



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 cross-linking. 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.

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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.

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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 [5–10]. 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

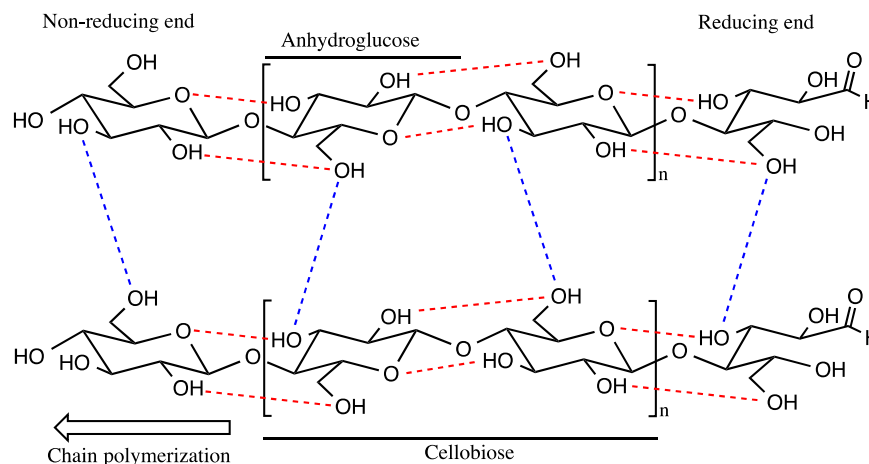


Fig. 1. Cellulose structure with the intra- (red) and inter-chain (blue) hydrogen bonds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

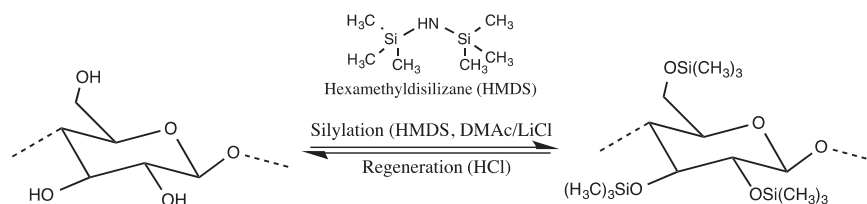


Fig. 2. Silylation reaction of cellulose with hexamethyldisilazane (HMDS) and the regeneration.

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 previously described 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 disilylzan (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), dextran (T1, MW of 1000 Da, Pharmacosmos) and aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$, Sigma Aldrich) were used as received. *N,N*-dimethylacetamide (DMAc, Acros) was dried for at least one day by 4 Å molecular sieve (Acros) before used and lithium chloride (LiCl, Fischer Scientific) was vacuum dried at 110 °C for 4 h. Porous polyacrylonitrile (PAN) 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 h at room temperature. Filtered cellulose was added to 600 ml DMAc in a round-bottom flask, stirred and heated to 165 °C. After 30 min, 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 h, a yellowish gel-like product was formed and it was separated by decantation. Purification was carried out by dissolution in *n*-hexane followed by centrifugation to obtain a completely clear polymer solution. Final product was precipitated from methanol and was vacuum dried at 60 °C.

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