Cellulose membranes for Organic Solvent Nanofiltration

Faqih Muhamad Sukma, P. Zeynep Culfaz-Emecen
Middle East Technical University, Chemical Engineering Department, Ankara, Turkey

Being a young yet promising technology, Organic Solvent Nanofiltration (OSN) has many potentials for different applications such as homogeneous catalyst recycling, recovery of organic solvents in food, painting, and pharmaceutical industries by allowing separations of organic mixtures by simply applying a pressure gradient over a membrane. However, limited number of suitable polymers that can withstand a wide range of organic solvents are available. Polyimide, among those is the polymer mostly studied [1]. Cellulose offers an alternative for this field of study.

Although abundant in nature, use of cellulose as a membrane polymer is hindered by the lack of suitable nonderivatizing solvent. Common solvent systems like NaOH/CS_2 or NMMO are either toxic or unstable. Recent studies showed that there is an alternative way of dissolving cellulose using ionic liquids [2].

The aim of this study is to process cellulose via phase inversion using ionic liquids as solvents to fabricate membranes for Organic Solvent Nanofiltration. 1-ethyl-3-methylimidazolium ([EMIM]OAc) is used as the ionic liquid to dissolve cellulose, while acetone is used as cosolvent and water as nonsolvent. Membrane percursor solutions and membrane types used in this study are listed in Table 1. For solution containing acetone, a cosolvent evaporation step was used to increase the cellulose concentration in solution before precipitation in water.

Table 1. Composition of cellulose solutions used to fabricate membranes

Membrane	**Membrane percursor solution (%wt)**	**Cosolvent evaporation before coagulation**
A	8% Cellulose – 92% [EMIM]OAc	No
B	8% Cellulose – 20% Acetone – 72% [EMIM]OAc	No
C	8% Cellulose – 20% Acetone – 72% [EMIM]OAc	Yes
D	12% Cellulose – 25% Acetone – 63% [EMIM]OAc	No
E	12% Cellulose – 25% Acetone – 63% [EMIM]OAc	Yes
F	20% Cellulose – 80% [EMIM]OAc	No

To study the retention of membranes, Bromothymol Blue (624 Da) and Brilliant Blue R (826 Da) solutions in ethanol are used. Besides, different solute-solvent system based on water are studied using Brilliant Blue R (826 Da), Blue Dextran (5 kDa), and Blue Dextran (20 kDa) as the probes.

It is observed that increasing cellulose concentration in the membrane precursor solution, either by having more cellulose in the starting solution or by evaporating the acetone prior to coagulation, decreases membrane permeance and increases rejection of Bromothymol Blue as shown in Figure 1. Drying post-treatment of membranes further increased the retention (Figure 1).

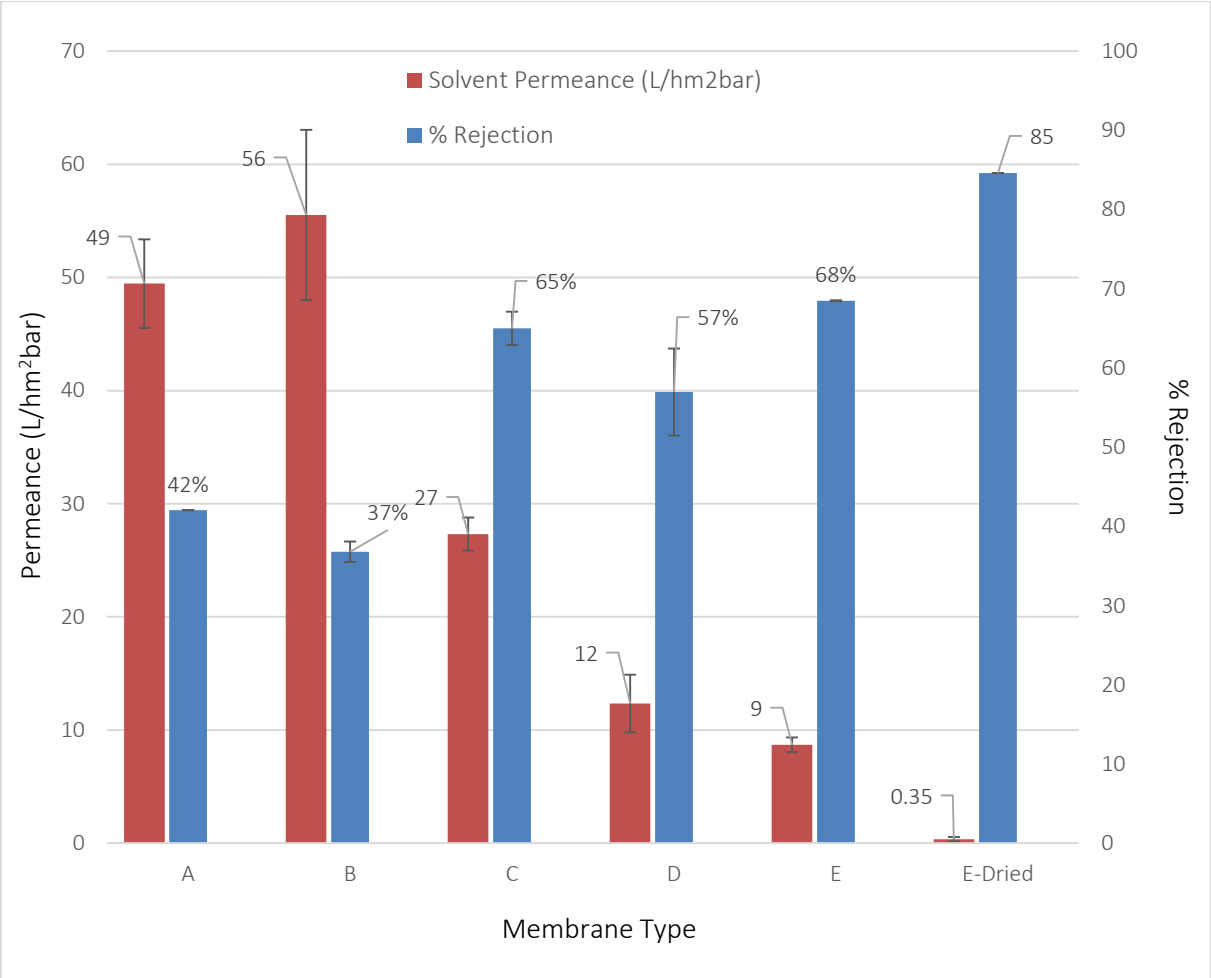


Figure 1. Bromothymol Blue rejection performance in five different non-dried membranes

It is noticed that solute-solvent-membrane interaction may hold an important role in determining the retention performance as a higher molecular weight dye (Brilliant Blue R, 826 Da) is retained less than Bromothymol Blue (624 Da) dissolved in ethanol, which may be related to the interaction of the ionizable groups in Brilliant Blue R with the membrane as shown in Figure 2. Change of solvent also affects the rejection as shown by higher value of Brilliant Blue R rejection in water compared to in ethanol, probably due to the presence of a hydration shell around Brilliant Blue R in aqueous solution and its ionized groups (Figure 2). Based on Blue Dextran retention, membrane E has MWCO between 5 and 20 kDa and membrane F lower than 5 kDa. Brilliant Blue R rejection in ethanol and water show differences due to solute-solvent, membrane-solvent, and membrane-solute interactions (Figure 2 & 3). Further increase of cellulose concentration to 20% combined with drying post-treatment increased Bromothymol Blue (in ethanol) rejection to 94%, Brilliant Blue R (in ethanol) rejection to 40%, and Blue Dextran 5 kDa (in water) rejection to 94% (Figure 3).

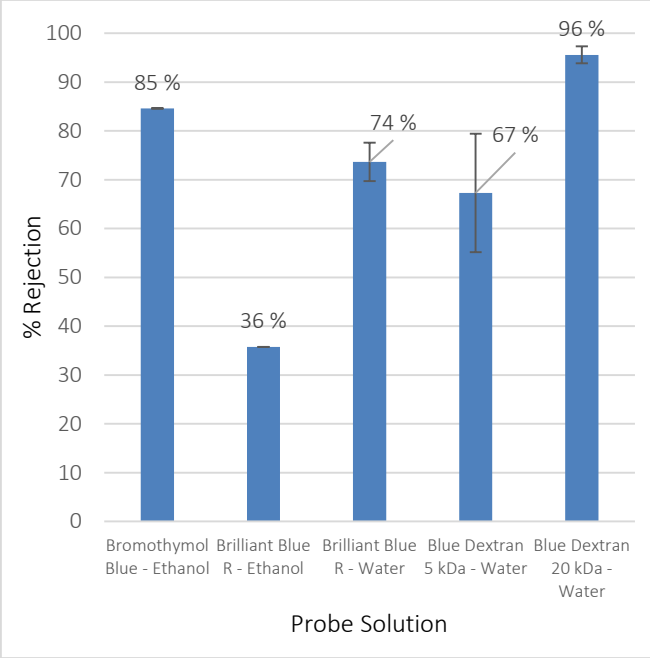


Figure 2. Rejection value on membrane E by using five different solute-solvent systems

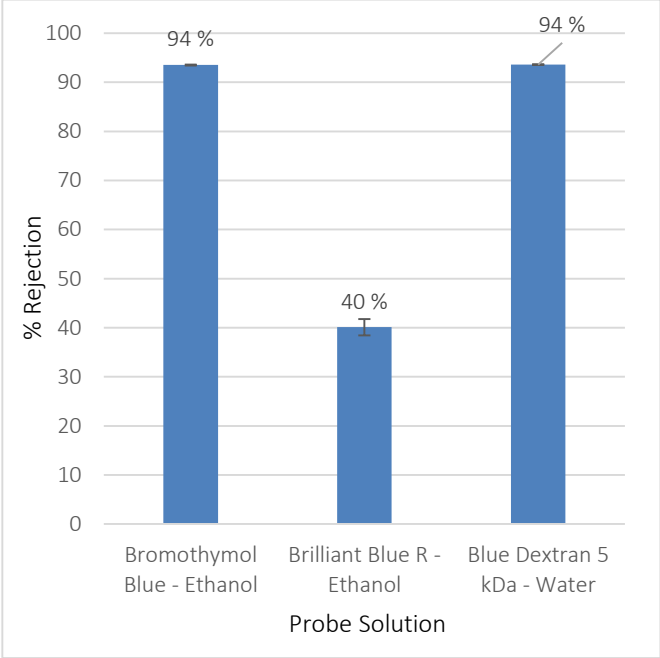


Figure 3. Rejection value on membrane F by using three different solute-solvent systems

References

[1] S. Hermans, E. Dom, H. Mariën, G. Koeckelberghs, and I. F. J. Vankelecom, "Efficient synthesis of interfacially polymerized membranes for solvent resistant nanofiltration," vol. 476, pp. 356–363, 2015.

[2] J. Vitz, T. Erdmenger, C. Haensch, and U. S. Schubert, "Extended dissolution studies of cellulose in imidazolium based ionic liquids," *Green Chem.*, vol. 11, no. 3, p. 417, 2009.