



Layer-by-layer assembly of anion exchange membrane by electrodeposition of polyelectrolytes for improved antifouling performance



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ABSTRACT

This study demonstrates the feasibility of layer-by-layer (LbL) assembly of poly(sodium 4-styrene sulfonate) (PSS)/poly(diallyldimethylammonium chloride) (PDADMAC) polyelectrolyte multilayers on an anion exchange membrane (AEM). The electrodeposition of (PSS/PDADMAC)_n multilayers on the AEM with a PSS layer as the top surface endows the surface with negative charges and increases the surface hydrophilicity, leading to a significantly improved antifouling performance in electrodialysis (ED) to an organic foulant, i.e., sodium dodecyl sulfate (SDS). The desalination rate during 180 min increased from 24.0% for the pristine AEM to 30.5% for a 5.5 PSS/PDADMAC bilayers modified AEM with 75 mg/L SDS in the initial solution. A SDS fouling layer was formed at the dilute side of the pristine AEM, causing a sharp increase of electrical resistance and restricting the ion transport through the AEM completely. Electrodeposition of 5.5 PSS/PDADMAC bilayers prevented the formation of the SDS fouling layer at the surface of AEM, which reduced the sharp increase of electrical resistance and kept the ion transport through the AEM unaffected. With 100 or 150 mg/L SDS in the initial solution, the desalination rate during 180 min increased from 24.1% or 15.4% for the pristine AEM to 28.4% or 26.8% for the 5.5 PSS/PDADMAC bilayers modified AEM.

1. Introduction

Membrane processes, including nanofiltration (NF) and reverse osmosis (RO) as well as electrodialysis (ED), are among the most effective technologies for water treatment, especially for unconventional water resources such as brackish water and seawater, and wastewater [1–5]. More and more attention has been paid to the application of ED in many fields, such as the recovery of organic acids [6–8], desalting brackish water [2,9], removing bromide ions [10], and treating wastewater effluent [11,12], because of the excellent characteristics of ion exchange membranes (IEMs): a high chemical stability, a low electrical resistance and a good mechanical strength. Nevertheless, membrane fouling, and in particular the organic fouling of anion exchange membranes (AEM), is a major obstacle to the sustainable application of ED because it increases energy consumption, deteriorates the membrane performance and shortens membrane lifetime [13–16].

Since most organic compounds in wastewater have negative charges, they will migrate to the surface of an AEM when an electrical

field is applied, and then deposit and form a fouling layer on the membrane because of the interaction forces (i.e., electrostatic interaction and affinity interaction) between these organics and the AEM [17–19]. Hence, optimizing surface characteristics (e.g., charge, hydrophilicity) of AEMs by a suitable surface modification provides an effective way to improve the membrane antifouling performance, because the formation of a fouling layer is affected by the membrane surface properties [20,21]. Several surface modification strategies, such as polyelectrolyte electrodeposition [22–24] and coating [25,26] have been reported to modify membrane surface properties, delaying membrane fouling, which allows for controlling membrane fouling to some extent. However, these studies measure the improvement of the modified AEMs indirectly by measuring the transition time (i.e., the time elapsed until the occurrence of fouling), without further exploring fouling properties and mechanisms [22]. More importantly, the thin layer formed on the membrane might become inadequate for foulants with stronger interactions, or when various types of foulants are simultaneously present [27].

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Layer-by-layer (LbL) assembly polyelectrolyte technique is a promising way to control membrane fouling because of its simplicity and it allows the gradual and controlled build-up of electrostatically cross-linked layers on the surface of the membrane [28]. Various LbL modified membranes have recently been developed for different specific purposes by selecting various polyelectrolyte species, adjusting fabrication conditions and altering surface functionalities [29–33]. These membranes showed a satisfactory antifouling performance in various circumstances [34–36]. For example, with poly acrylic acid (PAA)/Tobramycin (TOB) bilayers on a thin film composite (TFC) polyamide reverse osmosis (RO) membrane, a 37% and 26% higher flux compared to the virgin membrane was obtained after three fouling cycles with bovine serum albumin and sodium alginate solutions, respectively [35]. In these studies, layer-by-layer assembly was mostly employed to modify membranes for pressure driven separations. Only a few recent studies utilized layer-by-layer polyelectrolyte deposition to enhance the selectivity of ion exchange membranes [37–40]; more importantly, alternative electro-deposition LbL assembly modification method can further enhance the stability of the multilayer coated on the membrane [41]. For example, polyethylenimine (PEI)/PSS films were formed on a cation exchange membrane to generate a permselective layer, improving the $\text{Na}^+/\text{Ca}^{2+}$ selectivity by modifying the membrane surface properties [40]. However, the role of LbL assembly of polyelectrolytes in improving the antifouling performance of AEMs has not been widely studied.

In this study, diverse PSS/PDADMAC multilayers were electro-deposited on an anion exchange membrane (NEOSEPTA AMX) with the layer-by-layer assembly polyelectrolyte technique, in order to improve its antifouling performance to organics during electrodialysis. The modified AEMs were characterized by several surface analytical methods, and their surface characteristics were correlated with their resistance to organic fouling. The antifouling effect was firstly evaluated by investigating the changes in desalination performance without and with the foulant sodium dodecyl sulfate (SDS) in the initial solution. Then, the structural and electrochemical properties of the modified AEMs before, and after being fouled by SDS were characterized. The antifouling performance of LbL assembled AEMs to higher concentrations of SDS was also investigated.

2. Materials and methods

2.1. Materials

Poly(sodium 4-styrene sulfonate) (PSS, M_w 70,000) and sodium dodecyl sulfate (SDS) were purchased from Alfa Aesar (Shanghai, China). Poly(diallyldimethylammonium chloride) (PDADMAC, M_w 100,000–200,000, 20 wt% in water) was purchased from Aladdin (Shanghai, China). Other reagents such as Tris-HCl, NaCl (A.R), HCl (A.R), Na_2SO_4 (A.R) were used to prepare the experimental solutions. All solutions were prepared using ultra-pure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$, Milli-Q, Millipore). A commercial anion exchange membrane (AEM, NEOSEPTA AMX, Astom Corp, Japan) was used as the membrane support for LbL assembly modification. The cation exchange membrane (CEM, NEOSEPTA CMX) assembled alternately with AEM in the membrane stack was also provided by Astom Corp.

2.2. LbL membrane modification

The LbL assembly of a PSS/PDADMAC bilayer on the surface of the AEM was performed in an electrodialysis apparatus (Fig. S1). The PSS and PDADMAC solution for modification were prepared by dissolving 0.6 g/L of PSS or PSADMAC with 0.1 M NaCl (as a supporting electrolyte) in 10 mM Tris-HCl buffer (pH 7). The AEM and CEMs constituting the membrane stack were first immersed into the ultra-pure water for 24 h and then one AEM and two CEMs were alternately placed into the membrane stack. The PSS solution and 0.1 M NaCl solution was

circulated into the compartment 1 and 2, respectively, driven by the peristaltic pump with a flow rate of 100 mL/min. The process was performed at a current density of 0.25 mA/cm² for 1 h and PSS would be deposited on the surface of AEM facing to the compartment 1. Then the membranes were taken out to be rinsed by ultra-pure water for 2 min, and the sides of AEM into the membrane stack were changed (i.e., the PSS-deposited surface facing compartment 2). After that, 0.1 M NaCl solution and PDADMAC solution was circulated in compartment 1 and 2, respectively, under the same conditions with the previous process; PDADMAC would be deposited on the PSS-deposited surface. The PSS and PDADMAC electrodeposition were repeated in an alternating way to fabricate AEMs with multiple PSS/PDADMAC polyelectrolyte bilayers. The final membrane was stored in 0.05 M NaCl for further use.

2.3. Membrane fouling tests

Membrane fouling tests were carried out using SDS as the model foulant in the electrodialysis apparatus (Fig. S1). Two fresh CEMs and one fresh or modified AEM were placed into the membrane stack alternately in each test. The modified side of AEM was faced to compartment 1. A solution of 0.1 M NaCl containing 75 mg/L SDS and a 0.1 M NaCl solution was circulated into compartment 1 and 2, respectively, driven by a peristaltic pump with flow rate of 100 mL/min. The test was performed at a voltage of 4.0 V and the electrical conductivity of solution in the compartment 1 was online recorded as a function of time. The tests were repeated three times to ensure the reliability of data. The details were described in the previous study [17].

2.4. Membrane characterization

The chemical structure of the surface of the studied AEMs was characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, T27-Hyperion-Vector22, Bruker, Germany). The morphology and elemental mapping of the AEMs were obtained by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS, Hitachi SU8020, Japan). The contact angle of AEM was measured by the sessile drop method using a contact angle analyzer (OCA20, DataPhysics, Germany). The zeta potential of the AEMs was measured using a zeta potential measurement analyzer (Anton Paar, Austria) with 1 mM KCl solution as the background electrolyte at pH 6.0. The area electrical resistance of AEM was measured by an LCR Meter (IM3533, HIOKI, Japan) set at 100 kHz, 100 mV in 0.5 M NaCl at 25 °C. The electrochemical impedance spectroscopy (EIS) of the AEMs was measured using an Autolab electrochemical workstation (PGSTAT302N, Metrohm) with a four-electrode setup. A 10 mV amplitude sinusoidal potential perturbation was applied ranging from 100 kHz to 1 mHz at a rate of 60 measurements frequencies in 0.1 M NaCl solution at 25 ± 1 °C.

3. Results and discussion

3.1. Characterization of LbL assembly membrane

Different numbers (1.5, 3.5, 4.5 and 5.5) of PSS/PDADMAC bilayers were electrodeposited on the surface of AEMs, with the PSS layer as the top surface. Electrodeposition of PSS/PDADMAC bilayers did not cause changes in the overall surface morphology (Fig. S2) of the AEM (“ridge and valley”); however, increasing bright spots on the membrane surface in each SEM image observed with more bilayers could be attributed to the increased deposition of PSS. In addition, the increase of the content of S on the membrane surface with more bilayers (Table 1) also indicates that more PSS was deposited on the outmost membrane surface with an increasing number of bilayers. This observation indicates the relatively uniform deposition of PSS on the membrane surface. The successful LbL assembly of PSS/PDADMAC bilayers was further confirmed by ATR-FTIR spectra (Fig. 1a). The characteristic peaks at

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