



# Composite polyelectrolyte multilayer membranes for oligosaccharides nanofiltration separation

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## ABSTRACT

In the present work, composite polyelectrolyte multilayer (C-PEM) membranes were fabricated by using layer-by-layer (LbL) assembly technique for oligosaccharides nanofiltration (NF) separation. Specifically, the (chitosan/poly(styrene sulfonate) (PSS))<sub>3</sub> multilayers designated as the middle layer (ML) were first deposited on the hydrolyzed polyacrylonitrile (PAN) ultrafiltration membranes, which were designated as the support layer. Then, the (poly(allylamine hydrochloride) (PAH)/PSS)<sub>2</sub> multilayers designated as the top layer (TL) were deposited on the ML to form C-PEM membranes. When utilized for oligosaccharides NF separation, C-PEM membranes exhibited desirable performance compared to single-paired PEM membranes such as (PAH/PSS)<sub>5</sub> and (chitosan/PSS)<sub>5</sub> membranes owing to the collaboration of the TL and ML. In detail, C-PEM membranes acquired a permeation flux of  $3.7 \pm 0.3 \text{ L m}^{-2} \text{ h}^{-1}$ , 100% rejection of oligosaccharides and  $63.0 \pm 0.5\%$  rejection of glucose along with a high maltose/glucose selectivity of 46, demonstrating the promising potential for one-step membrane separation of oligosaccharides mixture.

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## 1. Introduction

Nowadays, oligosaccharides have been widely utilized as food and feed ingredients or additives (Xu, Chao, & Wan, 2009) owing to their great healthcare and nutrition functions (e.g. bifidus-stimulating activity, low calorific value, low cariogenic property, etc.) (Mussatto & Mancilha, 2007). Generally, oligosaccharides were mainly produced via biochemical reactions. And oligosaccharides product in the reaction mixture often possessed a yield of lower than 50 wt%, containing high content of monosaccharides (e.g. glucose, galactose, etc.). For functional foods applications, oligosaccharides with low content of monosaccharides were considered to be the target products and highly desired (Anderson & Hanna, 1999; López-Leiva & Guzman, 1995; Roberfroid, 1999). Therefore, an efficient separation of oligosaccharides and monosaccharides was indispensable. Nanofiltration (NF) has been demonstrated as a feasible technology for the separation and purification of oligosaccharides (Feng, Chang, Wang, & Ma, 2009; Goulas, Grandison, & Rastall, 2003; Kamada, Nakajima, Nabetani, Saglam, & Iwamoto, 2002; Li, Li, Chen, & Chen, 2004; Zhao et al., 2012). However, previous efforts were mainly focused on utilizing commercial NF membranes for obtaining high purity of oligosaccharides product.

Since these commercial membranes usually exhibited relatively low rejection of oligosaccharides, the feed solution must be recycled for a number of times to avoid the loss of oligosaccharides. Therefore, developing strategies for fabricating NF membranes displaying high rejection of oligosaccharides and high selectivity of oligosaccharides/monosaccharides has proven an urgent and challenging task.

Recently, layer-by-layer (LbL) assembly technique has developed rapidly as a facile and versatile surface modification technique for fabricating ultrathin polyelectrolyte multilayers (PEMs). Considering the merits of PEMs such as tunable pore size, ultrathin and controllable selective layer, facilitated mass transport, several research groups (Ahmadiannaminia et al., 2012; Jin, Toutianoush, & Tieke, 2003; Li et al., 2008; Miller & Bruening, 2004; Stanton, Harris, Miller, & Bruening, 2003) have exploited PEMs to fabricate NF membranes (Wang, Yao, Yue, & Economy, 2009). Till now, the application of PEMs in NF membrane fabrication was primarily focused on fabricating PEMs with only a single pair of polycation or polyanion such as poly(styrene sulfonate) (PSS)/poly(allylamine hydrochloride) (PAH) (PSS/PAH) (Stanton et al., 2003), PSS/poly(diallyldimethylammonium chloride) (PDDA) (Miller & Bruening, 2004), poly(vinyl amine)/poly(vinyl sulfate) (Jin et al., 2003) and sulfonated poly(ether ether ketone) (SPEEK)/PDDA (Li et al., 2008). These types of membranes usually exhibited desirable performance in rejection of one component or separation of binary mixture, but they might not well meet the requirements for separation of ternary mixture or mixture containing more than four kinds of components, especially for the mixtures with wide

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molecular weight range such as oligosaccharides mixture. For such a separation task, stepwise separation using a single sheet of membrane would be often expected.

In the present study, composite polyelectrolyte multilayer (C-PEM) membranes containing two different polyelectrolyte pairs as the active layer were prepared. Specifically, one pair was PAH/PSS, another pair was chitosan/PSS which was seldom utilized individually for fabricating PEMs due to the high hydrophilicity of chitosan (Beppu, Vieira, Aimoli, & Santana, 2007; Chen et al., 2008; De Oliveira, Fonseca, & Pereira, 2008). Hydrolyzed polyacrylonitrile (PAN) ultrafiltration membranes were selected as the support layer to ensure good adhesion. Isomaltooligosaccharides (IMO500) containing 41 wt% glucose, 27 wt% maltose and isomaltose (collectively called maltose hereafter) and 32 wt% oligosaccharides (trisaccharide and above) were chosen as the separation system. According to the literatures (Miller & Bruening, 2004; Richert et al., 2004) and our preliminary experiment, (chitosan/PSS)<sub>5</sub> membranes allowed an essentially complete passage of glucose with relatively high permeation flux and low rejection for oligosaccharides, while (PAH/PSS)<sub>5</sub> membranes displayed the opposite trend, possessing high rejection for glucose, maltose and oligosaccharides, but rather low permeation flux. Therefore, NF membranes with a unique structure were constructed for stepwise oligosaccharides separation. The (chitosan/PSS)<sub>3</sub> multilayers as the middle layer (ML) were firstly deposited on the support layer. Then, the (PAH/PSS)<sub>2</sub> multilayers as the top layer (TL) were deposited on the ML to form C-PEM membranes. The TL was served as the barrier for totally rejecting oligosaccharide and largely rejecting maltose, while the ML was mainly responsible for rejecting the residual maltose and passing the majority of glucose. Moreover, the chemical composition, structural morphology and NF performance of C-PEM membranes were detailedly characterized.

## 2. Material and methods

### 2.1. Materials

Polyacrylonitrile (PAN) powders were purchased from Shuguang Chemical Co. (Shanghai, China) and used without pretreatment. Chitosan with a degree of deacetylation of 90% was supplied from Zhejiang Golden-shell Biochemical Co. (Zhejiang, China). Dimethyl sulfoxide (DMSO), acetic acid and sodium chloride (NaCl) were obtained from Jiangtian Chemical Reagent Co. (Tianjin, China). Isomaltooligosaccharides (IMO500), that contained 41 wt% glucose, 27 wt% maltose and isomaltose (collectively called maltose hereafter) and 32 wt% oligosaccharides (trisaccharide and above), were supplied from Tianjun Co. (Tianjin, China). Polyethyleneimine (PEI,  $M_w = 25$  kDa, 50 wt% aq.), poly(allylamine hydrochloride) (PAH,  $M_w = 70$  kDa) and poly(styrene sulfonic acid) sodium salt (PSS,  $M_w = 70$  kDa) were purchased from Sigma-Aldrich Chem. Co. Deionized water was used throughout all the experiments.

### 2.2. Preparation of the hydrolyzed asymmetric PAN ultrafiltration membranes

The asymmetric PAN membranes were fabricated via phase inversion technique with 14 wt% PAN powders dissolved in DMSO. The polymer solution was cast on a glass plate and then immersed in deionized water. Subsequently, the hydrolyzed PAN membranes were obtained by immersing the PAN membranes in 1.5 M NaOH (aq.) at 60 °C for 1 h. The residual NaOH was removed by rinsing with large amount of water. Before fabricating the polyelectrolyte multilayer (PEM) membranes, the hydrolyzed PAN membranes

were first immersed in 3.6 wt% HCl for 0.5 h to convert  $\text{COO}^-$  group into  $\text{COOH}$  group.

### 2.3. Preparation of the PEM membranes

The hydrolyzed PAN membranes were completely soaked with water and then placed in a dead-end cell to ensure only one side of the membranes being exposed to the polyelectrolyte solutions. The fabrication of composite polyelectrolyte multilayer (C-PEM) membranes started with the immersion of the hydrolyzed PAN membranes in 2 gL<sup>-1</sup> PEI solution (pH 9.0, 0.5 M NaCl, aq.) for 10 min and rinsed with deionized water for 1 min. Then, the PEI-treated membranes were immersed in 2 gL<sup>-1</sup> PSS solution (pH 6.5, 0.5 M NaCl, aq.) for 10 min followed by rinsing with deionized water for 1 min. The middle layer (ML) which comprised three chitosan/PSS bilayers was constructed firstly with a 10 min immersion of the above substrate in 2 gL<sup>-1</sup> chitosan solution (pH 4.5, 0.5 M NaCl, acetic acid aq.) and then rinsed with deionized water for 1 min before a 10 min immersion in 2 gL<sup>-1</sup> PSS solution. The as-synthesized membranes were then capped with two PAH/PSS bilayers (2 gL<sup>-1</sup> PAH solution, pH 4.0, 0.5 M NaCl, aq.) to form the top layer (TL) following the same immersing and rinsing procedures.

For PAH/PSS or chitosan/PSS membranes, the hydrolyzed PAN membranes were only immersed in PAH/PSS solution or chitosan/PSS solutions. The deposition conditions (type and concentration of polyelectrolytes, pH value) and immersion time were chosen upon specific requirement (as shown in Fig. 1).

### 2.4. Characterizations

The surface and cross-sectional morphologies of the membranes were characterized by SEM (Philips XL-30 ESEM). ATR-FTIR spectra were measured in transmittance mode on a Nicolet, MAGNA-IR 560 instrument with a resolution of 4 cm<sup>-1</sup>. The thickness of the PEMs for C-PEM membranes was obtained by AFM (AJ-III, Aijian nanotechnology Inc., China) measurement, which was carried out in air under normal conditions. Solution viscosity was measured by using Viscometer (DV-1 Prime, Brookfield engineering laboratories Inc., USA). Considering the difficulty on measuring the surface zeta-potentials of C-PEM membranes as a function of layer number, PSS-doped CaCO<sub>3</sub> microspheres were utilized as the substrate instead of the hydrolyzed PAN membranes. The surface zeta-potentials of C-PEM microparticles as a function of layer number were measured in water by a Brookhaven zeta-potential analyzer.

### 2.5. Nanofiltration (NF) process

A dead-end stirred cell filtration system with a N<sub>2</sub> gas cylinder and solution reservoir connected was designed to testify the permeation flux of the membranes. The system consisted of a filtration cell (Model 8200, Millipore Co.) with a vertical-blade magnetic stirrer assembly. The impeller diameter (D) was about 49 mm and its distance to the membrane surface was set at about 40 mm during the filtration process. The volume capacity of the filtration cell was 200 mL and the inner diameter was about 62 mm. The effective area of the membranes was 28.7 cm<sup>2</sup>. The feed side of the system was compressed by N<sub>2</sub> gas. After fixing the membranes, the stirred cell was filled with IMO500 aqueous solution. The solution permeation flux ( $J$ , Lm<sup>-2</sup> h<sup>-1</sup>) was then calculated by Eq. (1)

$$J = \frac{V}{A \times \Delta t} \quad (1)$$

where  $V$  was the volume of permeated solution (L),  $A$  was the membrane area (m<sup>2</sup>), and  $\Delta t$  was the permeation time (h). Most of the NF experiments were carried out at a stirring speed of about 400 rpm, temperature of 25 ± 1 °C and operation pressure of 0.3 MPa.

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