionic species is better than non-ionic species.

To study the effect of the final layer charge we also performed rejection measurements with membranes terminated with a PAH (+) layer. Our results show a drop in rejection for all investigated micro-pollutants for the membrane [6.0/6.0] (Fig. 10). From contact angle measurements this membrane shows more hydrophobicity than all other membranes, so one could expect a different rejection behavior

from these membranes. These retention results are in line with reflectometry data (Fig. S1) where excess of monomers of PAH in this layer makes the layers swollen and highly permeable. Permeability of this membrane terminated with PAH is 3.0 ± 0.5 l m^{-2} h^{-1} bar^{-1} is higher than a PAA (-) terminated membrane (1.8 ± 1.6 l m^{-2} h^{-1} bar^{-1}). A higher permeability, after adding an extra polyelectrolyte layer, would suggest that the multilayer adopts a more open structure leading to a lower degree of size exclusion/steric hindrance and thus a lower rejections. We also studied the final layer effect for other two membranes [6.0/3.5] and [3.5/3.5], the retentions of which are given in Fig. S2. Similar to [6.0/6.0], the retention of membranes [6/3.5] and [3.5/3.5] was found to be significantly declined. Swelling of the layers after PAH adsorption makes them more permeable.

4. Conclusions

Growing public awareness about the presence and the health concerns associated with small organic contaminants in water, also increase the demand of membrane based processes in the water industry. Here hollow fiber NF membranes are especially promising as they require much lower operating pressures than for example RO, while their hollow fiber geometry makes them less susceptible to
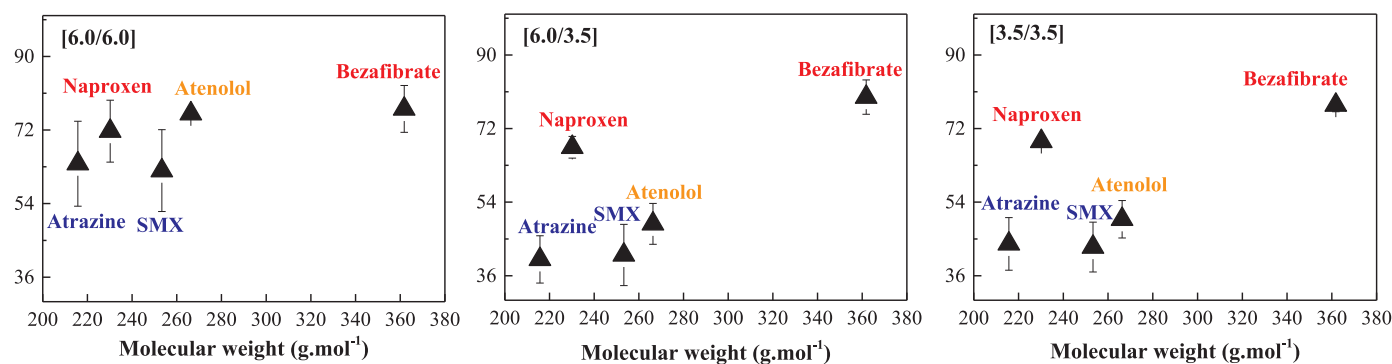

Fig. 8. Retention as a function of size of micro-pollutants. Micro-pollutants are color coded based on their charge: orange for positive (+) micro-pollutants, blue for neutral (0) micro-pollutants, and red (-) for negative micro-pollutants. Membranes are with 6 (-) bilayers PAH/PAA prepared with different combinations of pH [6.0/6.0], [6.0/3.5] and [3.5/3.5] and 50 mM ionic strength with 0.1 g l^{-1} polymer). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
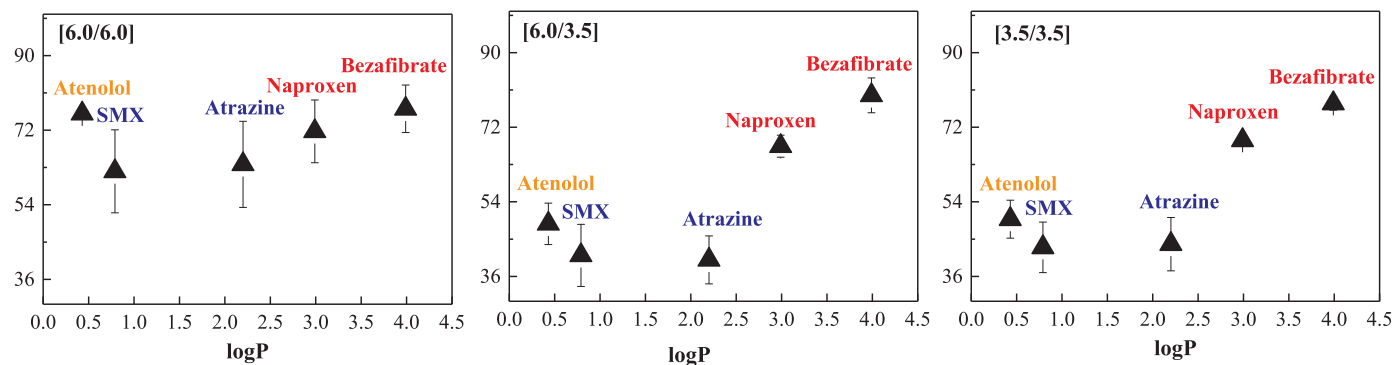
Fig. 9. Retention as a function of hydrophilicity of micro-pollutants. Micro-pollutants are color coded based on their charge: orange for positive (+) micro-pollutants, blue for neutral (0) micro-pollutants, and red for negative micro-pollutants. Membranes are with 6 (-) bilayers of PAH/PAA prepared with different combinations of pH [6.0/6.0], [6.0/3.5] and [3.5/3.5] and 50 mM ionic strength with 0.1 g l^{-1} polymer). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).
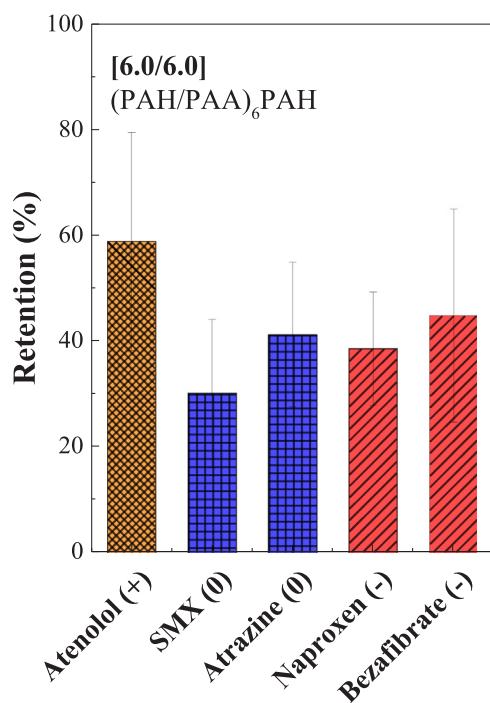

Fig. 10. Retention of different micro-pollutants at pH 5.8 PEMs membranes with 6.5 (+) bilayers (PAH/PAA)$_{6.5}$ prepared with different combinations of pH and ionic strength of 50 mM with 0.1 g l^{-1} polymer). Conditions for filtration experiments were: pH 5.8, Re ≈ 3100, and a TMP of 1.8 bar.

fouling than their spiral wound counterparts. This work investigates the use of weak PEMs for the preparation of low pressure, tunable NF membranes for micro-pollutant removal from water. Hollow fiber based PEM membranes were prepared with the layer-by-layer approach utilizing a combination of two weak PEs (PAH/PAA) at different pH conditions. Membranes prepared at pH [6.0/6.0] demonstrate a good retention for all the micro-pollutants due to the dense structure, coupled with an acceptable flux due to the thin PEM layer used. Membranes prepared with other pH combinations [6.0/3.5] and [3.5/3.5] with a more open layer structure demonstrated good retention only for the charged micro-pollutants. Overall the rejection mechanism was found to be dominated by steric hindrance, especially for the membranes prepared at pH 6. This study demonstrates a simple and versatile method to prepare weak PEM based hollow fiber NF membranes. We show that by varying the pH during coating one can tune the performance of the membranes towards specific applications. Moreover, the membrane prepared at pH 6, is especially promising as it combines a high MP rejection with low ion rejections. This membrane would be well suited to reduce the problem of micro-pollutants,

without significant alteration of the ionic composition of the feed.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2017.05.027.

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