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Crosslinked cellulose thin film composite nanofiltration membranes with zero salt rejection

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ABSTRACT

We report a new synthetic route of fabricating regenerated cellulose nanofiltration membranes. The membranes are composite membranes with a thin selective layer of cellulose, which was prepared by regeneration of trimethylsilyl cellulose (a hydrophobic cellulose derivative) film followed by crosslinking. Filtration experiments using mixtures of sugar and sodium chloride showed that solutes above 300 Da were highly rejected whereas practically no rejection was observed for NaCl. This is a big advantage for a complete desalination as the existing commercial nanofiltration membranes typically exhibit NaCl rejection in the range of 30-60%. Membranes with zero NaCl rejection are required for recovery and purification applications in food, chemical and pharmaceutical industry.

1. Introduction

Membrane processes are currently considered as one of the best viable technologies across a broad range of separation processes. Nanofiltration (NF) has been a rapidly expanding field leading to significant innovations in the last decade especially for treating aqueous effluents in various industries. About 75% of the total market share of NF membranes worldwide is dominated by water demineralization and wastewater treatment applications [1].

Many industrial chemical processes employ salts in aqueous systems for variety of purposes. Sodium chloride (NaCl) is one of the most largely used inorganic materials within the industry [2]. Separation of this salt from small molecular weight components is often required. This is not trivial especially when salt is present in high quantities or when a complete desalination is required [3,4]. Final products must fulfill specific purity; otherwise their values may get reduced. Furthermore, inadequate treatment can lead to substantial cost for further desalination thereby lowering the economics of the products. For the last few decades, various NF membranes have been developed. They typically have excellent rejection to small organic molecules (MWCO 150-500 Da) but they can also retain high amounts of NaCl in the feed. Therefore, such membranes are insufficient for products that require high purity since the contaminating salts are still present in the concentrate. Therefore, development of NF membranes capable of a complete separation of small molecules from NaCl solution is important.

Cellulose is a long-known biopolymer and is a well-established membrane material. The growing interest of this polymer for membrane technology lies on its abundant availability, low cost, excellent hydrophilicity, biocompatibility and its solvent resistance. Unfortunately, as cellulose structure is stiff and closely packed due to its intensive inter- and intra-chain hydrogen bonds (Fig. 1), it is insoluble in most organic solvents. Over the past decades, cellulose has been processed with the multistep and polluting viscose process, driving people to seek other options to process cellulose. To date, a limited number of solvents have been found and used for manufacturing cellulose membranes. *N*-methylmorpholine-*N*-oxide, sodium hydroxide/urea and sodium hydroxide/thiourea systems are among the popular ones. These solvents have been used successfully to generate porous cellulose membranes [5,6,7,8,9,10]. Derivatization of cellulose is an alternative; cellulose is modified into a more processable polymer and is transformed back to cellulose after film deposition. Here, the easiness of the derivatization and regeneration as well as its reversibility are very important to make the process attractive compared to the one step membrane processing.

We now report a newly developed cellulose composite NF membrane that was fabricated using trimethylsilyl cellulose (TMSC) as a precursor. TMSC is an attractive alternative to cellulose xanthogenate that was originally synthesized for making regenerated cellulose in order to replace the viscose process [11]. Trimethylsilyl (TMS) groups were

introduced to mask the hydrophilic properties of cellulose and to break down its strong crystallinity, resulting in trimethylsilyl cellulose (TMSC) with good solubility in common organic solvents such as *n*-hexane and chloroform at room temperature. The process is straightforward and a complete regeneration can simply be carried out by vapor-phase acid treatment to avoid direct exposure to water (Fig. 2). This is a convenient way to assemble thin film of cellulose with good deposition behavior and film morphology [12,13].

The preparation of cellulose composite membranes using TMSC has been described before by Timmermann [14] and Ali [15]. In Timmermann's work no crosslinking was performed. The resulting membranes were "tight" ultrafiltration membranes. Ali performed crosslinking using glyoxal. We noticed in our work that the glyoxal crosslinked membranes were not stable with time as the crosslinking is reversible, so in this study we switched to glutaraldehyde. In addition, we used a different support, another coating procedure and a modified cellulose regeneration method. The focus of our work is the development of a cellulose composite membrane with as low as possible molecular weight cut-off and zero or very low rejection to NaCl.

Rejection experiments using single solutes as sugars and a mixture of sugar-NaCl solutions demonstrated that the as-prepared crosslinked cellulose membranes had a molecular weight cut-off (MWCO) of about 300 Da while permeating all the salt. For the desalination of low molecular weight components these membranes can be operated at lower pressures than the conventional NF-membranes because the osmotic pressure generated by the salt has not to be overcome. These membranes could have applications in demineralization of lactose and whey protein in milk processing as well as in the recovery of small compounds (e.g. organic acids, antibiotics, heterocyclic drug derivatives, etc) from fermentation broths. These membranes may also be very attractive for the reuse of salty water from dyeing effluents.

2. Experimental Section

2.1. Materials

Cellulose (Avicel PH101, Fluka), hexamethyl disilyzane (HMDS, Sigma Aldrich), *n*-hexane (Sigma Aldrich), hydrochloric acid (Sigma Aldrich), glutaraldehyde as 25% solution in water (Sigma Aldrich), sodium chloride (Sigma Aldrich), glucose (Sigma Aldrich), sucrose (Sigma Aldrich), raffinose pentahydrate (Amresco) and dextran (T1, MW of 1000 Da, Pharmacosmos) were used as received. N,N-dimethylacetamide (DMAc, Acros) was dried for

at least one day by 4A molecular sieve (Acros) before its use and lithium chloride (Fischer Scientific) was vacuum dried at 110°C for 4 hours. Porous polyacrylonitrile ultrafiltration membranes were received from GMT GmbH (Germany).

2.2. Experimental procedures

Experiments include 2 main steps; (a) TMSC polymer synthesis – to enhance cellulose solubility and (b) thin film membrane preparation.

2.2.1. Procedure of TMSC synthesis

For the TMSC synthesis we followed with slight modification a procedure described by Schempp et al. [16]. Prior to the reaction, about 6 g of cellulose was swelled in water at 4°C for 1 day and in DMAc for 1 hour at room temperature. Filtered cellulose was added to 600 ml DMAc in a round-bottom flask, stirred and heated to 165°C. After 30 minutes, heating was stopped and when the mixture reached 100°C, 30 g LiCl was added. Stirring was continued until a clear solution was obtained. Solution was then heated to 80°C and 90 ml of HMDS was added by a dropping funnel under magnetic stirring. After 3-4 hours, a yellowish gel-like product was formed and it was separated by decantation. Purification was carried out by dissolution in *n*-hexane followed by filtration and centrifugation to obtain a completely clear polymer solution. Final product was precipitated from methanol and was vacuum dried at 60°C.

2.2.2. Procedure of membrane preparation

Spin coating solution was prepared by dissolving 2.2% (w/w) TMSC polymer in *n*-hexane at room temperature. PAN membrane was used as a support material. It was fixed to a glass plate prior to coating. 1.8 ml coating solution was dispensed onto the support membrane and the spinning was performed for 1 minute with a speed and an acceleration of 4500 rpm and 2500 rpm⁻¹ respectively. The spin coated TMSC membranes were regenerated back to cellulose by vapor-phase hydrolysis (VPH). They were exposed to the vapor above a 10% HCl solution for one day. An aqueous solution containing 1% glutaraldehyde and 0.02% Al₂(SO₄)₃ was used for crosslinking at 40°C for 1 hour followed by washing with water to remove any excess crosslinker followed by curing in oven for 3 hours at 50°C.

2.3. Polymer and membrane characterization

Polymer characterization was performed using a Bruker liquid state 400 NMR spectrometer using deuterated chloroform (CDCl_3) as a solvent. The degree of substitution (DS) was defined as average number of silyl groups present on every anhydroglucose unit (AGU) of cellulose. It can be calculated using eq. (1) where $A_{\text{TMS H}}$ and $A_{\text{cellulose H}}$ represent the peak area of protons in the silyl groups (around 0 ppm) and cellulose (2.9-5.5 ppm) [17,18] respectively.

$$DS = \frac{A_{\text{TMS H}}}{9} \times \frac{7}{A_{\text{cellulose H}}} \quad (1)$$

Membrane hydrophilicity before and after regeneration was determined by water contact angle (WCA) measurement using a Krüss drop shape analyzer – DSA100 with monochrome interline CCD camera. Analysis was performed using deionized water at ambient temperature. The ATR-IR spectra of membranes were collected using a Fischer Scientific Nicolet iS10 spectrometer and were recorded in the range between 650 and 4000 cm^{-1} over 32 scans. Surface and cross-section morphology of the membranes were analyzed by an FEI Magellan scanning electron microscope (SEM). Membrane samples were sputter coated with iridium for 20 seconds at 20 mA to minimize charging effects during SEM imaging. Atomic force microscopy (AFM) imaging of membranes with noncontact mode was performed with an Agilent 5400 SPM/AFM microscope (Agilent Technologies) over an area of $5 \times 5 \mu\text{m}^2$. After scanning the images were flattened to remove curvature and slope from the images. Roughness was given as the root-mean-square (R_{rms}) value based on the data standard deviation. Membrane surface zeta potential was tested using SurPASS electrokinetic analyzer (Anton Paar, Austria) with background of 10mM NaCl solution around neutral pH.

2.4. Membrane performance evaluation

All nanofiltration experiments were carried out with a dead end filtration system using an HP4750 stirred cell (Sterlitech Corporation, USA) with an effective area of 12.6 cm^2 pressurized by nitrogen gas. Permeates were collected after steady state and the permeance (J) was calculated using eq. (2).

$$J = \frac{V}{A \cdot t \cdot \Delta p} \quad (2)$$

where V is the volume of the permeate (L), A is the effective membrane area (m^2), t is the time (h) for permeate collection and Δp is the trans membrane pressure (bar). Rejection value (R) was determined using eq. (3), where C_p and C_{AFS} are the concentration of permeate and averaged concentration of the initial and final feed solution, respectively. In the sucrose/NaCl experiment, the sucrose yield obtained as a retentate (Y_r) was calculated according to eq. (4), in which the volume reduction (VR) is the ratio between the volume of permeate withdrawn and the initial feed volume.

$$R (\%) = \left(1 - \frac{C_p}{C_{AFS}} \right) \times 100 \quad (3)$$

$$Y_r = (1 - VR)^{1-R} \quad (4)$$

Single sugar (glucose, sucrose, raffinose and dextran) solutions with a concentration of 1000 ppm was used as feed. The corresponding MWCO curve was obtained from a plot of the rejection of sugars versus their molecular weights (Fig. 3). Membranes were also tested with mixed sugar-NaCl solutions, each at a concentration of 1000 ppm. Concentrations of sucrose and NaCl were analyzed using Dionex ICS 3000 high-performance anion-exchange chromatography with a pulsed amperometric detector and Oakton® pH/CON 510 conductivity meter, respectively.

3. Results and Discussion

3.1. Membrane structure and morphology

The silylation of cellulose resulted in TMSC with a degree of substitution of 2.2 as confirmed by NMR analysis (Fig. 3). The as-synthesized polymer had good solubility in a number organic solvents including *n*-hexane, cyclohexane, tetrahydrofuran, chloroform, toluene and acetone. The static water contact angle (WCA) decreased from 96° for the hydrophobic TMSC membranes to 26° for the corresponding regenerated cellulose (RC) films. These values are in good agreement with other studies [13,19,20], indicating the complete elimination of silyl groups.

ATR-IR analysis was performed on membranes to confirm the bonding configuration (spectra are shown in Fig. 1). The spectrum of TMSC membranes was broad and overlapped

especially between 700 and 1500 cm^{-1} , signifying the amorphous state of the polymer [21]. Sharp peaks at 746, 781 and 1247 cm^{-1} were exclusively attributed to Si-C bands, whereas those at 787 and 1113 cm^{-1} were for Si-O-C bands. There were also some unreacted hydroxyl groups indicated by the presence of a weak peak in the range of 3200 – 3700 cm^{-1} , as expected from the degree of substitution being less than 3. The substitution of TMS groups by hydrogen upon hydrolysis can be confirmed by comparing the spectrum of TMSC with RC membranes. There was a complete disappearance of Si-C and Si-O-C vibrations accompanied by a very strong presence of an O-H related peak, emphasizing the full cleavage of the silyl groups.

Glutaraldehyde has been found appropriate to crosslink polysaccharide including cellulose [22,23,24]. Compared to the spectrum of RC membranes, the spectrum of the crosslinked RC membranes showed the higher intensity of C-O stretching from 1050-1150 cm^{-1} that represents the existence of crosslinks. These linkages were formed between C-6 cellulosic hydroxyl as the most reactive site and diols, which were the hydrated regions of glutaraldehyde. Furthermore, there was no observable change in the O-H peak signifying the comparable amount OH related groups, which in other words, suggested that the crosslinking occurred via acetal bonds where every glutaraldehyde molecule binds four anhydroglucose units. The reaction is depicted in Fig. 5.

Besides the chemistry, the morphology of the selective layer is also important for the membrane separation performance. Surface and cross-section imaging of the crosslinked membranes were performed by SEM to observe any defects and to estimate the thickness (Fig. 6.a,b), while AFM was conducted to quantitatively examine the surface roughness (Fig. 6.c,d). The surface image (Fig. 6.a) showed a very smooth surface without any observable defects and its smoothness was also confirmed by the AFM analysis, giving a quite low root-mean square roughness (R_{rms}) of 3.8 nm (Fig. 6.c and 6.d), which was considered good for a spin coated cellulose film of this thickness. This is an important asset for NF membranes with respect to fouling mitigation. The cross-section image (Fig. 6.b) showed the presence of the crosslinked RC layer as a dense structure with a thickness of around 150 nm. This layer adhered strongly to the porous support and cannot be peeled off easily even after prolonged exposure to water. Hydrogen bonding among hydroxyl and nitrile groups at the interface and a slight intrusion of the cellulose coating into the membrane pores might be a reason for this stability.

Electrokinetic properties of the membranes were studied using the streaming potential method. Calculated zeta potential of the surface of hydrolyzed membranes was found to be around -25mV whereas the zeta potential of the crosslinked (RC) membranes was -43mV. Higher negative values were obtained upon prolonged exposure to HCl. Acid can easily attack the acetal cellulosic linkages in amorphous domains breaking up the 1-4 glycosidic bonds [25,26] resulting in shorter cellulose chains with more aldehydes which were eventually oxidized into carboxylic acids. During measurement, these groups were deprotonated leading to a negative zeta potential. The lower potential obtained for the crosslinked membranes was probably due to dissociation of the un-crosslinked aldehydes of the glutaraldehyde.

3.2. Membrane separation performance

Separation performance of the membranes was firstly evaluated by pure water filtration. The pure water permeance of the support membranes was around 200 L/m²hbar, whereas the steady state water permeance of the crosslinked cellulose membranes was around 1.2 L/m²hbar. This flux was maintained at multiple filtrations and was stable during the five days measurement time. This is a result of good mechanical properties of the membrane as well as excellent adhesion between the selective layer and the support so that the membrane did not detach or experience damage upon prolonged experiment. Compared to commercial NF-membranes the water permeance through our cellulose composite membranes is relatively low. The current thickness of the cellulose coating is about 150 nm. So far we were not able to reduce the thickness without sacrificing selectivity. In future experiments we will reduce the degree of crosslinking and we will switch to other support membranes.

Rejection experiments were performed to estimate the membrane MWCO. Different single-solutions of sugar species between 180 and 1000 Da (listed in Table 1) with concentration of 1000 ppm were employed as feed at 4 bar. In this study, sugar was chosen since its separation from salty solutions has emerged as an important membrane application. MWCO was estimated from the plot of their rejections over their molecular weights. The rejection increased with the molecular weight (Fig. 7), as one would expect, and the MWCO was estimated to be about 300 Da.

Table 1: Solute properties in aqueous solution at 25°C

Solute	MW (Da)	Stokes radii (nm)
Glucose	180.2	0.365
Sucrose	342.3	0.471
Raffinose	504.4	0.584
Dextran (T1)	≈950	0.650

The separation of neutral organic solutes from electrolytes is required in the food, pharmaceutical and chemical industry. For this reason, in this study the crosslinked RC membranes were investigated to separate sucrose molecules, whose molecular weights are slightly higher than the membranes MWCO, from NaCl. The feed were mixtures of 1000 ppm sucrose and 1000 ppm NaCl that was pressurized at 4 bar. For comparison, four representative commercial NF membranes listed in Table 2 were also tested using identical conditions.

Table 2 Representative of the commercial membranes

Series	Manufacturer	Material	J (L/m ² hbar)
XN45	Trisep	Polypiperazine amide	7.7
TS40	Trisep	Polypiperazine amide	3.8
DK	GE Osmonics	Polyamide	4.3
NF270	DOW Filmtech	Polyamide	6.9

From the results (Fig.8) it is seen that separation performances of the as-prepared membranes were different from those of the commercial membranes. Our membranes were able to retain more than 80% of sucrose with nearly zero rejection of NaCl. The sucrose yield was about 96% obtained at volume reduction of 0.2 (calculated from eq. (4)). The sucrose rejection in mixed-solute system was lower than that in the single-solute experiment (Fig. 3), which was 93%. This phenomenon has been investigated in similar studies [27,28,29,30] in which the sugar retention decreased due to the expansion of the membrane pores (pore swelling). This effect may be different in all cases depending mostly on the nature of the membrane sample used. Pore swelling is caused by the increasing concentration of counter-ions on the electrical double-layer and is more pronounced at higher salt concentration [28,31]. This mechanism can also explain the slightly higher permeance obtained in the sucrose/NaCl mixture compared to the flux of pure water. Compared to the commercial membranes, 80-95% sucrose rejections were achieved, yet the retention of NaCl was higher

with a range of 15-50%. In addition, although their permeances were higher, they all experienced permeance diminution with the presence of sucrose and NaCl compared to their water permeances (Table 2), contrary to our membranes. The effective pressure was reduced due to the NaCl-generated osmotic pressure. The permeance reductions were not exactly linear to the salt rejection as some membranes may undergo pore swelling as well. To obtain high purity products, further processing is entailed to eliminate the remaining salts, which will be more difficult as the stream has already been concentrated.

All commercial NF membranes have a low to moderate rejection for monovalent ions. Even though their pores are bigger than the ion size, monovalent salts are usually retained at various degrees. The ion exclusion mechanism can be explained as a result of Donnan exclusion and steric hindrance. Donnan exclusion takes place in membranes with fixed charges. Ions with the same charge as the fixed ions in the membrane material are repelled from the membrane surface.

Bowen et al. showed that salt transport could not be ascribed to charge effects alone [32]. Diffusion due to concentration gradient and convection due to pressure difference are also significant in salt transport mechanism. In some cases at which strongly charged membranes operated in low pressure, the effect of diffusion can even be predominant.

In this work, our crosslinked RC membranes have practically zero rejection to NaCl in spite of the negative zeta potential. The high salt permeability should be strongly associated with substantial contribution of diffusion and or convection. High diffusivity of the ions in the membrane can be expected because of the high hydrophilicity of the membrane material. In addition, the pore swelling may also contribute to the high salt passage by improving the convective flow and weakening the repulsion effect stemming from the membrane wall. Further investigations including analysis of the effective membrane pore size as well as the effect of different ion properties (concentration, valence and size) with respect to ion rejection need to be carried out in order to establish the transport mechanism. In addition, more research especially regarding the effect of hydrolysis period to the cellulose membrane performance with respect to its crystallinity should open additional opportunities to improve the membrane permeance.

4. Conclusions

Cellulose thin film composite membranes have been developed by coating trimethylsilyl cellulose (TMSC) on a porous polymeric support followed by cellulose regeneration using hydrochloric acid vapor and crosslinking with glutardialdehyde. The around 150 nm thick cellulose layer adhered strongly to the porous support even after prolonged filtration experiments. MWCO of the membranes was around 300 Da. Experiments using mixtures of sucrose and NaCl demonstrated the good separation of sucrose from NaCl as more than 80% of sucrose was rejected practically without rejecting the salt. This could not be achieved with commercial membranes using the same test conditions. Because of their selectivity, we anticipate that these membranes may be useful for separation, purification and desalination of valuable components from a saline process stream. In addition the smooth surface and the very hydrophilic character of the membrane surface will be beneficial for the fouling behavior.

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- Fig. 1** Cellulose structure with the intra- (red) and inter-chain (blue) hydrogen bonds.
- Fig. 2** Silylation reaction of cellulose with hexamethyldisilazane (HMDS) and the regeneration
- Fig. 3** ^1H NMR spectrum of TMSC using CDCl_3 as a solvent
- Fig. 4** ATR-RI of TMSC, regenerated cellulose (RC) and crosslinked RC membranes
- Fig. 5** Cellulose crosslinking by glutaraldehyde
- Fig. 6** SEM (^a surface, ^b cross-section) and AFM images (^c 2D phase, ^d 3D topography) of crosslinked RC membranes
- Fig. 7** MWCO determination using sugar solutions at 4 bar
- Fig. 8** Nanofiltration of solutions containing 1000 ppm sucrose and 1000 ppm NaCl at 4 bar

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Graphical abstract

Highlights

- Thin-film cellulose composite nanofiltration membranes are prepared.
- NF-membranes with 300 Dalton MWCO and zero salt rejection.
- Silylated cellulose as precursor for thin crosslinked cellulose films.

Accepted manuscript