Design of ultrathin nanostructured polyelectrolyte-based membranes with high perchlorate rejection and high permeability

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A B S T R A C T

The presence of perchlorate in drinking water sources is an issue of overwhelming concern in United States. Commercial reverse osmosis (RO) membranes show high rejection of perchlorate ions but with very low water permeability. We propose the modification of commercial nanofiltration (NF) membranes by layer-by-layer (LbL) assembly in order to enhance the ion rejection of these membranes to the same level as commercial RO membranes, but with much higher permeability. Poly allylamine hydrochloride (PAH) and poly acrylic acid (PAA) were the two polyelectrolytes used for surface modification. We found that, when both these polyelectrolytes were deposited on a NF 90 membrane at a pH of 6.5 and cross-linked with glutaraldehyde, we were able to achieve around 93% perchlorate rejection at a pressure of 5 bar with 10 ppm feed concentration. This was almost equal to the rejection offered by SW 30 membrane and higher than a BW 30 membrane under the same conditions of pressure and feed concentration. Most importantly, the modified membranes had 1.5 times the permeability of BW 30 membrane and 6 times that of SW 30. These membranes, therefore, had much superior permselectivity than the commercial membranes. In fact, this was one of the highest values of permselectivity reported so far for a PEM-based RO membrane targeting monovalent ion removal. Only 3 bilayers, with an overall thickness of just 20 Å, were sufficient to achieve such a high rejection. The mechanism of ion rejection by these modified membranes was based on size-based exclusion rather than charge-based separation.

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1. Introduction

In 1997 high levels of perchlorate were found in the drinking water supplies of the state of California. Ever since then, a number of other states within United States reported the presence of perchlorate in the groundwater as well as surface water supplies [1]. Recognizing the threats it poses to the environment and the health of millions of people, perchlorate has been added to the contaminants candidates list (CCL) as well as unregulated contaminant monitoring rule (UCMR) [2]. Perchlorate salts like ammonium perchlorate are used as oxidizers for missiles and munitions [3] which makes perchlorate ion an ubiquitous groundwater contaminant in areas close to NASA or other military settlements [4]. When taken in at higher than recommended levels, it interferes with Iodide ion thereby impairing the hormone secreting abilities of the thyroid gland. Studies have shown that Iodine deficiency in case of pregnant women can lead to lower IQ levels in their babies [5]. Improved methods of perchlorate detection have shown the

presence of perchlorate in at least 26 states all over United States [1]. The Colorado River which provides water for drinking as well as irrigation to almost 30 million people, has been known to be one of the most perchlorate-contaminated sites of the country [4]. Developing effective perchlorate removal strategies is therefore in urgent need.

As of now, the US EPA does not have any strict regulatory limits for perchlorate but according to recent reports they have initiated the process of regulating perchlorate to a uniform level throughout the nation under the Safe Drinking Water Act [3]. Various states like California, Massachusetts, Maryland, etc. have set their own individual standards between 1 and 2 μg/l [6]. Reports have indicated that as many as 11 million people in United States have been consuming drinking water with perchlorate concentration higher than 4 μg/l [6].

So far, the clean-up of some of the perchlorate contaminated sites has involved several billions of dollars. In 2014, the Nevada division of EPA allocated 1.1 billion dollars to a trust for cleaning up the perchlorate contamination in Lake Mead. This contamination originated from the manufacture of jet fuels by Ker McGee Chemical Company (KMCC) and it eventually led to the creation

of largest perchlorate plume in the nation [7]. Reports indicate that this perchlorate plume showed concentrations as high as 18,000 ppm prior to the cleanup, especially in areas closer to the industrial site [8]. In 2012, DOD and several other companies had to invest 50 million dollars for the cleanup of the perchlorate contaminated sites of Rialto, California [5]. Similar cleanup ventures were also taken up by NASA following the shutdown of several perchlorate-contaminated wells in Pasadena, California [9]. It is therefore quite clear that while developing the most viable treatment technique is essential, the latter also needs to be cost-effective in order to be actually implemented.

There are several wastewater treatment options available for the remediation of perchlorate, like fluidized bed biological reactor treatment, membrane-based processes like reverse osmosis (RO) and nanofiltration (NF), ion-exchange, ultraviolet laser reduction, etc. [3]. In this paper, we mainly focus on the pressure-driven membrane-based processes for removing perchlorate. Different research groups have tried out ultrafiltration (UF), nanofiltration (NF) as well as reverse osmosis (RO) membranes to assess their efficiency in reducing perchlorate [10–16]. Being a monovalent ion, perchlorate can be most effectively removed by a RO membrane [17]. However due to the inherently dense structure of the membrane, the latter offers a very low water flux. This makes RO a highly energy-intensive process with a low energy recovery percentage. Nanofiltration (NF) membranes require a much lower transmembrane pressure compared to RO but their monovalent ion rejection is not sufficiently high [18]. Our research focusses on the surface modification of commercial NF membranes in order to enhance their monovalent ion rejection capabilities to the level of RO membranes without significantly lowering down their permeabilities. These highly perm-selective membranes have the potential to replace the existing RO membranes and thereby reduce the energy/electricity costs involved in the RO process. The surface modification technique used in our research is the Layer-by-layer (LbL) assembly which involves the alternate deposition of oppositely charged polyelectrolytes (PE) on a surface [19]. This aqueous based thin film deposition technique was pioneered by Iler [20] and much later, in 1992 Decher et al. [21,22] brought to light the tremendous versatility of this technique. Over the last two decades this thin film deposition technique has found wide applications in the fields of sensors [23,24], fuel cells [25,26], gas barrier films [27,28], drug delivery [29,30] and membranes [18,31,32]. The wide choices of polyelectrolytes available, the deposition conditions used during the process and the number of bilayers are some of the tuning parameters that help in optimizing the performance of membranes [18].

PEM membranes have been widely employed to reject divalent/multivalent ions [33–38]. Comparatively fewer research groups have worked on the application of polyelectrolyte multilayer (PEM) membranes to typical RO applications involving the rejection of monovalent ions [39–44]. In order to fabricate PEM-based RO membranes, an approach commonly taken by a number of research groups is to modify a porous UF membrane using a considerably large number of PE bilayers. In most of these cases a high rejection value was reported but the permeabilities dropped down to values even lower than commercial RO membranes. A parallel approach was taken by Malaisamy et al., to make salt rejecting membranes by modifying a commercial NF 270 (Dow Filmtec, MI) membranes with just a few bilayers of polyelectrolytes [45]. A high value of permeability was attained; however the percentage removal of the target ion, i.e. fluoride ion was not as high as a commercial membrane. Overall, a good balance between high permeability and high rejection has not been achieved so far. In our work we used the NF 90 membrane (Dow Filmtec, MI) as the base membrane and PAH and PAA as the surface modifiers. We worked on optimizing the LbL process in terms of number of

bilayers and pH used for depositing the multilayers. The most optimized system was then compared with the commercial RO membranes in terms of permeability and perchlorate rejection. To our knowledge, this is the best combination of high permeability and high rejection of monovalent ions, as shown by a PEM based RO membrane, based on what has been reported in literature so far. Besides, the application of PEM based membranes for the removal of perchlorate ions has not been tried out before.

2. Experimental section

2.1. Materials

The nanofiltration membranes (NF 270 and NF 90) as well as the reverse osmosis membranes (BW 30 and SW 30) were purchased from Filmtec, Dow Chemical Company (Midland, MI). Potassium perchlorate salt, poly (acrylic acid sodium salt) (M_w 15,000, 35 wt.% solution in water) and poly (allylamine hydrochloride) (M_w 900,000) were purchased from Sigma Aldrich. Glutaraldehyde (50 wt.% solution) was obtained from Electron Microscopy Sciences (Hatfield, PA). All aqueous solutions were prepared using deionized (DI) water (>18.2 MΩ) supplied by a Barnstead Nanopure Diamond–UV purification unit equipped with a UV source and a final 0.2 μm filter. Unless specified otherwise all procedures were carried out at room temperature.

2.2. CF 042 cross flow membrane system

A CF 042 cross flow unit (Sterlitech, Kent, WA) with an effective surface area of 42 cm² was employed as the membrane module. This type of cross flow cell has a rectangular geometry, the flow channel being 3.62″ in length, 1.8″ in width and 0.09″ in depth. A positive displacement pump (Hydra-cell M03, Wanner Engineering, Minneapolis, MN) was used to deliver the feed from a conical 5-gallon feed tank. A variable speed drive (Emerson, St Louis, MO) was attached to the pump which controlled its speed. A part of the feed stream was directed back to the feed tank via a bypass valve. A back-pressure regulator was used to control the transmembrane pressure across the membrane module. The retentate stream was recycled back to the feed tank and the retentate flow rate was measured by a Site Read Panel Mount Flowmeter (Blue-White, Huntington Beach, CA). The permeate stream was collected and weighed on a measuring balance and the flow rate was determined gravimetrically. The temperature of the solution inside the feed tank was maintained at room temperature by a digital chiller (Polysciences, Warrington, PA). All the components of the cross-flow setup were obtained from Sterlitech (Kent,
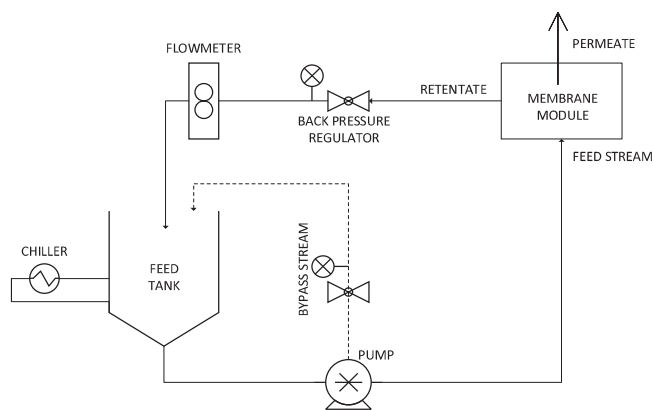

Fig. 1. Schematic representation of Sterlitech CF 042 cross flow system.

Washington) and assembled in our lab. A detailed schematic diagram of the above cross flow system has been shown in Fig. 1.

2.3. Experimental protocols

2.3.1. Filtration protocol

All membranes were soaked in DI water overnight. Initially, the membranes were compacted for 24 h by passing DI water across them at a pressure of 10 bar. The cross flow velocity was maintained at a value of 1 l/min. The flux was calculated by measuring the volume of water collected over a certain period of time. Following the DI water compaction stage, the perchlorate salt solution (10 ppm concentration) was made to flow across the membrane for another 24 h at a pressure of 5 bar. At the end of this stage a steady value of solution flux was recorded. The permeate samples were collected for half an hour following this stage. The percentage rejection (% R) was calculated as $\left(1 - \frac{C_p}{C_f}\right)$ where C_p and C_f are the concentrations of permeate and feed respectively. The concentrations were determined by a Q-Trap LC-MS/MS mass spectrometer in order to evaluate the membrane rejection. All experiments were validated using a minimum of three replicates for each type of membrane used.

2.3.2. Layer-by-layer (LbL) deposition process

Both PAH and PAA were prepared at a concentration of 10 mM. The pH of each of the solutions was adjusted to their desired values using 1 M HCl and 1 M NaOH. An Orion pH meter was used to read and adjust the pH of the solutions. The glutaraldehyde solution was prepared with a concentration of 1.5 wt.% without any pH adjustment. The permeate side of the membrane was covered, in order to make sure that the deposition only takes place on the feed side. The LbL was carried out using Carl Zeiss Slide Stainer which employs a robotic arm to move the sample from one solution bath to another. The dipping time in each polyelectrolyte solution was set to 10 min. After each dipping step the substrates were rinsed with DI water three times consecutively for 2 min, 2 min and 1 min respectively. Following the deposition of one bilayer, the sample was sonicated for 2 min. The protocol was repeated for the desired number of bilayers. Following the deposition of the polyelectrolyte multilayers the membranes were dipped in glutaraldehyde solution for 90 min. The sample was then washed with DI water three times for 15 min each and sonicated for 5 min to remove the excess glutaraldehyde. Following the LbL deposition, the membranes were soaked in DI water for at least 12 h prior to usage.

2.3.3. Quantification of perchlorate using LC-MS/MS

The perchlorate concentrations in the feed and permeate samples were quantified using Q-Trap 3200 LC-MS/MS. A prevail organic acid column (Grace Davison Discovery Sciences, Deerfield, IL) was used as the liquid chromatography column. Methanol and 10 mM ammonium acetate in a 9:1 methanol–water mixture were used as solvents. A flow rate of 0.1 ml/min was used and the perchlorate retention time was 6 min. Multiple reaction monitoring (MRM) was used to detect and analyze perchlorate ions. ANALYST software was used for quantifying the results from the mass spectrometry tests. The calibration range was selected between 0.5 mg/l and 50 mg/l. The perchlorate concentrations used for preparing the calibration standards were 0.5, 1, 2, 5, 10, 20 and 50 mg/l with three replicates of each. An R^2 value of around 0.98–0.99 was obtained in almost all cases. Before running any test the column was purged with the solvents and the instrument was equilibrated for at least 5 min.

2.4. Thin film characterization

The thickness of the deposited PE films was measured using a J.A Woollam M-44 Ellipsometer. For the purpose of this test, the polyelectrolyte films were deposited on gold coated glass slides (VWR International, Radnor, PA). These gold coated glass slides were treated with O_2 plasma for 20 min using a Harrick plasma cleaner (Harrick Scientific Corporation, Broading Ossining, NY) with 30 W RF power under 100 millitorr vacuum. Oxygen plasma treatment imparts hydrophilicity and leads to the formation of negatively charged gold-oxide on the surface [46]. Immediately after the plasma treatment, the gold-coated substrates were put in the slide stainer for the LbL surface modification, following the same protocol as described earlier (Section 2.3.2). For the PE films, the model for generic films (assuming refractive index as 1.5) was used. The surface zeta potential of the membranes was analyzed using an electrokinetic analyzer (BI-EKA, Brookhaven Instrument Corp., Holtsville, NY). A 1 mM Potassium chloride (KCl) solution was used as the electrolyte. A poly methyl methacrylate (PMMA) substrate was used as the reference material. All membranes were soaked in DI water overnight prior to being used for measurements.

3. Results and discussions

We based our research on the idea that if an existing NF membrane be modified by LbL we can essentially fabricate a RO membrane with high flux as well as high rejection of perchlorate ion. As the first step towards selection of the substrate, we tried out two types of commercial NF membranes. Under the same experimental conditions, we also tried out two types of RO membranes which helped us determine the target performance that we expected the PEM membranes to achieve.

3.1. Performance of commercial membranes

NF 270 and NF 90 were the two types of NF membranes and BW 30 and SW 30 were the RO membranes that we tested in the CF 042 cross flow system. NF 270 is a "loose" NF membrane with a poly piperazinamide based skin layer of 14–80 nm thickness while NF 90 is a "tight" NF membrane with a polyamide skin layer of around 134–214 nm [47]. Both the RO membranes are fully aromatic in nature. The skin layer of the BW 30 membrane is around 0.2–0.5 μm and that of SW 30 it is 0.6 μm [48]. All the tests were carried out at a transmembrane pressure of 5 bar under a cross flow velocity of 1 l/min with a perchlorate salt concentration of
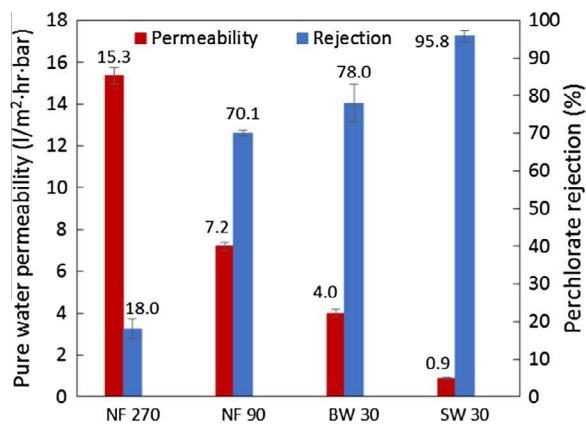

Fig. 2. Performance of the commercial membranes with respect to pure water permeability and perchlorate rejection.

10 ppm. Fig. 2 shows the performance trend of all the commercial membranes.

The results can be correlated very well with the structural properties of the respective membranes. As we move from NF 270 to SW 30 in the same order as shown in Fig. 2 the skin layer progressively keeps getting thicker and denser with a higher degree of crosslinking. Consequently the NF 270 membrane has the highest water flux but the lowest perchlorate rejection. On the other hand the SW 30 membrane showed a very high rejection of around 95% at 5 bar but with a very low permeability of 0.88 l/m^2 h bar. The NF 90 membrane showed an intermediate performance with a permeability of about 7.1 l/m^2 h bar and about 71% perchlorate rejection. We selected NF 90 as the substrate and fabricated the multilayers in a way that the rejection of the modified NF 90 could be equal to the perchlorate rejection of SW 30 but with higher permeability.

3.2. Performance of PEM membranes

The NF membranes, like NF 270 or NF 90 typically have pore sizes ranging between 1 and 5 nm [49]. The hydrated radius of perchlorate ion is around 1.37 Å, which explains the lower rejection offered by these membranes. The polyelectrolyte-based thin films layered on NF substrates can serve as nanothin barriers to the passage of ions. The challenge primarily lies in attaining a good permselectivity value which requires careful consideration of the choices of PEs used and their deposition conditions. Based on literature, it is quite an established fact that for weak PEs like PAH and PAA, the film properties like morphology, thickness, etc. are a strong function of the pH of the deposition solutions [50,51]. By tuning the pH conditions, we can build up thick loopy films wherein each layer measures up to 80 Å as well as very thin flat films with an average bilayer thickness of 3–5 Å [50]. The number of bilayers also plays a major role during the layer-by-layer buildup process. For the first few bilayers the film growth is linear, but beyond a certain critical number of bilayers, an exponential growth pattern creeps in [52], which can lead to lowering of the flux. These two polyelectrolytes were chosen as their properties can be varied to a large extent by changing some external parameters, adding considerable flexibility to the modification process. Polyelectrolytes swell in water. On swelling, the overall thickness of the film increases accompanied by an increase in the free volume between the polymer chains. This affects the flux as well as ion rejection of the membrane. Crosslinking the polyelectrolytes limits their swelling to a great extent [53]. We therefore chemically crosslinked the polyelectrolyte system by using glutaraldehyde to react with the amine groups of PAH thus limiting swelling to a certain extent [53–55].

3.2.1. Effect of pH of the polyelectrolytes

Depending on the pH of the polyelectrolytes, the type of interaction may be electrostatic or hydrogen bonding. According to literature, when both PAH and PAA are deposited at pH of 6.5, the film thickness is the lowest among all other pH conditions [50]. At this pH condition, both the polyelectrolytes are fully charged and are deposited on the surface as thin flat films via electrostatic interaction. On the other hand, when PAH is deposited at a pH of 8.5 and PAA at 3.5, both of them are partially charged and they are deposited as thick loopy films. We tried out 5 bilayers of each of the two polyelectrolyte systems to compare their performances. As shown in Fig. 3, the modified NF 90 membrane with 5-bilayers of PAH (pH 8.5) and PAA (pH 3.5) showed an extremely low permeability value of 0.45 l/m^2 h bar which was even lower than a commercial SW 30 membrane. Compared to that, 5 bilayers of PAH (pH 6.5) and PAA (pH 6.5) had almost 6 times higher permeability than SW 30 membrane. The rejection offered by the
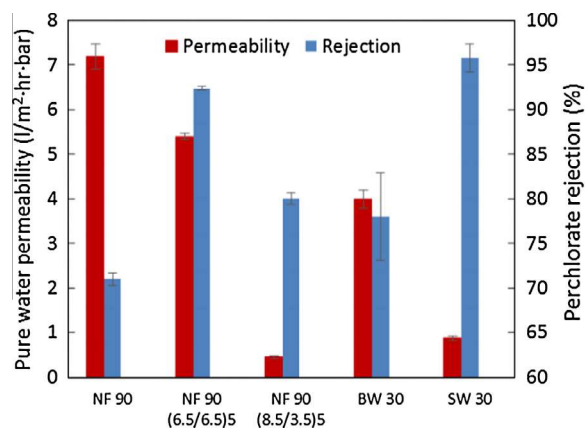

Fig. 3. Effect of the pH conditions used during the deposition of polyelectrolytes and the comparison of the modified membranes' performance with the commercial membranes. [NF 90(6.5/6.5)$_5$ represents NF 90 membrane modified with 5 bilayers of PAH (pH 6.5) and PAA (pH 6.5) and NF 90(8.5/3.5)$_5$ represents NF 90 membrane modified with 5 bilayers of PAH (pH 8.5) and PAA (pH 3.5)].

6.5/6.5 system was around 93% while for the 8.5/3.5 system it was around 81%.

A schematic representation of the above phenomenon has been shown in Fig. 4. The higher thickness of the 8.5/3.5 films results in lowering of the water flux. The swelling tendency of the 8.5/3.5 film is higher than the 6.5/6.5 film [56]. Cross-linking with glutaraldehyde reduces the swelling percentage to a certain degree in both the cases. However, glutaraldehyde only crosslinks the PAH layers leaving the PAA chains free to swell. An inherently higher degree of swelling for the PEMs under 8.5/3.5 condition as compared to the 6.5/6.5 condition, allows higher permeation of perchlorate ions across the film. In a previous study, a similar observation was made regarding the release of a certain cationic dye molecule from PEM films which were fabricated under different pH conditions [57]. According to the authors, the PAH/PAA films recorded a higher release rate when its degree of swelling was higher at the 2.0/2.0 pH condition as opposed to the 6.5/6.5 condition. In conclusion it can be said that the flat film configuration worked better both in terms of higher permeability as well as higher rejection in comparison to its loopy counterpart.

3.2.2. Effect of the number of bilayers

The number of bilayers is another important parameter which helps us tune the performance of the membranes. Fig. 5 shows the permeability and rejection of the modified membranes as a function of the number of bilayers.

The rejection of the bare NF 90 membrane was around 71%. With just 1 bilayer of [PAH (pH 6.5)/PAA (pH 6.5)] the rejection of the modified membrane increased to 86%, with only a 20% decrease in water permeability from the underlying membrane. On increasing the number of bilayers, we found that 3 bilayers are sufficient to enhance the rejection of NF 90 to almost the same value as shown by SW 30. As far as the flux is concerned, no significant change was observed on increasing the number of bilayers from 1 to 5. The slight difference in the flux of the membranes, modified with different number of bilayers, can be attributed to the very low thickness of the films. The thickness data from 3 bilayer onwards is shown in Fig. 6. The thickness values of one and two bilayers were too low to be detected, given the limited sensitivity of the ellipsometer. The layers grow linearly till 5 bilayers with an average bilayer thickness of 6 Å. This is in good agreement with previously reported data [50,56,58].

It can be assumed that with the deposition of the first bilayer, majority of the surface gets covered with the PEs which is the
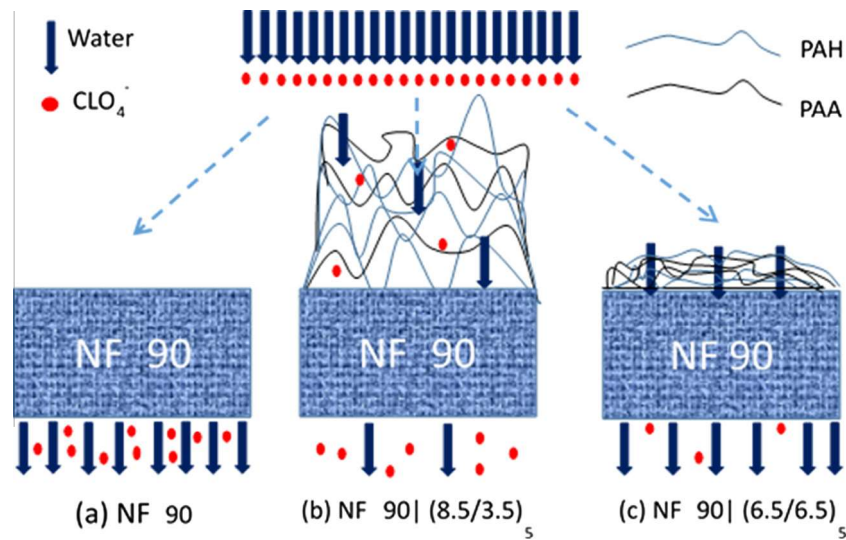
Fig. 4. Schematic representation of the effect of pH on the performance of the modified membranes in terms of permeability and rejection.
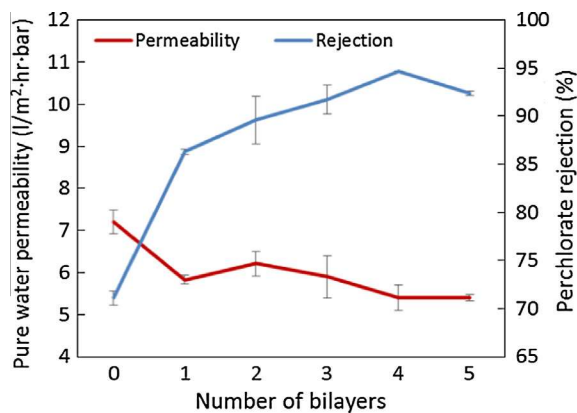

Fig. 5. Variation in the permeability and rejection of the modified membranes as a function of the number of bilayers.

cause behind the increase in rejection. The 20% reduction in permeability that was observed can be attributed to the covering up of the very fine pores on the NF 90 membrane with the first bilayer. After the deposition of 4 additional bilayers, a negligible
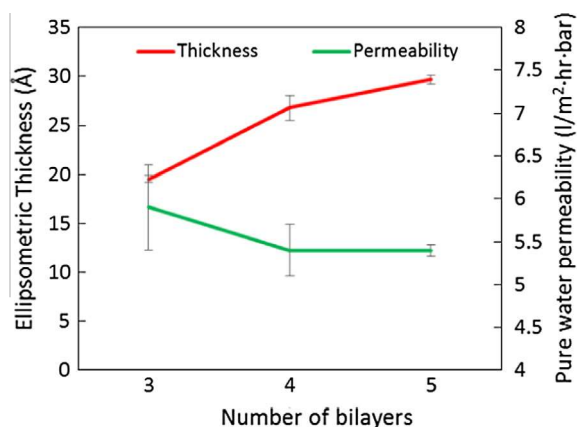
change in permeability was observed. The average value of permeability of the modified membranes was around 5.75 l/m^2-h bar. However in order to increase the rejection beyond 86%, we needed at least 3 bilayers. From 3 to 5 bilayers, no further improvement in rejection could be achieved as can be seen in Fig. 4. The minor differences in the performance of the 3, 4 and 5-bilayer systems can be attributed to certain unavoidable experimental fluctuations. For all practical purposes, the rejection of these three systems can be averaged out to a value of 93%. In this context, it should be noted here that the difference in the skin layer thickness between a commercial NF 90 membrane and SW 30 membrane is around 400 nm. For the modified membranes, only 20 Å of PEMs deposited on a NF 90 membrane, is enough to achieve the same level of rejection as SW 30.

3.2.3. Optimized membrane performance

Taking the 3-bilayer system as the most optimized one, we compare its performance with some of the commercial membranes as shown in Fig. 7. The permeability of the modified membrane is almost 6 times that of SW 30 membrane and 1.5 times that of BW 30. Its rejection is much higher than BW 30 and almost equivalent to SW 30. Therefore, we successfully designed a modified
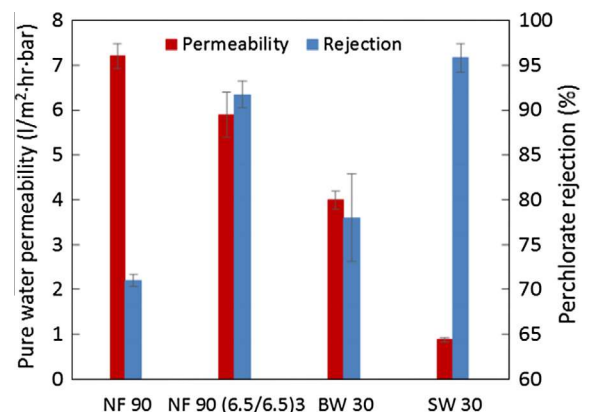

Fig. 6. Variation in the film thickness and the permeability with the number of bilayers (The thickness of the 1 and 2-bilayer systems could not be measured due to the lack of sensitivity of the ellipsometer used).

Fig. 7. Comparison in the performance of the optimized membrane with respect to the bare membrane and commercial RO membranes. [NF 90(6.5/6.5)$_3$ represents NF 90 membrane modified with 3 bilayers of PAH (pH 6.5) and PAA (pH 6.5)].

membrane system, having an excellent combination of high permeability as well as high rejection.

The level of perchlorate contamination varies significantly among different sites within the country. Consequently, the percentage rejection required to reduce the perchlorate concentration to the regulatory standards, also varies from one site to another. The state of California, which is notorious for perchlorate contamination, is an example. Here the concentration varies within a wide range of 18–280 ppb [4] and the maximum allowable concentration is around 1 ppb. This indicates that the same level of rejection is not required in all of the perchlorate contaminated sites. For the lower range of concentrations, just 1-bilayer of PAH (pH 6.5)/PAA (pH 6.5) is sufficient to effectively reduce the perchlorate concentration. For higher concentrations of perchlorate, however, the 3-bilayer system would be necessary to make sure the rejection is high enough to meet the standard requirements. Overall the LbL process presents a highly flexible modification technique, which can be tuned as per the application demands.

3.2.4. Mechanism of perchlorate rejection

The mechanism of ion rejection by PEM membranes can be either size-based [49] or charge-based [59] or most likely a combination of both. In order to find out the more dominant mechanism, we measured the streaming potentials of the modified membranes as a function of the number of bilayers. Fig. 8 shows the variation of surface zeta potential with the number of bilayers along with their corresponding rejections.

As expected, the bare NF 90 membrane shows negative charge under the tested conditions. All the modified membranes had PAA as their outermost layer; hence they were negative as well. A screening of the surface charge was observed following the deposition of the first two bilayers and the magnitude decreased further after three or more bilayers are deposited. But overall, the deposition of PAH/PAA multilayers did not alter the magnitude of the surface charge of NF 90 to any significant degree. On the other hand, a careful look at the rejection profile of the modified membranes reveals an increase from 71% to 86% on deposition of only one bilayer and kept increasing till we reached 3 bilayers. Given that, the charge does not vary to a significant extent with the number of bilayers, the streaming potential data and the rejection data cannot be correlated very well. Our hypothesis of surface coverage being related with the rejection seems to fit better with this situation. With higher surface coverage on going from 1 bilayer to 3 bilayers, higher perchlorate rejection was obtained. Following the deposition of three bilayers, the surface coverage reaches a plateau and so does the rejection. The surface charge, therefore, does not play any major role in determining the rejection behavior of these membranes. It is size-based exclusion that is the main perchlorate rejection mechanism for these modified membranes. This is in agreement with the findings of Bruening et al., regarding the rejection of Fluoride ion by PEM-based membranes [49].
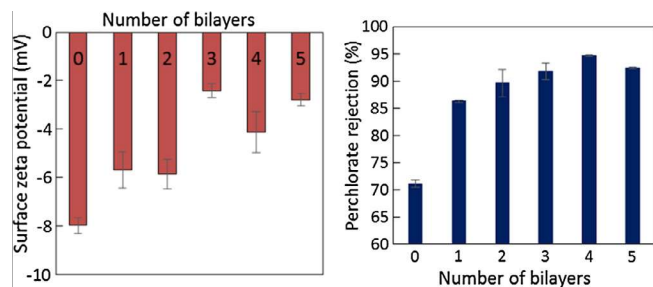

Fig. 8. Variation of surface zeta potential (left) as a function of the number of bilayers along with the corresponding variation in perchlorate rejection (right).

4. Conclusion and future work

For the first time, PEM based membranes were applied for removing perchlorate ions from drinking water sources. A high flux and high rejection membrane was fabricated by the surface modification of NF 90 membrane by the LbL assembly of PAH and PAA. The pH used during the deposition of the polyelectrolytes played a pivotal role in determining the permselectivity of the membrane. When both the polyelectrolytes were deposited at a pH of 6.5, the modified membrane had higher permeability as well as higher rejection than the case where PAH was deposited at a pH of 8.5 and PAA at 3.5. The effect of the number of bilayers deposited was also investigated. There was only about 20% reduction in the permeability of the bare membrane after depositing one bilayer and after that the value practically remained the same till 5 bilayers. As for rejection, the highest increase was seen on going from the bare membrane to 1 bilayer and after that there was only a slight increase till 3 bilayers. Overall, modification of NF 90 with 3 bilayers of PAH and PAA, both being deposited at pH of 6.5, gave the most optimum results with a perchlorate rejection of around 93% and permeability of 5.75 l/m^2 h bar. The modified membrane had 6 times higher permeability than SW 30 and 1.5 times that of BW 30. The perchlorate rejection of around 93% was also very close to what is shown by SW 30 and higher than that of BW 30 under the same conditions of feed concentration and pressure. The streaming potential results showed that the ion rejection mechanism barely depends on the surface charge of the outermost layer. This enabled us to conclude that size exclusion mechanism was more dominant than charge-based separation in this case.

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