Alginate-based membranes: Paving the way for green organic solvent nanofiltration

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ABSTRACT

In this study, green bio-membranes were investigated. Alginate membranes were prepared by crosslinking of sodium alginate in calcium chloride aqueous solution. By fabricating membranes simply using three abundant cheap materials i.e. sodium alginate, salt and water, we have demonstrated membranes with acceptable performance for OSN with excellent chemical stability. Membranes prepared on three different polymeric supports (PAN, crosslinked PAN and Cellulose) showed similar performance. The alginate membranes were also spun coated on glass plate and laminated on alumina support. Great chemical stability was observed towards various solvents including dimethylformamide and dimethylsulfoxide. Characterization tests with FTIR, SEM, AFM and contact angle were carried out. Using same support, many parameters were explored such as the alginate concentration and the post treatment such as drying, crosslinking or

precipitating in non-solvent. The range of the membranes permeance was 0.08 - 1.8 L/m² h bar depending on conditions used. The nanofiltration experiments revealed a molecular weight cut off of about 1,200 g/mol when tested with dyes such as Methyl Orange, Brilliant Blue and vitamin B12 in methanol. We initiated the preparation of fully green organic solvent nanofiltration membranes using green routes by preparing alginate selective layer on top of cellulose support. This study demonstrates that alginate membranes can be a promising candidate for green organic solvent nanofiltration.

Keywords: alginate membranes, NaAlg, organic solvent nanofiltration, green membranes, composite membranes, reaction-induced phase separation

1. INTRODUCTION

Membranes-based separation is an attractive method compared to the conventional processes (e.g. distillation and extraction) due to smaller footprint, lower costs, and higher energy efficiency [1-4]. The separation occurs without phase transition [5], concentration and pressure gradients across the membrane are the driving force. Nanofiltration (NF) membranes have pore diameters in the range of 0.5–2 nm with a molecular weight cutoff (MWCO) of 200 - 2000 g/mol; the MWCO is defined as the molecular weight at which 90% rejection is obtained. For organic solvent nanofiltration (OSN) the membranes must offer high chemical stability and attractive performance. Molecular separation with OSN is preferable as it is scalable and applicable for a wide variety of process conditions such as pH, temperature, solvent and pressure [6].

Various polymeric materials such as polyacrylonitrile (PAN) [7-8], polyimide (PI) [9-18], polythiosemicarbazide (PTSC) [19], polybenzimidazole (PBI) [20], polyaniline (PANI) [21-22], polysulfone (PSf)/sulfonated poly (ether-ether ketone) (SPEEK) blends [23], poly (ether-ether ketone) (PEEK) [24-25] and copolyazole [26] have been investigated as OSN membranes.

Coating and interfacial polymerization of polymers on top of chemically crosslinked supports were also studied as composite membranes [27-31]. However, little attention has been drawn to biopolymers.

The role of OSN, as a green technology, is limited by the waste generated during membrane preparation and the harmful solvents used. In addition to using biopolymers as raw materials, different strategies have been proposed to produce greener OSN membranes such as using greener solvents for casting or coating, using low toxicity chemicals, minimizing the number of steps in membranes production to reduce waste, and minimizing energy in preparing casting solutions [32].

OSN membranes with biopolymer selective layer were investigated in the literature. Cellulose, the most abundant organic biopolymer, does not melt or dissolve in ordinary solvents due to the strong hydrogen bonds between its chains. This qualifies cellulose as a very good candidate for organic solvent separation applications [33-35]. Sukma *et. al.* prepared cellulose OSN membranes from ionic liquid solution using phase inversion method. 94% Bromothymol Blue rejection in ethanol was obtained [36]. Catechin/cellulose composite OSN membranes were successfully prepared and tested. The polyester top layer was formed by interfacial polymerization between the bio-derived polyphenol (catechin) and TPC. The formation was executed through an environmentally

friendly route in efforts to prepare green membranes. The membranes were stable in DMF and showed a permeance of 1.2 L/m² h bar with MWCO of 500 g/mol [37]. Another bio-polyphenol was reported for the formation of composite OSN membranes. Morin was used to replace the toxic amine for the interfacial polymerization membranes prepared on crosslinked PAN support. The membranes showed an exceptional performance and resistance to NMP with a permeance of 0.3 L/m² h bar and a rejection of 96% of Brilliant Blue dye (825.97 g/mol) [38].

Sodium alginate (NaAlg) is a natural polysaccharide extracted from the cell wall of brown seaweed and it is the water-soluble salt of alginic acid. Alginate is an unbranched binary copolymer of 1-4 linked β -D- mannuronic acid (M) and α -L guluronic acid (G). In principle, alginate is built of G-G blocks, G-M blocks, and M-M blocks (Figure 1). These blocks can be found in different ratios and molecular weights, dictating the physical and chemical characteristics of the final polymers [39,40]. Crosslinked NaAlg has been a potential candidate for pervaporation applications since crosslinking is essential to increase the membrane stability toward water as well as to enhance the mechanical strength. A number of crosslinking agents have been reported including glutaraldehyde [41,42], toluene diisocyanate (TDI) [43], hexanediamine or jeffamine [44-47] and divalent cations such as calcium salts through ionic crosslinking [48].

Figure 1. Chemical structure of sodium alginate polymer with mannuronic (M) and guluronic (G) acid blocks.

In this work, sodium alginate composite membranes were prepared from NaAlg through the reaction induced phase separation technique [49]. Water was used as a solvent and an aqueous solution of calcium chloride was chosen as the crosslinking agent, aiming to improve the green characteristics of the membrane manufacture. Polyacrylonitrile (PAN), cellulose [50], non-woven polyester and alumina discs served as supports. The membranes were tested in various solvents including dimethyl sulfoxide, dimethylformamide, and tetrahydrofuran. This study provides a very simple way to not only manufacture highly stable OSN membranes with decent performance, but to also promote cheap and green materials in the advanced membrane technology.

2. EXPERIMENTAL SECTION

2.1. Materials

Sodium alginate (NaAlg) was purchased from MP Biomedicals LLC. Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was purchased from Fisher chemicals. Polyacrylonitrile

(PAN) (GMT, Membrantechnik GmbH, Germany), alumina disc (Anodisc 25, 200 nm pore size, Whatman Ltd.), and polyester (Sojitz Europe, Germany) were used as supports. The crosslinked PAN (XPAN) was prepared through crosslinking of the bare PAN support using hydrazine monohydrate (Sigma-Aldrich). Another support from cellulose was prepared by phase inversion. About 12% (wt/wt) cellulose (Avicel PH101, Sigma Aldrich) was dissolved in (1-ethyl-3-methylimidazolium acetate) (Sigma Aldrich) at 80 C. The solution was then cast (300 μ m clearance) on non-woven polyester followed by precipitation in water. Vitamin B12 (B12) (Sigma Aldrich), methyl orange (ACROS organics) and Brilliant Blue R-250 dyes (Fisher BioReagents), polyethylene glycols (Sigma Aldrich) were used as markers during rejection experiments. Solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), methanol, ethanol, toluene, NMP and acetone (all from Sigma Aldrich) were used without further purification.

2.2. Membrane preparation

First, NaAlg solution was prepared by dissolving NaAlg in water for 3-8 hours at room temperature depending on the polymer concentration.

2.2.1 Composite alginate membranes on polymeric support.

Composite membranes were prepared by casting NaAlg solution (150 μ m clearance) on top of PAN, crosslinked PAN (XPAN) or cellulose supports as illustrated in Figure 2. Next, the membranes were either left to dry at room temperature or were precipitated in acetone (Figure S4) or in a water bath containing calcium chloride for a

certain period of time then washed with pure water. The calcium ions act as crosslinking agents (Figure 3).

Figure 2. Preparation procedure of composite NaAlg (route 1) and CaAlg (route 2) membranes.

Figure 3. Chemical crosslinking reaction of NaAlg polymer and CaCl_2 salt solution

2.2.2 Freestanding alginate membranes on:

- a) Alumina support:

Freestanding NaAlg membranes were prepared by spin coating. Certain percentage of NaAlg solution was spin-coated on a glass slide at 1000 rpm speed and 1000 rpm s^{-1} acceleration for 1 min. After coating the glass plate was immersed in 5% CaCl_2 /water solution for 5 min where precipitation of the polymer occurred due to ionic crosslinking, resulting in the formation of CaAlg membranes. The glass plate was subsequently transferred to a pure water bath to stop the crosslinking reaction. The alginate layer was then detached from the glass plate and was transferred to the alumina support, the lamination step is tricky and further optimization is needed. The preparation is outlined in Figure 4.

Figure 4. Preparation procedure of freestanding CaAlg membranes.

b) Polyester support:

About 1 or 3% (w/w) NaAlg in water was prepared and cast on a polyester support directly with a thickness of 150 μm . The cast film was then precipitated in a crosslinker bath containing 5% CaCl_2 for 5 min and then transported to a water bath. Finally, the membrane was left to dry at room temperature; membranes were fixed in

filtration cells only once completely dry. This procedure has to be done carefully to avoid detachment of the alginate layer from the polyester.

Other membrane preparation methods are briefly mentioned in the supporting information (Figure S2).

2.3 Membranes characterization

2.3.1 FTIR analysis

The FTIR spectra were recorded on a Nicolet iS10 FTIR spectrometer with a Smart iTR Attenuated Total Reflectance (ATR) sampling accessory in the range of 500 – 3500 cm^{-1} at room temperature. The samples were fixed between a diamond plate and pressure tower with the separating layer facing the beam. Membranes were dried prior to measurements. Spectra of different membranes were compared.

2.3.2 SEM images

The surface of the studied membranes was characterized by high-resolution scanning electron microscope (Magellan) or (FEI Nova Nano) at 2 kV. The samples for cross-section images were obtained by fracturing the membrane in liquid nitrogen. Prior to the SEM imaging the samples were sputtered with a 3 nm thick (Magellan) or 5 nm (Nova Nano) Iridium coating using a Quorum Q150T S sputter coater under an argon atmosphere to achieve the necessary conductivity. The Magellan microscope was used to take the cross-section SEM images of the freestanding membranes; the samples were fractured carefully without liquid nitrogen since the support was too brittle to handle.

A Helios Nanolab 400S dual beam SEM equipped with electron beam (field emission source), focused ion beam (FIB) and through-the-lens secondary electron detector (TLD) was used to examine the freestanding membranes cross-section. Membranes were coated with a 7 nm of Pt/Pd inside a K575X sputter coater (Quorum Technologies). Two-steps coating with platinum was used to protect the top surface layer from ion beam-induced damage during subsequent cross-sectioning steps. The membrane surface was first coated with 200 nm of platinum using e-beam and additional 1200 nm of platinum coating using FIB. The cross-sectioned face of the membranes was imaged using TLD at 5 KV, 52-degree stage tilt angle and 3.9 mm working distance.

2.3.3 AFM analysis

The surface topographies were analyzed by AFM on an ICON Veeco microscope operating in the tapping mode using commercial silicon TM AFM tips (MPP 12100). Films were fixed on silicon wafer prior to experiment.

2.3.4 Contact angle measurements

Contact angle measurements were performed with an Easy- Drop Instrument (manufactured by Krüss) at room temperature using the drop method, in which a drop of water was deposited on the surface of a piece of membrane using a micropipette. The contact angle was measured automatically by a video camera in the instrument using a drop shape analysis software. All membranes were dried prior to the measurements. Three measurements were performed on different membrane pieces and the average values were reported.

2.3.5 Nanofiltration experiments

All nanofiltration experiments were carried out at 25 °C in a stirred dead-end filtration cell. The effective membrane areas were 12.6 and 4 cm² for composite and freestanding membranes respectively. Permeate samples for flux and rejection measurements were collected at steady state. Rejection studies were carried out using a feed solution of 20-ppm vitamin B12 (MW = 1,355 g/mol, size = 1.7 nm, charge = neutral) in methanol, DMF, DMSO and NMP. Also, 5 ppm of both methyl orange (MW = 327 g/mol, charge = -1) and Brilliant Blue R-250 (MW = 825, charge = -2) dyes were used. 0.2 wt% PEG's (600, 3K, 10K, and 35K g/mol) in water were used to characterize the rejection in water. The rejection of vitamin B12 and other dyes was monitored using a NanoDrop 2000/2000c spectrophotometer (Thermo Fisher Scientific). The rejection of PEG's was measured using GPC. Solvent permeance (J) was determined by measuring the permeate volume (V) per unit area (A) per unit time (t) per unit pressure (P) according to equation 1. The rejection (R_i) of dyes was calculated from equation 2, where CP_i and CF_i corresponded to the permeate and the feed concentrations, respectively. Each filtration experiment reported was at least repeated three times with three membranes.

$$J = \frac{V}{(A * T * P)} \quad (1)$$

$$R_i = \left(1 - \frac{CP_i}{CF_i}\right) * 100\% \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Membrane structure and morphologies

The FTIR spectra of the sodium alginate (NaAlg) and the crosslinked alginate (CaAlg) were recorded and compared in Figure 5. Spectrum of sodium alginate showed

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important absorption bands regarding hydroxyl, ether and carboxylic functional groups. Stretching vibrations of O–H bonds of NaAlg appeared in 3344 cm^{-1} shift. Stretching vibrations of aliphatic C–H were observed at 2932 cm^{-1} . Observed bands in 1602 and 1413 cm^{-1} were attributed to asymmetric and symmetric stretching vibrations of carboxylate salt ion, respectively. The bands at 1092 and 1031 cm^{-1} were attributed to the C–O stretching vibration of pyranose ring and the C–O stretching with contributions from C–C–H and C–O–H deformation. The calcium alginate spectrum showed changes in comparison with the IR spectrum of NaAlg. The absorption region of stretching vibrations of O–H bonds in CaAlg appeared narrower than in NaAlg. This difference arose from the participation of hydroxyl and carboxylate groups of alginate to the calcium induced chelate structure formation and a consequent decrease in hydrogen bonding between hydroxyl groups. Lower shifting for the asymmetric stretching vibration of carboxylate ion (1080 and 1021 cm^{-1}) was noted. This can be explained by the differences in the charge density, molecular weight and ion radius of the cations once calcium ions replace sodium ions as reported before [51].

Figure 5. FTIR- analysis of NaAlg and CaAlg alginate membranes.

SEM surface images of PAN support, NaAlg coated PAN, and CaAlg crosslinked membranes are presented in Figure 6. PAN porous supports have a pore size of around 50 nm (a). After NaAlg coating, the membranes exhibited full coverage of the PAN surface pores. There was no observable difference among all the membrane surfaces regardless their precipitation method (in acetone (b) or left to dry (c)). A full coverage of the PAN support was also obtained for CaAlg membranes (d) however minor ridges on the surface were spotted (SEM images in supporting information Figure S14). Higher magnification images were provided as insets to prove full coverage of the pores however increasing the magnification further resulted in destruction of the surface due to the alginate sensitivity to the beam (Figure S13). The thickness of 1% alginate on PAN estimated using AFM height mapping was about 1.7 μm (Figure S12).

Figure 6. SEM surface images of a) PAN support, b) 1% NaAlg coated PAN precipitated in acetone, c) 1% NaAlg coated PAN dried at room temperature and d) 1% NaAlg precipitated in 5% CaCl_2 for 5 min. Insets shows a higher magnification of the image.

The cross-sectional SEM image in Figure 7a and b shows the 1% CaAlg membranes sitting on top of a highly porous alumina support. From the AFM topography images in Figure 7 e and f, it is evident that the roughness of the alumina is imprinted on the surface of alginate even after the delamination of the layer from the alumina and relocation to silicon wafer. The alginate membrane on alumina exhibited a surface with the highest calculated roughness of 69 nm compared to other supports (Figure S11). An

alginate thickness of about 370 nm was estimated from the AFM height mapping on a silicon wafer. Figure 7 c shows the freestanding nanofilm on top of an alumina disc and Figure 7 d illustrates the alginate nanofilm fixed on a 2 cm diameter metal wire ring, demonstrating that the freestanding alginate film had a good integrity although it was only 370 nm thick.

Figure 7. 1% NaAlg spin coated alginate membranes on alumina (5% CaCl_2 , 5 min). a) and b) cross-section SEM images, c) Photograph of 1% alginate nanofilm crosslinked in 5% CaCl_2 for 5 min fixed on alumina, d) Photograph of 1% alginate nanofilm crosslinked in 5% CaCl_2 for 5 min fixed on a metal ring, e) and f) AFM surface topography of alginate layer after being separated from alumina and fixed on silicon wafer and g) the corresponding height profile.

In addition to using the aforementioned supports, we also prepared crosslinked alginate membranes on top of non-woven polyester. Although the alginate layer had poor adhesion to the support when in contact with some solvents (e.g. methanol, ethanol), we still managed to obtain good quality membranes whose performance is presented in the

next section. This can also be seen in the SEM surface images (Figure 8 b and a), which demonstrate that the 1 and 3% NaAlg (respectively) casting solution could cover the highly coarse surface of the polyester support without any observable voids. Figure 8 b showcase a low-resolution cross-section image of 3% alginate on polyester and c) and e) reveal the thickness of the alginate layer of 3% (1.3 μm) and 1% (700 nm) respectively. Although a full coverage of 1% alginate on polyester can be achieved, the film easily detached from the support as seen in the Figure 8 f, most likely due to the minimum polymer intrusion in the support pores. The thickness of 3% alginate on polyester was expected to be higher than the thickness of 1% alginate on PAN due to higher concentration, however (referring to Figure S12) the opposite is noted. The only possible explanation is that different supports were used. The 1% alginate was cast on the low porosity PAN support with a pore size of 50 nm, while the 3% alginate was cast on the highly open polyester. It is expected that some of the uncrosslinked polymer on the polyester dissolved during the 5-minute crosslinking time, whereas the entire polymer matrix was perfectly crosslinked for 30 minutes on top of the PAN support.

Figure 8. SEM surface images of the CaAlg membranes on polyester support where a) and d) represent surface images of 3% and 1% NaAlg concentration, b) and c) cross-section image of 3% NaAlg membrane, e) represent the cross-section of 1% NaAlg membrane and f) photograph of tested membranes with 1% and 3% concentration showing detachment of the film.

Contact angles were measured on the PAN support and the CaAlg on PAN. Figure 9 shows a contact angle of around 44° of the PAN support; while the 1% NaAlg coated membrane (crosslinked with 5% CaCl_2 for 30 min) had a contact angle of 25° , indicating the presence of the strongly hydrophilic alginate. Contact angle measurement of the uncrosslinked NaAlg membranes was not possible due to its high solubility in water.

Figure 9. Water contact angle measurement of a) PAN support, and b) 1% alginate crosslinked with 5% CaCl_2 for 30 min film on PAN support.

3.2 Nanofiltration performance

Figure S6 shows UV analysis of feed, permeate and retentate samples in methanol and DMF filtration containing vitamin B12. Filtrations were carried out at a pressure range of 5-15 bar. Two types of alginate composite membranes with two different concentrations were prepared on the PAN supports. Table 1 summarizes the permeances and rejections of the as-prepared NaAlg membranes. Different post treatment led to different membrane performance. Crosslinking rendered membranes with reasonable permeances and good rejections. For these membranes, coating with 1% NaAlg led to more than 98% rejection of vitamin B12 in methanol and DMF, while the rejection of the 0.5% membrane was slightly lower. Using 0.1% alginate concentration resulted in defective membranes indicated by the very low rejections. No decent rejections were obtained for the air-dried NaAlg membranes. Furthermore, the permeance of the acetone-precipitated membrane was very low most likely due to the formation of a dense skin layer resulted from the relatively lower affinity between solvent (water) and non solvent (acetone) compared to membranes precipitated in water / CaCl_2 crosslinking bath, a lower affinity between non solvent and solvent increases the coagulation time and favors a final

structure with a denser skin layer and smaller porosity in the sub-layer [52] (Figure S9 c). Using cellulose as a support (to provide a green option) resulted in similar rejections compared to the PAN supported membranes, while the lower permeance indicated the low porosity of the cellulose layer. For the experiments with DMF, membranes were prepared on the more stable XPAN support. Similar rejections to the values of the PAN supported membranes were obtained in DMF, indicating the good stability of the support that maintain the alginate sieving performance in the harsh solvent. However, the permeance value was compromised by the denser support structure (due to crosslinking). More study on this support was previously discussed in the literature [8].

Table 1. Performance of alginate composite membranes. ND: not detected.

NaAlg concentration (%)	Support	Post treatment	MeOH Permeance (L/m ² .h.bar)	20 ppm B12/MeOH	
				Permeance (L/m ² .h.bar)	Rejection (%)
1	PAN	Crosslinking 5% CaCl ₂ , 30 min	1.4 ± 0.2	1.27 ± 0.2	98 ± 2
0.5	PAN	Crosslinking 5% CaCl ₂ , 30 min	2.1 ± 0.1	1.46 ± 0.3	85 ± 3
0.1	PAN	Crosslinking 5% CaCl ₂ , 30 min		22.93 ± 5	34 ± 2
1	Cellulose	Crosslinking 5% CaCl ₂ , 30 min		0.38 ± 0.1	95 ± 1
1	PAN	Drying at room temperature		ND	-
0.5	PAN	Drying at room temperature	20 ± 2	17.19 ± 2	30 ± 3
0.1	PAN	Drying at room temperature		33.44 ± 4	0
0.5	PAN	Precipitation in acetone		0.08 ± 0.02	91 ± 1
				20 ppm B12/DMF	
				Permeance (L/m ² .h.bar)	Rejection (%)
1	XPAN	Crosslinking 5% CaCl ₂ , 30 min		0.21 ± 0.1	98 ± 1
0.5	XPAN	Crosslinking 5% CaCl ₂ , 30 min		0.85 ± 0.3	80 ± 3

It has been reported that in composite membranes, the mesoporous support layer imposes very significant resistance to the solvent transport [53, 54]. To better estimate the membrane performance and minimize the effect of support resistance, we prepared

freestanding membranes laid on top of a highly porous alumina disc (as seen in Figure 7 a). As the alumina support is stable in most solvents, the freestanding membranes on alumina were tested using various solvents. Visual observation of the freestanding films soaked for 3 days in solvents such as DMSO, DMF, NMP, and methanol confirmed the good stability of the films. A series of solvent permeances were tested using the same membrane are presented in the supporting information Figure S1. The water permeance was similar before and after harsh solvents filtration.

The permeance of the alumina supported membranes as compared to the ones on PAN support is expected to be much higher due to the high porosity of the alumina and the absence of pore penetration in the membrane surface pores. However, the values obtained were very similar to the composite membranes. This can only be attributed to the fact that these values represent the intrinsic permeances of the standalone alginate layer. This means that the composite membranes did not suffer from severe pore penetration.

Pure solvent permeances were recorded for the membranes supported by alumina and summarized in Table 2. Also rejection test was performed to identify the MWCO of freestanding membranes on alumina. Low permeances of solute/solvent were observed when compared to pure solvents. For instance, the permeance of methanol containing vitamin B12 was $1.60 \text{ L/m}^2 \text{ h bar}$ while pure methanol permeance was $1.8 \text{ L/m}^2 \text{ h bar}$. The common explanation for this finding is the competitive flow between solvent and solute, hindering the solvent molecules to permeate freely through the membrane, it is known from the literature that the transport through membrane is influenced by the solute-solvent-membranes interactions, parameters such as solubility,

dipole moment, surface energy, molecular size and hydrogen bonding can affect the performance [55,56]. No major visual adsorption of the dyes on the surface of the membranes was noted; this can be confirmed from the UV analysis in supporting information as well as the actual membrane photograph after being tested in Figure 8f.

Table 2 summarizes the permeance and rejection values of the alumina supported membranes using vitamin B12 in different solvents (Figure S7 present UV analysis). The highest permeance of 1.80 L/m² h bar was achieved using methanol, followed by NMP, DMSO and DMF, respectively. About 70%, 76% and 80% rejections were achieved with vitamin B12 in DMF, DMSO and NMP, respectively. These plausible values proved that the alginate membranes had a good stability in the tested solvents. Better performance could be obtained through careful optimization of the lamination step and membrane conditioning before testing. In comparison to 1% alginate membranes crosslinked in 5 % CaCl₂ prepared on PAN support (1.27 L/m² h bar, 98%); alumina alginate membranes (1.6 L/m² h bar, 90%) showed higher permeance and relatively lower rejection when tested for B12 in MeOH. Also 1% NaAlg. Crosslinked in 5 % CaCl₂ prepared on alumina support (0.25 L/m².h.bar, 70%) exhibited same behavior when tested for B12 in DMF when compared to alginate on XPAN (0.21 L/m².h.bar, 98%). The slightly higher permeance and lower rejection maybe as a result of membrane handling once laminated on -coarse surface- alumina, as the surface of alumina is rough with edges it might have created small defects on the membranes (see Figure S16). The reported results on alumina involved only 1% polymer solution; this was optimized based on the fact that higher concentrations~(3%) lead to very low permeance almost not detected and lower concentrations~(0.5%) were defective.

Table 2. Permeance and vitamin B12 rejection values of the membranes prepared from 1% NaAlg crosslinked with 5% CaCl₂ for 5 min on alumina support.

Solvent	Pure Permeance (L/ m ² .h.bar)	Mixture Permeance (L/m ² .h.bar)	Rejection (%)
MeOH	1.8 ± 0.2	1.6 ± 0.1	90 ± 2
DMF	0.77 ± 0.1	0.25 ± 0.02	70 ± 1
DMSO	0.8 ± 0.1	0.15 ± 0.05	76 ± 2
NMP	0.9 ± 0.05	0.11 ± 0.03	80 ± 3

In addition to PAN, cellulose and alumina support, we have also prepared alginate membranes by casting alginate solution directly on a non-woven polyester support. We aimed to produce greener membranes by eliminating the mesoporous middle layers (such as PAN and cellulose) -that are usually present in the normal composite membranes-and promote easier fabrication process. We expected to obtain higher permeance by lowering the resistance in the support. As this support posses a highly coarse and porous structure, we prevented the defect formation by using higher NaAlg concentration of 3% in addition to 1%, the crosslinking conditions were 5% CaCl₂ concentration for 5 min.

It can be seen from Figure 8 f that the 1% NaAlg resulted in defective membranes indicated by the zero vitamin B12 rejection. As expected, this was due to the highly rough surface of the polyester that created unwanted voids on the alginate layer. Fortunately, the vitamin B12 rejection of the cast 3% NaAlg membrane was between 92-94% (Figure S8), comparable to rejections of the NaAlg membranes supported by PAN (see Table 1) and alumina (see Table 2). This implied that all the resulting alginate structures were identical as they led to a similar sieving performance. Significant differences can be expected in terms of permeance due to variation of the transport resistance in the support. By testing the 3% NaAlg membrane on polyester, a 1,200 g/mol

MWCO was revealed and can be considered as the intrinsic property of the crosslinked alginate membranes prepared in this study. However, as the NaAlg concentration was much higher than the concentration used in the PAN supported membranes, lower permeances were obtained, given that polyester non-woven support has a very rough and open structure (see figure 8b). This is most likely due to severe polymer intrusion through the support pores, which will considerably diminish the preexisting open channels for the solvent permeation across the membrane. The mixture permeance of this membrane configuration was around 1, 0.1 and 0.45 L/m² hr bar in methanol, DMSO and water, respectively. Along the detachment problem and the folding effect, cracks on the surface of the membranes were also experienced (Figure S15). Optimization of conditions, parameters and fabrications steps is still needed to improve the performance of such membranes.

Table 3. Permeance and rejection values of dyes in methanol, DMCO and water tested through freestanding alginate membranes on polyester.

Membrane Type (crosslinked alginate on non-woven 5% CaCl ₂ 5 min)	20 ppm Dye/Methanol (MW g/mol)	Permeance (L/m ² .h.bar)	Rejection (%)
3% crosslinked alginate	Methyl orange (327)	0.96 ± 0.2	67 ± 3
	Brilliant blue (825)	1.14 ± 0.02	85 ± 2
	VB12 (1355)	1.06 ± 0.05	92 ± 1
1% crosslinked alginate	VB12 (1355)	794 ± 10	0
20 ppm Dye/DMSO (MW g/mol)			
3% crosslinked alginate	VB12 (1355)	0.13 ± 0.03	94 ± 1
0.2% PEG (MW g/mol) /water			
3% crosslinked alginate	(600, 3K, 10K, 35K)	0.45 ± 0.01	86 ± 2 (600 g/mol)

Despite many OSN membranes have been produced, our membranes are particularly interesting from the economical and environmental perspective as they are highly stable in harsh solvents, cheap, renewable and are easily manufactured using widely available harmless materials. Table 4 draws a comparison with other OSN composite membranes reported in the literature, information is taken from the review [5]. It is safe to say that alginate membranes performance is within the range of other OSN membranes.

Table 4. Comparison between alginate membranes and other OSN membranes. Adapted and modified from [5]. This work is in bold text.

	Membrane material	Solvent	Permeance (L/m ² .h.bar)	Marker (g/mol)	Rejection %
Polymeric composite membranes via coating	Cross-linked PI/crosslinked PI	DMF	0.7	Solvent Blue (350)	46
	Polypyrrole/PAN-H		0.05	Rose Bengal (1017)	98
	(PS-b-PEO/PAA)/ alumina		0.02	Polyethylene glycols (200–900)	80 (370 g/mol)
	Segmented polymer networks / PAN-H		2.7	Rose Bengal (1017)	99
	(SPEEK/PDDA)/ PAN		0.05	Rose Bengal (1017)	99
	(PDDA/PSS)/PAN (PDDA/PVS)/PAN		0.2	Rose Bengal (1017)	99
	(PDDA/SPEEK)/ PAN-H/Si		0.07	Rose Bengal (1017)	99
	Crosslinked Alginate /alumina	Methanol	0.25	Vitamin B12 (1,355)	70
	Crosslinked Alginate /XPAN		0.21	Vitamin B12 (1,355)	98
	PIM-1/PAN		6.0	HPB (535)	78
	(PIM-1/PEi)/PAN		3.6	HPB (535)	85
	(PS-b-PEO/PAA)/ alumina		0.1	Polyethylene glycols (200–900)	80 (370 g/mol)
	Crosslinked Alginate /alumina		1.6	Vitamin B12 (1,355)	90
	Crosslinked Alginate /PAN		1.27	Vitamin B12 (1,355)	98

4. CONCLUSIONS

Here we report the utilization of alginate as a promising biopolymer membrane for OSN. The membranes were prepared by depositing NaAlg on different supports followed by the one step precipitation-crosslinking reaction using CaCl₂ aqueous solution at room temperature. By simply crosslinking sodium alginate in aqueous salt solution, we

are able to fabricate nanofiltration membranes that can withstand harsh solvents such as DMF, DMSO and NMP with decent performance. The possibility of preparing alginate on polymeric support, alumina support as well as directly on non-woven packing was explored. We report the advantages of such membranes as follows:

- The polymer solution is prepared at room temperature.
- The polymer used is biodegradable, cheap and non-toxic.
- The solvent used is water.
- The support tested can be cellulose or directly polyester.
- The crosslinking bath is aqueous salt solution (non-toxic)
- Post treatment is drying at room temperature.

Whether porous polymeric or porous alumina support, the permeance and rejection values of alginate membranes were similar. The performance of alginate membranes reported here indicates the actual separation quality of the alginate film regardless of the support used or the method prepared which convey identical structure. The only determining factor is the membrane thickness, which result in different permeances. The thickness of each configuration is different due to the different factors like crosslinking time, alginate concentration or method of film applying such as casting or spin coating. Films, which were cast directly on a porous support, showed a similar performance as films, which were first, prepared free-standing and then laminated on alumina, this is indication of finding the intrinsic property of the alginate layer. The pure permeances of methanol, DMF and DMSO of alginate on alumina were about 1.8, 0.77, and 0.8 L/m².h.bar, respectively. The molecular weight cut off was about 1,200 g/mol tested on the cast alginate membrane on a non-woven polyester only if 3% alginate was used. Overall, this route offers a sustainable membrane fabrication for greener solvent

separations. Our study has demonstrated meaningful insight to prepare green and OSN-stable membranes from a cheap degradable material through a simple processing using two simple steps (polymer casting and crosslinking) and non toxic materials such as water (as solvent) and salt (as a crosslinker).

ASSOCIATED CONTENT

Supporting Information

SEM images, AFM images, solvent stability tests, UV-Vis analysis and rejection curves of the as prepared membranes are presented in the supporting information.

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ABBREVIATIONS

NaAlg, Sodium alginate; CaAlg, Calcium alginate; TFC, Composite membranes; MWCO, Molecular weight cutoff.

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