CELLULOSE MEMBRANES FOR ORGANIC SOLVENT NANOFILTRATION

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ABSTRACT

CELLULOSE MEMBRANES FOR ORGANIC SOLVENT NANOFILTRATION

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Cellulose is an alternative polymer that can be used in Organic Solvent Nanofiltration (OSN) where lack of chemically-stable membranes is a major problem. Cellulose, due to strong inter and intramolecular hydrogen bonding, is difficult to dissolve in many solvents, which is an advantage for OSN applications. Common solvent systems like Sodium Hydroxide/Carbon Disulfide (NaOH/CS_2) or N-Methylmorpholine-N-oxide (NMMO) for cellulose solubilization are either toxic or unstable. Recent studies have shown that there is an alternative way of dissolving cellulose using ionic liquids. The aim of this study is to fabricate cellulose membranes for OSN via phase inversion using ionic liquids as solvents. 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) was used as the ionic liquid to dissolve cellulose, while acetone was used as cosolvent and water as nonsolvent. Solutions of probe molecules in both ethanol and water were used to study the separation performance of membranes.

It was observed that increased cellulose concentration in the membrane precursor solution, decreased membrane permeance and increased rejection of Bromothymol Blue (BTB) and Cresol Red (CR) in ethanol. Solute-solvent-membrane interactions have an important role in determining the rejection performance as a higher molar volume dye, Brilliant Blue R (BBR), was retained less than CR, BTB, and Crystal Violet (CV) when dissolved in ethanol. Change of solvent also affected the rejection as was shown by a higher value of BBR rejection in water and the absence of rejection of CV as opposed to the behavior in ethanol. Drying the membranes increased the rejection but decreased the permeances by at least an order of magnitude. Compared to OSN membranes reported in literature, the membranes fabricated in our study have comparable performance.

Keywords: Cellulose Membranes, Organic Solvent Nanofiltration

ÖZ

ORGANİK ÇÖZÜCÜ İLE NANOFİLTRASYON UYGULAMALARINA YÖNELİK SELÜLOZ MEMBRANLARIN HAZIRLANMASI

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Selüloz, kimyasal olarak dayanıklı membranların azlığının önemli bir sorun olduğu Organik Çözücü ile Nanofiltrasyon (OÇN) uygulamaları için alternatif bir polimerdir. Molekül içi ve moleküller arası hidrojen bağlarından dolayı selüloz birçok çözücüde çözünmemekte, bu OÇN uygulamaları için bir avantaj oluşturmaktadır. NaOH/CS2 veya NMMO gibi yaygın selüloz çözücüleri toksik veya kararsız yapıda çözücülerdir. Yakın zamanda selülozu çözmek için iyonik sıvıların kullanılabileceği görülmüştür. Bu çalışmanın amacı, OÇN uygulamalarına yönelik olarak selüloz membranların iyonik sıvıda çözeltilerinden faz değişimi yöntemi ile üretilmesidir. İyonik sıvı olarak 1-etil-3-metilimidazolyum asetat, uçucu çözücü olarak aseton ve çözmeyen olarak su kullanılmıştır. Gösterge moleküllerin etanol ve suda çözeltilerinin filtrasyonu ile membranların ayırma performansı değerlendirilmiştir.

Membran hazırlama çözeltisindeki selüloz derişiminin artırılmasının membran geçirgenliğini düşürdüğü, ancak Bromotimol Mavi (BM) ve Kresol Kırmızı (KK) tutma oranını artırdığı görülmüştür. Çözünen-çözücü-membran etkileşimlerinin ayırma performansında önemli rol oynadığı, etanol içinde Parlak Mavi R (PMR) tutma oranının daha küçük moleküller olmalarına rağmen BM, KK ve Kristal Mor’dan (KM) az olduğu görülmüştür. PMR ve KM suda çözündüklerinde ise PMR tamamen tutulmuş, KM ise hiç tutulmamıştır. Membranların kurutulması geçirgenliği yaklaşık onda bir oranında düşürmüş, tutma oranlarını ise artırmıştır. Bu çalışmada üretilen membranların ayırma performansının literatürdeki ticari olan ve olmayan OÇN membranları ile benzer olduğu görülmüştür.

Anahtar Kelimeler: Selüloz membrane, Organik Çözücü ile Nanofiltrasyon

To Bunda, Ayah, Zahra, Taqwa

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NOMENCLATURE

[EMIM]OAc = 1-ethyl-3-methylimidazolium acetate

CR = Cresol Red

BTB = Bromothymol Blue

CV = Crystal Violet

BBR = Brilliant Blue R

BD5 = Blue Dextran 5kDa

BD20 = Blue Dextran 20kDa

V_F = Feed Volume

V_P = Permeate Volume

V_R = Retentate Volume

C_F = Concentration of solute in feed stream

C_P = Concentration of solute in permeate stream

C_R = Concentration of solute in retentate stream

K = Sorption coefficient

K’ = Modified sorption coefficient

SR = Swelling ratio

$C_{dye,\ membrane}$ = Concentration of dye in membrane

$C_{dye,\ solution}$ = Concentration of dye in solution

CHAPTER 1

INTRODUCTION

Separation processes hold a major role in chemical and pharmaceutical industries and are responsible for around 40-70% of both capital and operating costs [1]. Conventional processes such as distillation, evaporation, and crystallization require large amounts of energy. The importance of separation processes drives industries to provide more energy and material efficient as well as environmentally-friendly separation techniques. Membranes which are thin semi-permeable selective barriers used as an alternative for conventional separation processes, have been significantly advancing in separation process industries due to their low energy consumption, low chemical use, and easy installation. Being operated at ambient conditions and without using chemical additives are further advantages of using membranes as temperature and chemical sensitive substances are often handled in food and pharmaceutical industries.

A membrane selectively permeates chemical substances in contact with it at different rates. The substances which preferentially pass through the membrane are collected in the permeate stream while the rejected substances leave in the retentate stream [2]. Membrane processes are able to either replace or complement conventional separation processes such as adsorption, absorption, evaporation, distillation, or crystallization in industrial applications [1].

Classification of membranes based on retained solute can be done as follows [1,2]:

- **Microfiltration (MF) Membranes**

  Having large pore size, MF membranes are able to filter substances in the range of 0.1 – 10 μm such as bacteria or suspended solids. Transport and separation mechanism in MF membranes is characterized by size exclusion and described by pore flow theory.

- **Ultrafiltration (UF) Membranes**

  UF membranes retain solutes of size within the range of 2-100 nm. Transport and separation mechanism in UF membranes is characterized by size exclusion and described by pore flow theory.

- **Reverse Osmosis (RO) Membranes**

  RO membranes are nonporous and transport through them is characterized by solution-diffusion mechanism. RO membranes are typically used in desalination processes to retain all ions, i.e. mono and multivalent ions.

- **Nanofiltration (NF) Membranes**

  NF membranes lie between ultrafiltration and reverse osmosis membranes. They are occasionally called as loose reverse osmosis membranes, in terms of size of retained solute and their transport mechanism. Transport through them is rather complicated as both pore flow and solution-diffusion mechanisms affect the separation performance. In solution-diffusion mechanism, it is usually assumed that solute and solvent fluxes have no effect on each other. Chemical potential across the membrane is considered to be concentration dependent only. On the other hand, pore flow mechanism takes into account only pressure gradient as the factor for chemical potential gradient across the membrane. Solute flux is also affected by Donnan effect in nanofiltration membranes, which is an interaction between charged ions in solution and charged membrane [3].

Membranes can be either symmetrical (isotropic) membranes (Figure 1. 1) or asymmetrical (anisotropic) membranes according to their structure (Figure 1. 2). Symmetrical membranes have homogeneous composition and pore structure all throughout the cross-section of the membrane. Asymmetrical membranes are membranes having thin, selective skin layer supported on macroporous structure allowing high permeation flux which is desirable for industrial applications. Asymmetric membranes can be integrally skinned asymmetric (ISA) membranes, where thin skin layer and porous support are formed from a single material, and thin-film composite (TFC) anisotropic membranes, where thin surface layer and porous support are typically formed separately [2]. In thin film composite membranes, the support layer is typically fabricated by phase inversion method while the thin surface layer is produced by polymerization on top of it. In integrally skinned asymmetric membranes, membranes are directly produced by using phase inversion method in which the skin layer and porous support are of the same polymer. Skin layer, behaving as selective layer, is relatively dense because of fast phase separation.

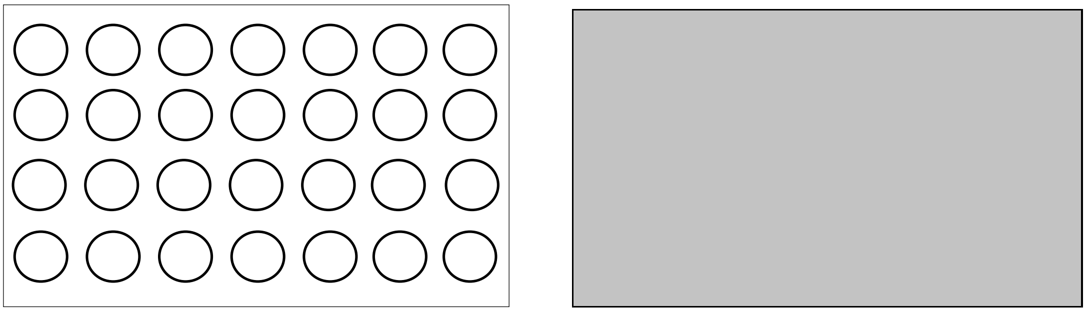


Figure 1. 1 Schematic representation of symmetric porous (left) and dense (right) membranes

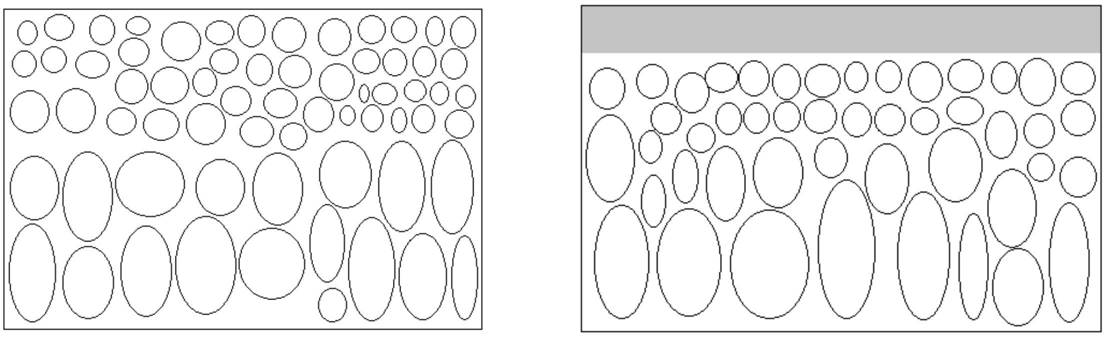


Figure 1. 2 Schematic representation of ISA (left) and TFC (right) membranes

Phase inversion (phase separation), first introduced by Loeb and Sourirajan in 1960s [4], is a common method used to fabricate polymeric membranes with various morphologies, from porous microfiltration membranes to dense reverse osmosis membranes. This method is the basis of most commercial polymeric membranes' production. It is a method in which a thermodynamically stable polymer solution is transformed into two separate phases, namely polymer-rich phase and polymer-lean phase in a controlled way. Polymer-rich phase forms matrix of membrane while polymer-lean phase forms membrane pores [5]. It can be induced by immersion precipitation (liquid induced phase separation), controlled evaporation, thermal precipitation, and precipitation from vapor [6]. Most basic system consists of a polymer, a solvent, and a nonsolvent (Figure 1. 3), which does not dissolve the polymer but is fully miscible with the solvent. Precipitation occurs due to diffusion of nonsolvent into the polymer solution and diffusion of solvent into nonsolvent medium, which brings the polymer solution into unstable, two-phase region.

Immersion precipitation method is mostly used for producing integrally skinned asymmetric membranes. It is both affected by thermodynamic and kinetic aspects of the system. The kinetic aspect of the process is mainly affected by rate of diffusion from nonsolvent into the casting solution and from solvent into nonsolvent medium.

Liquid-liquid demixing occurs when casting solution is in contact with nonsolvent medium and can be either instantaneous demixing or delayed demixing depending on several factors including size of diffusing molecules and viscosity of medium accommodating the mass transfer. In instantaneous demixing, a relatively porous skin layer with macrovoid formation in support layer is generally produced while a relatively dense skin commonly occurs in delayed demixing, though boundary between instantaneous and delayed demixing in nanofiltration membranes is still unclearly defined in literature, probably because this term coming from studies with microfiltration and ultrafiltration membranes [4].

From Figure 1. 3, typically the starting casting solution is either noted as point 1 or 2 in a thermodynamically stable region outside binodal region. Upon contact with nonsolvent medium, it will enter into binodal region. Then, polymer solution will enter metastable region between binodal and spinodal region where phase separation may occur via nucleation and growth or may be delayed until unstable region where phase separation is via spinodal decomposition. Polymer solution will phase separate into polymer-rich phase and polymer-lean phase indicated by A and A’ tie lines respectively [7].

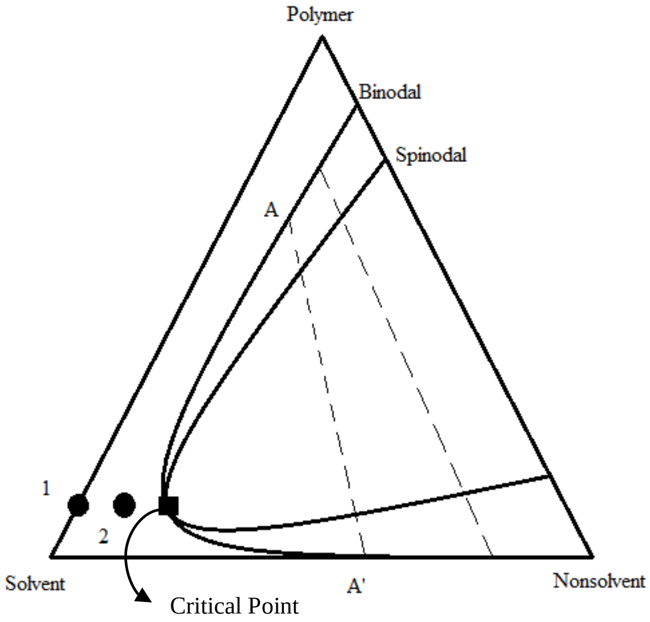


Figure 1. 3 Schematic diagram of phase inversion process

Phase inversion is also often used in fabricating the support layer of TFC membranes. TFC membranes consist of thin skin layer and porous support which are fabricated separately. Therefore, optimization can be done independently which is one of the advantages of TFC membranes. UF support is commonly fabricated via phase inversion acting as support layer for TFC membranes. The most common polymers used for porous support are polysulfone (PSf), polyethersulfone (PES), Polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polypropylene (PP), polyimide (PI), and polybenzimidazole (PBI). Ultrathin skin layer that is fabricated on top of membrane via interfacial polymerization or coating provides a relatively high solvent permeance compared to integrally-skinned asymmetric membranes of similar selectivity which usually have thicker skin layer.

In this study, cellulose membranes are fabricated from their solutions in ionic liquid, 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc), by precipitating them in water and their performance as organic solvent nanofiltration membranes is investigated.

CHAPTER 2

LITERATURE

2.1 Organic Solvent Nanofiltration

Membrane separations are abundant in aqueous applications. In recent years, there has been rapid developments of this technology for applications involving solutions in organic solvents. This new technique is considered to be the growing sub-field under membrane separation process technology where it can be applied in oil, petrochemical, food, bio-product, and pharmaceutical industries [8]. First attempt of producing Organic Solvent Nanofiltration (OSN) membranes has been reported back in 1964 by Sourirajan where cellulose acetate membranes were produced to separate liquid hydrocarbon mixtures [9], though it received more interest in the last decades.

Organic solvent nanofiltration can be applied in oil and petrochemical industries for dewaxing of lube oil, conditioning of liquid hydrocarbons, and biodiesel production. It can also be used in food and bioproduct industries for natural oil processing. Bulk chemistry, fine chemistry, and pharmaceutical industries can benefit from OSN applications, e.g. recovery of catalysts, purification of organic solvents, active pharmaceutical ingredients (API) concentration and purification, non-thermal solvent recovery, and non-thermal solvent exchange. It has been reported that large chemical companies like Exxon Mobil and Grace have been implementing OSN in their processes [8].

Organic solvent nanofiltration has complications not seen in aqueous applications. Challenges in OSN include robustness of membrane materials in aggressive solvent environment and in module preparation. Robustness of membranes towards swelling and leaching is also a major concern in OSN applications. In nanofiltration, since transport occurs through pores of a few nanometer size or through the free volume of the polymer, interaction between membrane, solutes, and solvent is an important factor in determining separation performance.

2.2 Organic Solvent Nanofiltration Membranes

Research related with material selection for organic solvent nanofiltration membranes focuses on using polymeric or inorganic materials. Organic solvent nanofiltration membranes should be mechanically, chemically, and thermally stable against a wide range of organic solvents in order to be specified as a good membrane. This is important to prevent membranes from compaction under high pressure which results in flux decline, from swelling due to solvent medium, and degradation under high temperature conditions [1]. Both polymeric and ceramic membranes have their advantages and disadvantages compared to one another. Mixed matrix membranes have also been studied in order to see if advantages of both types can be used synergistically.

2.2.1. Polymeric Membranes

Polymeric materials are mostly used for producing organic solvent nanofiltration membranes due to their wide variety of material selection. They are easy to fabricate and upscale. Polymeric membranes can be either integrally skinned membranes or thin film composites membranes. Polyimide (PI) membranes, produced via interfacial polymerization or phase inversion, are extensively used for OSN applications.

Soroko et al. [10] studied PI OSN membranes using phase inversion method by using four different types of PI including P84, HT P84, Matrimid 5218, Ultem 1000. P84 is already known for good separation in OSN application while HT P84 is usually used for recovery of aromatic solvents. On the other hand, Matrimid 5218 is commonly used for gas separation processes while Ultem 1000 is generally used for pervaporation and gas separation processes. Molecular weight cut off (MWCO), the smallest molecular weight with 90% rejection, curve was determined by using styrene oligomers dissolved in dimethylformamide (DMF). All PI polymers were dissolved in solvent/cosolvent pair of DMF and 1,4-dioxane respectively. Three solvent/cosolvent ratios (3/1, 1/1, and 1/2) were studied to determine the effect of selection of PI, as well as the effect of solvent and cosolvent on membranes performance. They observed that membranes made from P84 and HT P84 showed lower MWCO value compared to that of Matrimid and Ultem while flux of Matrimid and Ultem were found to be lower than that of P84 and HT P84 in all solvent/cosolvent ratios. In solvent/cosolvent ratio of 1/1, for example, the flux of Matrimid and Ultem was 13 and 4 L m^{-2} h^{-1} respectively, while 69 and 49 L m^{-2} h^{-1} of P84 and HT P84 respectively. Meanwhile, at solvent/cosolvent ratio mentioned earlier, MWCO of P84 and HT P84 was found to be 300 and 250 Da respectively where it was above 1200 Da for Matrimid and Ultem. Total solubility parameter was, then, considered involving polymer, solvent, and cosolvent where the higher the value, the higher solute is retained. They observed that total solubility parameter of P84 and HT P84 were higher compared to that of Matrimid and Ultem. They defined total solubility parameter as the combination of all mutual solubility parameters, i.e. solvent-nonsolvent affinity, polymer-solvent affinity, and polymer-nonsolvent affinity, exist in ternary system. Total solubility parameter was calculated by summing up polymer-solvent affinity and solvent-nonsolvent affinity and subtracted from polymer-nonsolvent affinity. Increase of total solubility parameter indicated tighter membrane structure. Solubility parameter itself is often defined as the parameter to describe the force interaction between molecules [11]. They also predicted that lower permeance value in Matrimid and Ultem was due to lower porosity in membranes fabricated from those polymers.

Soroko et al. studied further on PI OSN membranes to determine the effect of introducing evaporation step and the role of volatile cosolvent [12]. P84 polyimide was used with DMF as the solvent. 1,4-dioxane and Tetrahydrofuran (THF) were taken into consideration as volatile cosolvent. They observed that evaporation did increase rejection performance as PI concentration on surface layer increased. However, they also found that, there was optimum evaporation time as further evaporation only decreased porosity and flux without giving positive effect on rejection. They also concluded from their study that regardless of the nature of cosolvent, i.e. volatile or non-volatile, cosolvent should be present in casting solution for having high rejection performance, since it increased the solvent to nonsolvent diffusion rate ratio during phase inversion, hence triggering formation of skin layer via vitrification.

In the last series of their study on PI OSN membranes, Soroko et al. [13] tried to determine the effect of polymer characteristics such as molecular weight or alternated diisocyanate part of the PI chain. They used PI with similar structure but different molecular weight and found that rejection and permeance values for each PI were similar. However, they observed that using polymer with molecular weight that can produce sufficiently viscous casting solution is required in order to have defect-free membranes. A too viscous solution, however, can also prevent membrane formation. The optimum molecular weight of PI obtained from their study was around 35 kDa.

Besides polyimide, there are also studies by considering polysulfone (PSf) and polyether-ether ketone (PEEK) for OSN. PSf is commonly used for separation in mild organic solvent and known for its toughness and stability at high temperature due to amorphous thermoplastics structure, while PEEK is used due to its enhanced chemical stability towards harsh environment. Holda et al. [4] studied PSf OSN flat-sheet membranes in isopropanol environment by fabricating membranes made from casting solution of commercial PSf Udel polymer dissolved in N-methyl pyrrolidone (NMP) and Tetrahydrofuran (THF), as solvent and cosolvent respectively. Phase inversion method was used to fabricate membranes and they observed the effect of polymer concentration in casting solution and evaporation step time before coagulation both on membranes morphology and rejection performance. Rejection tests were done in dead-end filtration mode. Effect of increasing polymer concentration from 13 to 29% with increments of 2% was observed by keeping equal ratio of solvent/cosolvent (70/30) in all casting solutions and constant evaporation time of 30 s, while fixed casting solution of 21 wt% of PSf with solvent-cosolvent ratio of 70/30 was used to observe effect of evaporation time ranging from 0 to 120s. They used Rose Bengal (1017 Da) as the solute in isopropanol solution and found that with increasing polymer concentration and increasing evaporation time, Rose Bengal (1017 Da) rejection increased from 37% to 92% and from 47% to 76% respectively. At the same time, isopropanol permeance dropped from 9.7 to 0.07 L h^{-1} m^{-2} bar^{-1} and from 2.4 to 0.08 L h^{-1} m^{-2} bar^{-1} respectively. They observed that increasing of polymer concentration and introducing evaporation, while compromised isopropanol permeance, did increase Rose Bengal (1017 Da) rejection.

Another study with another polysulfone derivative was done by Darvishmanesh et al. [14] using polyphenylsulfone (PPSf) as the polymer. It is one of the types in polysulfone family possessing better impact and chemical resistance [15] than polysulfone and polyethersulfone. PPSf membranes were prepared from casting solution of PPSf dissolved in NMP, dimethylacetamide (DMA), and a mixture of DMF-NMP (50/50 wt %) while using Rose Bengal (1017 Da) solution in methanol to characterize the membranes. Increasing polymer concentration decreased methanol permeance while increased Rose Bengal (1017 Da) rejection in all membranes cast from different solvent. They also tried to test the stability of their membrane performance by exposing the membranes towards a wide range of solvents including ethyl acetate (an ester), n-hexane (an aliphatic hydrocarbon), toluene (an aromatic hydrocarbon), diethyl ether (an ether), isopropanol (an alcohol), and acetone (a ketone). Membrane exposed to acetone and toluene were damaged and the permeance could not be observed. Exposure to ethyl acetate, diethyl ether, and isopropanol increased membrane permeance thus decreased rejection. Exposing membranes to n-hexane almost did not alter the result of permeance and rejection. Those phenomena were explained by degree of swelling of each solvent towards membranes as acetone and toluene have higher value compared to other solvents.

While polymeric materials offers wide variety of polymer selection for membrane fabrication, they are generally weak mechanically and chemically without further post-fabrication treatment. Post-treatment of fabricated membranes is aimed to increase their life span and to enhance their separation performance, which is usually done by crosslinking, wet or dry annealing, drying by solvent exchange, or treatment with conditioning agents [1]. Common method is by performing crosslinking which can be thermal crosslinking, UV crosslinking, or chemical crosslinking. Fabrication of polymeric membrane is usually supported by nonwoven fabric to increase its mechanical strength. The nonwoven should have similar swelling degree with polymeric membranes to prevent formation of creases [1].

Jansen et al. [15] tried to increase solvent stability of PPSf membrane by blending PPSf and PI (Matrimid) in casting solution with NMP as solvent. They found that all fabricated membranes were stable in harsh environments, such as acetone and methyl ethyl ketone (MEK), and PPSf/Matrimid blend composition in terms of weight ratio affected solvent permeance through membranes. High permeance of alkyl acetates was obtained from 25/75 wt% blend, of acetone and MEK was achieved from 75/25 wt% blend, and of alcohol and alkanes from 50/50 wt% of PPSf/Matrimid blend. Their study involved Sudan II (276 Da) dissolved in methanol. The highest rejection value of Sudan II (276 Da) was obtained as 95% and 96.9% after exposing the membranes to MEK and acetone respectively.

Most studies observed rejection performances were affected by parameters including polymer concentration and treatment before coagulation. High rejection value usually compromises solvent permeance once polymer concentration in casting solution was increased due to thicker skin layer in structure of membranes. It is generally followed by reduced pore size and surface porosity [4]. Evaporation of volatile solvent in cast membranes also resulted in higher rejection but lower permeance values. This can be attributed to the elevated polymer concentration in skin layer thus denser skin layer was obtained reducing solvent penetration ability through membranes. Polymer concentration in casting solution affected exchange rate of diffusion of solvent and nonsolvent. Higher polymer concentration resulted in slower coagulation rate. As higher polymer concentration means higher viscosity of casting solution as well, higher entanglement in polymer chains may occur [4].

Burgal et al. [16] used polyether-ether-ketone (PEEK) to fabricate OSN membranes. PEEK was dissolved in a mixture of methanesulphonic acid and sulfuric acid. Immersion precipitation method was used to fabricate PEEK OSN membranes. They observed that resulted membranes showed excellent resistance towards polar aprotic solvents, acids, and bases. Membranes were characterized in THF and DMF, and THF showed higher permeance compared to DMF. This was attributed to higher viscosity of DMF compared to that of THF. In THF system, MWCO varied from 400 to 600 Da, while in DMF system, MWCO varied from 470-700 Da.

In TFC membranes, support layer is usually produced via phase inversion method while polymerization including interfacial or plasma polymerization or coating is applied for skin layer production. The main advantage of TCF membranes is skin layer and support layer can be optimized separately as they are made from different procedure.

Peyravi et al. [17] studied modified polysulfone ultrafiltration support for thin film composite organic solvent nanofiltration membrane. Commercial polysulfone membrane was modified with synthesized copolymers. Synthesized copolymers were made from three different monomers, which are 1,1’-Thiobis(2-naphthol) (TBN), 2,2’-Thiobis(4-methyl phenol) (TBMP), and Curcumin (CUR). Selective layer of the membrane was fabricated via interfacial polymerization of poly(ethyleneimine) (PEI) crosslinked with isophthaloyl dichloride (IPC). Methanol solutions of Bromothymol Blue (624 Da) and Crystal Violet (408 Da) were used to characterize the membranes. They observed that copolymer addition decreased the flux of pure organic solvent and dye solutions. Modified membrane based on CUR showed the lowest flux in methanol, ethyl acetate, and n-hexane. The result also exhibited higher solute rejection after modification of polysulfone layer. They concluded Crystal Violet was retained at a slightly higher rate that Bromothymol Blue as well.

2.2.2. Ceramic Membranes

Solvent resistance is one of most important factors in producing OSN membranes which can be provided by inorganic materials. However, due to their brittleness, difficulty in upscaling, handling, and fabricating as well as being more expensive than polymeric materials, most literature studies on OSN membranes are being done with polymeric materials rather than with inorganic materials. Also, the lowest MWCO that can be obtained from ceramic membranes is still higher than that of polymeric membranes. Nevertheless, its advantages still attract researchers to further study on how to develop OSN membranes from inorganic materials. Ceramic membranes possess important characteristics that are difficult to provide by polymeric membranes including superior chemical, mechanical, and thermal stability, not deforming or dissolving easily in organic solvents as well as not compacting under pressure. Compaction is a main drawback in polymer membranes causing flux decline during the course of separation process [1].

Rezaei et al. [18] studied the hydrophobisation of ceramic membranes by grafting the top layer of commercial ceramic TiO_2 membranes with Grignard chemistry. Mostly in literature related with ceramic OSN membranes, metal oxides such as alumina, zirconia, or titania are used for fabricating membranes and hydrophilic membranes are produced due to hydroxyl groups on the surface. This offers benefit in aqueous applications but certain modification is often required to make it applicable in non-aqueous applications. They compared separation performance of their fabricated membranes with commercial polymeric membranes of Starmem 240 and Duramem 300. Polyethylene glycol (PEG) and polystyrene (PS) as solute materials and a wide range of solvents including water, THF, toluene, and n-hexane were used to characterize the membranes. They observed that rejection result from their modified ceramic membranes produced a comparable result with regard to commercial polymer membranes used in study. They concluded that their fabricated membranes offered an alternative for a good non-swollen OSN membranes.

Zeidler et al. [19] studied ceramic organic solvent nanofiltration membranes fabricated by sol-gel technique from a mixture of titanium isopropoxide and zirconium n-propoxide. Hydrophobisation was done by introducing carbon into NF-membrane layer. A styrene oligomer mixture was used to characterize the membranes by dissolving it THF. Complexation agent of diethanol amine (DEA) was introduced to increase the amount of carbon thus enhancing hydrophobicity of membrane layer. They observed that rejection of solute in ceramic membranes is affected significantly by solvent system thus further studies are required for ceramic OSN membrane application in industry.

2.2.3. Mixed Matrix Membranes

Incorporating inorganic materials into polymeric membranes can be done in three different ways, which are dispersing the inorganic filler in the polymer solution, in-situ polymerization, and sol-gel method [20]. Generally, addition of inorganic materials into polymeric membranes reduces flux. Main problems with incorporation of inorganic materials into polymeric membranes are solubility and non-homogeneity issues. Gelation may also occur in the polymer solution.

Siddique et al. [20] incorporated γ-aminopropyltrimethoxysilane (APTMS) into PI membranes fabricated by phase inversion method. APTMS acted as a crosslinking agent while at the same time as organosilicone precursor to stimulate inorganic network. Casting solution composed of 22 wt% of PI, with solvent/cosolvent (DMF/1,4-dioxane) ratio of 3:1, 1:1, and 1:3. 2 wt % of maleic acid was also added into the casting solution. They observed the resulted mixed matrix membranes exhibited an enhanced stability compared to commercial Duramem 300 including its thermal stability due to inorganic network within the structure. Membranes were easy to handle and had consistent rejection performance in dichloromethane (DCM), DMF, and acetone over 72 hours.

2.3 Transport and Separation in Organic Solvent Nanofiltration

Literature studies focusing on transport mechanism in separation process is either by treating membranes as black box, meaning without considering how membranes interact with systems, or by considering the interaction between membrane, solute, and solvent [1]. Transport mechanism by considering the whole system can be either solution diffusion or pore flow models. Application of these models depends on type of membranes whether it is porous or dense membranes. In nanofiltration membranes, both models affect their separation process, thus describing transport is more complicated compared to other type of membranes. Solution diffusion model was introduced by several groups who emphasized chemical potential across the membrane as a concentration gradient only [1]. This model is often applied for dense membranes assuming solvent and solute fluxes are independent from each other. On the other hand, pore flow model considers that separation is mainly affected the pore size of membranes. It is assumed that concentration of solute and solvent throughout the pores is uniform. Potential gradient across is affected by pressure gradient [1]. Considering only solution diffusion model in NF membranes will contribute in failing to understand the exact phenomena as effect of applied pressure is neglected, while considering only pore flow model in NF membranes also is not accurate as concentration gradient and solvent-membrane and solute-membrane interactions are not taken into account.

Effect of interaction between membrane, solute, and solvent can be illustrated by the work of Soltane et al. [21] using commercial supported PDMS membranes characterized by six different solute molecules (dyes and hydrocarbon) and five different solvents covering a wide range of solubility parameters including ethanol, dimethylcarbonate (DMC), hexane, heptane, and toluene. They observed that solvent permeance was proportional to its affinity with membranes while degree of swelling did contribute to rejection of solute. They found that the highest rejection of solute came from the solvent which has highest degree of swelling towards membranes showing that solute-membrane interaction holds a decisive factor as well in separation performance. In another study done by Volkov et al. [22] using a polymer of intrinsic microporosity, Poly[1-(trimethylsilyl)-1-propyne] (PTMSP), as a material for fabricating polymeric OSN membranes, negative rejection occurred for neutral dyes (Solvent Blue 35 and Oil Red O) while high solute rejection was obtained for their selected negatively charged dyes (Orange II and Remazol Brilliant Blue R). They used their dyes in pair as Solvent Blue 35-Orange II pair and Oil Red O-Remazol Brilliant Blue R pair, both dissolved in ethanol. Their study showed physicochemical properties of each dye played part in determining the separation performance as both neutral dyes have a relatively higher affinity to the membranes compared to negative charged dyes. This affinity also overcame interaction between membranes and solvent (ethanol) as neutral dyes were more preferred than ethanol causing transport of ethanol being blocked by dyes molecules.

In the study of Bruggen et al. [23], four commercial membranes which are N30F, NF-PES-10, MPF-44, and MPF-50, were tested with three different solvent systems of water, ethanol, and n-hexane. As reported by the suppliers, other than MPF-50, the membranes have hydrophilic properties. Based on the experiment, it was also shown that ethanol flux was much higher compared to water flux in MPF-50. N30F and NF-PES-10, on the other hand, exhibited comparable ethanol and water flux, while in MPF-44, water flux was higher than ethanol flux. Flux of n-hexane in MPF-50 was also high while low flux was found in N30F and NF-PES-10. For MPF-44, the flux could not be recorded as membrane was damaged by n-hexane. For rejection performance, aqueous solutions of maltose (342 Da) and raffinose (504 Da) were used. Ethanol and n-hexane systems were also examined by using 2,2'-Methylenebis-(6-tert-butyl-4-methyl phenol) (340 Da) and DL-alpha-tocopherol hydrogen succinate (531 Da). For solutes having the similar molecular weight, they were not retained at the same rate by each membrane. Rather than only affected by solute size, there was also influence from membrane-solvent interaction. Darvishmanesh et al. [24] also further emphasized membrane-solvent interaction on solute rejection. Commercial membrane, STARMEM^{TM}122, was used in this study. Six different solvents, which are methanol, ethanol, acetone, methyl ethyl ketone, toluene, and n-hexane, were examined along with three different dyes of Sudan II (276 Da), Sudan Black (457 Da), and Sudan 408 (465 Da). Higher permeance were shown by polar solvents (methanol, ethanol, methyl ethyl ketone, and acetone) compared to nonpolar solvents (toluene and n-hexane) though membrane was reported to be hydrophobic. Depending on the solvent involved, solute rejection varied. Sudan Black and Sudan 408 were, then, further examined to study the effect of solvent. It was observed that with n-hexane negative rejection occurred, while methanol and ethanol system showed high rejection result around 90%.

Bhanusali et al. [25] studied characterization of polymeric membranes in polar and nonpolar organic solvents. Alcohols and alkanes were used to characterize commercial polymeric membranes, which are DS11AG (composite polyamide RO membrane, hydrophilic properties), Membrane D (composite dimethyl-silicone NF membrane, hydrophobic properties), and MPF50 (silicone based NF membrane, hydrophobic properties). They observed that polar solvents' flux was higher than nonpolar solvents' one in hydrophilic membranes, where flux of nonpolar solvents was higher than that of polar solvents in hydrophobic membranes. There was an indication from their study that molecular size of the solvents affected solvent transport through the membrane. As an example, methanol has higher flux when compared to ethanol and isopropanol. In another study [26], they mostly used commercial Membrane D to study solute transport through membranes. Using alcohols and alkanes as solvents, four solute compounds were used, which are Sudan IV (Dye, 384 Da), Fast Green FCF (Dye, 808 Da), Hexaphenyl benzene (534 Da), and Triglycerides. Five triglycerides (554 Da, 639 Da, 723 Da, 807 Da, and 890 Da) were used for characterization. Triglycerides were dissolved in n-hexane and it was shown that their rejection behavior was affected by their molecular size. Triglycerides having molecular weight of 890 Da showed 90% of rejection, while the one having 554 Da molecular weight showed 72% of rejection. In Hexaphenyl benzene, though they have similar molecular weight with one of the triglycerides compound, one having 554 Da, the rejection behavior was different.

Hexaphenyl benzene was rejected at 42% in hexane and they suggested that polar carbonyl group in triglycerides and aromatic group in Hexaphenyl benzene behave differently with the selected Membrane D.

Comparing the rejection behavior of two different nature of dye, Sudan IV (neutral) showed negative rejection in alcohols (methanol and ethanol), while Fast Green FCF (negative) exhibited high rejection values in alcohols. Sudan IV was also tested with n-hexane and resulted in 25% solute rejection. By using another commercial membrane (hydrophilic polyamide-based YK membranes), however, 86% rejection in methanol and 43% rejection in n-hexane were observed for Sudan IV. They concluded that solvent and membrane choice affected the solute separation performance.

In most of the studies for organic solvent nanofiltration, solute separation is not only affected by molecular size of the solute but also the interaction between membrane, solute, and solvent. Higher molecular weight of solutes is not necessarily retained at higher rate. Properties in the membrane also affect transport of solvent hence solute rejection behavior is also influenced as hydrophilic membranes are favorable for polar solvents, where hydrophobic membranes preferable for nonpolar solvents.

2.4 Cellulose as Membrane Material for Organic Solvent Nanofiltration

In this study, cellulose is proposed as an alternative material for producing polymeric OSN membranes. Cellulose is known as an abundant biopolymer with strong hydrogen bonds and crystallinity [27]. Hence, it is difficult to dissolve cellulose in common solvent like water and organic liquids [28]. This can be, however, an advantage of cellulose membranes for filtration in these solvents. Conventionally, cellulose is dissolved with $NaOH/CS_2$, also known as xanthogenate route, producing derivatized cellulose, which is cellulose xanthogenate, and byproduct of H_2S. Another common way to dissolve cellulose is by using N-methylmorpholine-N-oxide (NMMO) which is a thermally unstable. DMAc/LiCl solvent system, patented by McCormick in 1980s, is also frequently used to dissolve cellulose [29]. Solvent exchange of cellulose, since no water should be present, or distillation of the DMAc/LiCl/Cellulose system is often required in order for the interaction between DMAc/LiCl and Cellulose to take place. Its complication in the process may create infeasibility beyond laboratory scale application. Lack of suitable solvents makes it difficult to process cellulose into membranes as shown by only few literature studies related with cellulose membranes. Derivative of cellulose, however, in the form of cellulose acetate has been widely used as a membrane for reverse osmosis application typically for desalination process [27]. Alternative solvent to dissolve cellulose has been proposed in recent years in the form of ionic liquid.

Ionic liquids have attracted many applications considering the need for green solvents as an alternative to common solvents such as organic solvents (methanol, toluene, DMSO) and halogenated solvents (carbon tetrachloride, chloroform). Ionic liquids are liquids composed entirely of cations and anions, in which at least one ion possesses a delocalized charge and the other component is organic for preventing the formation of a stable crystal lattice, and mostly have melting points below 100°C [30]. They have negligible vapor pressure, and for this they are often regarded as more environmentally-friendly compared to typical organic solvents used to dissolve polymers. Regarded as tunable designer solvents, ionic liquids are versatile solvents that can be composed of various combinations of cation and anion. As a result, however, the properties of ionic liquids are difficult to be determined in general as they may differ according to the structure of anion and cation. Imidazolium ionic liquids are the most commonly used ionic liquids [31].

Ionic liquids are typically viscous and upon addition of polymers lead to highly viscous solutions. This intense interaction between ionic liquids and polymers affects structure of membranes compared to when polymers are dissolved with common solvents. High ratio of ionic liquids outflow to nonsolvent intrusion into the membrane leads to slow phase inversion. Xing et al. [9] observed this phenomenon by using 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) to dissolve polybenzimidazole (PBI).

Membranes with relatively dense skin layer supported by sponge-like structure were formed. Macrovoids were observed at the bottom of membranes.

There are some studies related with dissolution of cellulose in ionic liquids. However, only few of them turn the solution into cellulose membranes. 1-butyl-3-methylimidazolium coupled with various anions of Cl^-, Br^-, SCN^-, $[PF6]^-$, and $[BF4]^-$ has been studied to dissolve cellulose and found that mixing process cannot be done under ambient condition. High temperature around 100-110℃ is required for dissolution resulting in high viscous solutions [28]. Water content in ionic liquids also affects solubility of cellulose as non-dried ionic liquids reduce their ability to dissolve cellulose [32]. Ability of dissolving cellulose has also been studied by using other types of ionic liquids of 1-allyl-3-methylimidazolium chloride ([AMIM]Cl), 1-ethyl-3-methylimidazolium chloride [EMIM]Cl, 3-methylimidazolium chloride [BMIM]Cl, and 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc). [EMIM]OAc showed much stronger solubility for cellulose compared to the other studied ionic liquids while cellulose dissolved in [EMIM]Cl exhibited the best tensile strength character [33]. [EMIM]OAc is known for its high miscibility with water at any ratio thus can be easily leached out from cast membranes, recycled, and reused [9].

Livazovic et al. [27] fabricated cellulose multilayer membranes using ionic liquid, [EMIM]OAc, as solvent. Two methods were used to produce membranes. First one was by using silylated cellulose – THF solution as coating solution for porous substrate made by phase inversion. Polyacrylonitrile (PAN), polysulfone (PSf), polyetherimide (PEI), and polyvinylidene fluoride (PVDF), dissolved with DMAc, DMF, or NMP, were used as polymeric materials for the substrate. The second method by dissolving cellulose in 1-ethyl-3-methylimidazolim acetate ([EMIM]OAc) and then casting the solution on asymmetric porous supports (PAN, PSf, PEI, or PVDF) and polyester nonwoven respectively, or directly on glass plates. Phase inversion was also used to coagulate the cast solution. Interfacial polymerization of polyamide layer was done on top of cellulose membrane produced from the second method forming thin film composite membrane. Salt and PEG solution, to determine MWCO, filtration tests were done to characterize membranes. For the first method, they observed that with increase of cellulose concentration, coating thickness increased thus rising salt and PEG rejection and lowering water permeance and MWCO. They found that the lowest MWCO as 5000 Da with water permeance of 8.1 L h^{-1} m^{-2} bar^{-1} by using solution containing 1.6 wt% cellulose. For the second method, the lowest MWCO was 3000 Da with water permeance of 13.8 L h^{-1} m^{-2} bar^{-1} using PSf as the support.

Puspasari et al. [34] used trimethylsilyl cellulose as coating to PAN membrane support to produce cellulose composite nanofiltration membranes. This study was aimed to produce membranes that have low molecular weight cut-off with zero or very low salt rejection. N-hexane was used to dissolve trimethylsilyl cellulose. Crosslinking solution of aqueous solution containing 1 wt% of Glutaraldehyde and 0.02 wt% of $Al_2(SO_4)_3$ was used. Vapor phase hydrolysis was used to regenerate the coated trimethylsilyl cellulose membrane into cellulose. They observed membrane having dense structure layer on top of porous support. Sugar solution was used to determine MWCO and MWCO was found to be 300 Da. Finally, mixture of sucrose and salt solutions was used to further characterize the membranes and comparison was made with respect to four commercial membranes. Sucrose was retained at 80% while almost zero rejection of salt was obtained. Commercial membranes, on the other hand, retained higher sucrose but also achieved higher rejection of salt.

Mautner et al. [35] also studied the use of cellulose by fabricating cellulose nanopapers as tight aqueous ultrafiltration membranes. Four different types of nanocellulose was used as a material for producing nanopapers. A homologous series of PEG oligomer, molecular weight between 1 and 93 kDa, was used to characterize MWCO. The type of nanocellulose was observed to influence the permeance and MWCO values. The lowest MWCO value from the studied nanopapers was found to be 6 kDa. Earlier in another study [36], they studied the use of nanocellulose for organic solvent nanofiltration. The membranes were fabricated by paper making process. The permeance of THF, n-hexane, and water was measured and they found that n-hexane has the highest value. PEG solution in water and PS solution in THF, with molecular weight range of 1-13 kDa, were used to determine MWCO and found to be 3.2 kDa and 6 kDa based on PS and PEG respectively.

Yushkin et al. [37] utilized commercial cellophane membranes for organic solvent nanofiltration. Dyes, which are Solvent Blue 35 (350 Da, neutral dye), Orange II (350 Da, anionic dye), and Remazol Brilliant Blue R (626 Da, anionic dye), in ethanol and water solutions were used to characterize membrane separation performance. It was shown in the ethanol system that Solvent Blue 35 was less rejected compared to Orange II although having the same molecular weight. In both ethanol and water system, Remazol Brilliant Blue R was retained at the highest rate. Solvent Blue 35 has low solubility in water thus characterization with this dye was not done. It was also concluded that Orange II and Remazol Brilliant Blue R were rejected higher in water system compared to that in ethanol system. Rejection value for Orange II and Remazol Brilliant Blue R in water was 97% and 100% respectively, while it was 55% and 79% respectively when using ethanol solution.

The use of ionic liquids to fabricate membranes from other polymers via phase inversion has also been reported. Xing et al. pioneered the use of ionic liquids for membrane fabrication in 2010 [38]. They used 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN) to produce cellulose acetate (CA) flat-sheet and hollow fiber membranes via phase inversion in water. To observe the membrane morphology, freeze drying method was used and found that membrane with nodular structure was formed. As a comparison, cellulose acetate membranes produced from NMP and acetone solution were porous. Macrovoid free membranes were also detected from CA/[BMIM]SCN and CA/acetone solutions, while in CA/NMP solution macrovoids were formed. Thickness of membranes produced from CA/[BMIM]SCN solution was also the thinnest among them. They discussed that phase separation happened slower in CA/[BMIM]SCN system compared to CA/NMP and CA/Acetone systems hence dense nodular structure was formed. In another study, they tried 1-ethyl-3-methylimidazolium thiocyanate ([EMIM]SCN) to produce cellulose acetate membranes. Unlike in previous study, the interaction between ionic liquids and cellulose acetate was studied thus changing cation group. Effect of different coagulants was also investigated by using water and isopropanol. They observed that membranes coagulated in water showed dense nodular structure, while membranes precipitated by isopropanol formed closed-cell porous structure. In terms of their thickness, the one coagulated in water was thinner.

Kim et al. [39] studied the effect of cosolvent on cellulose acetate (CA)-[EMIM]OAc system. Acetone (Ac) was incorporated into the system as the cosolvent. Membranes were fabricated by phase inversion in water. Five polymer solutions were prepared which were 12 wt% CA-88 wt% [EMIM]OAc (Solution A), 12 wt% CA-35 wt% Ac-53 wt% [EMIM]OAc (Solution B), 18 wt% CA-33 wt% Ac-49 wt% [EMIM]OAc (Solution C), 12 wt%-88 wt% Acetone (Solution D), and 12 wt% CA-88 wt% NMP (Solution E). It was observed that membranes from solution B and E were thicker along with large macrovoids, while the others were thinner with sponge-like structure.

Xing et al. also studied the use of ionic liquid with different polymer than cellulose acetate [9]. Polybenzimidazole (PBI) membranes were produced via phase inversion in water. 1-ethyl-3-methylimidazolim acetate ([EMIM]OAc) was used as the solvent to dissolve PBI. Thermal treatment and chemical crosslinking were aimed to enhance the membrane performance. Glutaraldehyde (GA) and 1,2,7,8-diepoxyoctane (DEO) solutions were used as the chemical crosslinker. They observed that membranes with a relatively dense selective layer on top of a sponge-like were formed along with macrovoids formation at the bottom of the membranes. Water flux of membranes after crosslinking membranes was reduced implying reduced pore size. Five different solutes, which are Sudan IV (380 Da), Remazol Brilliant Blue R (627 Da), Eosin Y (648 Da), Brilliant Blue R (826 Da), and Rose Bengal (1018 Da), in organic solvents were used to characterize membrane separation performance. Ethyl acetate, DMSO, and ethanol were used as the solvents for filtration tests. It was observed that membranes crosslinked by GA showed higher solvent flux than that of membrane crosslinked by DEO. Test in DMSO was only done in membranes crosslinked in DEO, as the one crosslinked in GA dissolved in DMSO. Ethyl acetate flux was the highest in both types of crosslinked membranes. For ethanol and DMSO solutions, Sudan IV, Remazol Brilliant Blue R and Brilliant Blue R were used and result showed that rejection value was affected by molecular size. It was observed that rejection in DMSO was lower than in ethanol. Both membranes showed similar rejection behavior. For ethyl acetate solution, Sudan IV, Eosin Y, and Rose Bengal were used and Rose Bengal showed the highest rejection rate. In membranes crosslinked with GA, rejection of Sudan IV in all tested solvents was similar, while in membranes crosslinked with DEO, rejection rate in ethanol for Sudan IV was higher than that of ethyl acetate and DMSO.

Li et al. [40] used 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) to produce cellulose membranes. Deionized water at 10°C was used to coagulate the cast solution. Cross-flow filtration test was done by using aqueous dye solution to characterize separation performance. Dyes used in this study were Methyl Orange (327 Da), Congo Red (697 Da), and Brilliant Blue R (826 Da). The observed morphology was dense layered structure with no macrovoids. They also found the MWCO to be around 700 Da.

2.5 Aim of Study

This study proposes cellulose as an alternative material for OSN membranes to be fabricated via phase inversion method by using ionic liquid [EMIM]OAc as solvent. There are many studies on cellulose dissolution with ionic liquids. There are only a few on making cellulose into a membrane and none until now to use it for organic solvent nanofiltration. The aim of this study is to investigate fabrication parameters that affect membrane performance in separating several probe molecules from their solution in ethanol and water, which is used as a solvent for which solute-solvent interactions are better known. Cellulose concentration and volatile cosolvent in membrane casting solution, solvent evaporation before coagulation, and drying after coagulation were considered for varying membrane properties. Finally, swelling and probe sorption tests were done to get insight into the separation performance of the membranes.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Materials

Cellulose (Cotton Linter) and 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc, 95%) were purchased from Sigma Aldrich (Figure 3. 1).

Acetone (99%) was used as cosolvent and was provided from Sigma Aldrich as well. Cellulose was dried for at least two days at 80°C before using, while [EMIM]OAc and acetone were used as purchased. Reverse Osmosis water purified by Instant Purified Water (MC:DS) provided by ELGASTAT was used for coagulation as nonsolvent and for washing of cast membranes.

Figure 3. 1 Chemical structure of cotton linter cellulose (left) and [EMIM]OAc (right) used in this study

3.2 Solution Preparation

[EMIM]OAc was heated initially to 90℃ to evaporate water inside it as it can reduce the ability of [EMIM]OAc to dissolve cellulose [28].

Table 3. 1 Casting solutions prepared for membrane fabrication

Solution Type	**Composition**
Solution A	8 wt% Cellulose – 92 wt% [EMIM]OAc
Solution B	8 wt% Cellulose – 20 wt% Acetone – 72 wt% [EMIM]OAc
Solution C	12 wt% Cellulose – 25 wt% Acetone – 63 wt% [EMIM]OAc
Solution E	20 wt% Cellulose – 80 wt% [EMIM]OAc

3.3 Membrane Fabrication

Flat sheet membranes were fabricated by casting selected polymer solution onto glass plate by using a 250 μm casting bar. Membranes from solution E were cast hot while others were cast at room temperature. After casting, membranes were either put into N_2 (99.99% purity) bath or directly into coagulation bath containing water. After at least an hour of coagulation, membranes were washed by changing the water three times in which the last washing was done for 24 hours in order to remove residual solvent. Ethanol immersion of membranes was done following washing step. Membranes were either kept in ethanol or dried afterwards. Drying procedure was done by exposing membranes to ambient condition overnight.

Table 3. 2 Fabricated cellulose membranes

Membrane Type	**Evaporation Step**	**Casting Solution**
C8	No	A
C8A	No	B
C8AE	Yes	B
C12A	No	C
C12AE	Yes	C
C12AE-D	Yes	C
C20	No	E
C20-D	No	E

Solvent evaporation step was done to evaporate volatile cosolvent aimed to increase polymer concentration at the onset of coagulation in water. Membrane cast from selected solution was placed in evaporation bath (Volume ≅ 6 L) for 30 minutes. N_2 flow rate was controlled by a rotameter and set to be 0.6 L/min

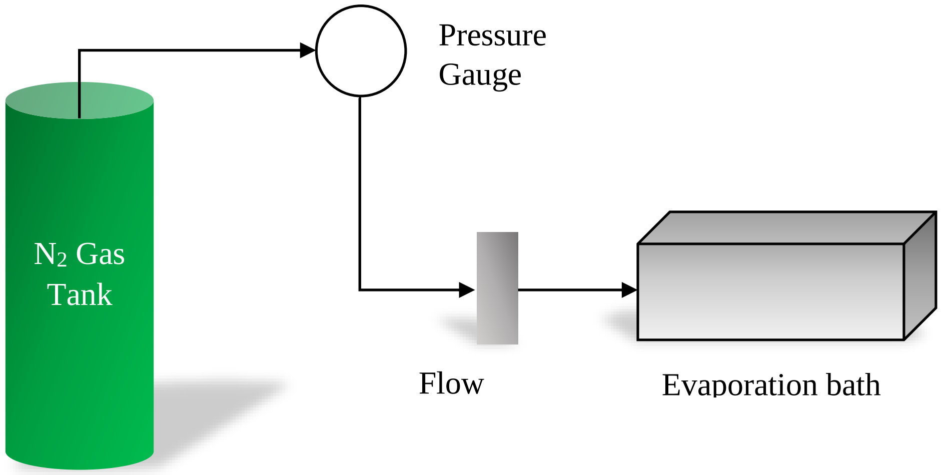


Figure 3. 2 Experimental set-up for solvent evaporation

3.4 Membrane Morphology Observation

Structure and surface morphology of membranes were determined by JSM-6400 scanning electron microscopy (SEM) in METU Metallurgical and Materials Engineering Department. Membranes were dried and broken with liquid nitrogen. Membrane samples were put onto SEM sample holders and stored in vacuum over the weekend. Before images were taken, samples were sputter coated with Au-Pd alloy to reduce sample charging under electron beam. Freeze drying technique (Christ, Alpha 2-4 LDplus, METU Food Engineering Department) was also used to observe the difference with regularly vacuum-dried membranes. Samples were frozen, then put in vacuum for two days before broken with liquid nitrogen.

3.5 Nanofiltration Experiment

Filtration tests were done in Amicon stirred cell of 10 or 50 ml volume. Dead-end filtration mode was set up at pressure of 1 and 4 bar along with 250 rpm of stirring to prevent concentration polarization. The tests were done at ambient temperature. All filtration tests were at least done in duplicate. As for the dried membranes, membranes were put back briefly into the water for loosening up the structure in order to ease placing the membrane in module, then immersed in ethanol before running the tests. Before filtration tests were done, solvent permeance was measured. A volume reduction factor of 2 was applied in filtrations. Feed, permeate, and retentate samples concentration were measured by UV-Vis Spectrophotometry (UV-1601 M). Permeance and rejection values were calculated as follows:

$$Permeance = \frac{Q}{A * \Delta P} \qquad (3.1)$$

$$\%Rejection = \left(1 - \frac{C_P}{\left(\frac{C_F + C_R}{2}\right)}\right) * 100 \qquad (3.2)$$

Table 3. 3 UV wavelength for each probe solution

Probe Solution	**UV Wavelength (nm)**
Cresol Red – Ethanol	432
Bromothymol Blue – Ethanol	423
Crystal Violet – Ethanol	590
Crystal Violet – Water	590
Brilliant Blue R – Ethanol	588
Brilliant Blue R - Water	595
Blue Dextran 5 kDa – Water	620
Blue Dextran 5 kDa – Water	620

Dye sorption during filtration test was calculated by material balance around the system as follows:

$$Mmol\ dye\ sorbed\ in\ membrane = C_F * V_F - \sum(C_P * V_P) - C_R * V_R \qquad (3.3)$$

Where C_P, $C_{F,}$ and C_R are concentration of solute in permeate, feed, and retentate streams respectively. %Rejection is calculated as a function of permeate volume (Appendix B.1). Q is described as solvent flux (L/h), while A (m^2) and ΔP (bar) are effective membrane area and transmembrane pressure respectively.

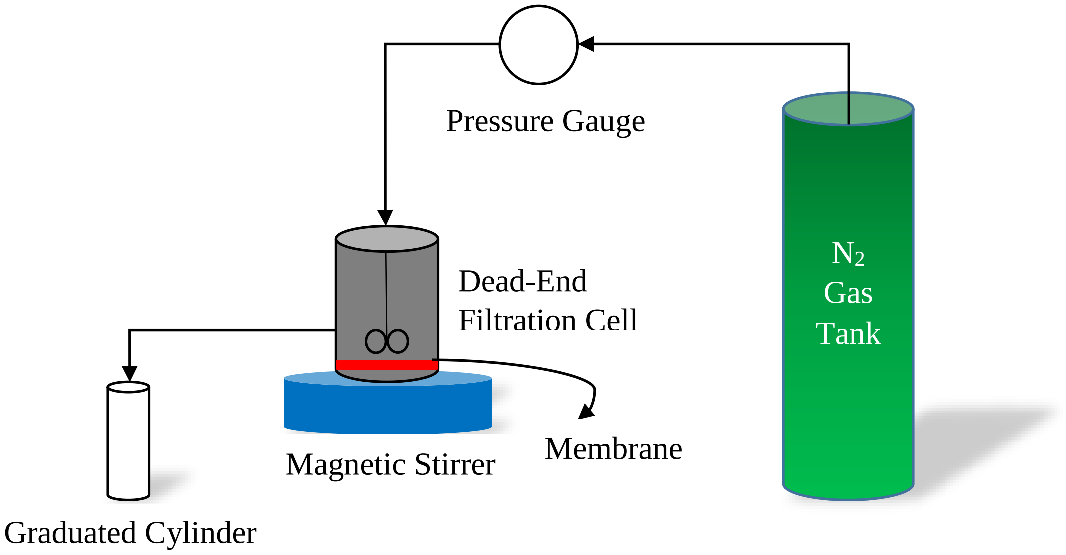


Figure 3. 3 Experimental set-up for permeance and rejection tests of all membranes

To study the rejection of membranes, Cresol Red (382 Da, 95%), Bromothymol Blue (624 Da, 95%), Crystal Violet (408 Da), and Brilliant Blue R (826 Da) solutions in ethanol are used. Besides, aqueous solutions of Crystal Violet (408 Da), Brilliant Blue R (826 Da), Blue Dextran (5 kDa), and Blue Dextran (20 kDa) were used. Crystal Violet was purchased from Merck while the rests of the probe were purchased from Sigma Aldrich. Brilliant Blue R can be dissolved partially in both ethanol and water. Hence, before the rejection tests were done, feed solution was filtered by commercial filter paper to ensure that no dye powder exists in the feed solution. Solute molecules were selected to investigate the effect of molar volume of solutes (pore flow mechanism), affinity of solute with solvent and membrane (solution diffusion mechanism), and charge of solute (charge interaction) on separation performance.

Feed concentration was ~0.05 mM for ethanol solutions of Cresol Red, Bromothymol Blue, Brilliant Blue R, and Crystal Violet. In aqueous solutions, feed concentration used was ~0.050 mM for Brilliant Blue R and Crystal Violet, ~0.16 mM for Blue Dextran 5kDa, and ~0.04 mM for Blue Dextran 20 kDa.

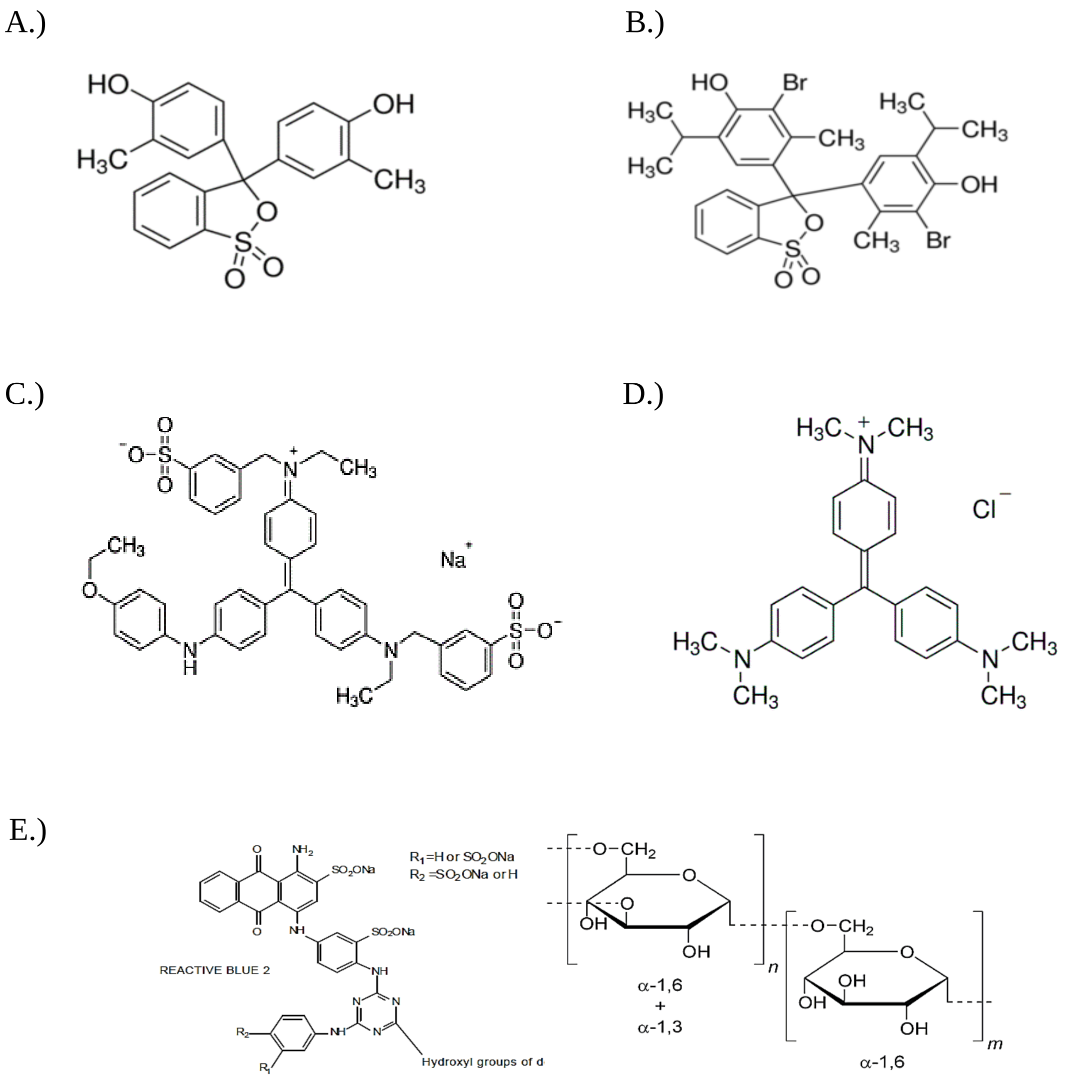


Figure 3. 4 Chemical structure of a.) Cresol Red, b.) Bromothymol Blue, c.) Brilliant Blue R, d.) Crystal Violet, and e.) Blue Dextran

3.6 Swelling Tests

Membranes were prepared following procedures mentioned above. After ethanol immersion, membranes were dried in ambient and further in vacuum for an overnight. Having dried the membranes, they were then immersed in solvents (ethanol, DMSO, hexane, and water). They were taken out of solvent, wiped briefly with tissue paper and weighed every day until the weight became constant, implying equilibrium between membrane and solvent was reached. Swelling ratio was defined as the ratio between difference of wet and dry weight over dry weight of membranes,

$$SR = \frac{Wet\ Weight\ (g) - Dry\ Weight\ (g)}{Dry\ Weight(g) * Solvent\ density\ (\frac{g}{cm^3})} \tag{3.4}$$

3.7 Sorption Tests

Sorption tests were done to calculate sorption coefficient (K) and modified sorption coefficient (K’), which are related to the solubility of the permeating molecule in the membrane according to solution-diffusion mechanism [22]. Six different solutions were used:

- Cresol Red – Ethanol Solution
- Bromothymol Blue – Ethanol Solution
- Crystal Violet – Ethanol Solution
- Crystal Violet – Water Solution
- Brilliant Blue R – Ethanol Solution
- Brilliant Blue R – Water Solution

Membranes were prepared following procedures mentioned above without drying. After ethanol immersion, they were briefly wiped to remove ethanol on the surface of membranes. Wiped membranes, then, were put into glass bottles containing selected solutions with 20 ml. Dye concentration in the solution was measured daily until steady value was observed, implying equilibrium solute sorption in membrane. Sorption coefficient (K) was calculated as follows,

$$K = \frac{C_{dye,membrane}}{C_{dye,solution}} \tag{3.5}$$

$C_{dye,membrane}$ = weight fraction of dye sorbed in wet membranes

$= \frac{m_{dye}}{m_{dye}+m_{solvent}+m_{dry\ membrane}}$

$C_{dye,solution}$ = final concentration in the solution the membrane is immersed (g/g)

$= \frac{m_{dye}}{m_{solution}}$

Here, m_{dye} was found using the difference in the initial concentration of the dye in solution and the final concentration. On the other hand, $m_{dye}+m_{solvent}+m_{dry\ membrane}$ was found by measuring the wet membrane at the end of the sorption test.

Modified sorption coefficient (K') from sorption test was also measured as follows,

$$K' = \frac{mmol\ of\ dye\ sorbed\ on\ membrane}{dry\ membrane\ weight} \tag{3.6}$$

Similar to modified sorption coefficient, sorption during filtration was calculated by dividing mmol of dye sorbed in the membrane over dry membrane weight. Weight of dry membrane in both modified sorption coefficient and sorption during filtration was obtained by putting the membrane in vacuum. Weighing was done until steady weight of membrane was observed.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Morphology of Fabricated Membranes

Images of membrane morphology were taken with scanning electron microscopy (SEM), both without freeze drying and with freeze drying steps before SEM analysis. Freeze drying step was done to remove water content within membranes by sublimation aiming to preserve the structure of membranes, and to see if the observed morphology was different than the regularly vacuum-dried membranes.

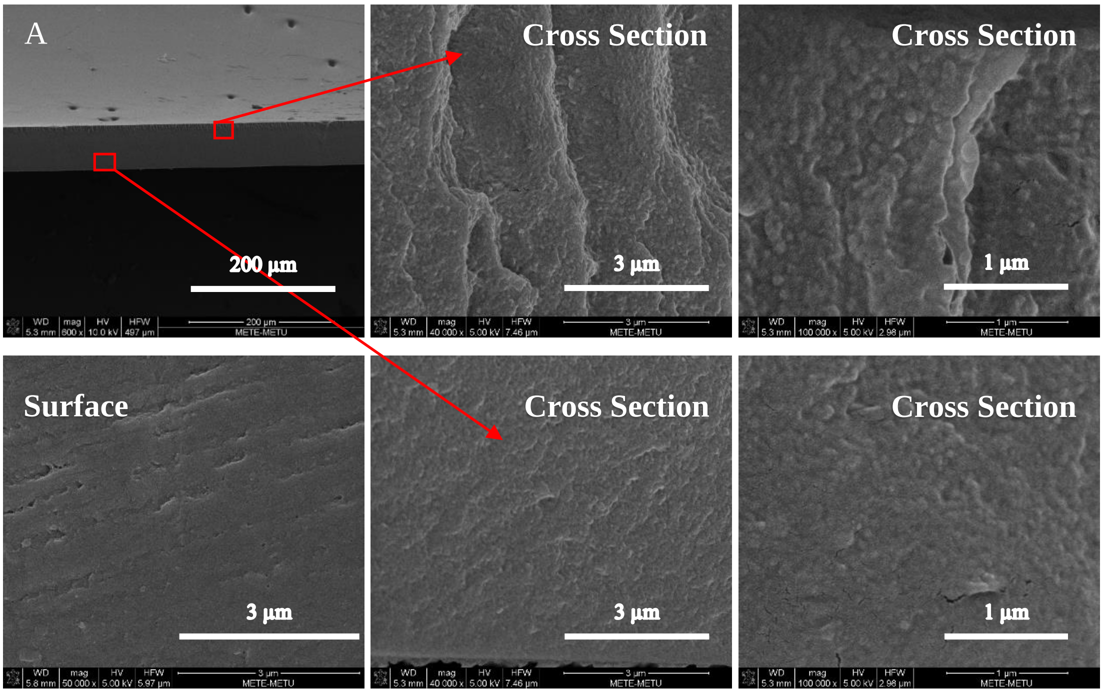
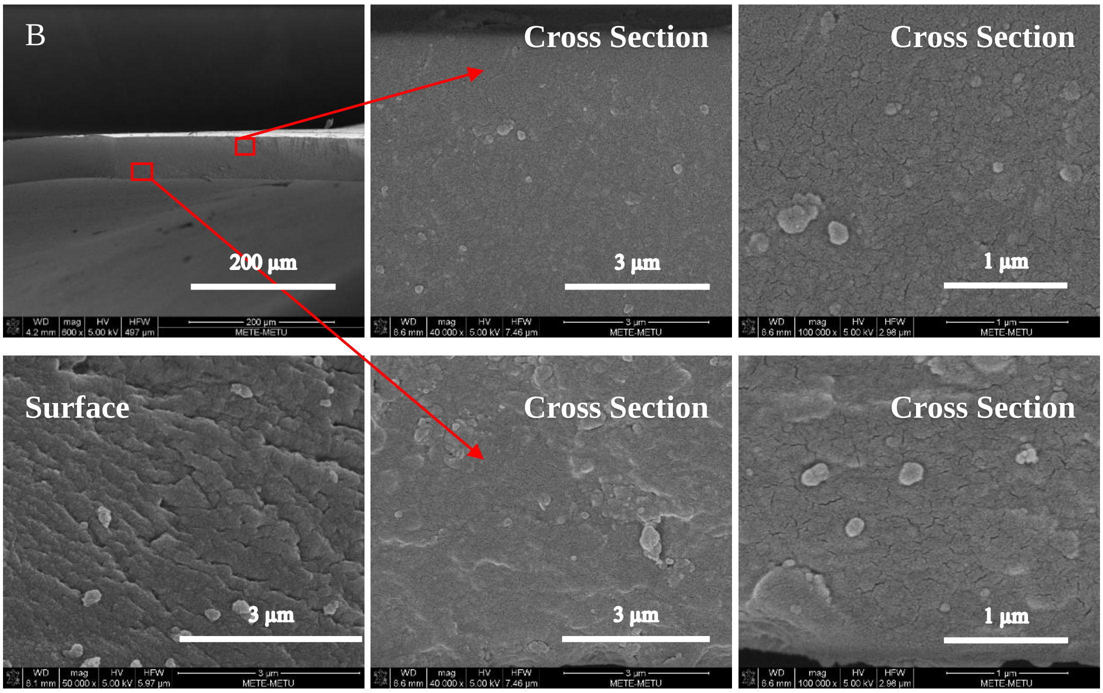


Figure 4. 1 Cross sectional, top and bottom cross sectional, and surface images of a.) C8 without freeze drying



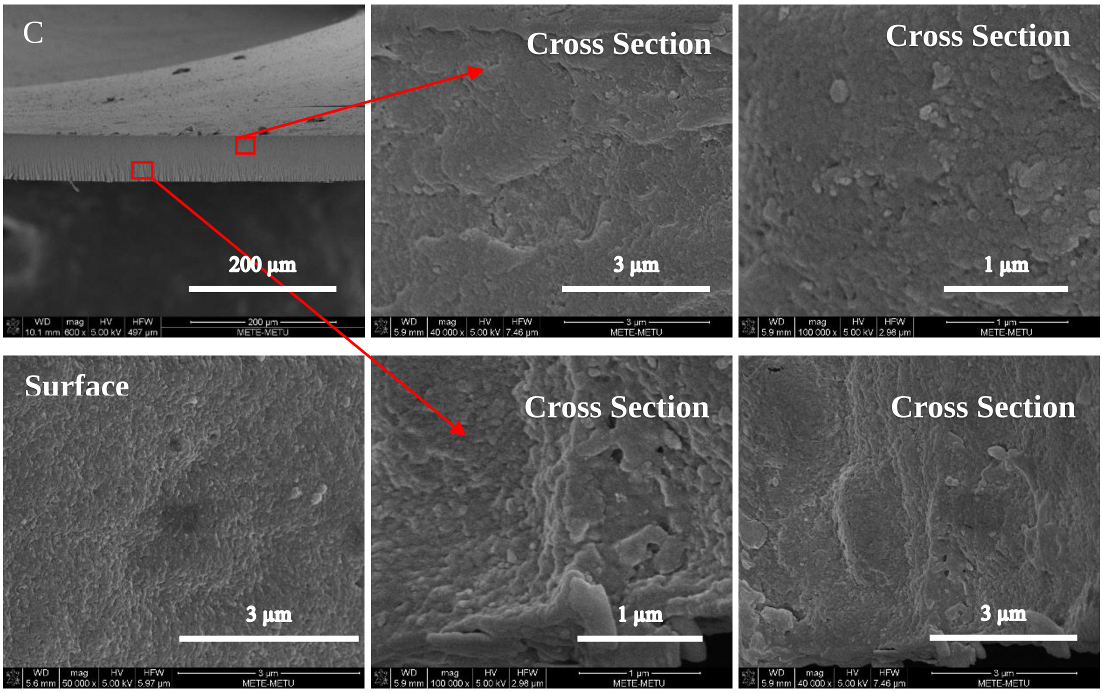
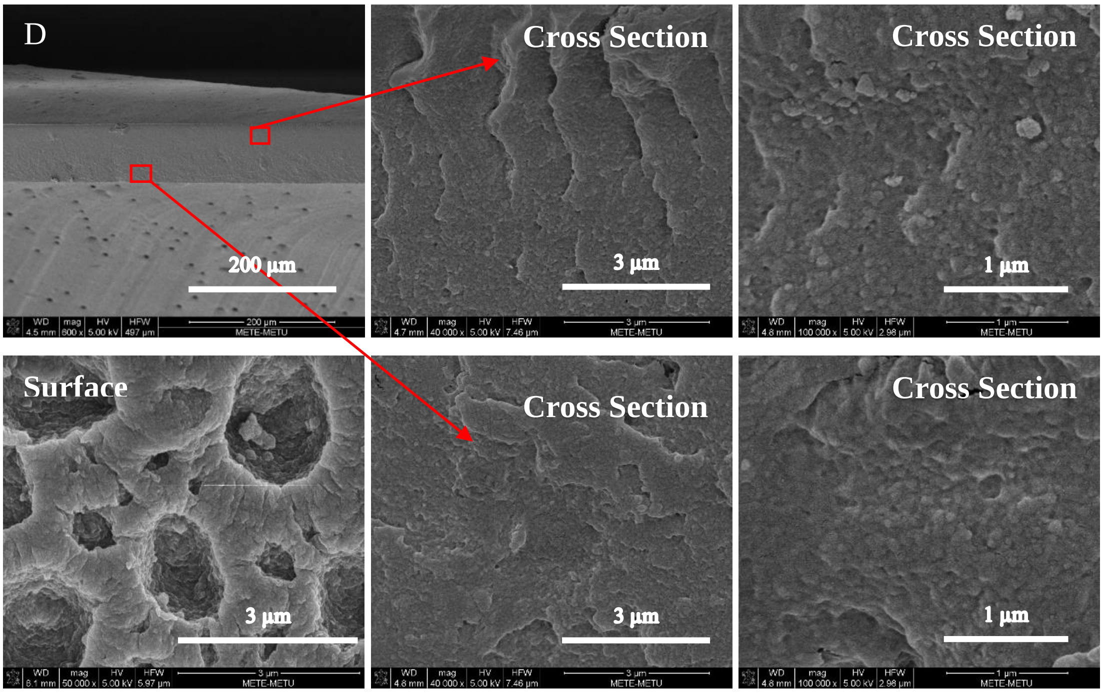


Figure 4. 1 (cont'd) Cross sectional, top and bottom cross sectional, and surface images of b.) C8A, and c.) C8AE respectively without freeze



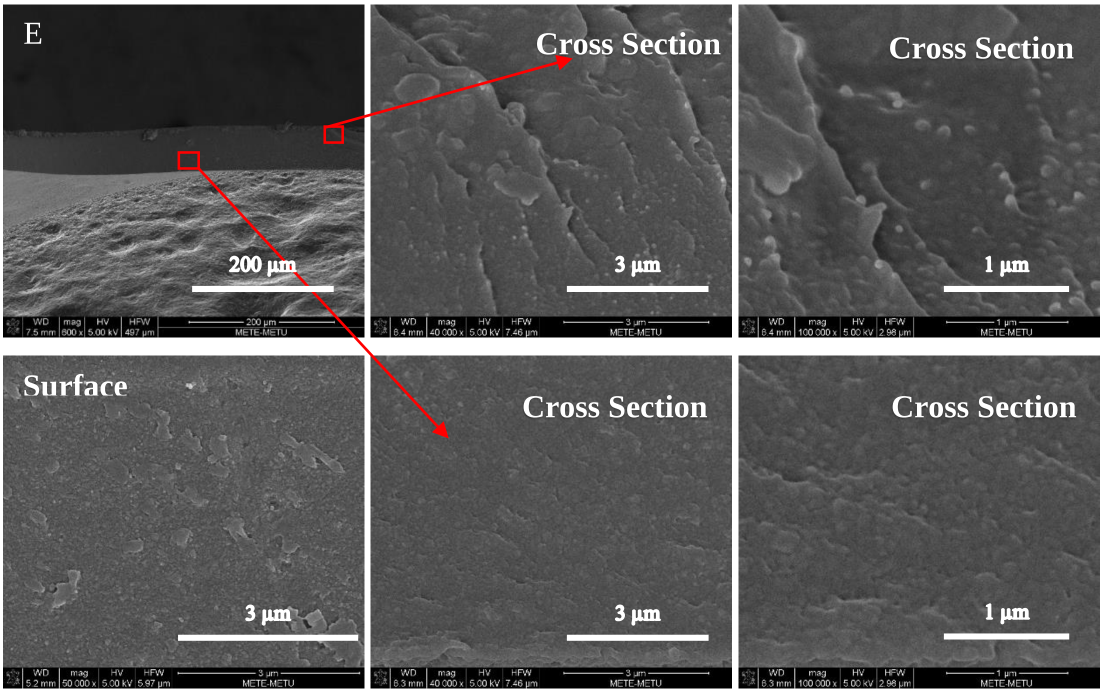


Figure 4. 1 (cont'd) Cross sectional, top and bottom cross sectional, and surface images of d.) C12A, e.) C12AE respectively without freeze drying

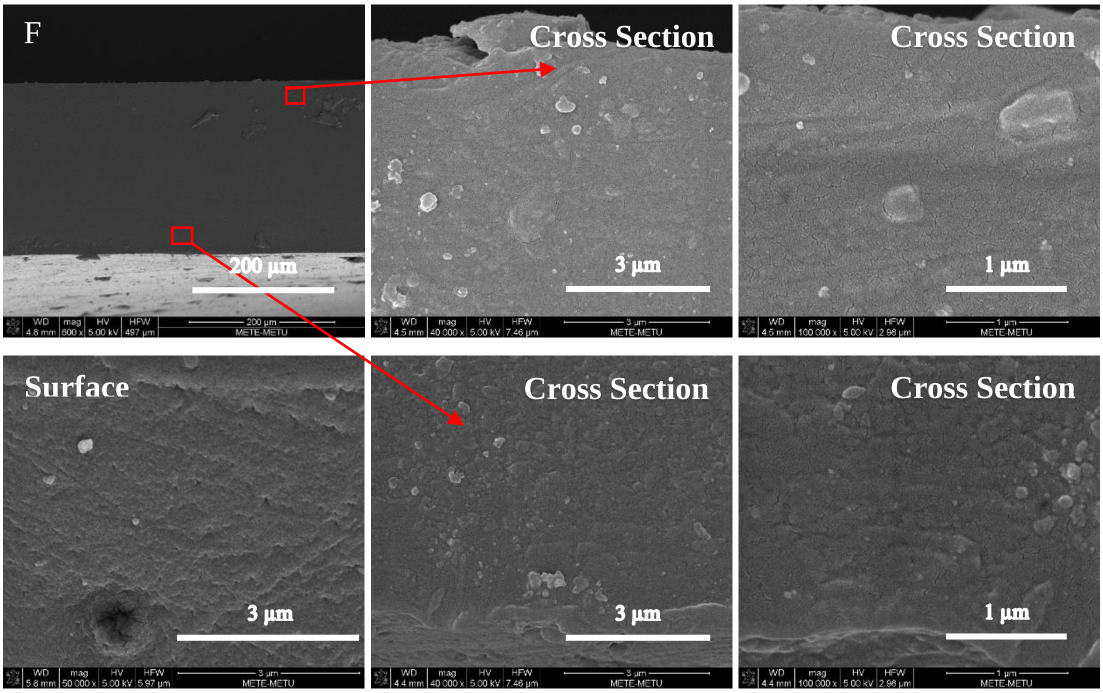


Figure 4. 1 (cont'd) Cross sectional, top and bottom cross sectional, and surface images of f.) C20 without freeze drying

From SEM observation, it was observed all membranes have no macrovoids within their structure with no skin layer (Figure 4. 1), such dense morphologies are common in membranes made of other polymers in ionic liquids via phase inversion [9]. Freeze dried membranes also showed similar morphology to the regularly dried membranes (Figure 4. 2). Dense structure of the membranes is typically attributed to the high viscosity of the ionic liquid and the casting solution. High viscosity of dope solution is considered to slow down the penetration of water into cast solution and results in a higher ratio of ionic liquid outflow over water inflow during phase inversion process [41]. From the SEM images, membranes may have structure in between dense to microporous (< 2 nm), since pores of a few nm would not be visible in SEM images. Effect of polymer concentration or cosolvent addition on casting solution could not be observed from the images as all membranes have relatively similar cross sectional structure compared to each other. Xing et al. [41] used 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) as the solvent for producing polybenzimidazole (PBI)/P84 blend membranes for ultrafiltration. In their study, they observed that all membranes have a relatively dense top layer with microporous sponge-like structure and some macrovoids at the bottom regardless of blend composition. They found that decreased viscosity from the dope solution resulted in more porous morphology.

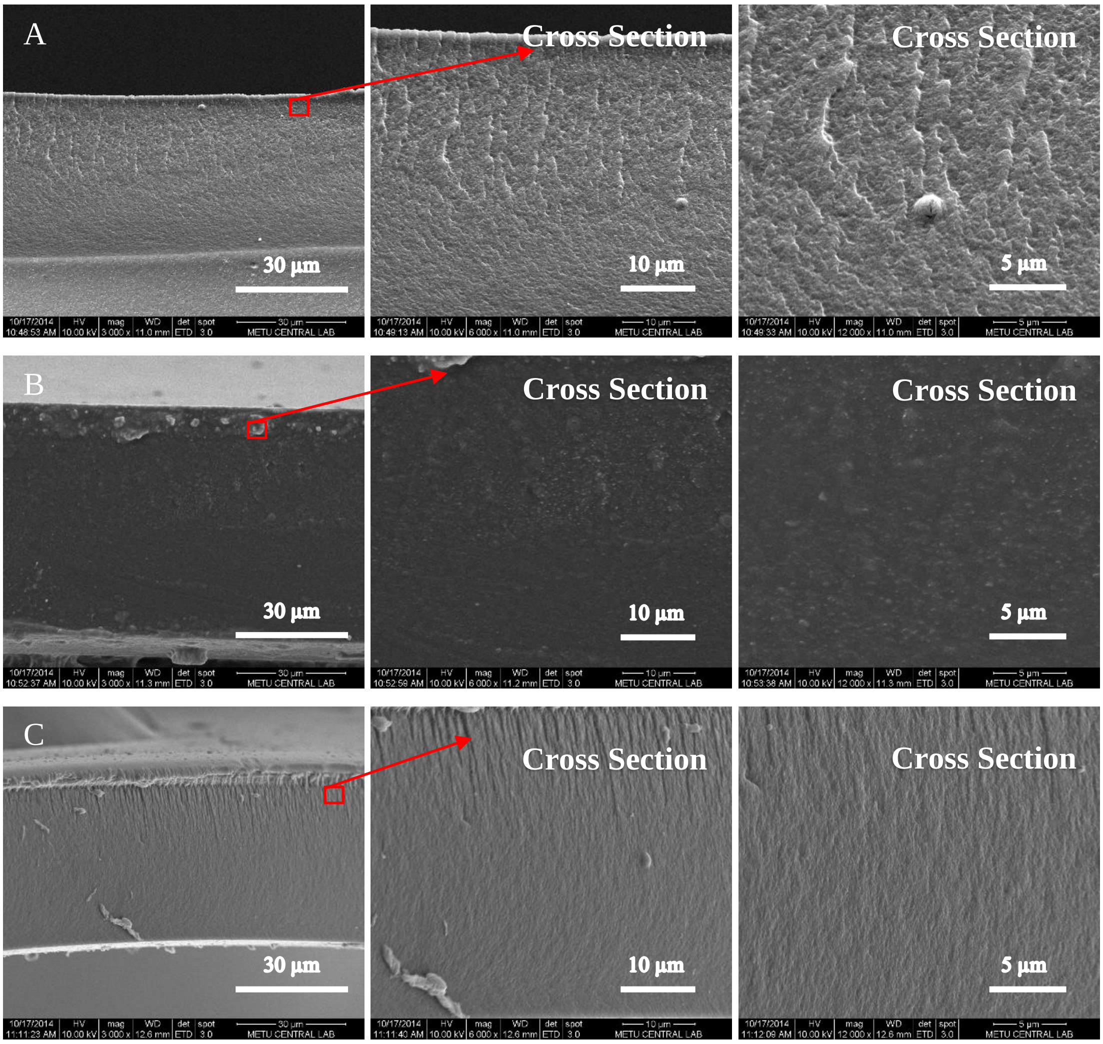


Figure 4. 2 Cross sectional and top cross sectional of a.) C8, b.) C8A, and c.) C8AE with freeze drying

Xing et al. [38] also studied another type of ionic liquid, which is 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN) to produce cellulose acetate (CA) membranes. They used also NMP and acetone to compare membrane morphology obtained by using ionic liquids. They observed that CA/[BMIM]SCN pair produced an entirely nodular structure while CA/NMP and CA/acetone pairs resulted in porous membranes. Membranes obtained from CA/[BMIM]SCN were also macrovoid free, which is desirable when considering mechanical strength of membranes, and also thinner in thickness compared to membranes obtained from CA/NMP and CA/acetone. Xing et al. [42], in another study, used 1-ethyl-3-methylimidazolium thiocyanate ([EMIM]SCN) to dissolve cellulose acetate (CA). They compared the structure formed from CA/[EMIM]SCN with water and isopropanol as the coagulants. They observed that membranes coagulated in water exhibited a dense nodular structure, while those coagulated in isopropanol have porous structure. They observed from SEM images of their membranes that using water as coagulant resulted in a thinner form of membrane compared to the one coagulated by isopropanol. Nodular structure was attributed to the higher tendency of [EMIM]SCN outflow to inflow rate of water thus suppressing the formation of macrovoids.

Thicknesses of each membrane were also measured from SEM images by ImageJ software.

Table 4. 1 Thickness of fabricated membranes observed by SEM

Membranes	**Thickness (μm)**
C8	61±1
C8A	59±1
C8AE	63±1
C12A	81±1
C12AE	60±1
C20	237±1

It was observed that thickness obtained from SEM images are higher than expected thickness of membranes considering all the polymer in the casting solution to precipitate in a dense layer from the initial 250 μm thick solution (Table 4. 1). This can be attributed to porosity and/or lateral shrinkage of the membrane during the drying process done before sample preparation. Based on rough calculation, C20 (for example), if it is completely dense, should have the thickness of 50 μm by multiplying polymer concentration (20%) in the casting solution with the casting knife thickness and assuming weight fraction is more or less the same with volume fraction. A porosity of 20%, which is typical for a microporous membranes, would make 63 μm, which is still thinner than what was observed. The same observation is valid for the other membranes as well. Drying process causes membranes to shrink, and therefore may have resulted in thicker membranes that were also smaller in area compared to their area before drying.

4.2 Effect of Polymer Concentration and Cosolvent Addition on Separation Performance

Rejection tests for all membranes were done in a stirred dead-end filtration setup. For undried membranes pressure of 1 bar was used, while for dried membranes 4 bar pressure was applied. The system was stirred throughout the test to prevent concentration polarization on membrane which may cause the observed rejection to be different than the intrinsic rejection of the membrane [2]. Volume reduction factor of 2 was applied meaning that only half of feed solution was allowed to permeate through the membranes. The remaining solution in the system was taken as the retentate sample. In all the tests, it was observed that permeate flux was constant and almost equal to the pure solvent flux (Figure 4. 3). This implies that concentration polarization and fouling on the membrane were negligible. It was observed during the test that some of the solute (dye) was sorbed by membrane since the membrane was visibly colored and from the material balance it was found that the initial amount of the dye fed to the cell was more than the sum of what was collected in the permeate and retentate. In order to distinguish between the effect of dye sorption and the actual rejection, feed was refreshed every day while leaving the system stirred with the dye solution and unpressurized overnight. Tests were done until dye sorption on the membrane diminished as observed from material balance calculation. It was observed from the data that dye sorption of membranes was happening at the early set for each experiment, as shown by Figure 4. 4 as an example. As the sets went on, membrane became saturated with the dye and sorption reached zero, after which the rejection stabilized. This value of the rejection was taken as the rejection of the membrane for the dye. Rejection value of membrane in each test was calculated from final retentate value to remove the influence of dye sorption in membrane (Appendix B.1). The amount of dye sorbed on the membranes was normalized by the dry membrane weight. Dry weight of the membrane was obtained by drying the used membrane after filtration in vacuum until a steady weight is reached.

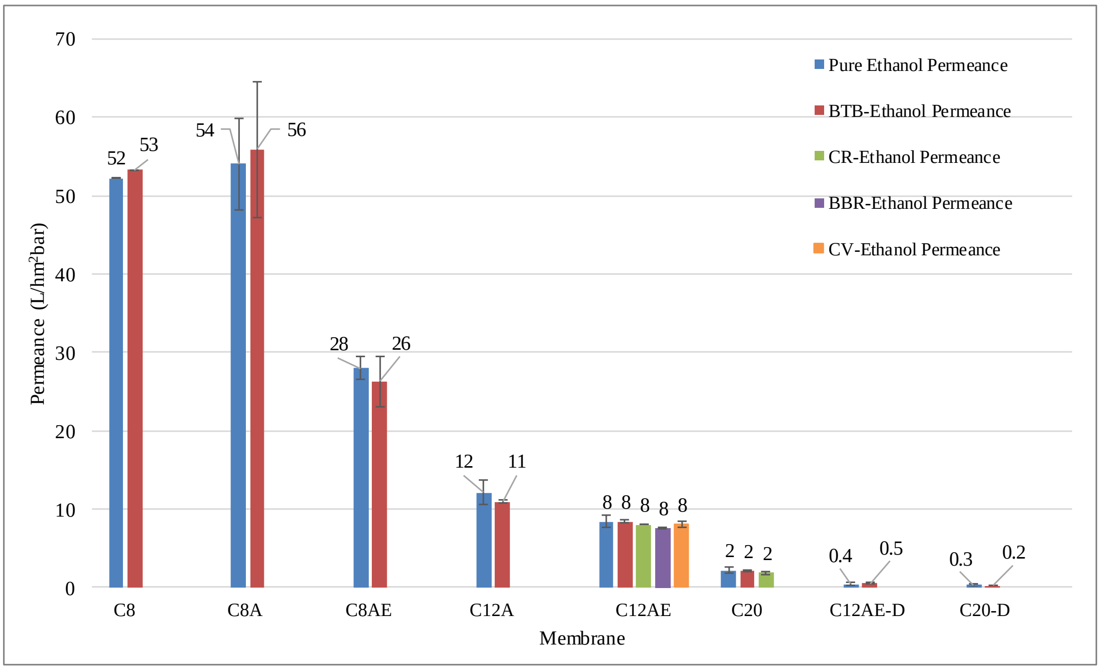


Figure 4. 3 Pure ethanol permeance and permeance during probe filtration of each membrane

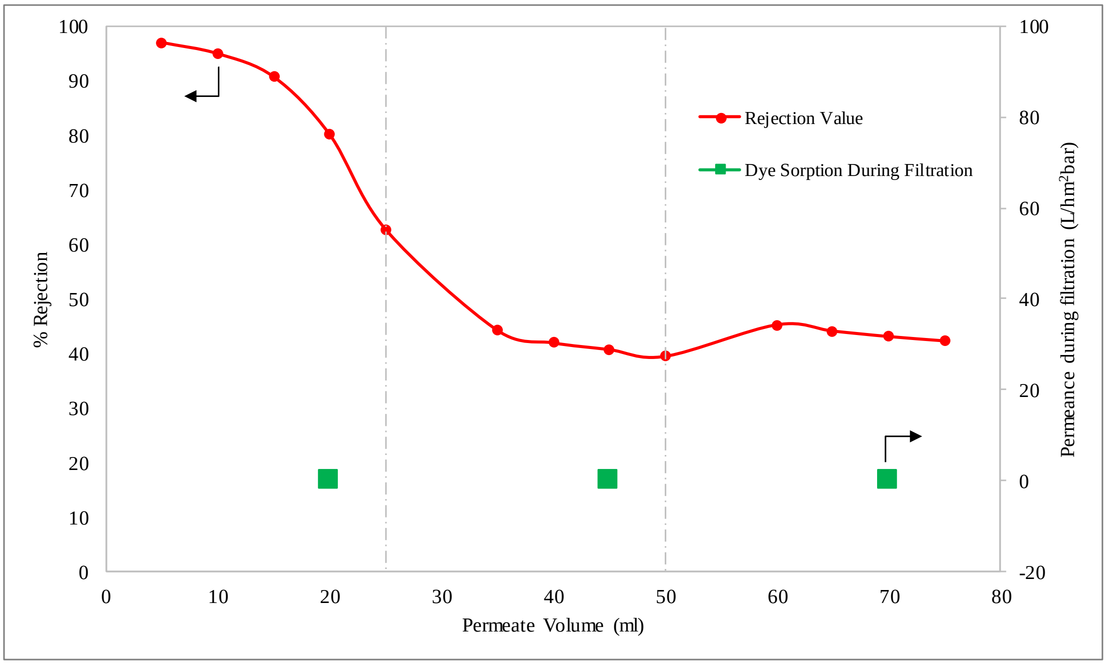


Figure 4. 4 Bromothymol Blue (624 Da) rejection in ethanol by undried C8 membrane

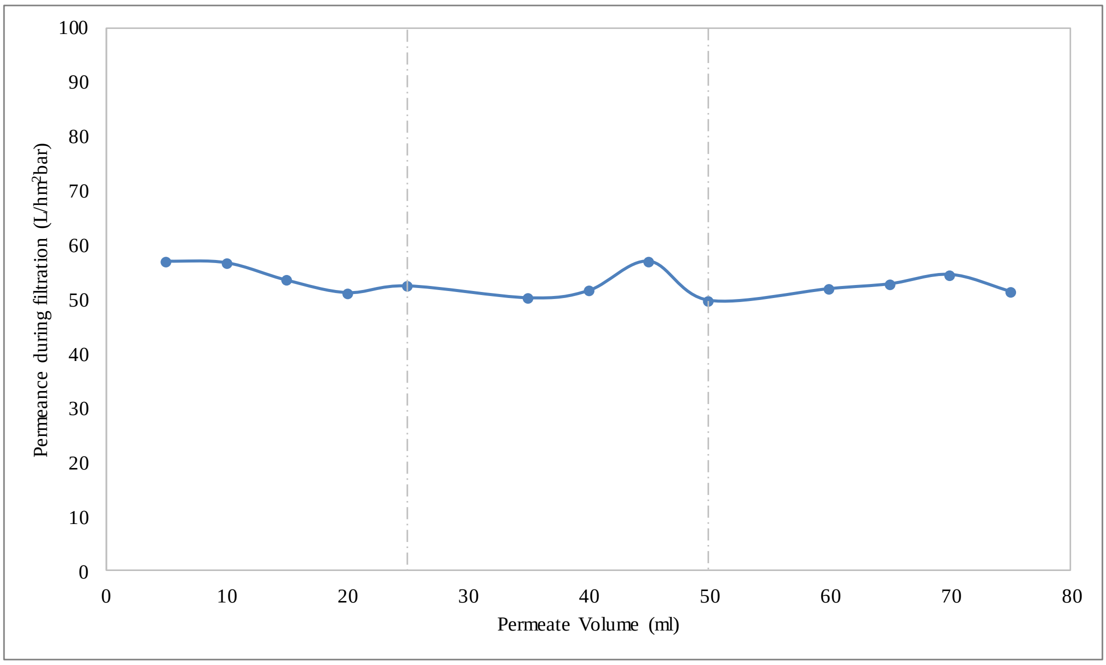


Figure 4. 5 Permeance during filtration of Bromothymol Blue (624 Da) in ethanol by undried C8 membrane

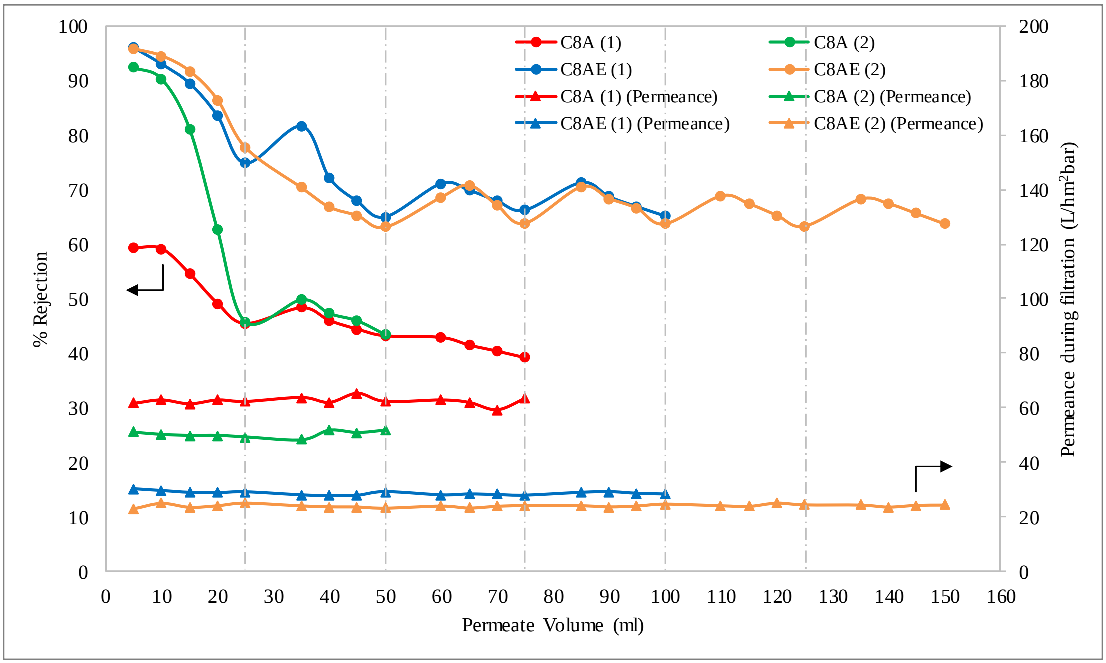


Figure 4. 6 Bromothymol Blue (624 Da) rejection in ethanol of undried membranes cast from solution B (containing 8 wt% Cellulose – 20 wt% Acetone – 72 wt% EMIM Acetate) without (C8A) and with (C8AE) evaporation step prior to coagulation

The effect of polymer concentration and presence of cosolvent were first examined to investigate how membrane morphology affects separation performance. From C8 to C8A, the only difference is that there is an introduction of cosolvent, acetone, while keeping the same weight percentage of polymer. As a result, the amount of solvent, [EMIM]OAc, was reduced. By using Bromothymol Blue in ethanol to characterize the membranes, it was observed that solute rejection and solvent permeance were similar (from 52 to 54±6 L/hm^{2}bar permeance; 41% and 43±3% rejection in C8 and C8A, respectively) (Figure 4. 4 and Figure 4. 6).

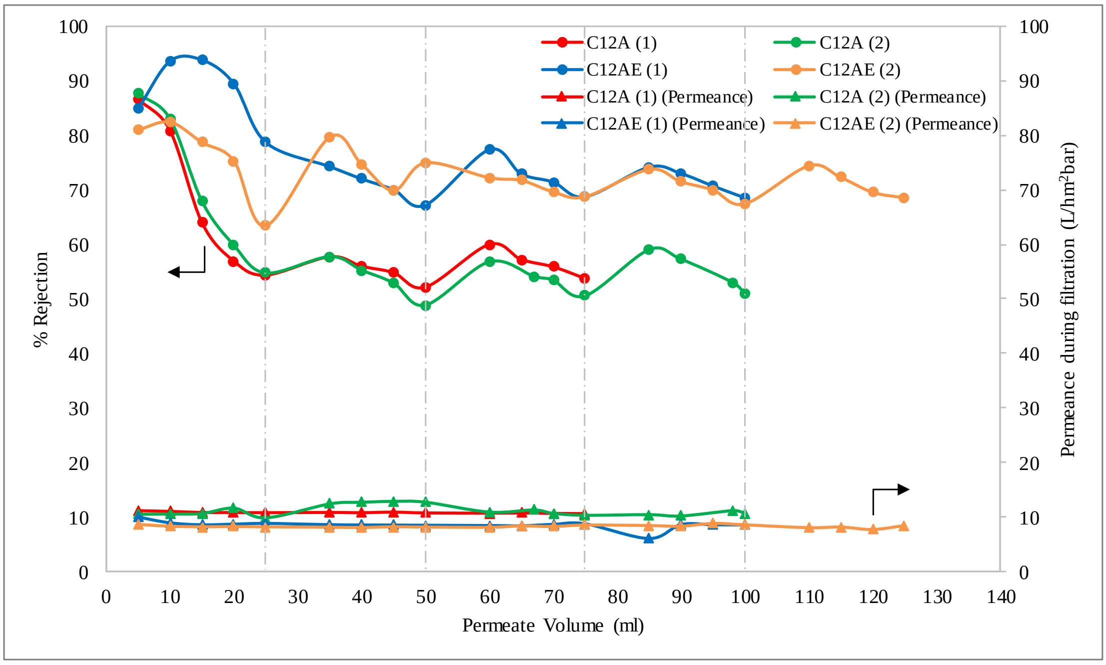


Figure 4. 7 Bromothymol Blue (624 Da) rejection in ethanol of undried membranes cast from solution C (containing 12 wt% Cellulose – 25 wt% Acetone – 63 wt% EMIM Acetate) without (C12A) and with (C12AE) evaporation step prior to coagulation

C12A having higher polymer concentration (12 wt% cellulose) showed higher rejection (53±2%) (Figure 4. 7) value compared to C8 and C8A (from 41% to 43±3%, respectively) having both 8 wt% of cellulose. Holda et al. [4] also showed similar result when they increased the concentration of polymer in casting solution. By using Rose Bengal as the studied solute, they increased the rejection value from 37% to 92% while decreasing solvent permeance 9.7 to 0.07 L/hm^{2}bar when increasing polymer (polysulfone) concentration from 13 to 25%. Polymer concentration above 25 wt% resulted in no measurable data as no flux was shown during the test. Kim et al. [43] also showed that their membrane rejection performance was increased when polymer (polyetherimide) concentration increased. This effect of polymer concentration can be attributed to the increase polymer concentration in polymer-nonsolvent interface [7] inhibiting inflow of nonsolvent to the cast membranes thus promoting delayed demixing resulting in a thicker and denser membranes with lower porosities. In general, more polymer concentration in dope solution slows down demixing process and at the same time higher selectivity is obtained [4].

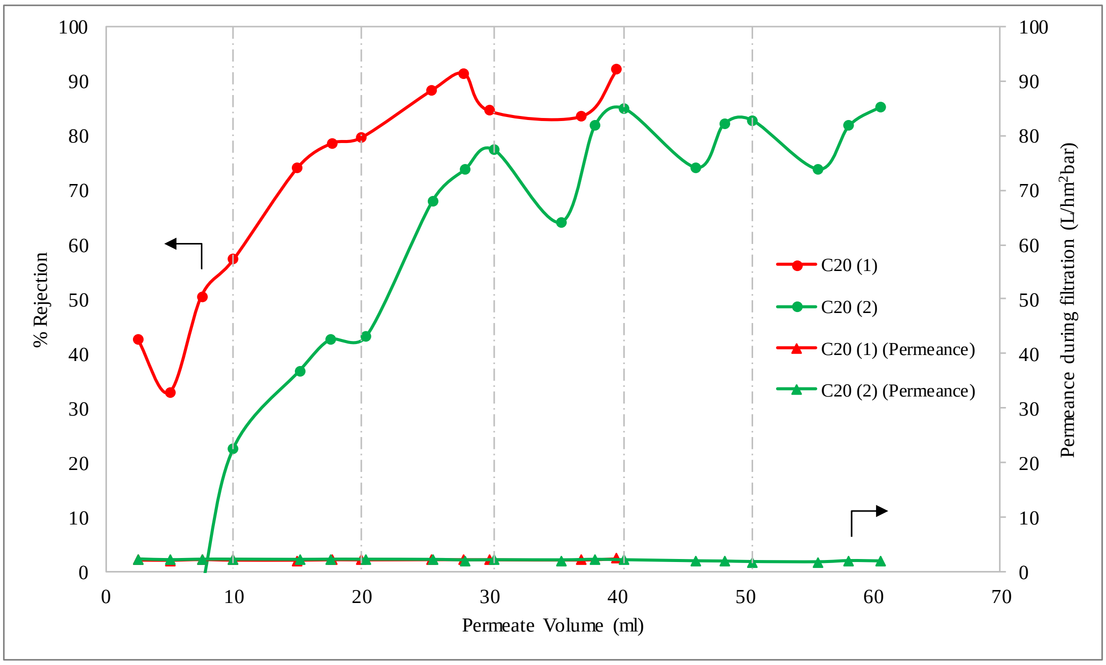


Figure 4. 8 Bromothymol Blue (624 Da) rejection in ethanol of undried membranes cast from solution E (containing 20 wt% Cellulose – 80 wt% EMIM Acetate) (C20)

Using more concentrated polymer solution, solution E, further increase of rejection (86±4%) and decrease of permeance (2.2±0.3 L/hm^{2}bar) were noticed in membrane C20 as shown by Bromothymol Blue (624 Da) (Figure 4. 8)

Introduction of evaporation step was done in order to obtain a polymer solution with elevated polymer concentration at the onset of coagulation in water [7]. In this study, volatile cosolvent, acetone, was evaporated in constant N_2 flow for 30 minutes. The cast film was put in the coagulation bath containing nonsolvent (water) after evaporation step. Preliminary studies were done in determining the necessary amount of time for evaporation (5, 15, and 30 minutes). It was observed that the result did not change significantly in terms of permeance and solute rejection hence 30 minutes of evaporation was used for future tests in order to maximize the amount of acetone that can be evaporated, although there is no quantitative data of how much the acetone evaporates during this step. From the data (Figure 4. 6 and Figure 4. 7), evaporation step did increase the solute rejection value while decrease solvent permeance. From C8A to C8AE, both membranes were cast from the same solution containing 8 wt% of cellulose, 20 wt% of acetone, and 72 wt% of [EMIM]OAc. The difference was that in C8AE, evaporation step was introduced. It was shown that rejection value increased from 43±3% to 66±1%, while solvent permeance dropped from 54±6 to 28±1 L/hm^{2}bar with the evaporation step. The same also occurred with C12A (without evaporation) and C12AE (with evaporation), both of which were cast from casting solution composed of 12 wt% of cellulose, 25 wt% of acetone, and 63 wt% of [EMIM]OAc. Rejection increased from 53±2% to 70±1%, while permeance decreased from 12±2 to 8±1 L/hm^{2}bar. Holda et al. [4] showed that solute rejection of their membrane increased while solvent permeance decreased when volatile solvent evaporation step was introduced. They also noticed that there was optimum evaporation time as evaporation time more than the optimum value only resulted in the drastic decrease of solvent permeance without increasing solute rejection. In our study, 30 minutes of evaporation did decrease the permeance but not as drastically as the study mentioned.

Drying post-treatment was introduced in order to improve dye rejection performance. Drying post-treatment contributed to the pore collapse within the membrane structure, which resulted in tighter membranes, which can increase the membrane selectivity. This, however, has a drawback as the solvent permeance of the membrane typically drops drastically. Burgal et al. [44] showed that their PEEK OSN membranes showed better rejection when drying post-treatment was applied. Pore collapse is attributed to the high capillary force inside the pores. Surface tension of solvent filling the membranes pores prior to drying determines membrane pore size after drying. The higher the surface tension, the more the pore collapse when subjected to drying. In this study, membranes were dried at ambient condition overnight after ethanol immersion. From the test, it was noted that drying post treatment did increase rejection value

(Figure 4. 9). From C12AE to C12AE-D, rejection of bromothymol blue increased from 70±1% to 87±3%, while solvent permeance decreased from 8.4±0.8 to 0.4±0.2 L/hm^{2}bar. It was a drastic decline for the solvent permeance and can be attributed to reduced porosity in the membrane structure. By using the more concentrated solution E composed of 20 wt% of cellulose and 80 wt% of [EMIM]OAc, bromothymol blue rejection of C20-D was further increased to 94, while the permeance was only slightly decreased compared to C12AE-D (Figure 4. 9). Comparison of undried and dried membranes cast from solution E (C20 and C20-D) showed increased rejection (from 86±4% to 94) and decreased permeance (from 2.2±0.3 to 0.3±0.1 L/hm^{2}bar) (Figure 4. 8 and Figure 4. 9). Summary of bromothymol blue rejection in ethanol by C8-C20, C12AE-D, and C20-D can be seen in Figure 4. 10.

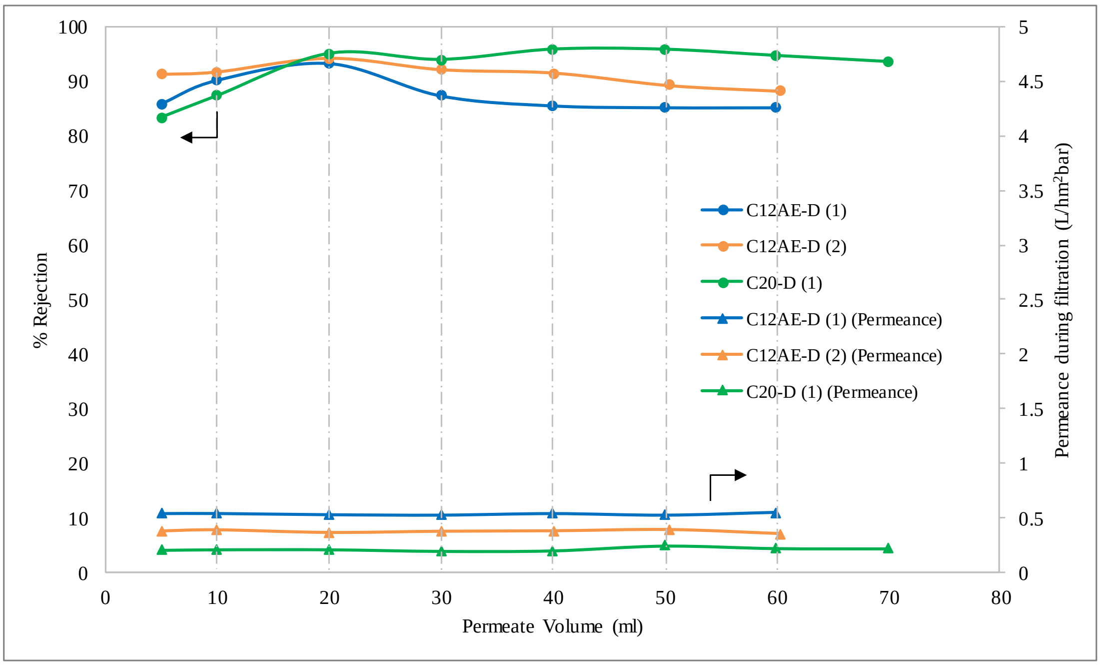


Figure 4. 9 Bromothymol Blue (624 Da) rejection in ethanol of dried membranes cast from solution C (containing 12 wt% Cellulose – 25 wt% Acetone – 63 wt% EMIM Acetate) with evaporation (C12AE-D) and cast from solution E (containing 20 wt% Cellulose – 80 wt% EMIM Acetate) (C20-D)

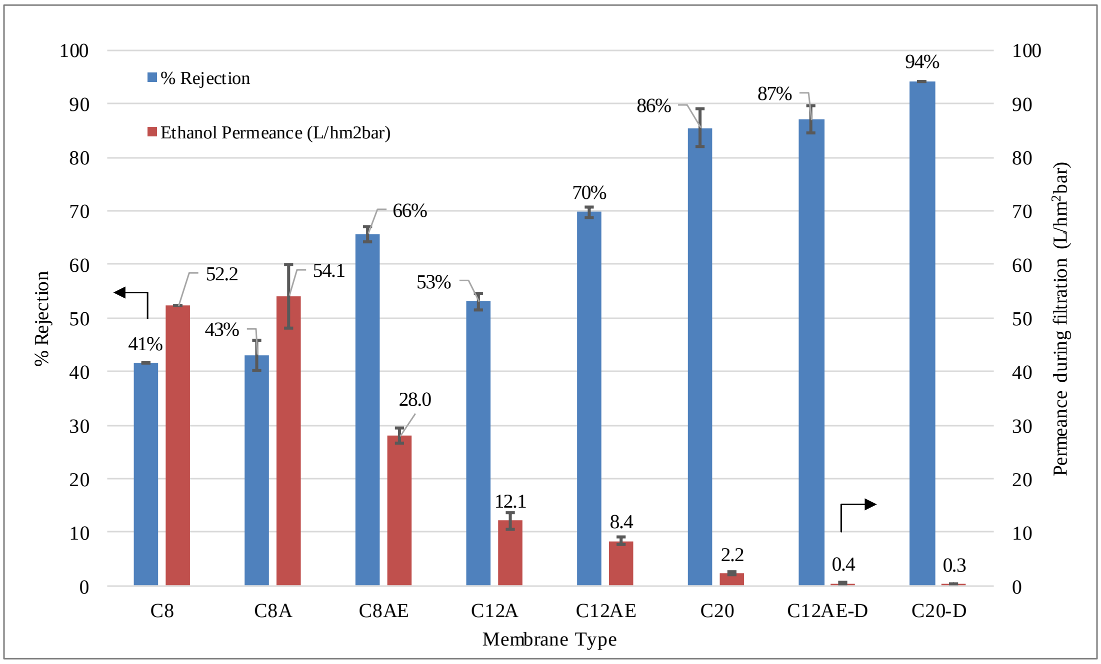


Figure 4. 10 Summary of Bromothymol Blue (624 Da) rejection in ethanol by undried C8-C20 membranes and dried C12AE-D and C20-D membranes

4.3 Effect of Solute and Solvent in Feed Solution

The important characteristic that distinguishes nanofiltration membranes from other types of membranes such as microfiltration, ultrafiltration, and reverse osmosis membranes is that their transport mechanism is in between pore flow and solution diffusion mechanisms. Hence, not only pore size of membranes affects the separation performance but also the interaction between solute, solvent, and membrane in the system. Physicochemical properties of solute, i.e. shape and size of molecules, charge, affinity with the solvent and the membrane contributes to the rejection performance of nanofiltration membranes. Molar volume of each dye (Table 4. 2), calculated by Molecular Modeling Pro software by Ayse Asatekin Group from Tufts University, is used as a measure of the size of the dyes since molecular weights are affected by large atomic mass ions such as Br, Cl, etc. in the structure. The effect of solute choice was studied first by comparing two solutes with similar nature but different molecular weight. Cresol Red and Bromothymol Blue were used and both of them were dissolved in ethanol. The tests were done with undried (C12AE and C20) membranes and dried (C12AE-D) membranes.

Table 4. 2 Molecular weight and molar volume of each dye

Dye	Molecular Weight (Da)	Molar Volume (cm^3/mol)
Cresol Red	382	140.1
Bromothymol Blue	624	251.1
Crystal Violet	408	253.7
Brilliant Blue R	826	421.3

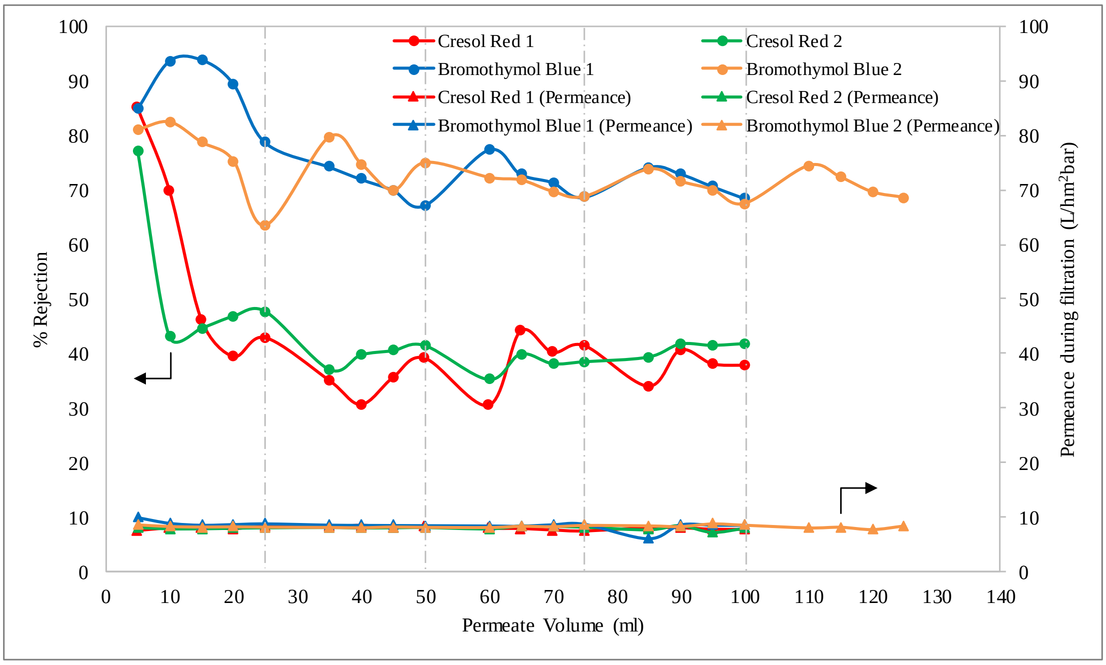


Figure 4. 11 Rejection performance of undried C12AE membranes cast from solution C (containing 12 wt% Cellulose – 25 wt% Acetone – 63 wt% EMIM Acetate) with evaporation step prior to coagulation with Bromothymol Blue (624 Da)-Ethanol solution and Cresol Red (382 Da)-Ethanol solution

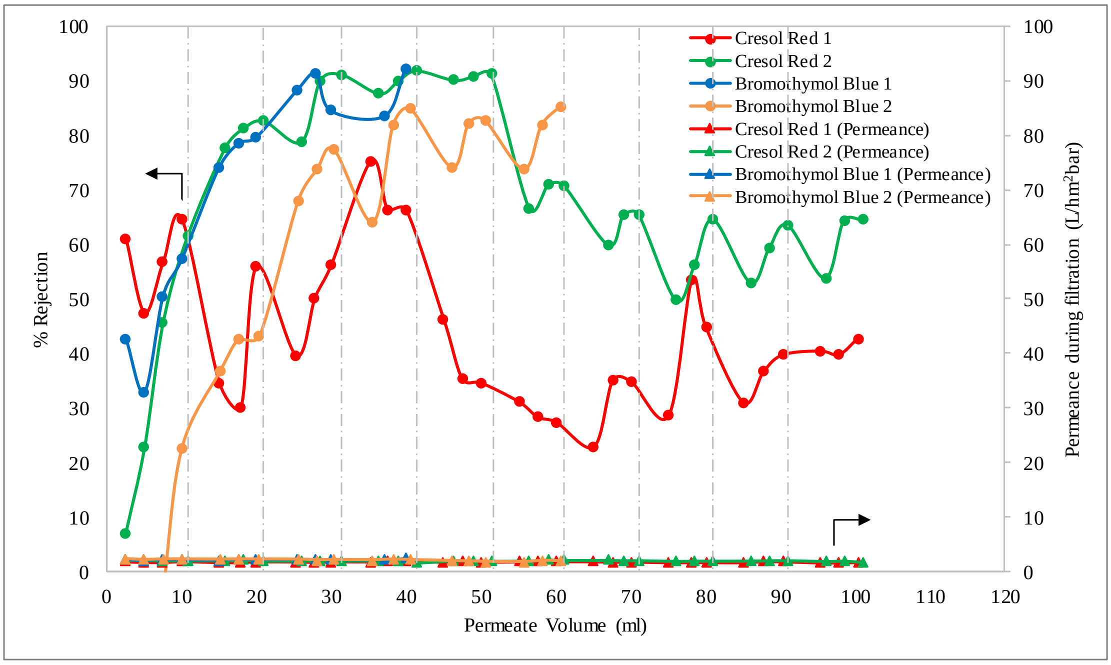


Figure 4. 12 Rejection performance of undried C20 membranes cast from solution E (containing 20 wt% Cellulose – 80 wt% EMIM Acetate) with Bromothymol Blue (624 Da)-Ethanol solution and Cresol Red (382 Da)-Ethanol solution

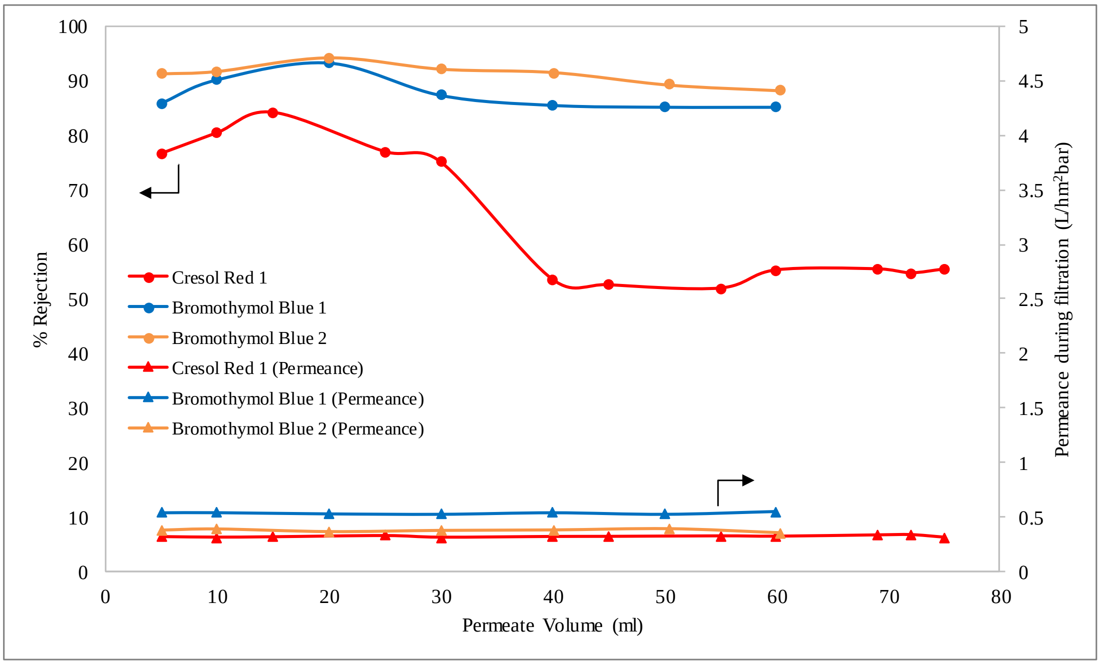


Figure 4. 13 Rejection performance by using Cresol Red (382 Da)-Ethanol and Bromothymol Blue-Ethanol solutions of dried membranes cast from solution C (containing 12 wt% Cellulose – 25 wt% Acetone – 63 wt% EMIM Acetate) with evaporation step prior to coagulation (C12AE-D)

It was observed that, Bromothymol Blue rejection is higher than that of Cresol Red in all cases (Figure 4. 11 - Figure 4. 13). Since both solutes are neutral and they have similar structure, it can be expected that both solutes have similar affinity towards the membrane compared to one another. In this case, size of molecules appears to be the determining factor in the separation performance of the membranes. However, this was not the case when negatively charges solute of Brilliant Blue R was tested. Although Brilliant Blue R is higher in molar volume compared to Cresol Red and Bromothymol Blue, it was not retained at all by the membranes (Figure 4. 14). Unlike Brilliant Blue R, Crystal Violet (408 Da), which is a positively charged dye, showed rejection value similar to that of Bromothymol Blue (Figure 4. 15). C12AE retained 40±2% of Cresol Red, 70±1% of Bromothymol Blue, 66±2% of Crystal Violet while it had almost no rejection of Brilliant Blue R.

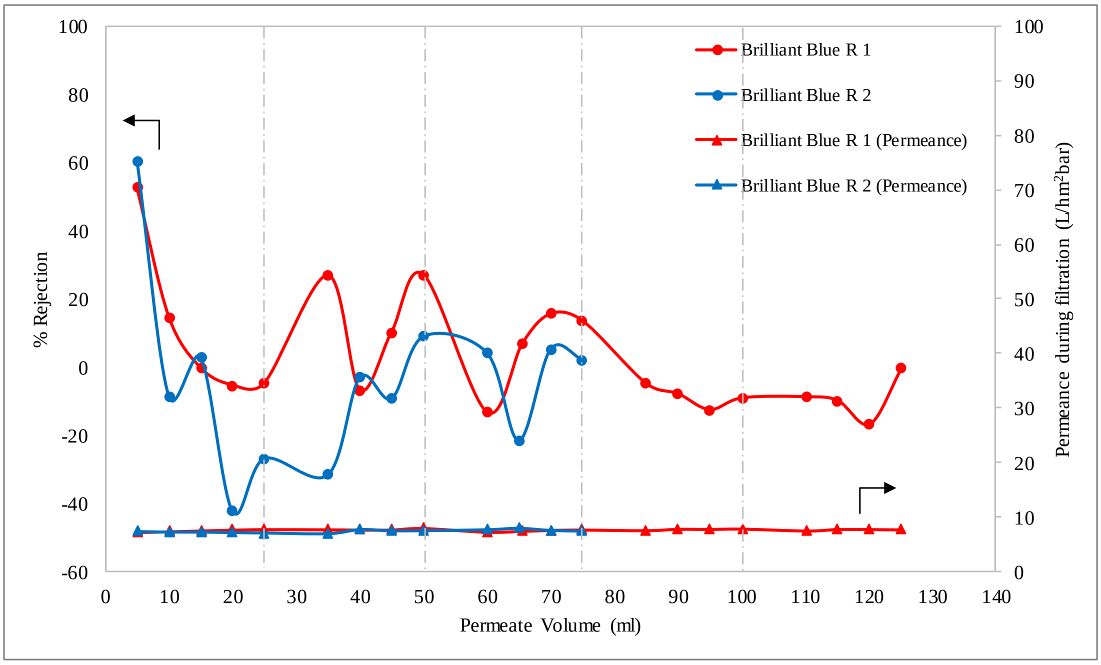


Figure 4. 14 Rejection performance by using Brilliant Blue R (826 Da)-Ethanol solution of undried C12AE membranes cast from solution C (containing 12 wt% Cellulose – 25 wt% Acetone – 63 wt% EMIM Acetate) with evaporation step prior to coagulation (C12AE)

The effect of solvent choice was investigated using Brilliant Blue R and Crystal Violet as solute and water as solvent. From the tests, it was observed that Brilliant Blue R in water was retained almost fully (Figure 4. 16) compared to Brilliant Blue R in ethanol which was not retained at all (Figure 4. 14). On the other hand Crystal Violet showed negative rejection in water (Figure 4. 17) while 66±2% was retained in ethanol (Figure 4. 15). Cellulose is negatively charged in neutral pH [45]. The high rejection of Brilliant Blue R and negative rejection of Crystal Violet in aqueous solution can be explained by charge interaction which causes negatively charged Brilliant Blue R to be almost fully retained by the negatively charged membrane while the positively charged Crystal Violet is fully permeated. In ethanol, cellulose is expected to have much less charge on the surface, if at all. Negative rejection implied faster rate of solute that permeated through membrane compared to the rate of solvent.

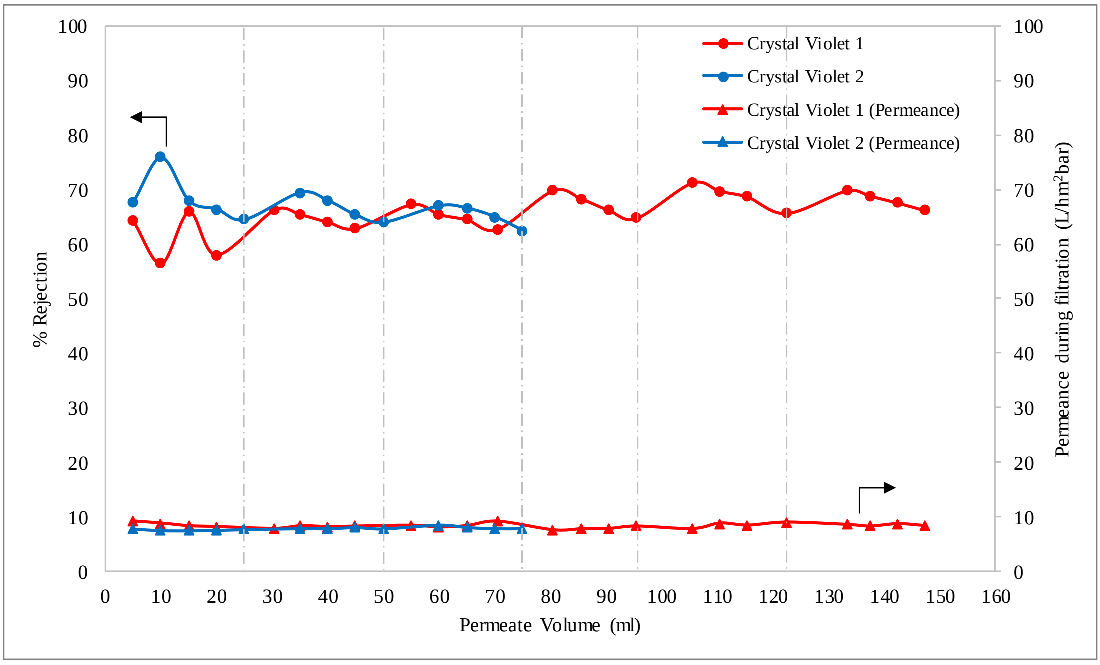


Figure 4. 15 Rejection performance by using Crystal Violet (408 Da)-Ethanol solution of undried C12AE membranes cast from solution C (containing 12 wt% Cellulose – 25 wt% Acetone – 63 wt% EMIM Acetate) with evaporation prior to coagulation (C12AE)

Considering the dye sorption on the membranes during filtrations (Table 4. 3), Crystal Violet appears to have almost no affinity to the membrane in its solution in ethanol. Considering the solution diffusion model, this low solubility may explain its rejection in ethanol solution. This result also implies that charge effects are not significant in filtrations where solvent is ethanol. Crystal Violet in water, however, sorbed everywhere including the cell thus the calculated dye sorbed on the membrane does not reflect the actual sorption during filtrations.

On the other hand, Brilliant Blue R, Bromothymol Blue, and Cresol Red seem to have similar affinities towards the membrane in their ethanol solutions. However, Brilliant Blue R is not retained at all while Bromothymol Blue and Cresol Red are. One explanation to this may be the neutral dyes, Bromothymol Blue and Cresol Red, appearing in aggregates in the solution as opposed to BBR, which would still ionize to some extent in ethanol and due to its ionized groups would have a lower tendency to aggregate. The larger size of the aggregates would imply a smaller diffusivity through the membrane based on the solution diffusion model or better sieving through the pores based on pore diffusion model. Summary of different separation performance by using undried C12AE membranes is shown in Figure 4. 18.

Table 4. 3 Dye sorbed during filtration test per dry weight of membrane

Feed Solution	Dye sorbed/dry membrane weight (mmol/g)
Cresol Red-Ethanol	0.018±0.003
Bromothymol Blue-Ethanol	0.010±0.002
Brilliant Blue R-Ethanol	0.016±0.006
Brilliant Blue R-Water	0.017±0.006
Crystal Violet-Ethanol	0.002±0.003

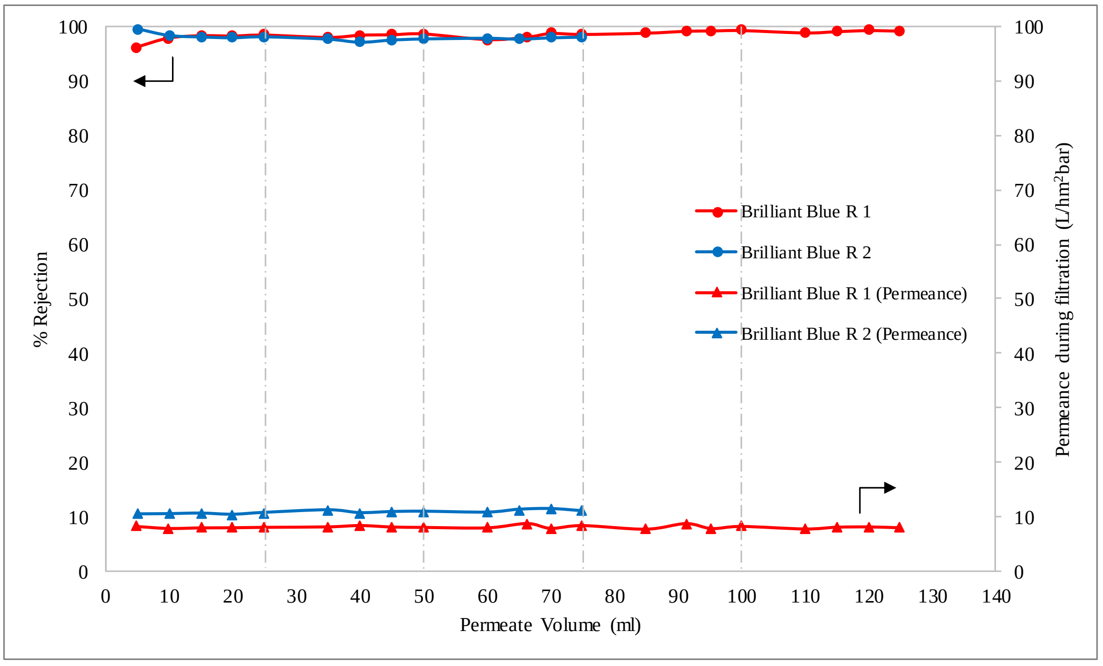


Figure 4. 16 Rejection performance by using Brilliant Blue R (826 Da)-Water solution of undried C12AE membranes cast from solution C (containing 12 wt% Cellulose – 25 wt% Acetone – 63 wt% EMIM Acetate) with evaporation step prior to coagulation

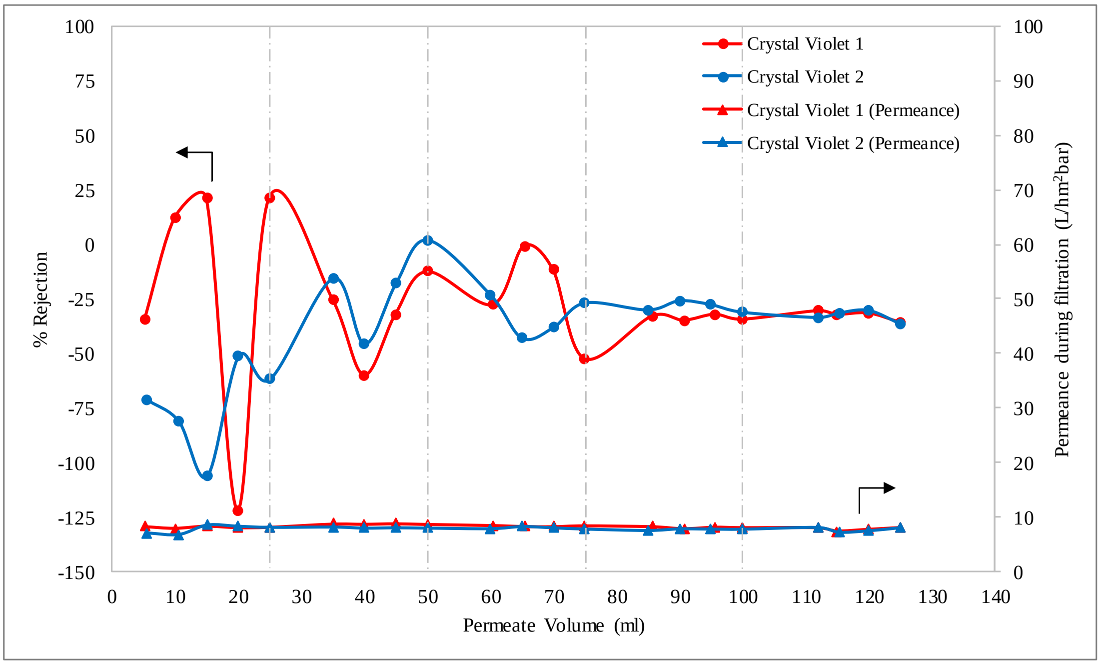


Figure 4. 17 Rejection performance by using Crystal Violet (408 Da)-Water solution of undried C12AE membranes cast from solution C (containing 12 wt% Cellulose – 25 wt% Acetone – 63 wt% EMIM Acetate) with evaporation prior to coagulation

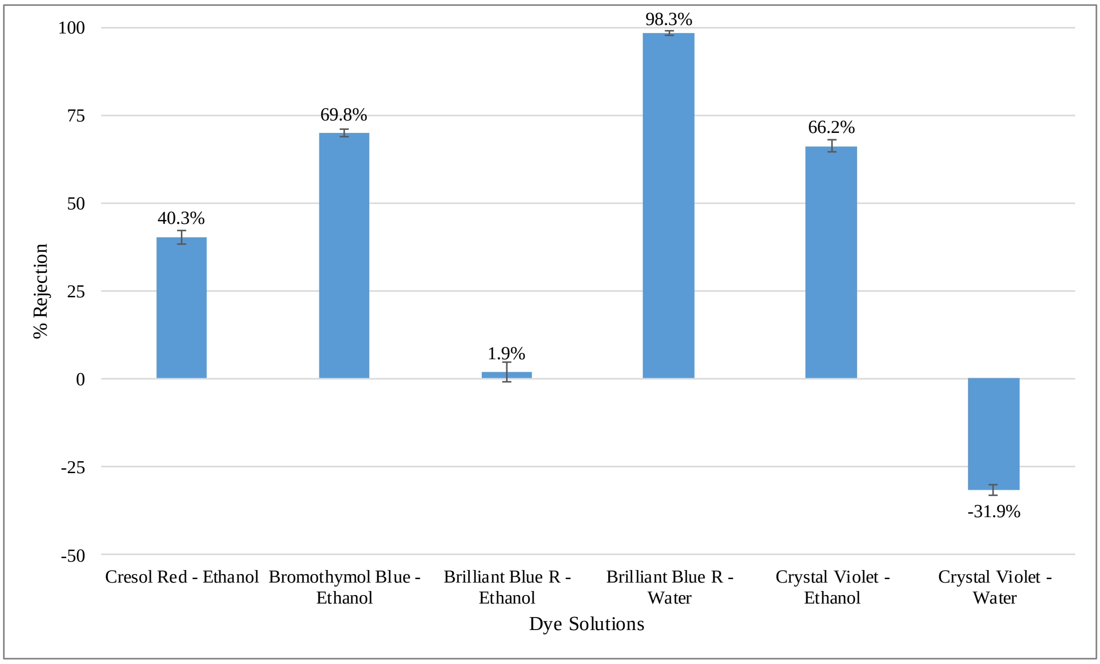


Figure 4. 18 Summary of rejection performance by using undried C12AE membranes in different dye solution

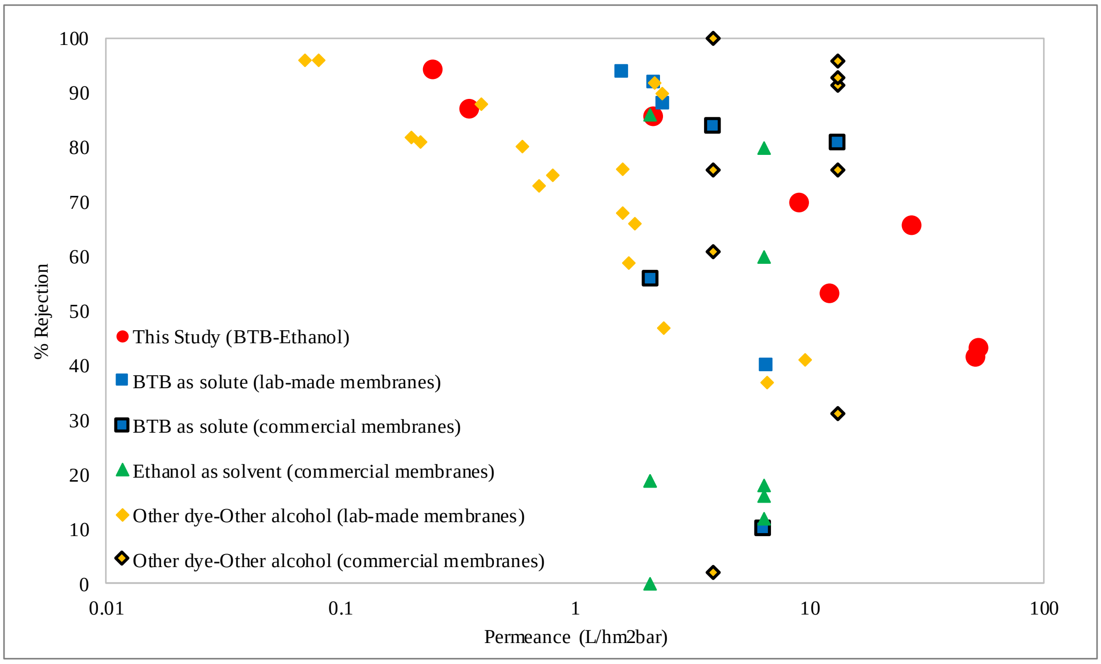


Figure 4. 19 Comparison of this study with other related studies; Darvishmanesh (2010 [24] & 2011 [14]), Peyravi (2012 [17]), Geens (2005 [46]), and Holda (2013 [4])

In membrane filtrations, rejection and permeance are both important factors and typically there is an inverse relationship, or trade-off, between these such that high rejections are generally accompanied by low permeances. Figure 4. 19 shows data on rejections and permeances of selected OSN membranes from literature and our membranes. The Bromothymol Blue rejection in ethanol solution of our membranes is compared to the performance of other membranes in Bromothymol Blue rejection, other dyes' rejection in ethanol, and other dyes' rejection in other alcohols. It can be seen that some of the membranes fabricated in this study have similar rejection in literature and the undried membranes have higher permeances that the rest while dried membranes have comparable permeance to other OSN membranes reported in literature. Considering the possibility of enhancing separation with multistage cascades, it can be said that all the membranes fabricated in our study are comparable to other reported OSN membranes.

Rejection study was also done for macromolecules of Blue Dextran having molecular weight of 5 and 20 kDa dissolved in water. Their result was compared to the result obtained from Brilliant Blue R in water (Figure 4. 16). Although Blue Dextran 5 kDa has higher molecular weight than Brilliant Blue R, it was understood from the test that it was less retained even when the membrane used in Blue Dextran 5 kDa test was dried prior to filtration test (Figure 4. 20). This may confirm that the rejection in aqueous solutions is mostly governed by charge interaction. Blue Dextran is negatively charged due to the reactive dye groups bonded to the dextran chain, but less than Brilliant Blue R. Blue Dextran 20 kDa was retained at a higher rate than Blue Dextran 5 kDa due to its molecular weight.

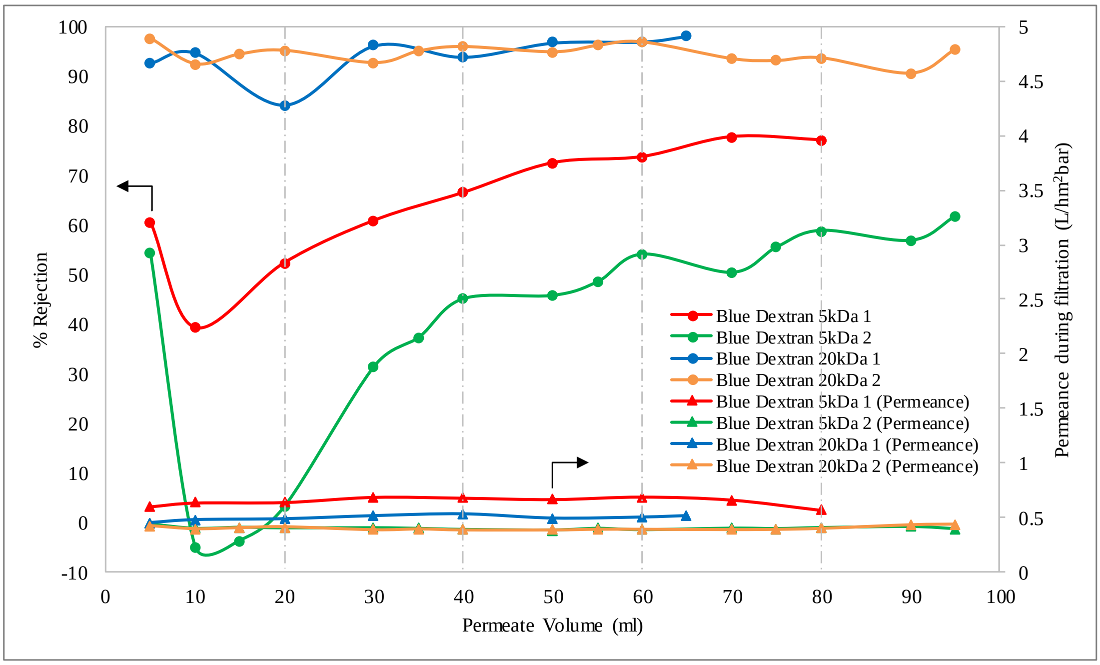


Figure 4. 20 Rejection performance by using Blue Dextran (5 kDa)-Water and Blue Dextran (20 kDa)-Water solutions of dried membranes cast from solution C (containing 12 wt% Cellulose – 25 wt% Acetone – 63 wt% EMIM Acetate) with evaporation step prior to coagulation (C12AE-D)

4.4 Swelling and Dye Sorption in Relationship with separation performance

Interaction between membranes, solutes, and solvent may be explained by using swelling ratio, sorption coefficient, and modified sorption coefficient values. Swelling test was done with undried C8 membranes, while sorption test was done with undried C12AE membranes to determine how all the three components interact with each other.

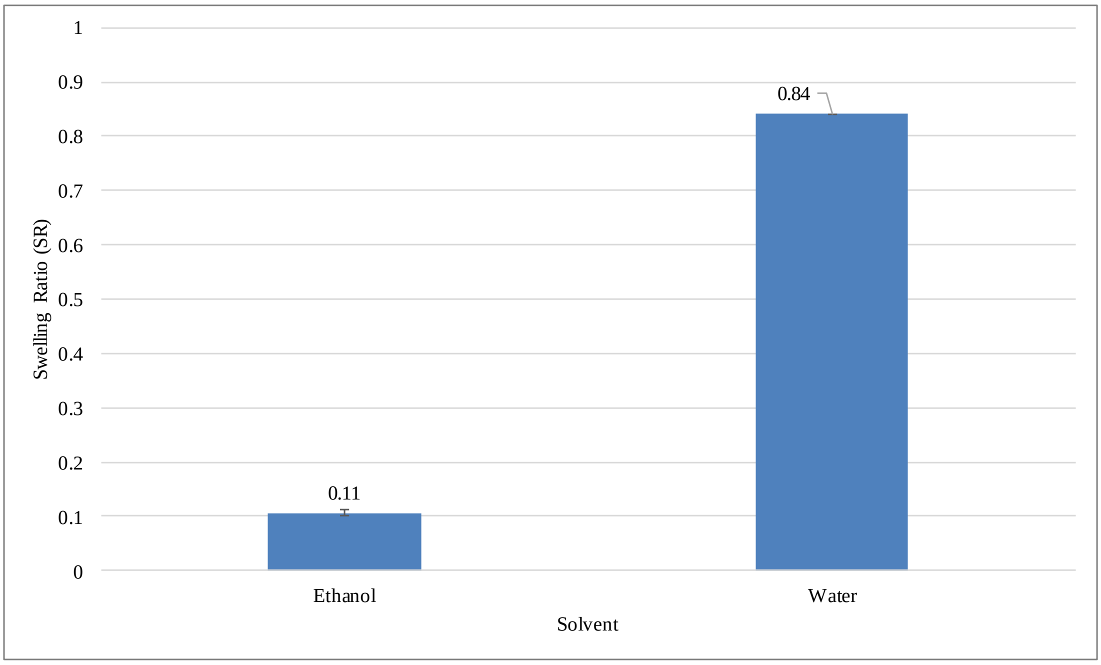


Figure 4. 21 Swelling test of C8 membrane with water and ethanol

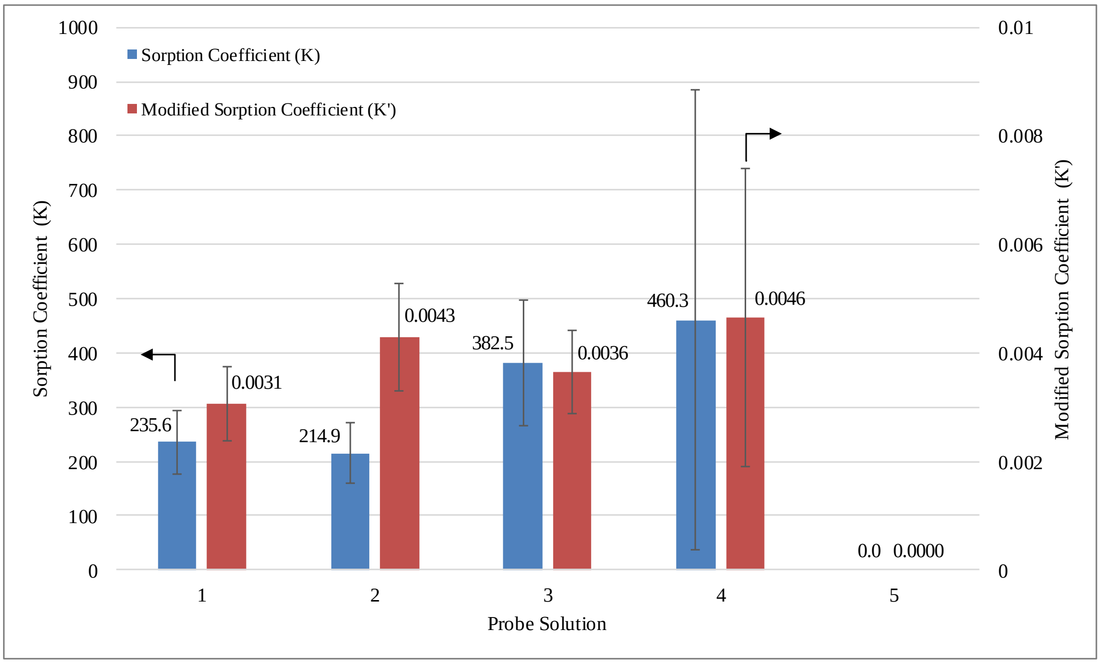


Figure 4. 22 Sorption coefficient and modified sorption coefficient of membranes with respect to rejection test feed solution

Bhanusali et al. [26] summarized that higher affinity of solute than solvent to membrane resulting in low rejection and vice versa. They also concluded that high affinity of solute to solvent leads to lower rejection of solute. From the sorption test result of our membranes, Crystal Violet showed no affinity to cellulose while Bromothymol Blue, Cresol Red, and Brilliant Blue R showed similar affinity. The ratio of dye sorbed on membrane over dry membrane weight, modified sorption coefficient (K'), also showed similar pattern with the sorption coefficient (Figure 4. 22). Pressure may affected the sorption amount as K' was obtained higher in filtration test than in sorption test. On the other hand, though having similar affinity based on sorption test result, Brilliant Blue R showed no rejection in ethanol compared to Bromothymol Blue and Ethanol. From this result, higher molar volume does not necessarily retained at a higher rate.

Higher rejection of Brilliant Blue R in water compared to in ethanol may also be explained with swelling test result. Swelling test result showed that water has a higher affinity to cellulose compared to ethanol (Figure 4. 21). Due to this, water may permeate faster than solute compared to when the solute dissolved in ethanol resulting in low solute concentration in permeate stream. This result is also similar with study done by Soltane et al. [21] as they observed that high rejection rate occurred with the solvent that has high swelling degree on membranes.. One of the solutes that they used in their filtration test, which is Sudan Blue (350 Da), showed negative rejection in ethanol although having the lowest degree of swelling. Hydration shell of Brilliant Blue R in water may also make its size larger compared to in ethanol. Study by Yang et al. [47] also showed that Orange II (negatively charged) was retained at a higher rate in aqueous solution compared to in methanol. They suggested that hydration shell in water makes the effective size of the solute larger.

Study of Volkov et al. [22] also showed the importance of interaction between membranes, solute, and solvent. They used Poly [1-(trimethylsilyl)-1-propyne] (PTMSP) as the polymeric material which is a glassy polymer with high free volume fraction. From their study, they calculated sorption coefficient and found that negative dyes of Orange II and Remazol Brilliant Blue R have low affinity to PTMSP membranes compared to neutral dyes of Solvent Blue 35 and Oil Red O. Obtained sorption result supported filtration tests as negative dyes were retained at a higher rate compared to neutral dyes.

Table 4. 4 summarized the separation performance for all the fabricated membranes by solute solutions in ethanol and water.

Table 4. 4 Summary of separation performance for all fabricated cellulose membranes

Membranes	Permeances (L/hm^{2}bar)		%Rejections							
	Ethanol	Water	Ethanol Solution				Water Solution			
			CR	BTB	BBR	CV	BBR	CV	BD5	BD20
C8	52.2	-	-	41.5	-	-	-	-	-	-
C8A	54.1±5.9	-	-	43.0±2.8	-	-	-	-	-	-
C8AE	28.0±1.4	-	-	65.7±1.3	-	-	-	-	-	-
C12A	12.1±1.6	-	-	53.1±1.5	-	-	-	-	-	-
C12AE	8.4±0.8	8.1±0.6	40.3±2.0	69.8±1.0	1.9±2.7	66.2±1.6	98.3±0.6	-31.9±1.6	-	-
C12AE-D	0.4±0.2	0.5±0.1	55.2	87.0±2.6	-	-	-	-	66.3±12.7	95.9±2.1
C20	2.2±0.3	-	52.6±16.4	85.6±3.6	-	-	-	-	-	-
C20-D	0.3	-	-	94.1	-	-	-	-	-	-

4.5 Effect of Applied Pressure, Coagulation Medium, and Type of Cellulose on Separation Performance

The effect of type of cellulose, liquid coagulant, and the effect of applied pressure during filtration tests were also briefly investigated throughout the study and are summarized here by using undried C12AE membranes (Figure 4. 23). In most of membrane fabrication, cotton linter cellulose was used as the polymer. Bromothymol Blue (624 Da)-Ethanol solution was used to characterize the membranes. It was observed, as the cast solution was coagulated in ethanol, solute was retained at a lower rate (54% compared to 70±1% for coagulation in water). Permeance was higher for membrane coagulated in ethanol than coagulated in water (22 to 8±1 L/hm^{2}bar). This implies that the membrane has a looser structure when the cellulose solution is coagulated in ethanol. The effect of applied pressure was also measured and it was found that as the pressure increased, solute rejection slightly decreased. Rejections were 70±1% and 61% at 1 and 4 bar respectively. The effect of type of cellulose was also examined by changing the polymer to Avicel (microcrystalline cellulose). Membranes fabricated from Avicel showed a slightly lowered rejection value compared to the one produced from cellulose cotton linter.

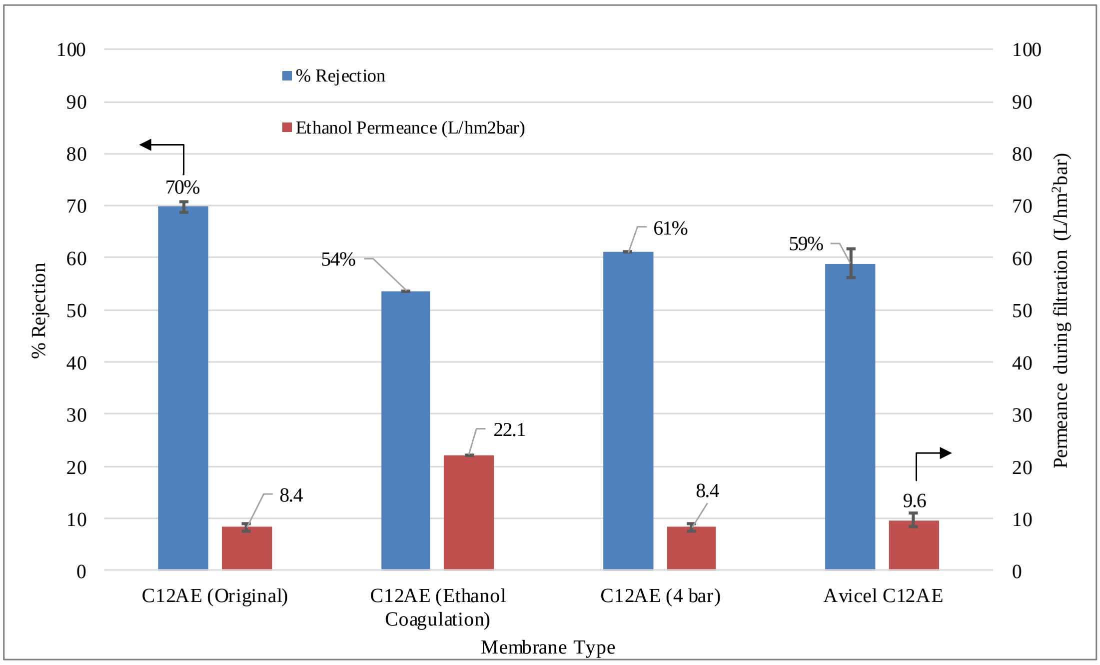


Figure 4. 23 Effect of applied pressure, coagulation medium, and solvent prior to drying, and type of cellulose on Bromothymol Blue rejection in ethanol

CHAPTER 5

CONCLUSIONS

In this study, cellulose membranes were fabricated for organic solvent nanofiltration via phase inversion using ionic liquids as solvents. Cellulose was dissolved with 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc), while acetone was used as cosolvent and water as coagulant. Morphology characteristics of fabricated membranes was observed by SEM images. Separation performance was investigated as well with probe solutions in both ethanol and water. Cresol Red, Bromothymol Blue, Crystal Violet, and Brilliant Blue R were used for ethanol system, while Crystal Violet, Brilliant Blue R, Blue Dextran (5 kDa and 20 kDa) were used for water system.

Fabricated membranes showed similar morphology as no macrovoids formation occurred within their structure and no skin layer. Effects of cosolvent in addition in dope solution, polymer concentration in cast solution, volatile solvent evaporation prior to coagulation, and drying post-treatment after membrane fabrication on separation performance were observed. Cosolvent addition while keeping the same amount of cellulose resulted in similar rejection result of Bromothymol Blue in ethanol. Increase of polymer concentration from 8 wt% to 20 wt% of Cellulose improved Bromothymol Blue rejection in ethanol from 41% to 86±4% while reduced ethanol permeance from 52.2 to 2.2±0.3 L/hm^{2}bar. This observation was also noticed from Cresol Red rejection in ethanol as solute rejection increased from 40±2% to 53±16%. This can be attributed to the denser structure of the membrane as polymer concentration in the precursor solution is increased. Evaporation prior to coagulation also affected separation performance of Bromothymol Blue in ethanol. C8A and C8AE were cast from the same solution with cosolvent evaporation in C8AE being the only difference. It was observed that Bromothymol Blue rejection increased from 43±3% to 66±1% while ethanol permeance reduced from 54±6 to 28±1 L/hm^{2}bar when evaporation was introduced. Similar observation was also noticed from C12A (without evaporation) and C12AE (with evaporation) as rejection increased from 53±2% to 70±1% while ethanol permeance decreased from 12±2 to 8±1 L/hm^{2}bar. Evaporation of volatile solvent contributed to denser membrane structure. Drying post-treatment after membrane fabrication collapsed pore structure in membrane. From filtration test of dried C12AE and C20 membranes, it was observed that Bromothymol Blue rejection in ethanol increased from 70±1% to 87±3% (C12AE and C12AE-D respectively) and from 86±4% to 94% (C20 and C20-D respectively). Ethanol permeance reduced from 8.4±0.8 to 0.4±0.2 L/hm^{2}bar (C12AE and C12AE-D respectively) and from 2.2±0.3 to 0.3±0.1 L/hm^{2}bar (C20 and C20-D respectively).

Transport mechanism in nanofiltration membrane is affected by both pore-flow and solution-diffusion mechanism. Higher molar volume of solute is not necessarily retained at a higher rate. Solute affinity with membrane and solvent and solvent affinity with membrane affect the separation performance. Brilliant Blue R (2±3%), having higher molar volume, showed almost no rejection compared to that of Bromothymol Blue (70±1%), Cresol Red (40±2%), and Crystal Violet (66±2%) when dissolved in ethanol using C12AE membranes. However, when water was used the solvent, Brilliant Blue R and Crystal Violet showed opposite result from their respective rejection in ethanol. In water, Brilliant Blue R showed very high rejection, 98±1%, while negative rejection was observed in Crystal Violet (-32±2%). This may be due to charge interactions as cellulose is negatively charged in water. Having a positive charge, Crystal Violet was attracted towards cellulose resulting in negative rejection. Compared to OSN membranes reported in literature, the membranes fabricated in our study have comparable performance.

RECOMMENDATIONS

Nanofiltration cellulose membranes have been fabricated via phase inversion method using ionic liquid as solvent. Solute solutions in ethanol and water were used to characterize the membranes. Suggestions on what can be done in the future in addition to what has been done in this study are as follows:

- Mixture of solute solutions with the same solvent can be used as a feed to characterize the membranes, *i.e.*, mixture of Bromothymol Blue – Brilliant Blue R in ethanol or mixture of Crystal Violet – Brilliant Blue R in water.
- Dead-end filtration setup was used in this study. Characterization in cross-flow filtration setup can be applied to observe the separation performance using either single solute solution or mixture of solute solution
- Integrally skinned asymmetric (ISA) cellulose membranes were fabricated in this study. Thin film composite (TFC) membranes based on cellulose may also be prepared since TFC membranes have an advantage in which skin layer and porous support can be tuned independently.

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APPENDICES

APPENDIX A

CALIBRATION CURVES

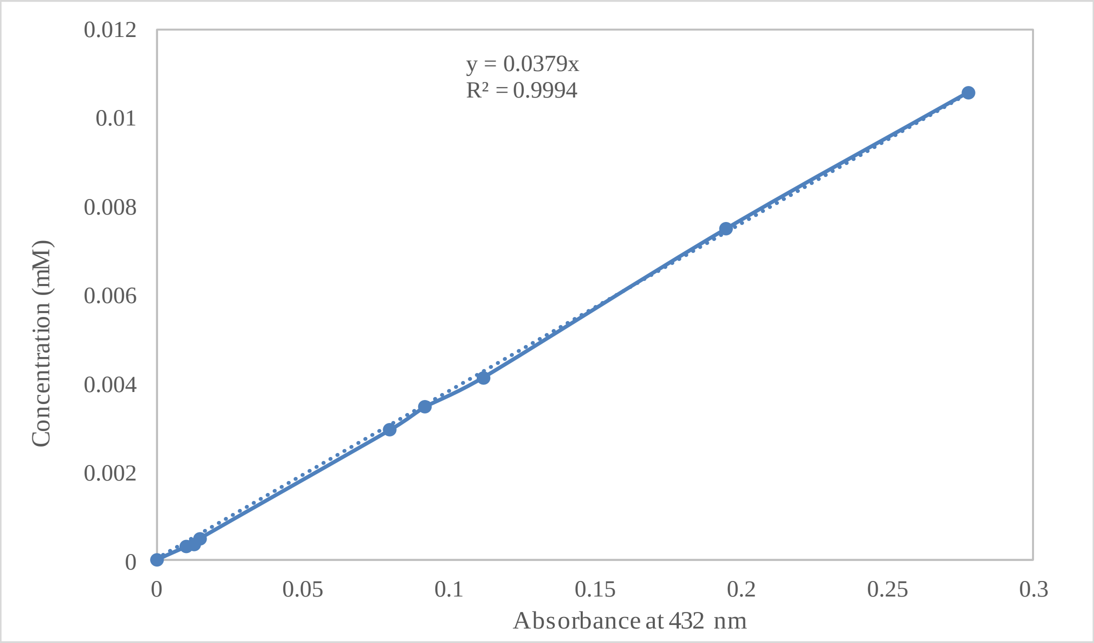

Figure A. 1 Calibration curve of Cresol Red in Ethanol

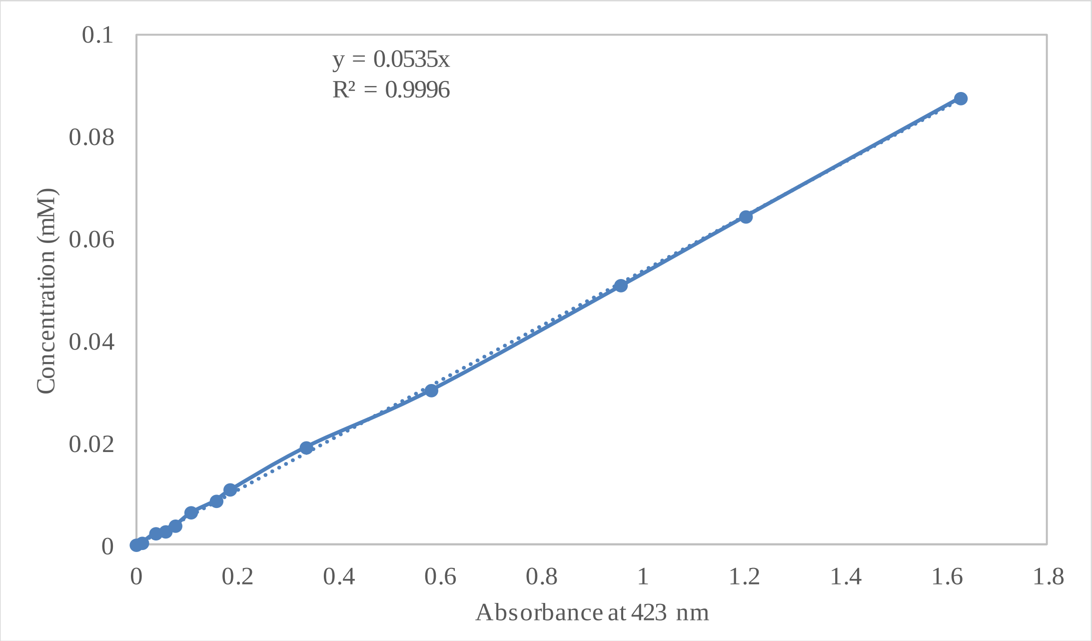

Figure A. 2 Calibration curve of Bromothymol Blue in Ethanol

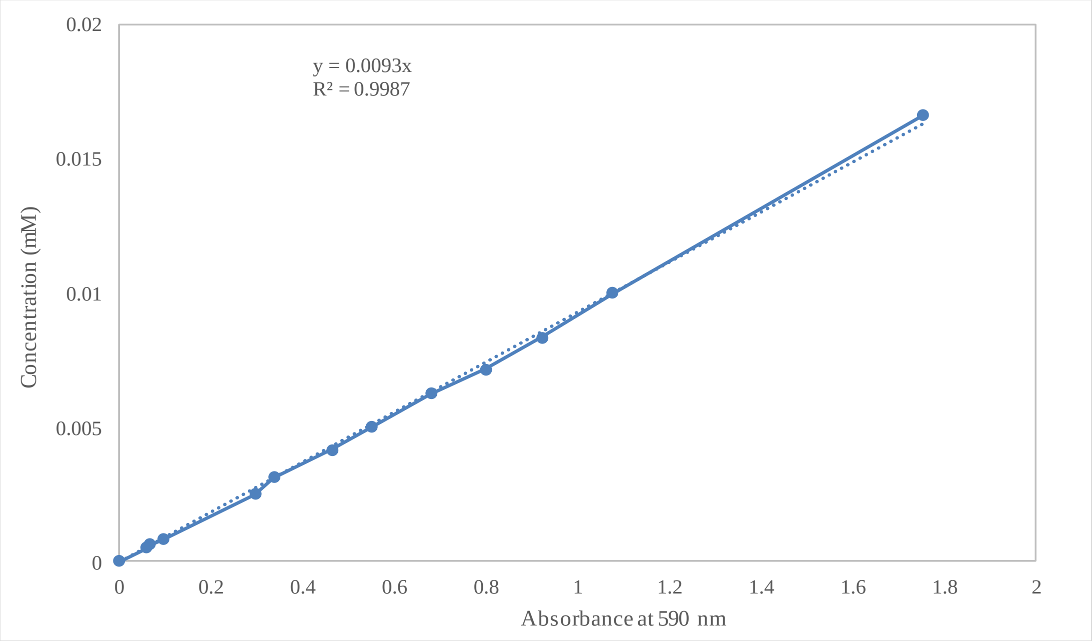

Figure A. 3 Calibration curve of Crystal Violet in Ethanol

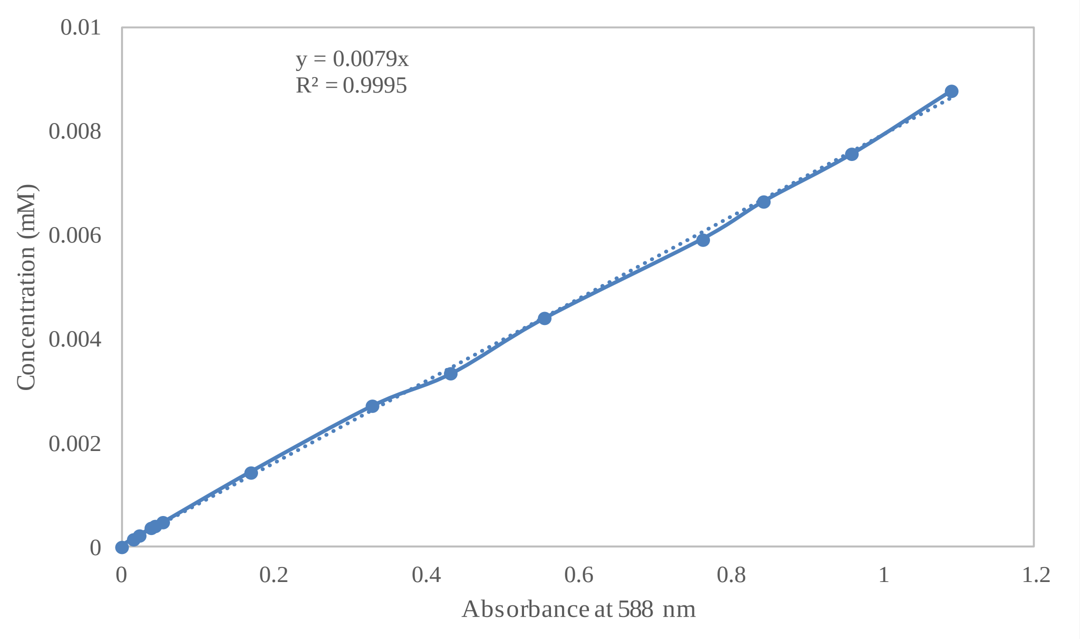

Figure A. 4 Calibration curve of Brilliant Blue R in Ethanol

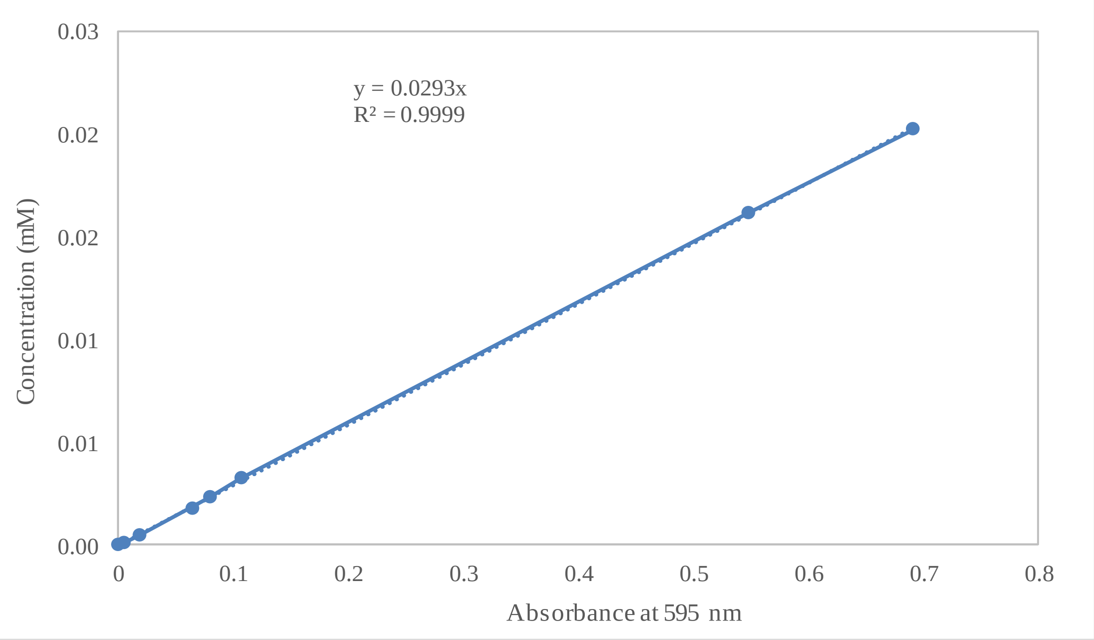

Figure A. 5 Calibration curve of Brilliant Blue R in Water

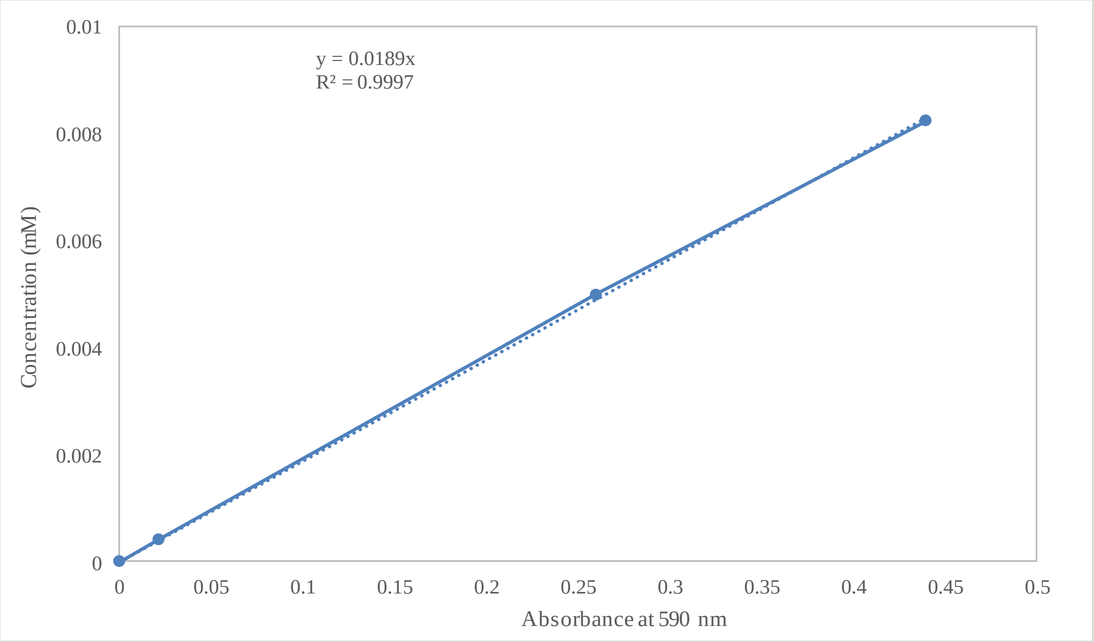

Figure A. 6 Calibration curve of Crystal Violet in Water

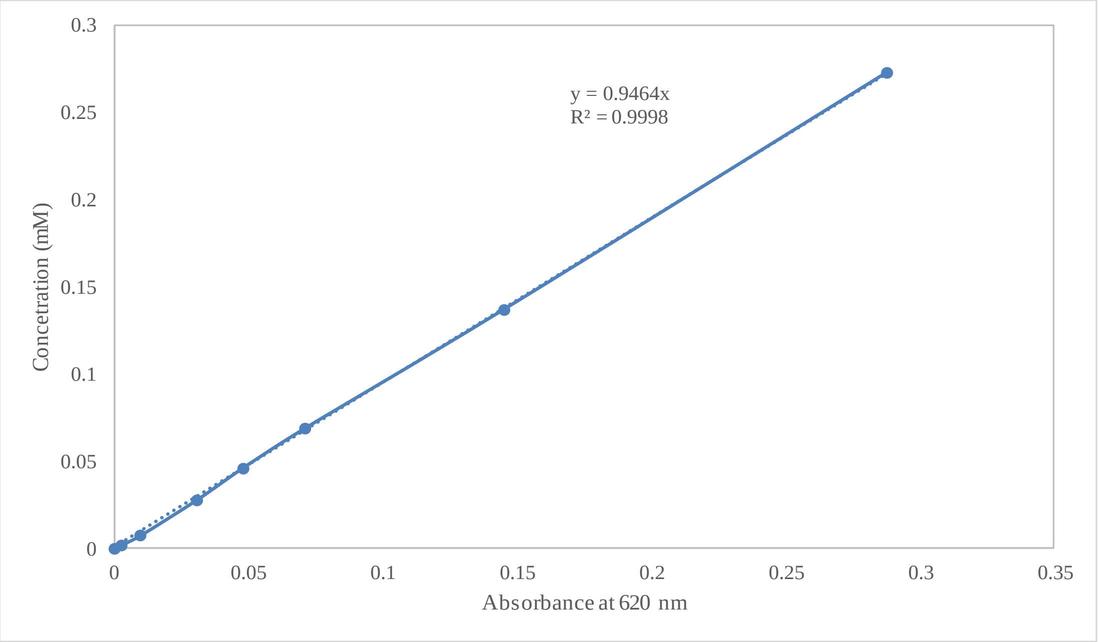

Figure A. 7 Calibration curve of Blue Dextran (5kDa) in Water

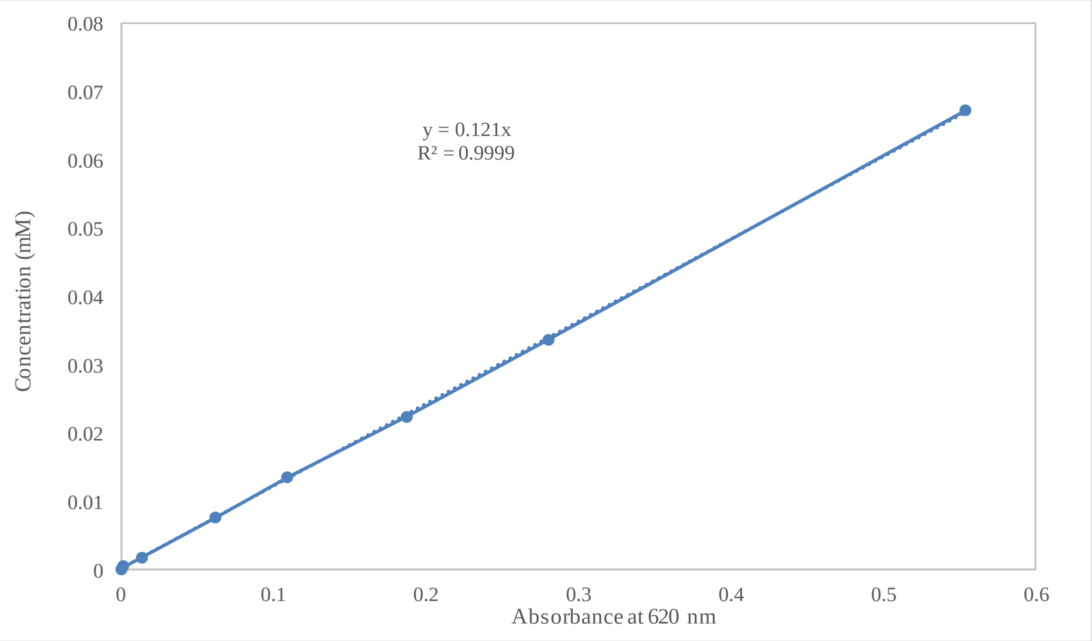

Figure A. 8 Calibration curve of Blue Dextran (20kDa) in Water

APPENDIX B

SAMPLE CALCULATION

B.1 Determination of %Rejection from Back Calculation in Rejection Test

Example: First Set of C8

Feed fed to the system= 0.0509 mM

Retentate value obtained at the end of first set of experiment= 0.0585 mM

Feed Volume= 50 ml (Volume reduction of 2)

Back calculation was done to calculate the amount of feed by removing the sorption effect on membrane.

Feed (F) Volume (ml)	**Permeate (P) Volume (ml)**	**Retentate (R) Volume (ml)**	**Feed (F) Conc. (mM)**	**Permeate (P) Conc. (mM)**	**Retentate (R) Conc. (mM)**	**%Rejection**
50	5	45	0.0330	0.0010	0.0365	97.07
45	5	40	0.0365	0.0019	0.0408	95.02
40	5	35	0.0408	0.0040	0.0461	90.77
35	5	30	0.0461	0.0097	0.0522	80.18
30	5	25	0.0522	0.0206	**0.0585**	62.77

*measured at the end of the filtration by UV measurement

$$Feed\ Concentration = \frac{(C_R * V_R) + (C_P * V_P)}{V_F}$$

- $C_{F,5} = \frac{(C_{R,5} * V_{R,5}) + (C_{P,5} * V_{P,5})}{V_{F,5}} = \frac{(0.0585 * 25) + (0.0206 * 5)}{30} = 0.0522$

  Feed from the 5th sample is the retentate for the 4th sample

- $C_{F,4} = \frac{(C_{R,4} * V_{R,4}) + (C_{P,4} * V_{P,4})}{V_{F,4}} = \frac{(0.0522 * 30) + (0.0097 * 5)}{35} = 0.0461$

  Feed from the 4th sample is the retentate for the 3rd sample

- $C_{F,3} = \frac{(C_{R,3} * V_{R,3}) + (C_{P,3} * V_{P,3})}{V_{F,3}} = \frac{(0.0461 * 35) + (0.0040 * 5)}{40} = 0.0408$

  Feed from the 3rd sample is the retentate for the 2nd sample

- $C_{F,2} = \frac{(C_{R,2} * V_{R,2}) + (C_{P,2} * V_{P,2})}{V_{F,2}} = \frac{(0.0408 * 40) + (0.0019 * 5)}{45} = 0.0365$

  Feed from the 2nd sample is the retentate for the 1st sample

- $C_{F,1} = \frac{(C_{R,1} * V_{R,1}) + (C_{P,1} * V_{P,1})}{V_{F,1}} = \frac{(0.0365 * 45) + (0.0010 * 5)}{50} = 0.0330$

$$\%Rejection_1 = 1 - \frac{0.0010}{\frac{(0.0330 + 0.0365)}{2}} * 100 = 97.07\%$$

$$\%Rejection_2 = 1 - \frac{0.0019}{\frac{(0.0365 + 0.0408)}{2}} * 100 = 95.02\%$$

$$\%Rejection_3 = 1 - \frac{0.0040}{\frac{(0.0408 + 0.0461)}{2}} * 100 = 90.77\%$$

$$\%Rejection_4 = 1 - \frac{0.0097}{\frac{(0.0461 + 0.0522)}{2}} * 100 = 80.18\%$$

$$\%Rejection_5 = 1 - \frac{0.0206}{\frac{(0.0522 + 0.0585)}{2}} * 100 = 62.77\%$$

B.2 Sorption Test

Example: One of sorption tests for Cresol Red in Ethanol

Sorption Feed = 0.09 mM

Sorption Volume = 20 ml

MW of Cresol Red = 382.43 g/mol

Final concentration in the solution the membrane is immersed in= 0.0038 mM= 0.0000018 g/g

$$K = \frac{C_{dye,membrane}}{C_{dye,solution}}$$

$C_{dye,solution} = 0.0000018\ \mathrm{g/g}$

$$C_{dye,membrane} = \frac{\text{The difference between initial and final solution concentration}}{Wet\ weight\ membrane}$$

$$C_{dye,membrane} = \frac{(\text{Feed Conc} - \text{Sample Conc}) * \text{Sorption Vol} * \text{MW of dye}/1000}{Wet\ weight\ membrane}$$

Wet weight membrane after test= 0.088g

$$C_{dye,membrane} = \frac{(0.09 - 0.0038) * 20 * 382.43/1000}{0.088}$$

K=36

$$K' = \frac{mmol\ dye\ sorbed\ on\ membrane}{dry\ membrane\ weight}$$

Dry membrane after vacuum = 0.0292 g

Mmol dye sorbed on membrane = 0.00011 mmol

K’=0.004 mmol/g

B.3 Swelling Test

Example: One of the tests with Ethanol by using uncrosslinked C8

Initial Weight of Membrane = 0.0745g

Final Weight of Membrane after swelling = 0.0796 g

Density of Ethanol = 0.789 g/cm^3

$$SR = \frac{Final\ Weight - Initial\ Weight}{Initial\ Weight * density\ of\ solvent}$$

$$SR = \frac{0.0796 - 0.0745}{0.0745 * 0.789}$$

$$SR = 0.087\ \frac{cm^3}{g}$$