Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.0666

69 (2017) 84–92
March

Surface modification of polyamide membranes using the layer-by-layer technique: characterization and antifouling potential

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Received 16 June 2016; Accepted 29 August 2016

ABSTRACT

In this paper, modification of NF90 and BW30 polyamide membranes via layer-by-layer deposition of polycationic and polyanionic polyelectrolytes of different molecular weights is reported. Three anionic polyelectrolytes: sodium salt of poly(sodium 4-styrene sulfonate), poly(4-styrene sulfonic acid-co-maleic acid) sodium salt, poly(acrylic acid) sodium salt, and two cationic polyelectrolytes: poly(diallyldimethylammonium chloride) and poly(ethylenimine) were used for membrane modification. The effects of deposition time, the number of polyelectrolyte layers, chemical nature and molecular weight of the polyelectrolytes on the degree of membrane modification were evaluated. The surface morphology of the prepared composite membranes were studied using atomic force microscopy. An enhanced resistance to membrane biofouling of the modified membrane samples was shown during seawater treatment in the non-continuous regime. A possible mechanism of the bactericidal action of the modified membranes is discussed.

Keywords: Layer-by-layer modification; Polyelectrolytes; Membrane biofouling; Contact angle; Atomic force microscopy

1. Introduction

The main problem arising upon water treatment and desalination using pressure-driven membrane processes such as microfiltration, ultrafiltration, nanofiltration (NF) and reverse osmosis (RO) is membrane fouling that seriously hampers the application of the membrane technologies [1]. Depending on feed water composition, several types of fouling can occur in membrane systems, which include inorganic fouling (or scaling), particulate/colloidal fouling, organic fouling and biofouling [2].

From all types of membrane fouling, the biofouling is the most difficult to cope with [3]. Biofouling is a dynamic process of microbial colonization and growth, which results in the formation of microbial biofilms on the membrane surface [3,4]. The membrane biofouling is initiated by irreversible adhesion of bacteria to the membrane surface followed by fast growth and multiplication of the cells in the presence of feed water nutrients [4]. With time, the initial sessile microbial population can eventually form a biofilm, which consists of a confluent lawn of bacteria on the membrane surface surrounded by a protective excretion of polysaccharides and other macromolecules. As fouling progresses, membrane flux sharply declines; higher operating pressures and more energy must be expended to achieve the desired throughput [1].

In general, membrane fouling is mainly determined by the foulants' ability to adsorb on the membrane surface influenced by hydrophobic interactions, hydrogen bonding, van der Waals attractions, or electrostatic interactions [5].

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Presented at the EDS conference on Desalination for the Environment: Clean Water and Energy, Rome, Italy, 22–26 May 2016.

Therefore, one of the main approaches to mitigate membrane fouling is to minimize adhesion interactions between a foulant and a membrane [5,6]. It was reported that chemical modification of the membrane surface with hydrophilic and charged monomers makes it possible to increase resistance of membranes to organic fouling and biofouling [7–11]. The majority of the previous studies in this field were performed using photo-initiated surface grafting, plasma treatment, chemical vapour deposition or other rather complex modification techniques [6–8].

The surface coating of the membranes via *layer-by-layer* (LbL) deposition of polyelectrolytes seems to be a simple and flexible technique to improve the membrane fouling resistance [12]. In this method, polycationic and polyanionic polyelectrolytes are alternately deposited on a membrane surface mainly due to electrostatic and hydrophobic interactions. The attractive features of the LbL technique are that hydrophilicity and thickness of a deposited layer can be well controlled and the membrane's properties can be optimized by varying of the polyelectrolyte type [12–15]. It should be also highlighted that LbL assembly might be used for membrane modification directly "*in situ*" in commercial membrane elements.

Also, LbL polyelectrolyte membranes made of positively charged poly(allylamine hydrochloride) and negatively charged poly(sodium 4-styrenesulfonate) (PSS) or blend of poly(acrylic acid) and PSS deposited on hydrolyzed polyacrylonitrile porous support or on polyethyleneimine (PEI) modified Torlon substrates have been successfully demonstrated as forward osmosis membranes with good rejection toward NaCl [16,17].

The majority of the previous studies on LbL membrane modification have been dealt with mitigation of membrane fouling with organic compounds [18–22]. LbL assembly between PSS and poly(allylamine hydrochloride) was used to reduce RO membrane fouling with bovine serum albumine (BSA) [18]. It was reported that the antifouling resistance of modified membranes increases with a number of deposited polyelectrolyte layers due to decreasing of the surface roughness. Malaisamy et al. [19] showed that an absolute value of the zeta potential of polyamide membranes modified with PSS/poly(diallyldimethylammonium chloride) (PDADMAC) increased with numbering of polyelectrolytes bilayers on the membrane surface. By changing a type of a terminated polyelectrolyte layer and a number of bilayers, the membrane zeta potential and antifouling properties of the membranes can be adjusted.

Su et al. [20] used both static and dynamic adsorption for LbL deposition of PDADMAC and PSS on the surface of polysulfone membranes. It was shown that the membrane hydrophilicity was improved when more than five bilayers were adsorbed onto the membrane surface. Zhou et al. [21] modified a RO polyamide membrane by electrostatic self-assembly of poly(ethylenimine) (PEI) on the membrane surface. The charge reversal on the membrane surface due to the deposition of the PEI layer was shown to increase the fouling resistance to cationic foulants due to increased surface hydrophilicity and enhanced electrostatic repulsion between the membrane surface and the foulant.

Ba and Economy [22] deposited a layer of negatively charged sulfonated poly(ether ether ketone) onto the surface of a positively charged NF membrane. The modified membrane showed better fouling resistance compared with positively or negatively charged membranes during filtration of BSA, humic acid and sodium alginate solutions due to the reduction of the charge interaction between the membrane and the foulants.

Cellulose acetate NF membranes cast by phase inversion were surface modified by adsorption of alternated layers of sodium alginate and chitosan [23]. Comparing performances of the unmodified and modified membranes, it was shown that the flux of the modified membrane increases by 15% during filtration of BSA solutions. This phenomenon was explained in terms of repulsive electrostatic interactions between the outermost polyelectrolyte layer and the protein that prevents the membrane pore obstruction by BSA molecules.

Tang et al. [24,25] characterized several commercial RO and NF membranes by atomic force microscopy (AFM), transmission electron microscopy and streaming potential technique, and found that some RO membranes were coated with an aliphatic polymeric alcohol, which seemed to be polyvinyl alcohol (PVA). They found that the PVA-coated membranes have a neutral, more hydrophilic, and less rough surface compared with the membranes without PVA coating. Due to such surface properties during filtration, the coated membranes are less prone to fouling with organic compounds.

In addition to the previously published LbL papers [18–25], which have been focused on reduction of membrane fouling with organic compounds, the purpose of this study is to evaluate the potential of LbL-modified membranes toward mitigation of the membrane biofouling. In the attempts to reduce membrane biofouling described in this paper, NF90 and BW30 composite polyamide membranes (Dow/Filmtech, USA) were modified via the LbL approach using deposition of various polycationic and polyanionic polyelectrolytes of different molecular weights. Three anionic polyelectrolytes such as: PSS, poly(4-styrene sulfonic acid-co-maleic acid) sodium salt (PSScoMA), and poly(acrylic acid) sodium salt (PAA), and two cationic polyelectrolytes such as PDADMAC and PEI were used for modification. The surface morphology of the prepared composite membranes was investigated using AFM, zeta potentials and water contact angles on the membrane surface before and after modification have been also studied to provide addition information regarding membrane fouling issues.

2. Materials and methods

2.1. Membrane modification

NF90 and BW30 polyamide membranes supplied by Dow/FilmTec (USA) were used in the work. An active layer of these membranes was prepared by copolymerization of 1.3 phenylenediamine and benzenetricarbonyl trichloride [24,26]. Different anionic polyelectrolytes such as: PSS (molecular weight [MW] of 70 kDa), PSScoMA (MW of 20 kDa), and PAA (MW of 1.2 kDa), and cationic polyelectrolytes such as PDADMAC (MW of <100 kDa) and PEI (MW of 60 kDa) were used for modification. All polyelectrolytes were purchased from Sigma-Aldrich (USA) and used without further purification. The chemical structures of the used polyelectrolytes are presented in Fig. 1.

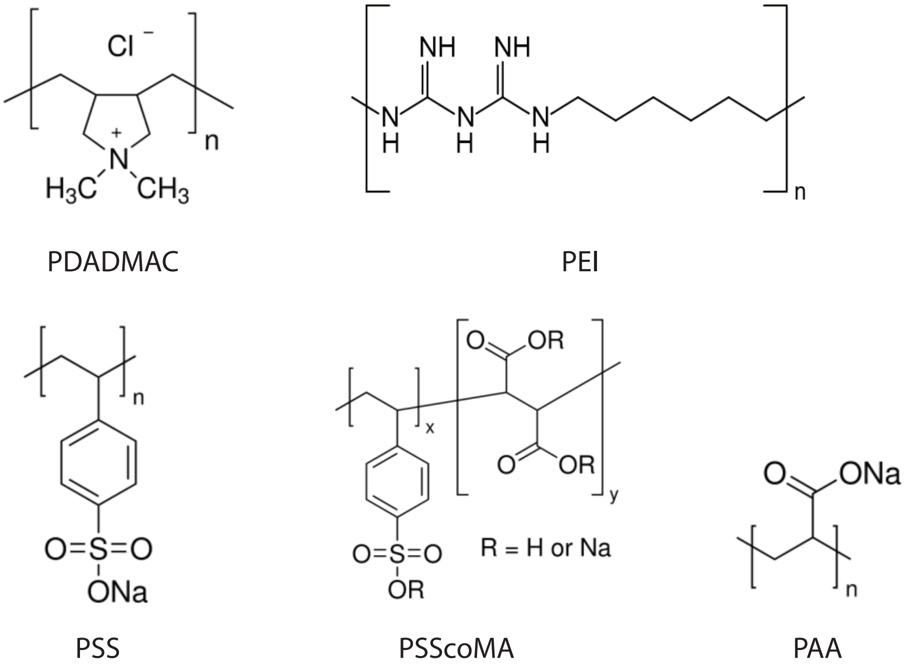

Fig. 1. Chemical structures of cationic and anionic polyelectrolytes used for LbL membrane modification.

Prior to modification, the membrane samples were soaked in Milli-Q water for a minimum of 4 h, replacing the water every hour. The electrostatic deposition of the polyelectrolytes layers on the membrane surface was initiated by immersion of a membrane in 0.05–0.5 M polycation/polyanion solution in 0.5 M NaCl (solution 1) for 5–30 min (step 1). The membrane surface was then rinsed with Milli-Q water for 1 min (step 2) before being exposed to 0.05–0.5 M polyanion/polycation solution in 0.5 M NaCl (solution 2) for 5–30 min (step 3). The membrane was then rinsed with Milli-Q water for 1 min (step 4). The completion of these four steps results in deposition of one polycation/polyanion bilayer on the membrane surface. This process was repeated "*n*" times to obtain membranes modified with "*n*" polyelectrolyte layers.

The degree of modification (DM) of the membrane was calculated from the difference between the weights of a membrane sample before and after modification as follows:

$$DM = \frac{W_m - W_0}{W_0} \times 100\% \tag{1}$$

where W_m and W_0 are the weights of a modified and initial membrane samples, respectively.

2.2. Membrane testing and characterization

A Sterlitech HP 4750 membrane cell of dead-end mode with an effective membrane area of 14.6 cm^2 was used to measure the membrane flux. The membrane flux (J) was calculated by measuring the time needed to collect a measured volume of permeate using the following equation:

$$J = \frac{V}{At} \tag{2}$$

where J represents flux (L/m^{2}h); V is volume of permeate (L); A is the effective membrane area (m^2) and t is the time taken to collect the permeate (h).

The amount of permeate collected as a function of time was measured by a digital balance (XB 3200C, Precisa, Switzerland) interfaced to a computer through a user-friendly software (Education Program, Version 3.02, Precisa).

The AFM technique was used to analyze the surface morphology and porous structure of the membranes. AFM images were obtained on a Multimode AFM with Nanoscope IIIa controller (Veeco, USA) using manufacturer supplied software. Tapping mode in air was used for the membrane imaging. Silicon cantilevers (TESP tapping mode probes, Bruker, USA) with high aspect-ratio tips of typical radius of curvature of 8 nm were used to scan the membrane surfaces. Membrane surface parameters such as the root mean square roughness (RMS) were obtained from the images. RMS is defined as the square root of the mean deviations of height values from the mean height of all the image pixels:

$$\text{RMS} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(Z_i - Z\right)^2} \tag{3}$$

where Z_i is the current Z-value, while Z and N are the average of Z-values and the number of points within the area, respectively. Full details of this imaging mode and RMS measurement are described elsewhere [27].

The surface and cross-section membrane images were taken by scanning electron microscope (SEM) Hitachi S-4800II, Japan. The polymeric membrane sample was frozen rapidly, and then fractured by simply breaking or by cutting using a new clean razor blade from the reverse side while maintained at liquid nitrogen temperature. The sample was mounted onto the stub, then coated with approximately 10 nm of gold (sputtering coating system) to make it conductive, and finally, the sample stub was inserted to the chamber in high vacuum mode to take an image.

Zeta potentials of the membranes were determined using an electrokinetic analyzer SurPass 3 from Anton Paar KG, Austria. Zeta potential value was calculated from the slope of streaming potential vs. operating pressure based on the Helmholtz–Smoluchowski equation [28]:

$$\zeta = \frac{\Delta E \mu k}{\Delta P \varepsilon_0 \varepsilon_r} \tag{4}$$

where ΔE is the streaming potential; ΔP is the transmembrane pressure drop; μ is the viscosity of the solution; k is the electrolyte conductivity; ε_0 is the permittivity of a vacuum and ε_r is water dielectric constant at 25°C. In the experimental setup, 1 mM KCl solution with pH of 5.3 ± 0.2 was pumped through a measuring cell, where two pieces of a membrane were placed with a narrow gap in between. The electrical potential difference was measured continuously by two Ag-electrodes. The pH of the KCl solution was adjusted with 0.1 M HCl or 0.1 M NaOH. The zeta potentials were averages of three measurements taken at each pH value.

A Ramé-Hart goniometer/tensiometer model 500 (Ramé-Hart instrument Co, USA) was used to measure the contact angle of a water drop of 5 µl volume on the membrane surface. The device is equipped with a high-speed video camera to monitor the side images of the drop profile as a function of time. Five measurements were conducted at different locations of membranes, and the average values for contact angle were reported.

Fourier transform infrared (FTIR) spectra of the membrane surface were measured with Spectrum Two FTIR Spectrometer (PerkinElmer, USA).

3. Results and discussion

The FTIR technique was used to confirm that LbL deposition of the polyelectrolyte layers on the membrane surface had taken place. Fig. 2 shows that FTIR spectra of unmodified and modified BW30 membrane samples differ essentially both in the position and intensity of the adsorption bands depending on chemical nature of the used polyelectrolytes.

The most significant changes in the spectra of BW30 membrane modified with PSS/PEI layers are the peaks at 1,244, 1,035 and 1,008 cm^{-1}, which can be assigned to asymmetric and symmetric stretching vibration of SO_3 groups of PSS in the modified layer, and the peaks at 1,576 cm^{-1}, which correspond to –N-H bending in PEI [29]. The broad adsorption band at 3,440 cm^{-1} is supposed to correspond to –OH group of the water adsorbed in the sample due to highly hydrophilic sulfonic acid groups. These aforementioned peaks are not presented in the spectra of the unmodified BW30 membrane, and their appearance confirms that PSS and PEI polyelectrolytes were deposited on the membrane surface.

It was found that DM values of the membrane samples depend on the immersion time of a membrane in the polyelectrolyte solutions, on a number of deposited polyelectrolytes layers and on the chemical type and molecular weight of used polyelectrolytes. As seen in Fig. 3a, the prolongation of a modification procedure (steps 1 and 3) lead to an increase in DM values, presumably, because larger amounts of polyelectrolytes are deposited on the membrane surface. The most pronounced increase in the DM value was found

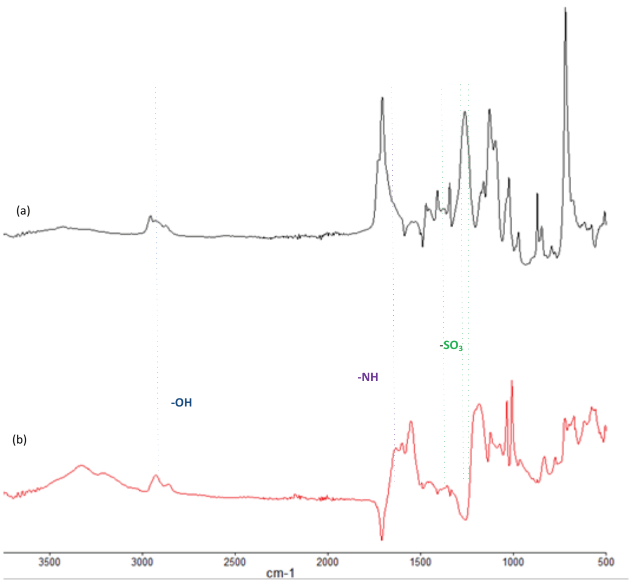

Fig. 2. FTIR spectra of the surface of unmodified initial BW30 membrane (a) and LbL-modified membranes with $(PSS/PEI)_4$ layers (b).

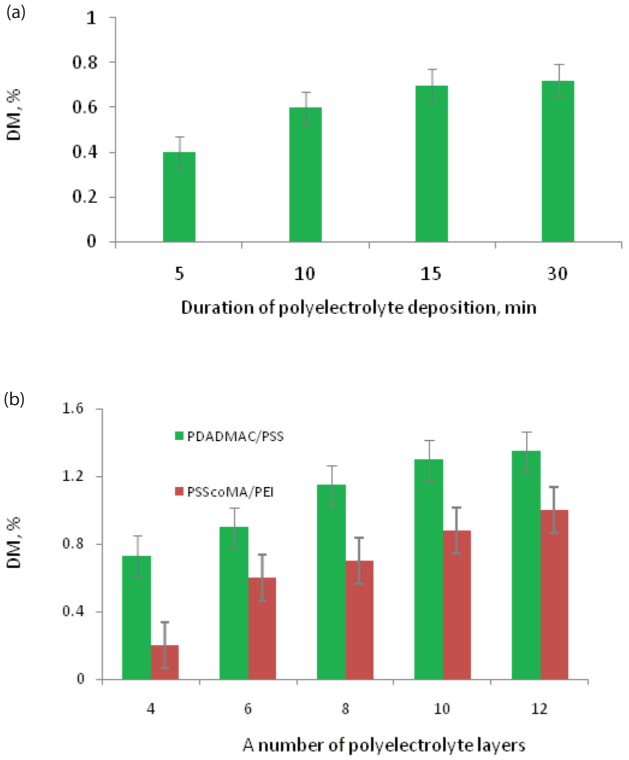

Fig. 3. Modification of NF90 membrane via LbL assembly between PDADMAC and PSS: DM vs. the modification time (a) and DM vs. a number of deposited polyelectrolyte layers (b).

when duration of membrane immersion in the polyelectrolyte solution changed from 5 to 15 min, while a further increase in modification time did not essentially change the DM of the membrane sample. It may be seen in Fig. 3(b) that an increase in the number of LbL layers on the membrane surface leads to a gradual increase in the DM of the membranes. It should be noted that higher DM values were obtained for the membranes modified with PDADMAC/PSS polyelectrolyte pair compared with PSScoMA/PEI pair (Fig. 3(b)). This finding might be explained by the fact that a first deposition stage plays an important role for LbL modification. When PDADMAC (a cationic polyelectrolyte, which is positively charged over a wide pH range owing to the quaternary ammonium groups) is used for a first coating step, the electrostatic attraction between the negatively charged surface of NF90 and BW30 membranes [26] and positively charged PDADMAC macromolecules facilitates the adsorption of cationic polyelectrolyte on the membrane surface. The higher PDADMAC adsorption on the membrane surface in this first coating stage, the large amount of polyanion (PSS) is capable of depositing on the membrane surface in the following modification stage. When LbL assembly starts from PSScoMA adsorption, electrostatic repulsion of similarly (negatively) charged polyelectrolyte molecules and the membrane surface reduce the amount of adsorbed polyelectrolyte, and this reduces the DM values for PSScoMA/PEI-modified membranes compared with the PDADMAC/PSS-modified one. On the other hand, quite high DM values for PSScoMA/PEI-modified membranes (Fig. 3(b)) suggest that polyelectrolyte adsorption on the membrane surface is not solely based on attractive electrostatic interactions. Obviously, other non-ionic interactions (e.g., hydrophobic, π-π, dipolar and van der Waals forces) between polyelectrolyte macromolecules and the membrane surface may also contribute to the LbL deposition process.

It was also found that DM values depend on molecular weight of polyelectrolytes used for LbL deposition. As seen in Fig. 4, when a cationic polyelectrolyte such as PDADMAC was used for membrane modification in combination with the polyanions of different molecular weights, the DM value of modified membrane samples increase with an increase of molecular weight of polyanionic macromolecules used for modification: PAA (MW of 1.2 kDa) < PSScoMa (MW of 20 kDa) < PSS (MW of 70 kDa).

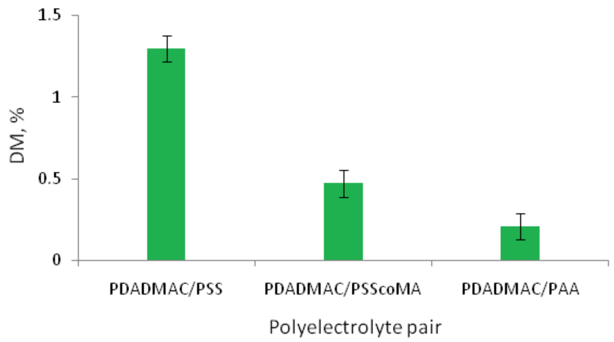

Fig. 4. LbL assembly between PDADMAC and various anionic polyelectrolytes on the surface of NF90 membrane: effect of a polyanion's molecular weight on DM values of the modified membrane samples.

Fig. 5 shows the zeta potential of the unmodified NF90 and PDADMAC/PSS-modified membranes with a different number of the polyelectrolyte layers. The unmodified NF90 membrane at pH 5.6 has a negative zeta potential of –14 mV, and after deposition of the first PDADMAC layer, the zeta potential reversed to +6 mV and then switched back to a negative value of –21 mV when alternated with a PSS layer. Thus, the surface charge of LbL-modified membrane can be switched between positive and negative after coating with a cationic or an anionic polyelectrolyte. These results are another clear indication of a polyelectrolyte coating on the membrane surface. The absolute values of zeta potential slightly increase with increasing the number of polyelectrolyte bilayers and for six or more deposited bilayers, the magnitude of zeta potential reaches +20 mV for the PDAMAC terminated membrane and –29 mV for the PSS-terminated membrane.

The water contact values for modified membrane samples with a different number of polyelectrolyte layers are shown in Fig. 6. It is seen in this figure that the water contact angle was strongly affected when the outermost polyelectrolyte layer was changed. This finding might be explained by the fact that wettability of a polymer film is generally determined by the first 5–10 A° of the polymer outermost surface [30]. If the outermost layer is changed, the wettability of the membrane changes too. The unmodified membrane exhibited an average contact angle of 55°, indicating that the surface is moderately hydrophobic. The contact angle increased to 74° when the PDADMAC

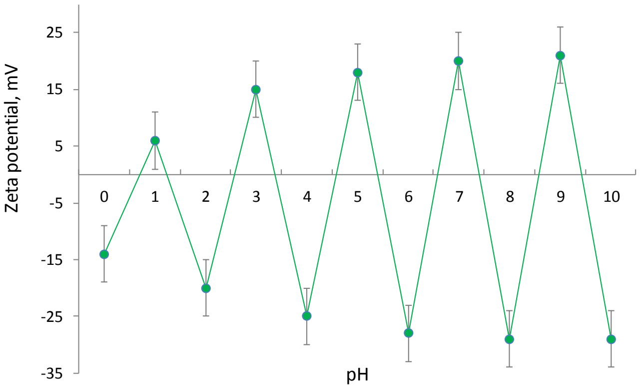

Fig. 5. Zeta potential of NF90 membrane modified by LbL deposition of PDADMAC and PSS polyelectrolytes after each coating stage. pH = 5.6. 1 mM KCl.

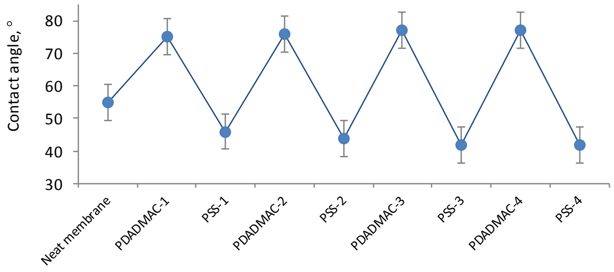

Fig. 6. Water contact angles on NF90 membrane modified by LbL deposition of PDADMAC and PSS polyelectrolytes after each coating stage.

layer was coated and decreased to 46°C for the PSS-coated membrane. Further deposition of PDMMAC and PSS layers on the membrane surface results in similar variation of the contact angles. It is seen from the presented data that PSS terminated membranes are more hydrophilic than the membranes with the PDADMAC outermost polyelectrolyte layer. This might be explained by the fact that PDADMAC macromolecules contain quaternary ammonium groups with hydrophobic character [31]. On the other hand, the presence of polar sulfonate groups in PSS macromolecules increases the hydrophilicity of the modified membrane surface. It was also reported that polycation-terminated multilayers are more hydrophobic than polyanion terminated ones as a result of lower electric charge density when polycations form the outermost layer [32].

The contact angles of unmodified NF90 and BW30 membranes and LbL samples modified with an increasing number of terminated PSS layers are presented in Fig. 7. As can be seen in this figure, the contact angle on the membrane surface reduced when the number of deposited layers increases from 2 to 4 but further deposition (8 deposited layers and more) did not practically change the contact angle value. It might be concluded that more homogeneous coverage of the membrane surface is reached when the number of modification layers increases. The hydrophilization of the modified membranes might reduce their fouling with organic compounds and microorganisms as it has been shown that membranes with hydrophilic surfaces are less susceptible to fouling compared with more hydrophobic samples [5–7].

To gain a better understanding of the features of LbL layers deposited on the membrane surface, AFM and SEM techniques were used to visualize surfaces and cross-sections of LbL-modified membranes.

Fig. 8 shows high-resolution AFM images of unmodified NF90 membrane and the modified samples with a different number of LbL layers on the membrane surface. AFM images are presented in perspective view over an area of 1 µm × 1 µm. The colour density in Fig. 8 shows the vertical profile of the sample with the light regions being the highest points and the darkest regions being the lowest points on the membrane surface. The rough surface morphology of the commercial NF90 membrane is clearly vis-

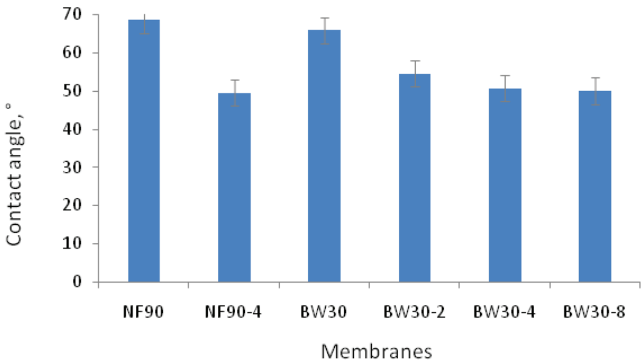

Fig. 7. The contact angles of initial NF90 and BW30 membranes and LbL-modified samples with a different number of deposited PEI/PSS polymer layers: 2 (BW30-2); 4 (NF90-4 and BW30-4) and 8 (BW30-8).

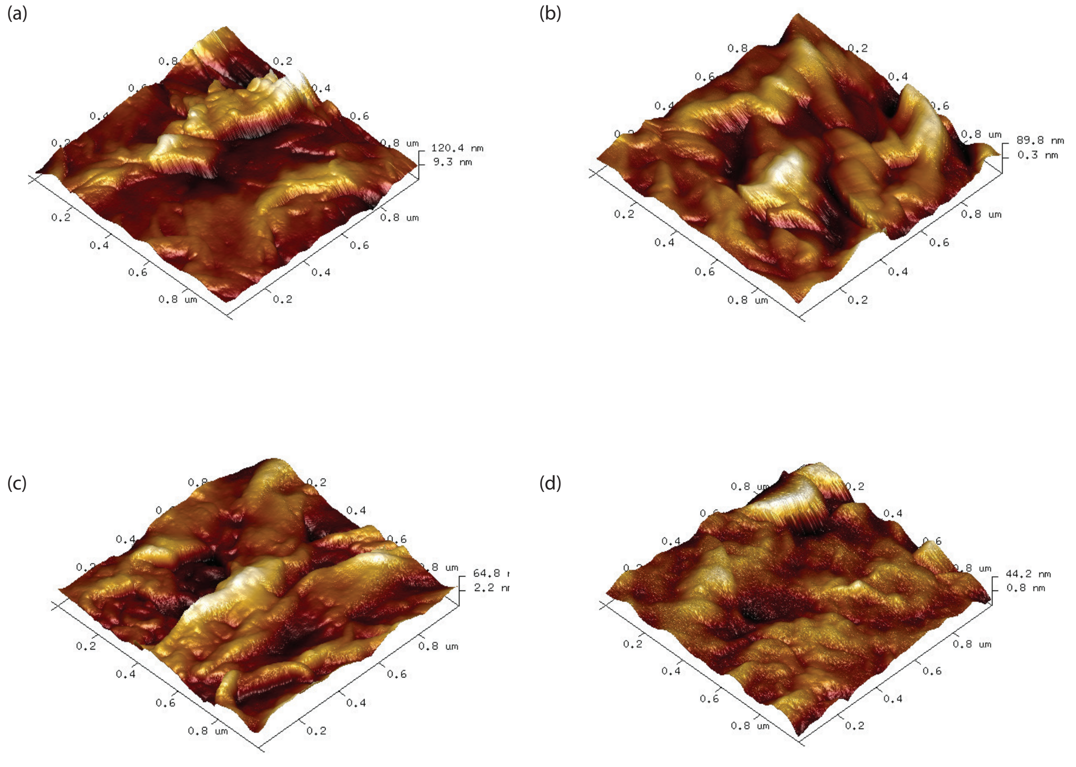

Fig. 8. AFM images of initial NF90 membrane (a) and LbL-modified samples with a different number of PSScoMA/ PEI layers: (b) - 2 layers; (c) – 4 layers; (d) – 8 layers.

ible in Fig. 8(a). The membrane surface becomes smoother as the number of modified layers increases and the valley parts of the rough surface morphology of the initial membrane are filled in with the deposited polyelectrolytes (Figs. 8(b)–(d)). The RSM values for unmodified NF90 membrane, the polyelectrolyte multilayered NF90-(PSScoMA/PEI)$_2$ and NF90-(PSScoMA/ PEI)$_4$ membranes are 21.82; 18.62; and 12.64 nm, respectively. This smoothening of the membrane surface might contribute to some extent to the reduction of membrane fouling as lower roughness most often associated with a decrease in surface fouling [33].

Fig. 9 shows the SEM images of the outer surface and a cross-section of initial and PSScoMA/PEI-modified NF90 membranes. It is seen in these images that the membranes surface topology becomes smother after LbL deposition and the thickness of a modified layer is about 1 µm (Fig. 9(b)). It should be noted that some exfoliation of the deposited layer is possible while the cross-section preparation by breaking the membrane sample at liquid nitrogen temperature (the upper-right corner in Fig. 9(d)).

Water fluxes for NF-90 membranes with a different number of deposited polyelectrolyte layers are presented in Fig. 10. As seen, the water fluxes are proportional to the applied operating pressure fluxes. The fluxes for LbL-modified membranes are somewhat lower than the fluxes of the unmodified membranes, for example, at operating pressure of 10 bar the flux declines from 62 to 50 l/m^{2}h and from 53 to 42 l/m^{2}h after deposition of four PSS/PEI layers on initial NF90 and BW30 membranes, respectively.

The performance of unmodified BW30 membrane and LbL-modified membrane samples during treatment of Arabian Gulf seawater was compared in the non-continuous regime when the filtration cycle (1 h) alternates with stops (the membranes were kept for 24 h at room temperature in the seawater). This non-continuous regime was used to minimize the possible effect of organic and colloidal fouling during filtration tests. As seen in Fig. 11, the average flux values for the initial SW30 membrane are reduced with time more rapidly than for modified membrane samples. This might be explained by antibacterial properties of LbL-modified membranes, which can inhibit the bacterial growth and reduce the formation of the biofouling layer on the membrane surface. The antimicrobial action of membrane samples with deposited cationic polyelectrolytes might be explained by penetration of polycationic chains into the bacterial cell walls [36]. Most microbial cells carry a negative surface charge [4,35]. It can be assumed that the rapid electrostatic attraction of cationic polymeric chains on the surface of the modified membrane and the negatively charged bacterial cell contributes to the membrane antimicrobial properties. In this sense, the mechanism of antimicrobial

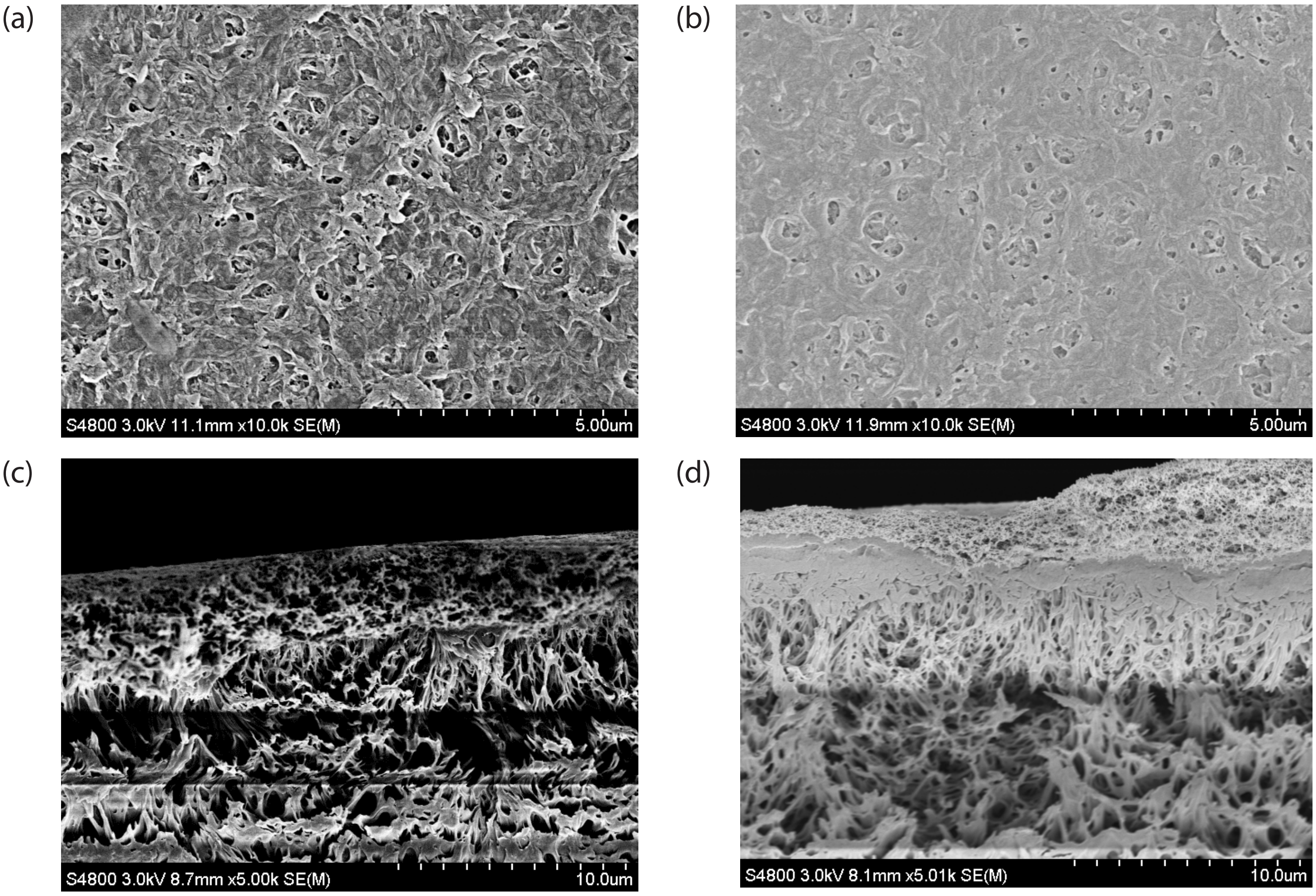

Fig. 9. CEM images of initial NF90 (a,c) and modified NF90-(PSScoMA/PEI)$_5$ membranes (b,d): the membrane surface (a,b) and the cross-sections (c,d).

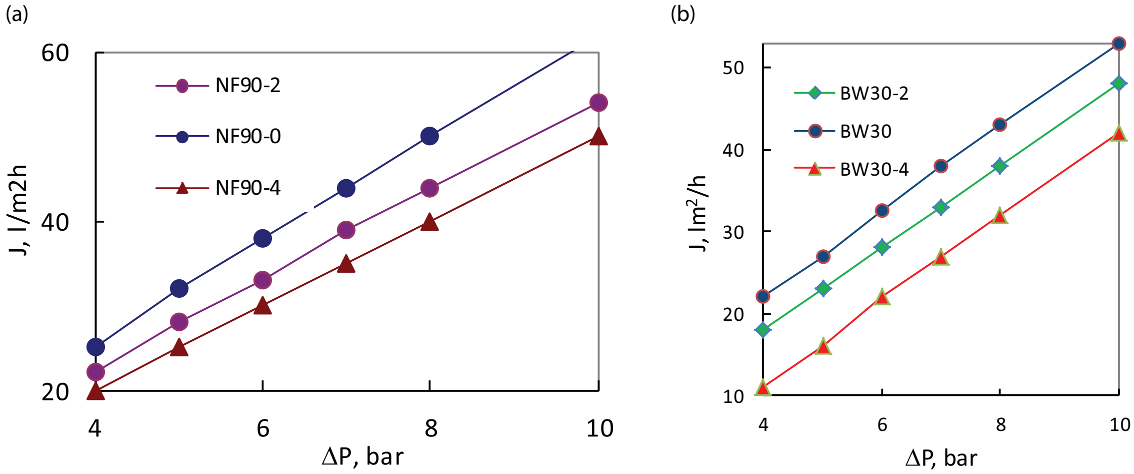

Fig. 10. Pure water fluxes vs. operating pressures for unmodified and modified NF90 (a) and BW30 membranes (b) with the different number of deposited PSS/PEI polymer layers: 2 (NF90-2 and BW30-2) and 4 (NF90-4 and BW30-4).

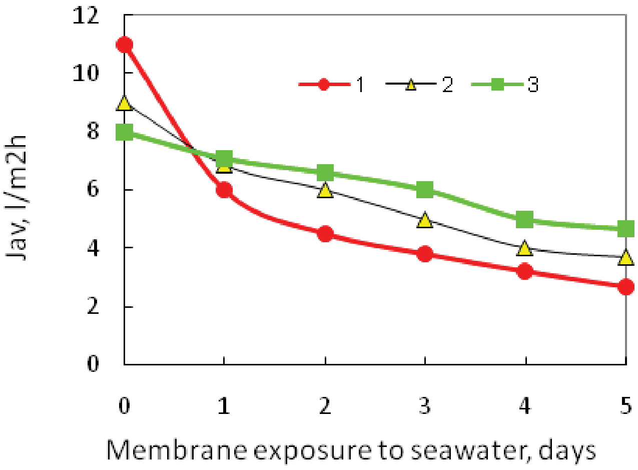

Fig. 11. The average fluxes for initial BW30 membrane (1) and polyelectrolyte multilayered BW30-(PSS/PEI)$_4$ and BW30-(PSS/PEI)$_8$ membranes vs. time of the membranes exposure to Arabian Gulf seawater (Doha). The duration of the filtration cycle is 1 h at operating pressure of 40 bars. The total dissolved solids and total organic carbon contents in sea water are 44.250 mg/L and 54.2 mg/l, respectively, pH 7.8, temperature 23°C.

action of PEI chains is similar to the one for the biguanides-based biocides [36]. Charged polycationic chains displace the divalent cations that hold together the negatively charged surface of the lipopolysaccharide network disrupting the outer membrane of gram-negative bacteria [37]. It was shown by electron microscopy that these antimicrobial agents bring about changes in the outer-membrane integrity of gram-negative bacterial cells and can induce leakage of low molecular weight cytoplasmic components from the bacteria cells [38]. The reflux up to 40% of potassium content of the bacterial cells was reported when contacting with polycationic biguanides [39]. It was also reported inhibition of biomembrane-bounded enzymes such as adenosyl triposphatase due to interaction between the cationic biocide and phosphates entities on the bacterial cell [40].

It should be also noted that the membrane fluxes slightly increase with the number of deposited PSS/PEI-modified layers (Fig. 11, curves 2, 3). This might be explained by better coating of the membrane surface with an increase of a number of deposited polyelectrolytes layers as was indicated by contact angle measurements (Fig. 7). Also, as was shown, the surface membrane roughness decreases as a number of modified LbL layers increases, and this might also improve the antifouling capability of the polyelectrolyte multilayered membrane.

4. Conclusions

Composite polyamide NF90 and BW30 membranes were modified using LbL deposition of different anionic and cationic polyelectrolytes on the membrane surface. It was found that DM values of the membranes grow with the modification time, with an increase in the number of LbL layers on the membrane surface and with molecular weight of polyelectrolytes used for modification. With AFM, it was shown that the surface membrane roughness decreases significantly as a number of modified LbL layers on the membrane surface increases. Measurement of contact angles on the membrane surface has proved that modification of the membrane surface via LbL polymer deposition leads to hydrophilization of the membrane surface. A distinct difference in the performance of the initial membrane and LbL-modified membrane samples was found during treatment of seawater in the non-continuous regime. This might be explained by antimicrobial properties of the modified membranes to inhibit the growth of bacteria on the surface and thereby minimize the formation of the biofouling layer. However, it should be noted that the active biocide cites on the membrane surface might be blocked because of adhesion of the bacterial cells. The long-term performance and stability tests for LbL-modified membranes in salty solutions as well as possibility of regeneration of the membranes' antimicrobial properties should be further addressed in future studies.

Acknowledgment

The authors are grateful to the Qatar Environment and Energy Research Institute (QEERI), Hamad Bin Khalifa University (HBKU), Qatar Foundation for financial support under project WGC-4000.

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