Development of nanofiltration membrane with high salt selectivity and performance stability using polyelectrolyte multilayers

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HIGHLIGHTS

- Polyelectrolyte solution ionic strength can improve membrane salt selectivity.
- Polyelectrolyte layers stability can be affect by solution ionic strength.
- PDADMAC and PSS possessed hydrophobic and hydrophilic properties, respectively.
- Polyelectrolyte layers stability can be studied by back-flushing the membrane.
- Polyelectrolyte layers can smoothen the membrane surface.

ARTICLE INFO

ABSTRACT

A selective nanofiltration membrane was engineered layer-by-layer (LBL) from polydiallyldimethylammonium chloride (PDADMAC) and polysodium-4-styrenesulfoate (PSS) polyelectrolytes. Thickness for 5 bilayers of PDADMAC/PSS was 321.00 ± 11 nm and showed $73.87 \pm 7\%$ rejection of $MgSO_4$, $22.52 \pm 2\%$ rejection of NaCl and satisfactory flux of 12.33 $L.m^{-2}.h^{-1}$ at 5 bar. Formation of PDADMAC/PSS multilayers using 1.5 M of supporting electrolyte produced nanofiltration membrane with the best $NaCl/MgSO_4$ selectivity of 2.97. In addition, the stability of polyelectrolyte multilayers was evaluated through membrane back-flushing. Modified membrane using polyelectrolyte solutions of moderate ionic strength (by adding 1.5 M NaCl) displayed the best performance stability in which the $MgSO_4$ retention capability reduced for only 4%.

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1. Introduction

Common materials used in the synthesis of nanofiltration (NF) membranes include polyamide, cellulose acetate, polyimide and polyethersulphone (PES). Among polymers, PES is an attractive material for NF membranes as it possesses high thermal stability, lower production cost, good mechanical strength and good chemical stability [1]. However, the low surface charge density and great surface roughness of polyethersulphone membranes limits their separation performance and antifouling properties [2]. One of the most effective means to improve the membrane rejection capability and anti-fouling property is surface modification as it can be conducted on the existing commercialized membranes. Various improvement techniques such as plasma treatment, UV-induced grafting and adsorption have been reported. Applications of NF could be widened further in various industries such as wastewater treatment, metal recovery, pulp and paper, and seawater treatment through improvements in membrane characteristics.

Self-assembly of charged molecules on membrane surfaces through adsorption is selected in this study as it offers further advantages such as being less time consuming, requiring less energy and cheaper production costs [3]. Smooth surfaces obtained after surface modification may provide good antifouling properties [4] which can prolong the membrane lifespan. Electrostatic adsorption of polyelectrolytes onto the substrate depends on several factors [5] such as the charge distribution along the chain, the molecular weight of polymer, substrate charge and some other non-electrostatic affinity between the substrate and the molecules. Factors affecting polyelectrolyte-modified membranes including number of bilayers, solution concentration [6] and the deposition pH [7]. Ionic cross-links in polyelectrolyte membranes could be

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List of symbols

C_f	concentration of feed solution (ppm)
$C_{f,1}$	feed concentration of component 1 (ppm)
$C_{f,2}$	feed concentration of component 2 (ppm)
C_p	concentration of permeate solution (ppm)
$C_{p,1}$	permeate concentration of component 1 (ppm)
$C_{p,2}$	permeate concentration of component 2 (ppm)
C_w	membrane wall concentration (M)
D	diffusion coefficient of solute at infinite dilution (m^2 s^{-1})
J	permeate flux ($L.m^{-2}.h^{-1}$)
J_v	solution flux per unit area of membrane (m^3 m^{-2} h^{-1})
k	mass transfer coefficient (m s^{-1})
k'	mass transfer coefficient (m s^{-1})
N	order number
r	radius of stirred cell (m)
R_1	rejection of component 1 (%)
R_2	rejection of component 2 (%)
R_{obs}	observed rejection (%)
R_{real}	real rejection (%)
S	effective membrane area (m^2)
$S_{1/2}$	selectivity of solute 1 over solute 2
S_a	averaged surface roughness
S_q	root-mean-square value
t	operating time or duration (hr)
V	volume of permeate (L)
v	kinematic viscosity (m^2 s^{-1})
ω	angular velocity (rad s^{-1})
$\bar{z}$	average of the z value in the given area
z_i	current z value

maximized by adjusting the deposition pH close to the average pKa values of the polyelectrolytes. Recently, several self-assembly methods such as static, dynamic and cross-flow dynamic-static were compared [8]. They found that the dynamic self-assembly method was able to improve the membrane rejection capability albeit with a significant reduction in the solution flux produced. However, limited studies on the stability of polyelectrolyte-modified membranes have been reported [9,10]. Polyelectrolyte molecules are characteristically adsorbed to a polymeric substrate only in small amounts due to the electrostatic repulsion between molecules that tends to reduce the build-up of molecules with the same charge. According to Coulombic interactions, the addition of a low molecular weight supporting electrolyte to the medium from which the polyelectrolyte molecules are adsorbed can reduce this phenomenon when the electrostatic forces are screened, within the limit of high electrolyte concentrations. The addition of supporting electrolyte has been used in this work to control the deposition of polyelectrolytes onto the PES membrane substrate. Higher amount of adsorbed polyelectrolytes potentially leads to instability of the multilayers formed thus it is important to determine the suitable amount of supporting electrolyte that can be employed for the formation of stable polyelectrolyte multilayers.

For membrane filtration to be cost and energy-effective, membrane fouling management is important in ensuring consistent separation performance with minimal cleaning and membrane replacement. In general, membrane performance can be affected by irreversible and reversible fouling. Irreversible fouling can be diminished through chemical cleaning, whereas the reversible fouling can be diminished through back-flushing [11] (for a short duration to reduce energy consumption) to minimize the accumulated foulants from the membrane surfaces to recover the filtration performance [12,13]. Thus, durability of polyelectrolyte-modified membranes during cleaning processes, in terms of performance changes after back-washing, is important

to ascertain the stability of polyelectrolyte layers. Back-washing of polyelectrolyte-modified membranes for stability evaluation has not been reported previously. In this work, NF membrane was engineered using polydiallyldimethylammonium chloride (PDADMAC) and polysodium-4-styrenesulfoate (PSS) for multilayers construction on commercial PES20 membrane through self-deposition method to improve the membrane surface roughness, hydrophilicity, solute retention capability and selectivity. The NF membrane characteristics such as salt retention capability, salt selectivity, morphological structures and surface roughness were evaluated. The membranes were also tested in terms of stability after back-washing.

2. Materials and methods

2.1. Materials

Commercial UF membrane (PES20) (with a nominal MWCO of 20,000) and NF membrane (NF1) were purchased from Amfor Inc. PSS (average molecular weight of around 1,000,000) and PDADMAC (average molecular weight of 400,000–500,000) solutions were purchased from Sigma-Aldrich. NaOH, NaCl and MgSO₄ were obtained from Merck.

2.2. Zeta potential analysis and polyelectrolyte solution preparation

The Zetasizer Nano series was used to describe the electro-kinetic potential in PDADMAC and PSS dispersions at room temperature [14]. Preparation of polyelectrolyte solutions were previously reported [6]. Polyelectrolyte solutions (1 wt.%) were prepared with different supporting electrolyte concentrations as shown in Table 1. Membrane M_c (PES20) and M_N (NF1) were commercial ultrafiltration and NF membranes employed in the characterizations.

2.3. Membrane surface modification

All membranes were modified with 5 bi-layers of the polyelectrolytes using static deposition method [3] on commercial PES20 membrane, in which the concentrations of NaCl in polyelectrolyte solutions were varied from 0 to 2 M. Although large numbers of polyelectrolyte bi-layers (as high as 59 to 61 bi-layers) have previously been reported [15], such a strategy was not employed in this work in view of the current trend in minimizing the number of bilayer but exhibiting similar performance [16].

2.4. Membrane pure water permeability measurement

Membrane permeabilities were determined using pure water flux measurements at pressures ranged from 2 to 5 bar in which the pressure was supplied by compressed nitrogen cylinder. Sterlitech HP4750 Stirred Cell [17–19] was used at ambient temperature to calculate the water flux of membrane with an active surface area of 14.6 cm² (which was preliminary compacted at 6 bar for 60 min) using Eq. (1) as reported [20–22], in which J is the permeate flux ($L.m^{-2}.h^{-1}$), V is volume of permeate (L), S is effective membrane area (m²) and t is

Table 1
Different concentrations of the supporting electrolyte in polyelectrolyte solutions.

Membrane label	Concentration of NaCl in polyelectrolyte solutions (M)
M_N	Unmodified NF1 membrane
M_c	Unmodified PES20 membrane
M_0	0
$M_{0.5}$	0.5
$M_{1.0}$	1.0
$M_{1.5}$	1.5
$M_{2.0}$	2.0