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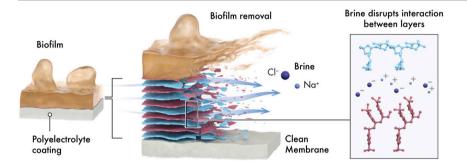
Sacrificial coating development for biofouling control in membrane systems

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GRAPHICAL ABSTRACT



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ABSTRACT

Current cleaning strategies for biofouling control on spiral wound membrane systems used for seawater desalination are not effective and can hinder long-term membrane performance. To enable effective cleaning of a membrane, we examined the in-situ application and the use of a sacrificial multilayer polyelectrolyte coating on the membrane surface. The membrane coating was based on a layer-by-layer assembly approach using two nontoxic linkers, poly (diallyl-dimethyl ammonium chloride) and poly(sodium-4-styrene sulfonate). This polyelectrolyte coating was effectively applied on the membrane surface under cross-flow conditions, and it was stable on the membrane surface under continuous operation. Coating removal requires only a concentrated sodium chloride solution (synthetic brine in our study) adjusted to pH 11. Using this procedure, both the biofilm and the sacrificial layer could be simultaneously removed, leaving a clean surface compared to the non-coated membrane. Biofouling tests showed that the coated membrane had two-fold higher permeate flux recovery than the control non-coated membrane. The used polyelectrolyte sacrificial coatings avoided the use of toxic linkers and harsh cleaning chemicals, and thus it is a suitable technique for biofouling control on reverse osmosis spiral wound membranes.

1. Introduction

During the past few decades, reverse osmosis (RO) membrane desalination has become widely recognized as a relatively energy-efficient method of freshwater production using seawater. RO membranes can reject up to 99% of a variety of elements such as monovalent and multivalent ions, viruses, bacteria, and suspended solids [1]. Even though the use of membranes is now a preferred method of seawater

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desalination, the technology has some critical drawbacks. One of the most significant concerns of RO membrane operation is the reduction of performance due to fouling. The fouling type which is the hardest to control is biofouling due to the growth, accumulation, and regrowth of biomass on the surface of the membrane [1-4].

Various chemical cleaning agents are broadly used and should be chosen specifically for the fouling composition on the membrane system. For example, caustic solutions are used for organic fouling by hydrolysis followed by solubilization [5]; chelating agents are used to weaken the structural integrity of divalent cations such as Extracellular Polymeric Substances (EPS) [6]; the use of surfactants aids on the formation of micelles for macromolecules and the use of acid solutions dissolve scaling, destroy the integrity of the cell wall and precipitate proteins [7–9]. Chemical cleaning efficiency is highly dependent on temperature, exposure time, hydrodynamic conditions, the concentration of the cleaning agents, and the age of the fouled layer [6]. Nevertheless, operational key performance as the increase in pressure drop and decrease in permeability, are still observed after the use of the specific cleaning agents becoming an economic burden for desalination plants [7,9,10].

Membrane surface modification has been previously reported as a possible solution to mitigate fouling [7,8,11]. The physicochemical characteristics of the membrane surface, such as roughness, hydrophilicity, and surface charge, impact the extent of membrane fouling [12]. For example, roughness is correlated with increased colloidal fouling, hydrophilicity limits the hydrophobic interaction between the membrane and fouling elements (e.g., proteins and some microorganisms) decreasing the fouling potential, and the surface charge determines which fouling component attaches to the membrane [12-14]. A hydrophilic membrane with a neutral surface charge can affect permeability, decrease surface charge, increase hydrophilicity, and decrease surface roughness [8,15]. Popular techniques for membrane surface modification include surface coating (e.g., amphiphilic copolymers, silver nanoparticles, and polyelectrolytes), chemical treatment using covalently coupled polymers, UV irradiation and plasma treatment to hydrophilize the surface [13,16–18]. Since the polyamide layer of the RO membrane is highly reactive towards oxidizing agents causing performance decay, Cho et al. [17] developed a surface modified polyelectrolyte membrane to be chlorine-resistant and, therefore, enabling biofouling control. However, to apply the coating, the authors use toxic chemical linkers such as glutaraldehyde, which is unsuitable for practical applications in water treatment. To remove the toxic linkers from the coatings, the bond between membrane and coating needs to be non-covalent, such as by electrostatic interactions. For example, a sacrificial coating created by layer-by-layer (LbL) deposition avoids the need of strong binding, eliminating the need of toxic linkers.

Membrane surface modification by LbL deposition is known to have good adhesion due to the amount of charged groups and the ability to adhere to any rough surface without the need for toxic linkers [16,19]. Nevertheless, a significant disadvantage of the coating strategy to prevent biofouling is the possible leach of the coating over time [13,20–22]. As an alternative, removable coatings for fouling control have been previously proposed and analyzed by flux recovery [16,18,20]. These studies observed a complete recovery of the permeate production on the coated membranes while the non-coated membranes suffered a 28% irreversible reduction in permeability [16,18]. In polyamide membranes, a coating with sacrificial properties was recently developed by Son et al. [20]. The coating was applied by spraying the polyelectrolytes on the membrane, followed by the use of alginate as a model fouling compound, and subsequently by removing the coating with brine in a high shear environment. The results showed a 97% flux recovery of the coated membrane, while the non-coated membrane only reached 83% flux recovery [20,23]. However, this approach was only examined under short-term dead-end filtration conditions, which is not relevant to continuous cross-flow operation of RO membranes. Since the coating was not applied under operational cross-flow conditions, it is not known based on these previous studies if the technique would be suitable for RO desalination and water treatment systems that operate under cross-flow conditions.

In this study, the application and removal of a polyelectrolyte coating on a polyamide membrane used for desalination under cross-flow operational conditions were examined using different techniques to assess the application and removal of the coatings. The importance of testing the coating on the membrane surface under cross-flow was to avoid the need for membrane treatment prior to placing the membrane in the modules and to ensure that the coating could be applied in-situ to regenerate the coating for multiple applications. Also, the potential of the sacrificial coating used for biofouling control was demonstrated using a membrane fouling simulator (MFS) to examine its use as a solution for biofouling of membrane systems.

2. Materials and methods

2.1. Chemicals

Poly(diallyl-dimethyl ammonium chloride) (PDDA) (CAS Registry No. 26062-79-3), poly(sodium-4-styrene sulfonate) (PSS) (CAS Registry No. 25704-18-1) were purchased from Sigma-Aldrich (US). The polyelectrolytes used are not hazardous substances according to the safety data sheets provided by Sigma-Aldrich and were used without further purification for membrane coating. Sodium Chloride (NaCl) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich (US) and were used without further purification for the removal of the coating and biofilm from the membrane surface. Sodium acetate, sodium nitrate, and sodium phosphate were purchased from Sigma-Aldrich (US) and were used without further purification as nutrients to enhance biofilm growth in the membrane systems.

2.2. Membrane coating

Both of the polyelectrolyte solutions (PDDA and PSS) were prepared at a concentration of 10 gL⁻¹ in deionized (DI) water. The following steps were performed to ensure the formation of the five-bilayers. First, the membrane was rinsed with DI water under cross-flow for 30 min. Second, the first polyelectrolyte (PDDA), which interacts with the polyamide membrane, was recirculated through the system under crossflow conditions for 5 min. DI water was rinsed through the membrane to remove the excess of PDDA (the part which did not interact with the surface) out of the membrane system. The rinsing was followed by the second polyelectrolyte (PSS) recirculation. The excess of PSS (the polyelectrolyte that did not interact with the previous layer) was removed out of the membrane system by rinsing with DI water. These coating steps were repeated five times per polyelectrolyte until the five bilayers were achieved.

To validate the formation and stability of the polyelectrolyte coating under cross-flow conditions, quartz crystal microbalance with dissipation (QCM-D) (Q-sense AB, Gothenburg, Sweden) measurements were performed. The analyses were done using a gold quartz sensor with a fundamental frequency of 5 MHz, at 22 °C under a continuous flow (0.15 mL·min⁻¹). Before the measurements the sensors were cleaned with 0.01 M NaOH, followed by 0.01 M HCl and rinsed with DI water.

The MFS was used to apply the coating on commercial polyamide RO membranes (BWRO, Dow Chemical). The five bilayer coating of the PDDA and PSS polyelectrolytes was applied under cross-flow velocity (0.163 ms^{-1}) representative for practice [24]. By increasing the number of layers the coating stability increases, but the membrane performance will be negatively affected [20]. Therefore, increasing the number of bilayers higher than five would not be feasible for practical applications. The chosen number of layers for this study was shown to be stable without significantly hindering the membrane performance for desalination. During the coating application, the MFS was fully assembled containing a feed channel spacer, a polyamide membrane, and

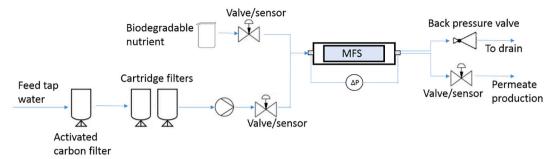


Fig. 1. Experimental setup of the membrane fouling simulator (MFS), operated under cross-flow conditions with permeate production. Biodegradable nutrients were dosed into the MFS feed water to enhance biofilm formation.

a permeate channel spacer. However, because of the feed spacer material (polypropylene), there was no electrostatic interaction between the polyelectrolytes and the spacer surface. In other words, the feed channel spacer would not be expected to be coated by the applied technique.

To evaluate the coating stability under cross-flow conditions, the MFS was operated for eight days with tap water at pH 7 at a cross-flow velocity of 0.16 m·s⁻¹. To test the sacrificial property of the coating, the removal of the coating was performed by adding sodium chloride (NaCl) at a concentration of 70 g·L⁻¹ (synthetic brine) under elevated cross-flow conditions (0.32 m·s⁻¹) for 10 min. Transmission electron micrographs (TEM) (Titan Themis Z, ThemoFisher Scientific, US) were acquired to verify the formation, stability, and removal of the polyelectrolyte coating. All coating experiments were done at 22 °C.

2.3. Biofouling studies

The experimental set-up for the membrane experiments included an MFS with a feed-water pump, a biodegradable nutrient dosage pump, a permeate flow meter, a back pressure valve, and a feed channel differential pressure sensor (Fig. 1). The MFS is a lab-scale flow cell that has been proven to be representative of spiral-wound membrane modules used in practice [24]. The MFS contained a reverse osmosis polyamide membrane sheet with an active membrane area of 20 cm \times 3 cm. A 34 mil (864 μ m) thick feed channel spacer and a 250 µm thick permeate channel spacer were used at the feed and permeate channels. Both the feed and permeate channel spacers were taken from an 8-in. diameter spiral wound reverse osmosis membrane module. The MFS is operated under cross-flow conditions fed with tap water at 22 °C with permeate production, at a cross-flow velocity of 0.163 $\,\mathrm{m\,s^{-1}},$ the representative for practice, with a constant transmembrane pressure of 1.5 bar [13,24,25]. Since tap water was used for the studies, the transmembrane pressure was adjusted to achieve a characteristic permeate flux for RO practice. However, it has been shown that biofouling studies under no or low transmembrane pressure are representative of spiral wound membrane systems [24]. All the experiments were fed with tap water to avoid organic and inorganic fouling (scaling), and only a small amount of acetate was dosed to enhance biofilm growth. Permeate production was monitored over the experimental period.

Biodegradable nutrients were dosed into the MFS feed water to enhance biofilm formation. The biodegradable nutrients (C:N:P) were applied at a ratio of 100:20:10 with a final carbon concentration of $500 \ \mu g \ C \cdot L^{-1}$. The biodegradable nutrient solution consists of sodium acetate, sodium nitrate, and sodium phosphate. To avoid any growth of bacteria in the biodegradable nutrient stock solution, pH was adjusted to 11 with 1 M NaOH solution. To analyze the residual fouling after cleaning and removal of the biofilm on a coated a non-coated membrane, the membranes were removed from the MFS, cut into coupons, and placed in 30 mL of autoclaved DI water. The samples were placed in an ultrasonic water bath for 2 min, followed by mixing on a Vortex for 1 min to remove fouling from the membrane and to provide a homogeneous sample for biofilm characterization and quantification. The samples were analyzed for active biomass by Adenosine Tri Phosphate (ATP) measured using an ATP Celsis Luminometer (Charles River, USA). ATP has been shown to be a suitable parameter for biofouling diagnosis and quantification of the amount of biomass. In a study in which a range of biomass parameters was compared to membrane performance decline it was found that ATP was clearly the best parameter to quantify biofouling and predict the performance decline [26]. The biofouling studies were repeated three times.

2.4. Coating removal and membrane cleaning

To clean the biofouled membranes a high salinity solution (synthetic brine) of sodium chloride (70 gL⁻¹, 1.2 M) at pH 11 was recirculated at a $0.32 \,\mathrm{m\,s}^{-1}$ cross-flow for 24 h for both coated and noncoated membranes. To adjust the pH of the cleaning solution, sodium hydroxide, which is commonly used for conventional Cleaning in Place (CIP) RO cleanings, was used here. The difference between the cleaning protocols presented in this study, compared to the conventional CIP, is the elevated salt concentration and the absence of cleaning with acid. The elevated cross-flow velocity enhances biofilm removal by the increased shear force. An increased shear force is commonly applied in conventional full-scale RO plants [27,28]. A 0.45 µm pore-sized filter was placed at the inlet of the flow cell to avoid the biomass re-entering the membrane system. To evaluate the cleaning efficiency, permeate production was measured under cross-flow conditions for 24 h without nutrient dosage.

3. Results and discussion

3.1. Monitoring polyelectrolyte addition using QCM-D

The addition of the polyelectrolyte coating on a polyamide surface was analyzed by QCM-D. This technique allows observing by the oscillation of the sensor the variation in relative frequency. The relative frequency decreases proportionally to the attachment of a mass in the surface sensor, forming a thin film that can be applied under low flow $(0.15 \text{ mL}\cdot\text{min}^{-1})$.

The polyelectrolyte coating was successfully applied under crossflow conditions based on QCM-D analysis (Fig. 2a). The decrease in the relative frequency observed indicated that the deposition of each of the polyelectrolytes (PDDA and PSS respectively) formed bilayers by electrostatic interaction. After forming the fifth bilayer, the coating stability was evaluated by continuous flow with DI water. After the fifth bilayer, the decrease in frequency can be attributed to water incorporation into the coating layers. The coated surface proved to be stable over time since there was no significant variation in the relative frequency after 20 h of continuous cross-flow operation (Fig. 2b).

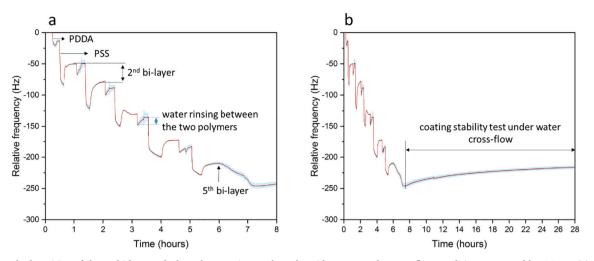


Fig. 2. Five-cycle deposition of the multi-layer polyelectrolyte coating on the polyamide sensor under cross-flow conditions measured by QCM-D (a) and coating stability under continuous 20 h cross-flow condition (b).

3.2. Sacrificial layer addition and removal under in practice cross-flow velocities

Due to equipment limitation, the cross-flow velocity used in the QCM-D is much lower than that used in practice (0.163 m·s – 1). Therefore, additional tests with MFS were performed under more realistic operational conditions where a polyamide RO membrane was used, with feed spacer and at a cross-flow velocity of 0.163 m·s⁻¹. The PDDA/PSS coating was applied using the same method as the QCM-D tests. The coating of the membrane was successfully applied under cross-flow conditions, as shown by images of the membrane using TEM. The characteristic polyamide structure of a virgin membrane was compared with the coating shown as a thin white layer (bright contrast) on top of the characteristic polyamide layer of the membrane (Fig. 3a and b). The coating layer covers the polyamide structure homogeneously with a thickness of-200 nm.

After the RO membrane was coated, stability tests were performed to ensure that the coating remained bound to the membrane under continuous cross-flow conditions as used in practice. After eight days of continuous operation, TEM images show a bright contrast cover on top of the characteristic polyamide structure, confirming the presence of the coating (Fig. 3c). The removal of the PDDA/PSS coating with NaCl (70 g·L^{-1}) at 0.32 m·s⁻¹ cross-flow velocity was also evaluated by TEM. The cleaned membrane had the characteristic polyamide structure, without the bright contrast homogenous cover, similar to the one shown in the virgin membrane, meaning that the coating layer was not anymore fully present in the RO polyamide membrane (Fig. 3d). In summary, these results showed that the coating of reverse osmosis polyamide membranes with polyelectrolytes (PDDA and PSS) is applicable under cross-flow conditions. Moreover, the coating remains attached to the membrane surface under long-term operating conditions representative of practice. By applying high salinity brine solution and increased shear, the coating can be removed and the initial membrane performance is restored.

Full removal of the sacrificial coating with brine would lead to complete recovery of the membrane permeate production. Sodium chloride at high concentration penetrates the polyelectrolyte coating increasing the distance between the layers, causing the detachment of polyelectrolytes from the membrane surface [8]. The used polyelectrolytes in this study have a stronger supramolecular interaction with the high salinity solution than the one with the membrane surface [20].

The effect of the coating on the membrane surface on permeate production is shown in Fig. 4. Due to the coating, a 15% flux decline was observed compared to the non-coated membrane. The applied coating slightly reduces the salt rejection (< 1%), as was previously

demonstrated by Son et al. [20]. The salt rejection was not evaluated due to the low salt concentration of tap water during the cross-flow experiments.

Full flux recovery (99%) was achieved by cleaning with a 1.2 M NaCl solution at pH 11. Cleaning with 1.2 M sodium chloride solution at pH 7 resulted only in 80% flux recovery, indicating only partial removal of the coating. The results are in agreement with the previously reported flux recovery under dead-end filtration conditions [20]. The fact that the coating was not entirely removed by 1.2 M sodium chloride solution suggests that the salinity of seawater (0.6 M) for cross-flow conditions used in practice would not be sufficient for the removal of the coating, making the coating suitable for seawater desalination. The efficiency of the removal of the sacrificial coating could be attributed to two factors: the disassociation of the polyelectrolytes pairs due to the high salinity and high pH of the cleaning solution and the high shear induced by the elevated cross-flow.

3.3. Biofouling control

In practice, biofouling occurs mainly in the lead elements of the spiral wound membrane installation [24]; hence the stability of the sacrificial coating in the later elements is of less importance for biofouling control. For this study, tap water with biodegradable nutrients was dosed into the MFS feed water to enhance biofilm formation. Seawater and freshwater pretreated for RO filtration and drinking water in distribution networks are examples of very nutrient-poor environments where oligotrophs can grow on minute concentrations ($< \mu g$ C·L⁻¹) of biodegradable nutrients in the water up to total bacterial cell concentrations of about 10^3 – 10^6 cells·mL⁻¹ [29]. Studies have shown that typically many different bacterial species are present in such oligotrophic environments [30,31]. The use of rich nutrient media to quantify bacteria from such oligotrophic environments has a very low vield (several log units lower) compared to a total bacterial cell count [29]. Use of the autochthonous bacterial population of drinking water as the feed water of our MFS studies provides (i) a broad variety of bacteria species, (ii) sufficient bacteria numbers, (iii) a continuous bacteria supply during the study, and (iv) bacteria common to the oligotrophic environment, which is in agreement with RO systems in practice. It has been demonstrated that such inoculation of autochthonous bacteria in drinking water for biofilm studies leads to biofilm formation that is well predicted and reproducible [24,32-34].

After biofouling occurred in the membranes, the removal of the biofilm and the coating was evaluated. The cleaning potential of the sacrificial coating was previously studied by simulating the impact of biofouling with the use of alginate as model foulant [20]. Even though

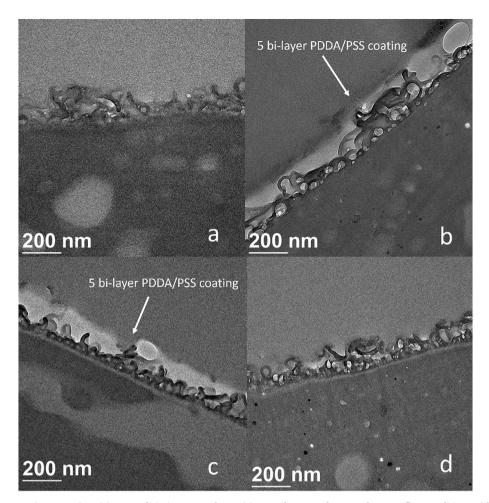


Fig. 3. Transmission electron microscopy (TEM) images of virgin RO membrane (a), coated RO membrane under cross-flow conditions with a thickness of ~200nm (bright contrast) (b), coating stability during eight days with cross-flow conditions (0.16 ms⁻¹) (c) and coating removed with NaCl (70 gL⁻¹) at elevated cross-flow velocity (0.32 ms⁻¹) (d).

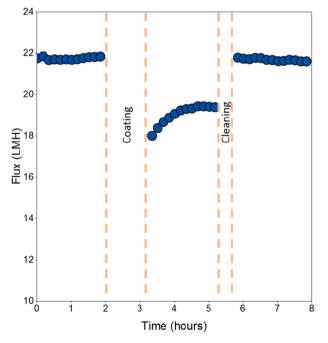


Fig. 4. Effect of the polyelectrolyte coating on the flux and coating removal after the addition of NaCl (70 g L^{-1}) at pH 11. Full recovery of the flux was observed after the cleaning time of the coating.

alginate is a broadly used model foulant for biofilms it does not simulate all biomass components such as proteins and bacterial cells. Therefore, biofouling studies were performed using the MFSs with and without coated membrane sheets to observe the cleaning potential of the coating with biofilm growth. Both MFSs were operated in parallel under the same conditions (feed water composition, cross-flow velocity, temperature, nutrient dosage, and transmembrane pressure). After a five days research period a biofilm developed on the coating, and subsequently the cleaning potential of sodium chloride at pH 11 was tested. The cleaning was performed continuously for 24 h at 0.32 ms⁻¹ cross-flow velocity using a 1.2 M sodium chloride solution at pH 11 for both coated and non-coated membranes. The 24 h cleaning time was needed to allow the sodium chloride (synthetic brine) to penetrate the biofilm and reach the coating. The efficiency of the cleaning strategy was evaluated by monitoring the permeate flux under normal crossflow conditions without nutrient dosage (Fig. 5a), as well as the residual active biomass on the membrane (Fig. 5b). The permeate flux presented in Fig. 5a is normalized by the initial flux value before starting nutrient dosage (J/J_0) . Even though at the beginning of the nutrient dosage (day 1) the coated membrane had a lower initial flux induced by the coating (approximately 15%), it had less flux reduction due to biofilm growth compared with the non-coated membrane. After both membranes were cleaned, the coated membrane had 80% flux recovery, while the coated membrane had only 40% flux recovery. Overall, the coated membrane had a lower flux decline and, after cleaning, had a two-fold flux recovery compared to the non-coated membrane. Also, the amount of residual active biomass after cleaning

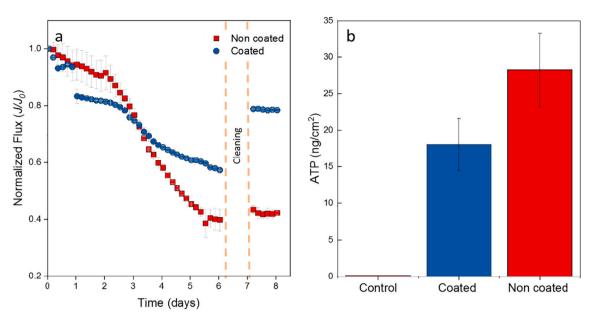


Fig. 5. Normalized flux decline in time caused by biofilm growth on coated (blue circles) and non-coated (red squares) RO membranes under cross-flow conditions and flux recovery of coated and non-coted membranes after 24 h cleaning with NaCl (70 g·L⁻¹) pH 11 at 0.32 m·s⁻¹ cross-flow velocity (a). ATP analysis from the coated and non-coated membrane after cleaning (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

was less for the coated membrane than the non-coated membrane. These observations may have two explanations: i) the biomass attached to the coated membrane surface was removed together with the coating during cleaning, and therefore the coated membrane had a higher cleaning efficiency; ii) due to the coating less biomass accumulated in the same amount of time, which is in agreement with previously reported studies on membrane coatings [13,35].

Relatively long cleaning periods (24 h) in RO water treatment plants are occasionally applied [36]. Moreover, a long cleaning period is needed when a well-developed biofilm is present on the membrane surface. By the time the cleaning with sodium chloride was performed the biofilm impact on membrane performance decline was approximately 50%. In practice, it is recommended to perform membrane cleaning before a 10% performance decline is reached [37]. Cleaning in an earlier phase of biofilm growth would significantly reduce the cleaning time and increase membrane performance recovery.

The presented sacrificial coating has the potential to be used in other types of membrane systems, such as ultrafiltration. In ultrafiltration, besides removing the foulant, the coating could avoid the need for NaClO and thus avoid the formation of halogenated by-products [38]. However, the impact of the sacrificial coating on membrane performance for UF systems has yet to be evaluated. The polyelectrolyte coating deposition occurs due to the electrostatic interaction between the polyelectrolyte and the polyamide layer of the membrane. The polyelectrolytes have the potential to be recovered by precipitation and can be reused for membrane re-coating, making it an environmental friendly technology.

The material of the feed spacer (polypropylene) commonly used in spiral wound membrane modules does not have the correct properties to interact with the polyelectrolytes. These polyelectrolytes do not form electrostatic interactions with the polypropylene due to lack of formal charge and its absence of heteroatoms. The development of a sacrificial coating that can also interact with the feed spacer might enhance the biofouling cleaning potential of the coating since biofouling does not occurs only on the membrane but also on the feed spacer surface [21,39].

Additional studies should assess the impact of the polyelectrolytes on biofilm development (e.g., surface charge), concentration polarization, and optimization of the number of coating layers. The number of bilayers has to be optimized, taking into account the decline of flux, concentration polarization, and removability. Moreover, the application of biocides in the sacrificial coating might be a technique for delaying the biofilm growth, and can be re-applied with the coating, conserving the biocide properties.

4. Conclusions

The polyelectrolyte coating of PDDA and PSSS proved to be effectively applied for RO polyamide membranes under cross-flow conditions used in practice. The layer-by-layer electrostatic interaction of the polyelectrolytes avoids the need for toxic linkers such as glutaraldehyde, and it can be applied, removed, and reapplied. The coating is stable under operational cross-flow conditions ($0.16 \text{ m} \text{s}^{-1}$) typical for spiral wound membrane systems. Also, the use of high salinity water (e.g., brine) by recirculation and high shear could be a solution for an effective cleaning process that does not affect the integrity of the membrane. The application of the sacrificial coating, with the use of brine at high pH as a cleaning agent, enhances the cleanability of biofouled membrane systems.

Author statement

All authors contributed to conceptualization, reviewing the data, and with editing and writing final manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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