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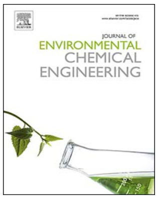

# High fouling-resistance of polyamide desalination-membrane modified with PEI/PAH polyelectrolyte multilayers

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## ABSTRACT

Membrane fouling is a persistent problem in reverse osmosis (RO) process which leads to higher operating pressure, quality deterioration, and frequent chemical cleaning of the membranes. The objective of this paper is to prepare a fouling-resistant RO desalination membrane while keeping high salt rejection and permeate flux. Polyamide (PA) membranes were prepared and modified using spin assisted Layer-by-Layer assembly of polyelectrolytes (PEI/PAH), characterized and tested in a cross-flow desalination setup. The effect of preparation conditions (number of coating layers, concentration and pH of the polyelectrolyte solutions) on the performance of the membrane was also investigated. SEM micrographs showed that the surface of the PA membrane is rough and has typical ridge and valley structure. However, images of the modified membranes showed smoother surfaces as the number of polyelectrolyte bilayers was increased which was verified using the AFM analysis. In addition, contact angle measurements suggested that the surfaces of the modified membranes became more hydrophilic due to the presence of hydrophilic hydroxyl and amine groups. Permeation results showed comparable salt rejection under saline feed water of 2000 ppm. 50 bilayer modified membrane having 110 mg/L of polyelectrolyte solution, possess permeability of 0.83 L/m$^2$ h bar with 95% salt rejection. However, 27 bilayer modified membrane having 200 mg/L of polyelectrolyte solution, possess greater permeability of 1.78 L/m$^2$ h bar with 96% salt rejection. Fouling experiments showed that after three hours of filtration, functionalized membranes retained more than 88% of water flux compared to pristine polyamide membrane which suffered from more than 42% flux drop.

## 1. Introduction

The main technologies to accomplish desalination can be broadly classified into two: thermal and membrane technologies. Currently, the largest percentage of desalination plants is based on RO membrane-technology [1]. The reason behind greater contribution of RO is its lower electrical energy requirements of 2–3 kWh/m$^3$ [2] compared to the high demand of 15.5 kWh/m$^3$ for MSF thermal desalination. The marketplace for RO equipment and membranes by the end of 2014 was around $5.4 billion and it is expected to stretch to $8.8 billion by 2019 with a compound annual growth rate of 10.5% [3]. This development is due to the efficient utilization of energy during the last decade for the RO processes along with the development of new and efficient membranes [4].

Membranes can effectively remove contaminants from drinking water. However, fouling is a prominent problem [5]. RO membranes suffered with scaling, particulate fouling, biofouling and organic fouling. These various mechanisms are commonly observed in membranes either at the surface or in the pores [6]. Membrane fouling is a complex phenomenon for which the membrane experiences blocking or coating by some components present in the processed stream, which eventually results in permeate flux decline [7]. Therefore, different membrane-surface modification methods have been implemented to decrease the extent of fouling such as surface coating [8–11], surface grafting [12–14], plasma treatment [15–17], UV irradiation [18] or by incorporation of nanomaterials [19–22].

Nano-fabrication of polyelectrolyte multilayer-films via layer-by-layer assembly (LbL) has now been recognized as a versatile technique

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*Abbreviations:* SPEEK, sulfonated poly (ether ether ketone); PAH, poly (allylamine hydrochloride); PEI, poly (ethylene imine); PSS, poly (styrene sulfonate); PEG, poly (ethylene glycol); BSA, Bovine Serum Albumin; MSF, Multistage Flash Distillation; MPD, m-phenylenediamine; TMC, trimesoylchloride; DMAc, dimethylacetamide; LbL, Layer by layer; TFC, thin film composite; DI, deionized water

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to control the surface structure and properties at the nanometer scale [23–25]. It can be achieved by dip-coating, spray-coating or spin-coating. More details about the LbL assembly of polyelectrolytes can be found in our recent review article [26]. Excellent control of film thickness and ability to optimize film properties via changing the polyelectrolyte has make the LbL assembly a very attractive method for the surface modifications of membranes.

Researchers have used the LbL assembly of polyelectrolytes to modify ultrafiltration membranes [24,25], nano-filtration membranes [27], commercial RO membranes [28], and gas separation [29]. Ishigami et al. [30] modified a commercial RO membrane using multiple layers of PSS/PAH. It was found that the permeate flux was decreasing with the number of layers while the salt rejection was marginally increasing. When the number of polyelectrolyte layers reached 12, the permeate flux decreased more than 40% compared to the unmodified membrane. However, the fouling resistance was enhanced in the modified membranes. Under fouling conditions and after 120 min of filtration using BSA, the unmodified membranes lost almost 45% of its initial permeate flux while the modified membrane with 12 bilayers lost around 10%.

Wang et al. [31] investigated the antifouling ability of composite membrane by depositing SPEEK/PEI (branched) on hydrolyzed membrane. Performance of the prepared membrane with 3 bilayers was determined by dead end filtration system using different foulants. The polyelectrolyte-multilayer-membrane demonstrated nearly constant performance in terms of normalized flux with time, whereas commercial NTR 7450 membrane showed a slight flux drop during filtration. It was anticipated that improved fouling resistance was the result of hydrophilic ionic crosslinks that were present in the polyelectrolyte layers. Contact angle and surface roughness were not studied to further explore the antifouling characteristics.

Kentish et al. [32] studied the fouling behavior of modified polyamide RO membrane by depositing Polyethylene glycol acrylate multilayers. AFM analysis revealed that there was no improvement in the surface roughness after 2 bilayers deposition while the contact angle was decreased to 41°. The increased surface-hydrophilicity made the modified membrane more resistant to fouling.

To the best of our knowledge, very few studies were found in literature that used the spin-assisted LbL assembly of polyelectrolytes to modify the RO membranes. Moreover, those studies did not pay attention to the tuning parameters for membrane modification including effect of pH and concentration of the depositing polyelectrolyte solutions.

Therefore, the aim of this study is to prepare a polyelectrolyte-modified RO membrane with adequate water flux and salt rejection using the LbL assembly of polyelectrolytes: Polyethyleneimine/Poly (allyamine hydrochloride) PEI/PAH. The effect of layer number, concentration and pH of both polyelectrolyte solutions on the membrane performance will also be investigated.

## 2. Materials and methods

### 2.1. Materials

All chemicals were purchased from Sigma-Aldrich. Polysulfone pellets with molecular weight of 35 kDa were used for membrane casting as a base polymer. Dimethylacetamide (DMAc) was used as a solvent for preparation of polysulfone base membrane. Polyester non-woven fabric support [Novatexx–2413] was purchased from [Freudenberg Filtration Technologies (Germany)]. Millipore deionized water was used throughout the research. m-phenylenediamine (MPD) ( > 99%) and trimesoylchloride (TMC) ( > 98%) were used to prepare the polyamide membrane. Hexane ( > 95%) was used as a solvent for TMC and also served as rinsing agent. PEI (25,000 g/mol) and PAH (120,000–180,000 g/mol) were used for membrane modification. Sodium Chloride ( > 99.5%) was used to prepare a model saline water. Bovine Serum Albumin (BSA) with molecular weight of 66 kDa and pH of 7 was used as a model foulant.

### 2.2. Preparation of polysulfone support

The 20 wt.% solution of polysulfone was prepared in DMAc with stirring at 60 °C for 6 h. The solution was left overnight for degassing. Solution casting was done using a micrometer adjustable casting blade at ambient temperature with constant thickness of 150 μm. After casting, the prepared polysulfone membrane was immediately immersed into a water coagulation bath at ambient temperature for one day to complete the phase inversion process.

### 2.3. Preparation of TFC membrane

Polysulfone support was dipped in 2 wt.% MPD solution for 10 min and the excess solution was removed by rolling with a rubber roller. Then, it was dipped in 0.15 wt.% TMC solution for 30 s to complete the synthesis reaction of polyamide layer. Hexane was used as the rinsing agent to remove unreacted/excess TMC solution. The polyamide membrane was then kept in an oven for 10 min at 70 °C to increase the cross-linking. Finally, the polyamide membrane was stored in DI water until further use.

### 2.4. LbL modification of TFC membranes

The LbL technique includes an alternating coating of the membrane surface with the two polyelectrolytes (PEI and PAH) using a custom made spin-coater (Absolute Nano Inc., USA). The membrane sample of the size 64 $cm^2$ was held in place on a rotating disc through a vacuum pump and spun coated with the polyelectrolytes at a rotation speed of 1000 rpm.

The time of each step along with other parameters was adjusted using the instrument software. The coating started with PEI for 10 s with a volumetric rate of flow 0.4 mL/s, followed by drying for 15 s. This dried film was rinsed for 10 s with deionized water to remove weakly bound/attached polyelectrolyte and then dried for 15 s. PAH was deposited the same way and the cycle was repeated until the desired number of layers was coated. Then, the membrane was removed and stored in deionized water.

### 2.5. Characterization

The surface morphology and cross-section of the prepared membranes were studied by TESCAN Field Emission Scanning Electron Microscopy (FE-SEM), Model JSM6400. In order to measure membrane thickness, samples were fractured by liquid nitrogen and analyzed using TESCAN FE-SEM. The extent of wettability of membrane surface was studied by measuring the contact angle using the sessile drop method (DM-501, Kyowa Interface Science Co.) on a dry membrane sample of at least 2 × 2 $cm^2$. The water drop (2 μL) contact angles were measured at least three at three different positions and the average value was reported. The membrane surface-roughness was studied and calculated using Atomic Force Microscope (AFM) with Veeco Dimension of 3100 SPM. TA instrument SDT Q600 was used for Thermo-gravimetrical analysis (TGA) to investigate the thermal stability of membranes. Fourier Transform Infra-red (FTIR) in ATR mode of (Nicolet 6700, Thermo scientific) was used to investigate the functional groups of unmodified and 50 bilayer modified polyelectrolyte membrane surface.

### 2.6. Membrane testing

The filtration experiments were conducted in a cross-flow apparatus using Sterlitech CF-042 membrane cell with an effective membrane area of 42 $cm^2$. Fig. 1 show cross flow test unit which consisted of a feed tank, chiller, pump, bypass and control valves, membrane assembly and