

CELLULOSE MEMBRANES VIA ALKALINE HYDROLYSIS OF
CELLULOSE ACETATE MEMBRANES AND THEIR APPLICATION IN
ORGANIC SOLVENTS

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CELLULOSE ACETATE MEMBRANES AND THEIR APPLICATION IN
ORGANIC SOLVENTS**

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ABSTRACT

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Cellulose, the most abundant polymer in nature, is an attractive membrane material. Hydroxyl groups in the polymer chain make it hydrophilic, which makes cellulose membranes fouling resistant. Intra and intermolecular hydrogen bonding due to these groups on the other hand gives cellulose solvent resistance which is an attractive property for membrane filtration in organic solvents. Although cellulose is insoluble in many solvents, ionic liquids dissolve cellulose so that cellulose membranes can be prepared by phase separation. Molten salts which are in liquid form below 100 °C are called as ionic liquids. In this study, 1-ethyl-3-methyl-imidazolium acetate (EMIMAc) is used as ionic liquid. Alternatively, by deacetylation of cellulose acetate membranes in alkaline media, regenerated cellulose membranes are obtained without any necessity of ionic liquids. Sodium hydroxide solution serves as regenerating agent due to its hydroxide groups. Effect of deacetylation duration and solution concentration on the regeneration efficiency is examined by FTIR spectra. Increasing NaOH concentration and time until 24 hours increased the degree of deacetylation. Firstly, cellulose and regenerated cellulose membranes are fabricated in flat sheet geometry. Drying medium effect on membrane morphology and separation performance of flat sheet cellulose membranes was evaluated and drying from ethanol was chosen as best method. In order to find out deacetylation and annealing effects on separation performance of cellulose acetate membranes, filtration tests were performed with

Bromothymol Blue (624 Da)-ethanol solution. Annealed cellulose acetate membranes showed >80% dye rejection while this value decreased after deacetylation.

Membrane modules which are made of hollow fiber membranes have much higher surface area comparing with flat sheet membrane modules. In the view of limited sources, producing and characterizing cellulose hollow fiber membranes for OSN applications is very important for the chemical industry. In this study, cellulose and regenerated cellulose hollow fiber membranes for OSN applications are produced. Polymer solution, bore liquid and coagulation bath temperatures were varied to arrange skin layer of hollow fibers. Separation performances are evaluated with Bromothymol Blue (624 Da) retention.

As an application of cellulose membranes in solvent recovery, annealed and regenerated membranes were used to recover aprotic solvents from their 1 g/L and 10 g/L PES solutions. Experiments were performed in DMSO, NMP and DMF at 10 bar and 40 bar. Annealed and regenerated cellulose membranes have over 99% PES rejections approximately in all solvents. Also these membranes were stable in DMSO for over 10 days, in NMP and DMF for over 25 days.

Keywords: Organic solvent nanofiltration, Cellulose, Alkaline hydrolysis

ÖZ

SELÜLOZ ASETAT MEMBRANLARIN ALKALİN HİDROLİZİ İLE SELÜLOZ MEMBRANLAR VE ORGANİK ÇÖZÜCÜLERDE UYGULANMASI

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Doğada en yaygın bulunan polimer olan selüloz ilgi çekici bir membran malzemesidir. Polimer zincirlerindeki hidroksil gruplarından dolayı hidrofiliktir ve bu sayede kirlemeye karşı direnç gösterir. Moleküller içi ve moleküller arası hidrojen bağları sayesinde çözücüye dayanıklı olmasından dolayı organik çözücüde filtrasyon uygulamaları için uygundur. Selüloz çoğu çözücüde çözünmemesine rağmen iyonik sıvılar selülozu çözer. Böylelikle selüloz membranlar faz değişimi yöntemi ile hazırlanabilir. Bu çalışmada iyonik sıvı olarak 1-ethyl-3-methyl-imidazolium acetate (EMIMAc) kullanıldı. Alternatif olarak selüloz asetat membranların alkalın ortamda rejenerasyonu sonucunda da iyonik sıvıya gerek kalmadan selüloz membranlar elde edilir. Sodyum hidroksit çözeltisi, rejenerasyon sırasında, rejeneratör ajan olarak görev yapar. Deasetilasyon süresinin ve çözelti konsantrasyonunun rejenerasyon verimine etkisi FTIR ile incelenmiştir. Artan NaOH konsantrasyonu ve 24 saate kadar artan süresi deasetilasyon derecesini arttırmıştır. İlk olarak selüloz ve rejenere selüloz düz tabaka membranları üretilmiştir. Kuruma ortamının membran morfolojisine ve ayırma performansına etkisi gözlemlenmiş ve etanolden kurutma en iyi şart olarak belirlenmiştir. Deasetilasyon ve tavlamanın selüloz asetat membranların ayırma performansına etkisini incelemek amacıyla Bromothymol Blue (624 Da)-ethanol çözeltisi kullanılarak filtrasyon testleri yapılmıştır. Tavlanan selüloz asetat

membranların boya tutma oranı 80% iken bu değer deasetilasyondan sonra düşmüştür.

Kovuklu elyaf membranlar kullanılarak yapılan membran modülleri düz tabaka membranlara kıyasla daha yüksek yüzey alanına sahiplerdir. OÇN uygulamaları için selüloz kovuklu elyaf membranların üretimi önemli yere sahiptir. Bu çalışmada OÇN uygulamaları için selüloz ve rejenere selüloz kovuklu elyaf membranlar üretilmiştir. Polimer çözeltisi, kovuk sıvısı ve koagülasyon banyosu sıcaklığı değiştirilerek kovuklu elyafların seçici tabakası düzenlenmiştir. Ayırma performansı amacıyla Bromothymol Blue (624 Da) tutuculuğuyla test edilmiştir.

Selüloz membranlarla bir çözücü geri kazanımı uygulaması olarak tavllanmış ve rejenere edilmiş membranlar, aprotik çözücüleri 1 g/L ve 10 g/L PES çözeltilerinden geri kazanmak için kullanıldı. Deneyler 10 bar ve 40 barda DMSO, NMP ve DMF'de yapıldı. Tavllanmış ve rejenere edilmiş selüloz membranlar, tüm solventlerde yaklaşık olarak 99% PES tutma oranına gösterdiler. Ayrıca, bu membranlar DMSO'da 10 gün boyunca, NMP ve DMF'de 25 gün boyunca stabil kaldı.

Anahtar Kelimeler: Organik çözücü nanofiltrasyonu, selüloz, alkaline hidrolizi

To My Family and Friends

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LIST OF ABBREVIATIONS

ABBREVIATIONS

NF	: Nanofiltration
OSN	: Organic Solvent Nanofiltration
OSU	: Organic Solvent Ultrafiltration
ISA	: Integrally Skinned Asymmetric
TFC	: Thin Film Composite
MWCO	: Molecular Weight Cut Off
PSP	: Pure Solvent Permeance
TMP	: Trans Membrane Pressure
[EMIM]OAc	: 1-ethyl-3-methylimidazolium acetate
DMSO	: Dimethyl sulfoxide
NMP	: N-methyl pyrrolidone
DMF	: N, N-dimethylformamide
BTB	: Bromothymol Blue
PES	: Polyether sulfone
NaOH	: Sodium Hydroxide
AA	: Acetic Acid
ChOH	: Choline Hydroxide
ChAc	: Choline Acetate
SEM	: Scanning Electron Microscope
UV	: Ultraviolet
FTIR	: Fourier Transform Infrared Spectroscopy
Da	: Dalton
μm	:Micrometer
nm	:Nanometer

CHAPTER 1

INTRODUCTION

Separation processes are widely used in the pharmaceutical and chemical industries to concentrate or purify chemicals and pharmaceuticals, exchange and recycle solvents. The costs of separation processes have crucial role as they constitute 40-70% of both capital and operating costs (Marchetti, 2017). For this reason separation processes have to be elaborated to satisfy both cost effective and efficient separation performance. By comparing with conventional separation techniques such as distillation, crystallization and extraction, membrane processes have advantages which are low energy and chemical requirements, low operation temperature, easy installation and scaling up. Although membrane processes provide efficient and eco-friendly separation, there are some drawbacks such as fouling, short lifetime, low selectivity, low permeance and chemical incompatibilities with operating solvent. Selection of appropriate membrane material and optimization of selectivity and permeability are important for filtration applications.

A membrane is a selectively permeable barrier which permeates certain species in a mixture faster than others under a driving force and transportation of other species through the membrane is slow or hindered. As seen in the Figure 1.1, the feed stream is separated into the retentate stream in which species retained by the membrane are collected and the permeate stream in which species passing through the membrane are collected.

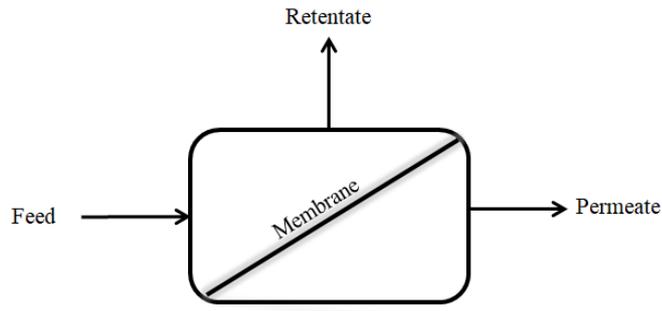


Figure 1.1. Schematic of Membrane System

According to pore size of membrane or size of rejected species, there are four main groups of membrane filtration processes, driven by pressure difference between feed and permeate, which are ultrafiltration, microfiltration, nanofiltration and reverse osmosis. Typical groups of retained solutes by each process are illustrated in the Figure 1.2.

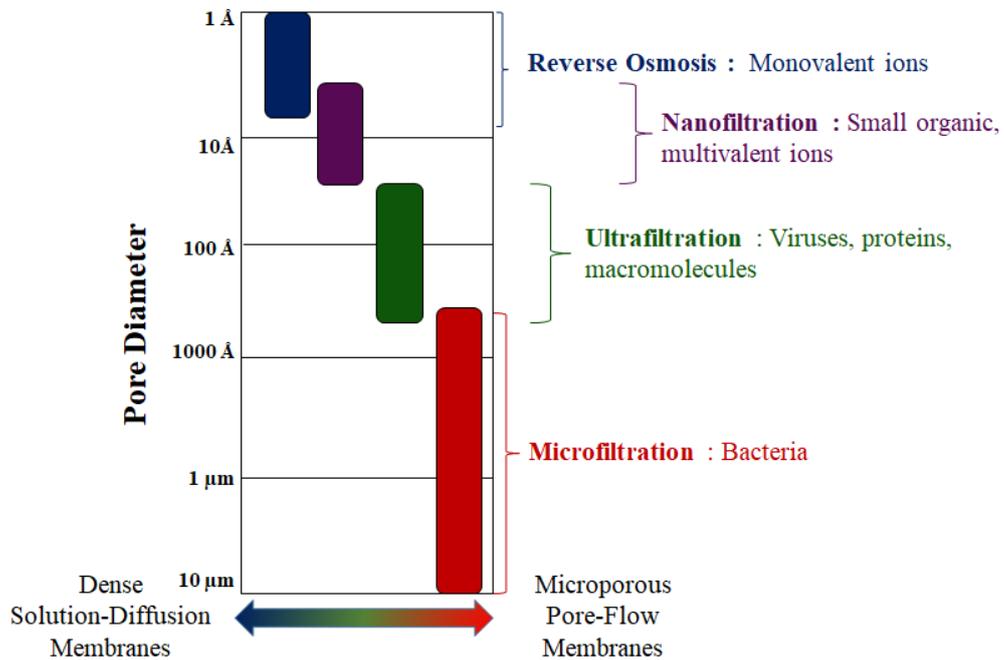


Figure 1.2. Classification of membrane processes according to retained solutes with different size

In order to explain separation mechanism, there are two models which are pore flow model and solution diffusion model. Separation mechanism of ultrafiltration and microfiltration membranes can be expressed by pore flow theory. In pore flow mechanism, membrane has a porous structure and separation occurs by size exclusion. Species which have smaller diameter than pore diameter of membrane permeate through the membrane due to pressure gradient across the membrane. Also, species which have similar diameter with pore diameter of membrane can be partially rejected. Larger species are rejected by membrane or captured in the membrane depending on pore structure. microfiltration and ultrafiltration membranes are classified as screen filters and depth filters. If a membrane has pores on the membrane surface and these pore are small enough to reject the particles, it is called as screen filter. Otherwise if particles are captured in the membrane; membrane is called as depth filter.

Membranes used in microfiltration processes are porous and separate particles above 0.1 μm in diameter such as bacteria and suspended solids. In order to reject colloids, viruses and dissolved macromolecules such as proteins, which are within range of 2-100 nm, ultrafiltration membranes are used.

In solution diffusion mechanism, separation occurs due to solubility and diffusivity difference of species in the membrane. Species dissolve in the membrane and diffuse at different rates from feed side to permeate side. The product of solubility and diffusivity of a species in the membrane is the species' permeability. The interactions between solute, solvent and membrane materials such as swelling of membrane in the solvent, sorption of solute in membrane, charges of solute and membrane are parameters that affect species' permeability.

Separation mechanism of reverse osmosis is characterized by solution diffusion mechanism. In order to desalinate seawater or groundwater, reverse osmosis membranes which have nonporous structure are commonly used. Nanofiltration membranes have characteristics of both pore flow model and solution diffusion

model. Therefore, during nanofiltration, species can pass through the pores by pressure gradient as in pore flow mechanism or species can dissolve in membrane and diffuse to permeate side by concentration gradient as in solution diffusion mechanism (Baker, R.W, 2004).

1.1. Nanofiltration

Nanofiltration term was firstly used to define the reverse osmosis processes in which ionic solutes in feed partially permeated through the membrane cross section. In the first NF membrane application of in nonaqueous media, cellulose acetate membrane was used and hydrocarbon solvents were separated. This innovation started by Sourirajan and his colleagues, was continued with separation of organic solvents mixtures during nearly two decades. Industrial developments which are applied by major chemical companies such as Union Carbide and oil companies such as Shell and Exxon increased interest on membrane applications with organic solvents. The first large scale industrial success was the WAX-DEWAX process which was founded at Exxon Mobil refinery by aiming to recover dewaxing solvents.

Organic solvents are frequently used as raw materials, cleaning agents and reaction media for products in industry. Organic syntheses are mostly performed in organic solvent media which contain valuable products and reactants. For all cases, it is very essential that, organic solvents have to be recovered at the end of all processes. Separation and recovery costs of organic solvents form an important part of operational expenses. At that point, membranes come into consideration as effective and cost-efficient separation method (Marchetti, 2014). Due to its low energy requirement, providing continuous and efficient separation quality, membrane separation have a good position in competition with conventional separation techniques (Priske, 2015). In the literature, there are several studies which are focused on organic solvent filtration for petrochemistry applications (White,2006; Tarleton,2009; Namvar-Mahboub, 2014), food and bioproduct application (Subramanian, 2001; Stafie, 2004; Tres, 2009) pharmaceutical applications (Sheth,

2003; Shi, 2006; Kim, 2014) and catalyst recovery applications (Scarpello, 2002; Luthra, 2002; Van der Gryp, 2010; Peddie, 2017).

Generally commercial membranes and polymeric membranes were used in these studies. Post treatments are necessary for most of the polymeric membranes to enhance stability. The development of new membrane materials is needed to generate more stable membranes having high rejections and permeabilities in organic solvents.

1.2. Membrane Filtration in Organic Solvents

Membrane material plays a crucial role in membrane performance. Therefore selection of which materials will be used is one the most important decision for membrane performance. Polymeric membranes are commonly used for membrane filtration applications in organic solvents. These applications require chemically stable membranes. Although ceramic membranes meet these requirements due to their chemical, thermal and mechanical stability and not swelling in organic solvents, there are major drawbacks. By comparing with polymeric membranes, ceramic membranes have high cost, brittle structure. Due to their flexible structure and lower cost, polymeric membranes are preferred in organic solvent applications as well as other applications. Polymeric membranes are divided into two groups which are integrally skinned asymmetric (ISA) membranes and thin film composite (TFC) membranes. Phase inversion method is used to produce the integrally skinned asymmetric membranes (Kim, 2002; Vanherck, 2010; Hwang, 2012). This method was developed by Loeb and Sourirajan (Loeb, 1963). The temperature change, evaporation of volatile solvent from cast polymer solution or immersion of cast polymer film into nonsolvent can induce phase inversion. According to non-solvent induced phase inversion technique, cast polymer solution is immersed in a nonsolvent bath which consists of commonly water. While immersing in water, polymer solution loses solvent and water as nonsolvent diffuses into the polymer solution and polymer solution composition moves into two phase region on the

ternary phase diagram (Figure 1.3). In the two phase region polymer solution is not thermodynamically stable and it is separated into two phases which are polymer rich phase and polymer lean phase. Membrane matrix is generated from polymer rich phase and polymer lean phase creates pores of membranes. By changing casting solution polymer to solvent ratio, coagulation bath temperature and content, evaporating volatile nonsolvent in casting solution before phase inversion and adding additives to regulate pore size membranes which have different morphologies are obtained (Baker, R.W,2004).

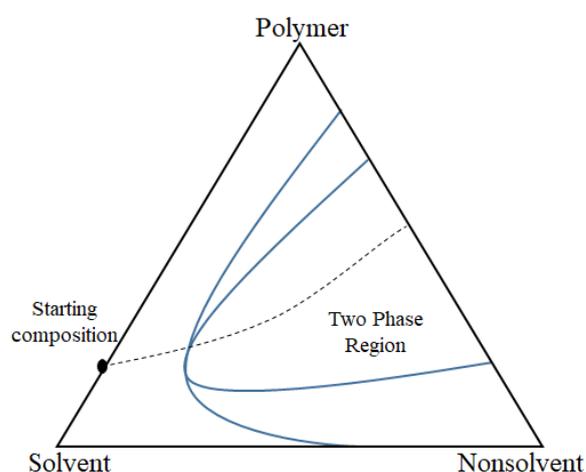


Figure 1.3. Ternary phase diagram for polymer-solvent-nonsolvent system

Integrally skinned asymmetric membranes have a selective dense top layer and porous support layer which are produced from the same polymer. In order to prepare ISA membranes for membrane filtration applications in organic solvents, chemically stable polymers are used or post treatments are done to enhance polymer stability in solvent (Marchetti, 2014).

Zhang et. al. produced integrally skinned polyetherimide(PEI) asymmetric nanofiltration membrane. They tested membrane performance with methylene blue-

ethanol mixture. Rejection of methylene blue (373 Da) increased with addition of 2 % polyvinyl pyrrolidone (PVP) additive from 80% to 95%. PEI membrane with 8% PVP additive is stable in common solvents which are ethanol, isopropyl alcohol , carbon tetrachloride and hexane and have high dye rejection (97%) in ethanol medium by comparing with commercial solvent resistant nanofiltration membranes(Zhang, Y., 2017). Polysulfone(PSf) membranes which were produced by Holda et al. were stable at isopropanol with 92% Rose Bengal rejection (Holda, 2013).

Polyimide(PI) is commonly studied polymer in the literature to produce ISA membranes and use in OSN applications (White, 2002; Vandezande, 2005). DuraMem Membranes and Starmem Membranes are the most used commercial crosslinked PI membranes (Vanherck, 2013). However, these polymeric membranes are not resistant to harsh solvent medium. In order to enhance stability of polymeric membranes in harsh solvents such as DMSO, n-methyl pyrrolidone(NMP), dimethyl formamide(DMF), tetrahydrofuran(THF) , post treatment is needed. Crosslinking is an effective method to provide chemical stability to membrane. In chemical crosslinking method, several chemicals are used to crosslink membrane polymer. Vanherck et. al used a 10 wt./vol.% methanolic solution of p-xylylenediamine to crosslinked PI membrane. See Toh et. al crosslinked integrally skinned PI membrane by using different aliphatic diamines as crosslinker. Crosslinked PI membranes have resistance to many harsh organic solvents have good separation performance in DMF (Varherck, 2008; See Toh, 2007).

Crosslinked polyvinylidene fluoride (PVDF) membranes in a methanol solution of 4.5 wt% of sodium hydroxide, 18.2 wt% of para-xylylenediamine and 9.1 wt% of magnesium oxide were tested in different solvents such as ethanol, iso-propanol, acetonitrile, DMF and toluene. Due to high affinity of aprotic solvents to PVDF, after immersing the membrane in DMF for 5 days, weight loss was calculated as 7%. Crosslinked membranes were dried form methanol and their Rose Bengal rejection in DMF reached 78% approximately (Mertens, 2018).

Crosslinked polybenzimidazole(PBI) membranes with dibromoxylene (DBX) and dibromobutane (DBB) are also resistant to extreme pH conditions and harsh organic solvents such as acetonitrile, DMF (Valtcheva, 2014). Crosslinked polybenzimidazole (PBI) and polyphenylsulfone (sPPSU) blend membranes have also good stability in THF and DMF. These membranes were produced by mixing sPPSU and PBI when preparing polymer solution. Then double crosslinking were performed by using α,α' -dibromo-p-xylene (DBX) and hyperbranched polyethylenimine (HPEI). Crosslinking with DBX improved solvent stability while HPEI restricted pore size. Tetracycline (444 Da) rejection of these membranes in DMF was 66% and in acetone was 81%. (Asadi Tashvigh, 2018).

The crosslinking is also done by UV radiation method or thermal treatment. The produced UV crosslinked PSf membranes have 96% Rose Bengal rejection in isopropyl alcohol (Strużyńska-Piron, 2014). Stability of PAN membranes was improved after thermally crosslinking with air at 180°C. However, flux decline occurs due to reducing membrane porosity during thermally crosslinking (Lim 2017). The spiral wound modules were prepared by chemically and thermally crosslinked PAN membranes which were stable in acetone, THF and DMF (Sairam, 2010).

Da Silva Burgal et. al dissolved native poly(ether ether ketone) (PEEK) with methanesulphonic acid and sulphuric acid to fabricate membrane via phase inversion. PEEK is a solvent-resistant polymer which does not dissolve in common organic solvents, including polar aprotic. In this study a strongly acidic medium was used to dissolve it for the fabrication of solvent-resistant membranes. Resulting PEEK membrane have resistant to DMF and THF, high and low pH conditions and high temperatures (Da Silva Burgal, 2015).

The second group of polymeric membranes for membrane filtration in organic solvents is thin film composite(TFC) membranes. These membranes consist of thin selective layer and porous support layer which is produced by mainly phase

inversion. Solvent resistant polymers such as polyether sulfone (PES), PAN, PVDF and PI are used as support layer. Thin selective top layer is produced by interfacial polymerization or coating porous layer. Polyimide membranes that are chemically crosslinked and have improved separation performances via solvent activation are commonly used to produce TFC membranes for OSN applications. Jimenez Solomon et al. observed that these membranes were stable in DMF and after solvent activation, separation performance of crosslinked PI TFC membrane was improved (Jimenez Solomon, 2012). In addition to solvent activation, Li et al also immersed PI membrane in Dopamine solution before interfacial polymerization to enhance separation performance. Their membranes were stable at NMP and DMF during two weeks (Li, 2018)

Peinemann group used crosslinked PAN membranes with hydrazine hydrate solution (Pérez-Manríquez, 2015) and crosslinked polythiosemicarbazide (PTSC) membranes with α,α -dibromo-*p*-xylene (DBX) in acetone (Aburabie, 2015) to fabricate TFC OSN membranes. These membranes were resistant to harsh solvents and showed high separation performance. Solvent stability of PAN membrane was tested in DMF and PTSC membrane was tested in DMF, THF, DMSO, DMAc and NMP.

Consequently, polymeric membranes are mainly used for OSN applications due to their easy scaling up and variety of available polymeric material. However, polymeric membranes require post-treatment such as thermal annealing and crosslinking in order to be robust in harsh solvents and have sufficient separation quality. These additional steps that take place after membrane fabrication requires energy and high amount of chemical usage as well as increasing fabrication time of solvent resistant membrane. There is a high demand for polymeric OSN membranes which are fabricated without any post-treatment.

Generally solvent resistant membranes are used for organic solvent nanofiltration applications. Besides nanofiltration applications solvent resistant membranes can be also used in ultrafiltration applications for recovery of organic solvents. In

photolithography organic solvents are used as cleaning agents to remove uncrosslinked polymers and photoresists. In polymer synthesis applications organic solvents perform as reaction media and contain both polymers and monomers. Also there are other applications in which organic solvents are contaminated with polymers such as their use in removal of polymer coatings. These solvents can be recovered by separating them from the polymer or polymer-solvent mixture can be concentrated depending on requirements by using solvent resistant membranes. Development of solvent resistant membranes may provide an efficient way to separate molecules in ultrafiltration range.

1.3. Separation and Transport Mechanism in Organic Solvent Nanofiltration

Separation performance is related with transport mechanism of solvent and solute through membrane. For organic solvent nanofiltration because membranes may be both porous and nonporous or a combination of them, two transport models must be considered: pore flow mechanism and solution diffusion mechanism. In pore flow mechanism, solutes which have smaller size than pores of membrane pass through to permeate side with solvent. Pore flow mechanism works as a sieving process and feed viscosity, membrane pore size affect separation performance. In solution diffusion mechanism, solvent and solute pass through membrane via free volume elements which are located in between polymer chains. The interactions between solute, solvent and membrane affect separation performance of membrane. In nonaqueous systems, because transport mechanisms may be more complex depending on the solvent property, these interactions construct limitations of membrane separation performance. In the literature, there are many studies on solute, solvent and membrane interactions in nonaqueous systems.

Yang et al examined effect of solvent medium on hydrophilic membrane performance by using dyes with same molecular weights (350 Da) and different charges (negatively charged Orange II, positively charged Safranin O, and neutral Solvent Blue 35). Orange II and Safranin O had high rejection in aqueous medium around 100%. Then these three dyes were tested by both hydrophilic membrane and hydrophobic membrane in methanol medium. In methanol, Orange II and Safranin O had 90% rejection and Solvent Blue 35 had 80% rejection approximately in both hydrophilic and hydrophobic membranes. For hydrophobic membrane, Neutral dye Solvent Blue 35 rejection in ethyl acetate were lower than Solvent Blue 35 rejection in methanol and toluene. For hydrophilic membrane the lowest Solvent Blue 35 rejection was observed in toluene. The reason of higher rejection is attributed to enlargement of solute molecules size because of complexation of solvent with solutes. By taking into account sieve effect, increasing solute size in water is a reasonable explanation for higher rejection in water. Also, solvent Blue

35, which is a neutral dye, has lower rejection than other two dyes in methanol. The rejections of Orange II and Safranin O were similar in methanol medium in both positively charged and negatively charged membranes (Yang, X., 2001). Different transport mechanism may take place in organic solvent systems. They stated that in order to explain this mechanism changing interactions between membrane, solvent and solute should be evaluated.

Effective molecular size of solute varies in different solvents due to solute-solvent interactions. If filtration is performed with the solvent in which solute has higher effective molecular size, higher rejection values are obtained as a result of size exclusion. Geens et al. proved that by calculating effective molecular sizes of different solutes and observing higher rejections with larger solutes in both methanol and ethanol. However there were some exceptions. Although Victoria Blue has smaller effective molecular size, its rejection was higher than the rejection of Vitamin E. The highest rejection value belonged to solute with smallest molecular size which was Erythroine B. They stated that, as well as solvent-solute interactions which change effective molecular size of solute, separation mechanism is also affected by solvent-membrane and solute-membranes interactions (Geens, 2005).

Solvent affinity to membrane is another determining parameter of membranes performance. As solvent affinity to the membrane increases, it has been observed that in several studies that transportation of solvent occurs more easily than solute that results in high rejection of solute and high permeance of solvent. Soltane et al. used five different solvent such as Toluene, DMC, hexane, heptane, ethanol to investigate the effect of affinities of solvent and membrane on membrane performance. Although membrane- solvent affinity was close to hexane and heptane in which Sudan Blue has positive rejection, negative rejection was observed in ethanol. The reason was explained as preferred transportation of solute because ethanol affinity to membrane was lower than ethanol affinity to Sudan Blue. Also solute affinity to solvent is a significant factor for membrane performance. In hexane and heptane due to solute having a similar affinity for both solvent and

membrane, rejections were very close. The highest Sudan Blue rejections were observed in Toluene and DMC due to higher affinity of solute to solvent than membrane. It was concluded that as stability of solvent-solute mixture increases, less solute transports through the membrane and rejection increases. (Soltane, 2016)

Bhanushali et al. worked with Sudan IV (neutral, 384 Da) and observed interactions of solute dye in between membrane in polar and nonpolar medium. Composite dimethyl silicone NF membrane had dye rejection about 25% in nonpolar solvent which was hexane. However, in polar solvent, ethanol and methanol, Sudan IV rejection had negative values with the same hydrophobic membrane which were explained by high affinity of solute to the membrane and consequently solute transport through the membrane was more preferential. By using a hydrophilic aromatic polyamide based membrane, 86% and 43% dye rejection was obtained in respectively methanol and hexane medium. Flux of polar solvent was higher through the hydrophilic membrane, as expected. (Bhanushali, D., 2002).

These studies show that besides size exclusion of solute molecules, affinities of solute-solvent-membrane, effect of polarity, charge and swelling which occur due to solute, solvent and membrane interactions are effective in membrane separation in organic solvents.

1.4. Hollow Fiber Membranes for Organic Solvent Nanofiltration

Hollow fiber membrane has an important advantage over flat sheet membranes because membrane modules which are prepared by hollow fiber membranes have very high surface areas. Hollow fibers are produced by the help of spinneret in which bore liquid passes through the capillary tube at the inside and polymer solution passes through the outside of capillary tube. The image and schematic of spinneret is given in Figure 1.4. The first spinneret was designed by Henry I. Mahon at Dow Company. Since first contributions of Mahon and the group at Dow Chemical in 1966, hollow fiber membranes made progress and they are used almost

in every application field. Hollow fibers are fabricated by two methods which are wet spinning and dry-wet spinning. If hollow fibers directly enter a coagulation bath which contains nonsolvent, this process is called as wet spinning. If a polymer solution which is extruded from the spinneret, is exposed to a certain air gap before entering into a coagulation bath, this process is called as dry-wet spinning. (Baker, R.W,2004)

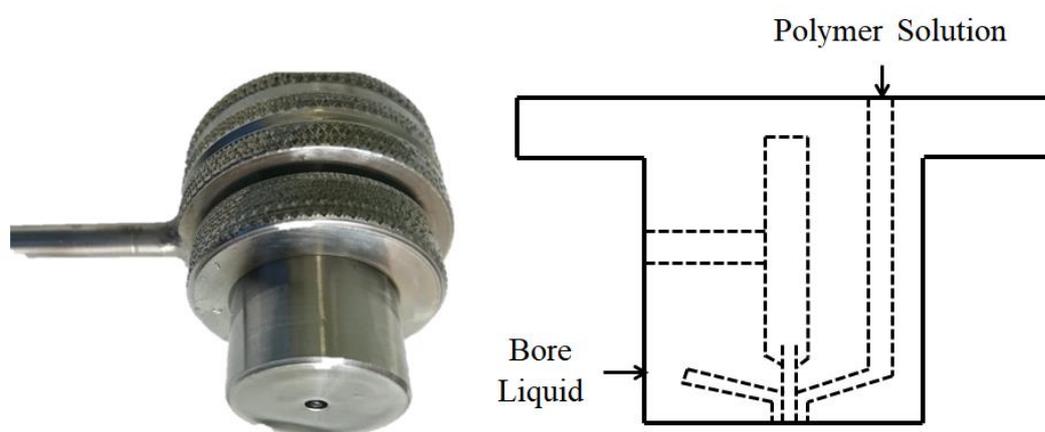


Figure 1.4. Image and schematic of spinneret

In the literature, there are several studies on hollow fibers for OSN applications. The first reported TFC hollow fiber membranes for OSN were polypropylene (PP) hollow fiber membranes. Kosaraju et al used microporous PP hollow fiber to produce TFC nanofiltration membranes by interfacial polymerization. These membranes had 88% Brilliant Blue R rejection in methanol (Kosaraju, 2008).

Loh et. al fabricated PAN hollow fiber membranes by using maleic acid doped PAN, NMP and 4-methylpiperidine solution. After thermally crosslinking fibers at 180 °C for 1 h they were stable in acetone, methanol, THF and DMF. MWCO of crosslinked fibers was found as 350 g mol⁻¹ approximately (Loh, 2008).

Darvishmanesh et al. produced nanoporous hollow fiber membrane via dry wet spinning by using a chemically stable polymer which is polyphenylsulfone (PPSf) as

membrane polymer. As polymer concentration in dope solution increases, maximum pore size decreased and increased dye rejection. Hollow fiber membranes had 98% Rose Bengal and 73% Bromothyl Blue rejection in isopropanol medium. They were stable in methanol, ethanol, n-hexane, isopropanol and n-heptane (Darvishmanesh, S., 2011).

Dutczak et. al combined hollow fiber fabrication with chemical crosslinking with the help of a triple orifice spinneret. PI, NMP and glycerol were used in the dope solution. Poly(ethylene imine) (PEI), NMP and water were used as bore liquid and NMP-water mixture was used as shell liquid. PEI functioned as crosslinker. External coagulant was water. The stability of crosslinked hollow fibers was evaluated by immersing NMP for eleven days and it was observed that the most stable fiber lost 20% of its mass. The MWCO of produced organic solvent filtration membranes was 3000 Da in toluene (Dutczak, 2012).

Lim et. al used polyamide-imide (PAI), NMP and lithium chloride dope solution to produce PAI hollow fiber membranes by dry-jet wet spinning. PAI hollow fibers crosslinked with (3-aminopropyl)trimethoxysilane (APTMS). By adjusting dope solution composition, crosslinking time and temperature, Rose Bengal rejection in DMF of crosslinked PAI hollow fibers reached 98% at 2 bar (Lim, 2016).

Tham et al. aimed to produce hollow fiber membranes which are resistant to operation conditions of organic solvent nanofiltration. Firstly they produced polyacrylonitrile(PAN) hollow fiber membranes in ultrafiltration range with minimum macrovoids. By adjusting polymer concentration, adding polymeric additive which prevents macrovoids formation and applying high take up speed, PAN hollow fibers with minimal macrovoids were produced. Then they crosslinked hollow fiber membranes by using a hydrazine monohydrate as cross linker to make them solvent resistant. They observed that as crosslinking time increases, pore size was getting smaller and more uniform pore size distribution was obtained.

Crosslinked hollow fibers were tested with Remazol Brilliant Blue R(626 Da) – ethanol solution and they performed excellent separation. (Tham, H.,2017)

Tashvigh et al. introduced a crosslink method in which wt 2% H₂SO₄ in isopropanol solution was used to enhance solvent stability of polybenzimidazole (PBI) hollow fiber membranes. This method did not require high temperature and high acid concentrations. After producing PBI hollow fibers by dry-jet wet-spinning method, they immersed in acid solution. Due to hydrogen bonds and proton transfer between PBI chain and sulphuric acid, strong network of polymer was formed. Hollow fibers with smaller pore size and high solvent resistance were obtained. Separation performances of these hollow fibers were evaluated with tetracycline/methanol and L- α -lecithin/hexane feed solutions. The rejection values of acid treated hollow fibers were higher than 98% (Asadi Tashvigh, A.,2019).

Poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA) PI hollow fiber membranes were obtained with chemical imidization of produced PMDA-ODA polyamic acid (PAA) hollow fiber membranes. These membrane have 96.7% Rose Bengal rejection in DMF(Li,2019).

The development of new methods and use of solvent resistant polymers to produce hollow fiber membranes for OSN applications will have great contribution to limited source in the literature.

1.5. Cellulose Membranes for Organic Solvent Nanofiltration

Cellulose is the most commonly found polymer in nature. Due to strong hydrogen bonds in its structure, cellulose does not dissolve in ordinary solvents. This property of cellulose makes it a favorable alternative membrane material for filtrations in organic solvents. In order to prepare polymer solution for membrane casting, cellulose has to be dissolved in a solvent. In 2002, Rogers' group stated that by using chloride containing ionic liquids cellulose can be dissolved up to 25% wt without derivatizing the cellulose (Swatloski, R. P, 2002). After this study, cellulose was

shown to dissolve in many other ionic liquids. Molten salts which are in liquid form below 100 °C are called ionic liquids. Vitz et al, investigated a wide range of ionic liquids from the point of the ability of dissolving cellulose. Among the various ionic liquids, ones with chloride, phosphate and acetate counter anions dissolved cellulose the most efficiently. (Vitz, J., 2009) In the literature, there are a few studies on fabrication of membranes by using cellulose solutions in ionic liquids.

Li et. al used 1-allyl-3-methylimidazolium chloride (AMIMCl), to prepare 8 wt% cellulose solution. They fabricated cellulose NF membranes by phase inversion. Although there was no significant change in chemical structure, the crystallinity of cellulose decreased after membrane production. Due to dense layer and no macrovoids in the membrane matrix, cellulose membranes have high dye rejections in water. Membrane was tested by using aqueous solutions of dyes with different size such as Brilliant Blue R (826 Da) and Congo Red (697 Da), and Methyl Orange (327 Da) and it was seen that membrane was able to reject the species which have molecular weight less than 700 Da. (Li, X.,2011)

Livazovic et. al reported cellulose multilayer membranes which were produced by interfacial polymerization on a cellulose support membrane. Support layer were produced with two different approaches. First approach was dip coating of an asymmetric porous membrane with dissolved silylated cellulose in THF. Hydrochloric acid was used to regenerate cellulose. Second approach was producing cellulose membrane with phase inversion by casting cellulose solution on asymmetric porous support. Cellulose solution was prepared by dissolving cellulose in ionic liquid, 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc). Then TFC membranes were produced by interfacial polymerization of selective polyamide layer. These membranes have MWCO in nanofiltration range. They also tested stability of cellulose coatings by immersing them into THF, hexane, DMF, NMP and DMAc. As a result, cellulose membranes were insoluble in these solvents (Livazovic, 2015).

Çulfaz-Emecen group produced cellulose membranes by phase inversion method for organic solvent nanofiltration applications. Durmaz et. al used DMSO as cosolvent and [EMIM]OAc as solvent and prepared dope solutions containing 8% cellulose. These membranes had dense and symmetric structure. While dried membranes have high dye rejection, dye rejection of non-dried membranes decreased with increasing DMSO composition in polymer solution (Durmaz, 2018). Sukma et. al used [EMIM]OAc as solvent and acetone as cosolvent. As evaporating acetone which was volatile solvent or raising cellulose concentration in the casting solution, dye retention of cellulose membrane increased. Depending on charge of dye molecules, their rejection changed due to changing affinity to membrane. The highest rejection of a neutral dye, Bromothymol Blue (BTB, 624 Da), was found as 94% by using a dried membrane poured from a polymer solution containing 20 wt% cellulose in [EMIM]OAc. With no need for additional crosslinking steps; these cellulose membranes were stable in even aprotic solvents (Sukma, F., 2018). Konca et. al evaluated the interaction between cellulose membranes and solute with three different dyes with varying size and charges. By comparing rejections of three different dyes in ethanol and DMSO, it was observed that molecular size of solute was not the only parameter to identify separation performance of cellulose membrane but also charge of solute and membrane and their interactions were determining parameters. After crosslinking of cellulose membranes with a polycarboxylic acid, interaction between membrane and solute was changed due to adding groups on membrane which affect membrane charge. They also showed that cellulose membranes were stable in acetone, ethyl acetate, hexane, toluene, THF and NMP (Konca, 2019). The summary of these studies are given in Table 1.1.

There are limited number of studies for cellulose hollow fiber membranes. Ma et. al dissolved bamboo pulp by using 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) as solvent and Dimethylsulfoxide (DMSO) as cosolvent to arrange viscosity of solution and fabricated hollow fiber membranes by dry wet spinning technique. Hollow fibers had porous cross section; however due to surface of hollow fibers

were dense, retention of bovine serum albumin was 98% (Ma, B.,2013). Falca et. al recently fabricated cellulose hollow fiber membranes by using there different ionic liquids which were [EMIM][Ac], 1,3-dimethylimidazolium dimethyl phosphate ([DMIM][DMP]), 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM][DEP]), 1-ethyl-3-methylimidazolium chloride ([EMIM][Cl]) to dissolve cellulose. Water was used as bore liquid and external coagulant. Hollow fibers that prepared by using [EMIM][DEP] and [DMIM][DMP] have 90% rejection of negatively charged dye Congo Red(696 Da) in ethanol. Also membranes prepared by using [DMIM][DMP] were stable in THF, NMP, and DMF while membranes prepared by using [EMIM][DEP] and [EMIM][Ac] were partially stable (Falca, 2019).

Peinemann group worked on cellulose composite membranes for OSN. They dissolved 12.5% cellulose in [EMIM]OAc and produced cellulose support layer by NIPS method. Then composite membranes were produced by interfacial polymerization between terephthaloyl chloride(TPC) and catechin(Abdellah, 2018) or quercetin(Abdellah, 2018). MWCO of catechin/cellulose and quercetin/cellulose composite membranes were 500 Da and 330 Da in DMF, respectively.

Anokhina et. al also studied on cellulose composite membranes (Table 1.1.). It is known that monohydrate form of N-methylmorpholine-N-oxide (MMO) can dissolve cellulose up to 13%. In order to prepare membrane casting solution containing 12 % cellulose, MMO in monohydrate form is used. Composite membrane was produced by casting this solution on polyester support with the help of laminator bar and coagulating in 40% MMO-water solution. Composite membranes were tested by using Orange II(350 Da) and Remazol Brilliant Blue R (650 Da) as solute and acetone, THF, DMF, NMP and DMSO as solvent. The highest separation quality were achieved in DMSO systems as 85% rejection of Orange IIand 93% rejection of Remazol Brilliant Blue R with 0.098 L/(h.m².bar) permeance value. Solvent that swells up membrane more, such as DMSO, NMP and DMF, caused a decrease in pore size of cellulose composite membrane. They stated that separation performance of membrane was affected by the interaction between

membrane and solvent (Anokhina, 2016). Then they dissolved the cellulose in [Emim]OAc and DMSO mixture and produced composite membranes. They observed that as cellulose concentration in the [Emim]OAc-DMSO mixture increased from 6 to 16 wt %, Remazol Brilliant Blue R rejection increases from 42% to 82% (Anokhina, 2017). This group also studied on delamination problem of cellulose layer from the support after DMF filtration. Firstly, polyester support was etched by using a chlorinating agent before cellulose layer casting. However this method could not prevent detachment of cellulose layer. Secondly, post treatments were done by precipitating produced composite membranes in 20% glycerol-water solution. Although this method prevented adhesive failure, separation performance was worsening after post treatments (8% 51% Remazol Brilliant Blue R rejection in DMF). Immersing the composite membrane in ethanol and hexane was tried and this post treatment method was chosen as optimal method due to ensure both a strong composite membrane and 51% Remazol Brilliant Blue R rejection in DMF (Anokhina, 2018). In Table 1.1., results are summarized.

Table 1.1. *Cellulose membranes in the literature*

Reference	Fabrication Technique	Performance			
		Solvent	Solvent Permeance (L/h.m ² .bar)	Probe	Rejection
Sukma et al., 2018	Phase Inversion	Ethanol	0.3	Bromothymol Blue	94%
Durmaz et al., 2018	Phase Inversion	Ethanol	0.2	Bromothymol Blue	80%
Konca et al., 2019	Phase Inversion	DMSO	0.067	Rose Bengal	93%
Anokhina et al., 2016	Composite Membrane	DMSO	0.098	Orange II	85%
				Remazol Brilliant Blue R	93%
Anokhina et al., 2017	Composite Membrane	DMSO	0.21	Remazol Brilliant Blue R	82%
Anokhina et al., 2018	Composite Membrane	DMF	0.28	Remazol Brilliant Blue R	51%

In the light of these literature data, our aim is to produce cellulose and cellulose acetate based flat sheet and hollow fiber membranes and to apply organic solvent filtrations.

1.6. Regenerated Cellulose Membranes by Alkaline Hydrolysis of Cellulose Acetate Membranes

As an alternative way to produce cellulose membranes, cellulose acetate membranes can be regenerated to cellulose by deacetylation of cellulose acetate. Deacetylation is performed via alkaline hydrolysis. During regeneration process, acetate groups in cellulose acetate are removed. Regeneration mechanism by alkaline hydrolysis is shown in Figure 1.5. In this study, deacetylated cellulose membranes are called as regenerated cellulose membrane.

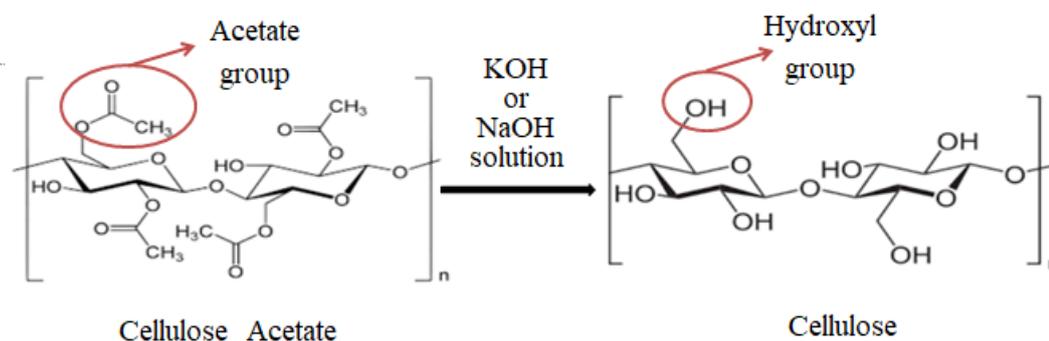


Figure 1.5. Schematic drawing of deacetylation mechanism

By this way, cellulose based membranes were produced with no need for ionic liquids which are expensive and highly viscous. Due to high viscosity of ionic liquids, processing of cellulose solution by using them is difficult. Regeneration method can be used in both flat sheet membranes and hollow fiber membranes. In literature there are a number of studies on regeneration of cellulose acetate to cellulose by alkaline hydrolysis. Firstly, cellulose acetate fibers were produced by electrospinning and then cellulose fibers were produced by deacetylation of cellulose acetate fibers in NaOH-ethanol, NaOH-water (Liu, H.,2002) and in KOH-ethanol

solution (Son, W. K., 2003). Regeneration quality was verified via the FTIR spectra by comparing the peaks represent hydroxyl bonds with the peaks represent acetate bonds.

In order to achieve high separation performance by cellulose acetate membranes for nanofiltration applications, selective layer of membrane has to be dense enough. The literature studies show that pore size of cellulose acetate membranes could be adjusted by thermal annealing. Free volume between polymer chains decreased during thermal annealing. Mahendran et al. observed annealing effect on BSA separation performance of a cellulose acetate –sulfonated polysulfone blend membrane. It was seen that rejection of BSA increased from 95% to 99% and 100% after annealing at 70 °C and 80 °C, respectively. (Mahendran, R., 2004) Su et al. stated that after annealing of cellulose acetate membranes, there were a significant decline in the pore size from 0.63 to 0.3 nm (Su, J., 2010).

1.7. Aim of the Study

Production of solvent resistant cellulose membranes by phase inversion for organic solvent filtration applications is the main objective of this study. Because cellulose is stable in many solvents; it is a good polymer choice as an organic solvent filtration membrane material. 1-ethyl-3-methylimidazolium acetate which is an ionic liquid was used to prepare cellulose solution. Membranes were produced in both flat sheet and hollow fiber membrane geometry and nanofiltration membrane performances were evaluated. Effects of polymer solution, bore liquid, coagulation bath temperature on hollow fiber morphology were evaluated. Alternatively, regenerated cellulose membranes were produced by alkaline hydrolysis of cellulose acetate membranes. By this way solvent resistant membranes were produced without ionic liquids. Progress of regeneration with respect to time and alkaline concentration was verified by FT-IR spectra. In order to improve membrane performance, regenerated membranes were annealed. Effects of regeneration and annealing on nanofiltration performance of flat sheet membranes were observed. Morphologies of cellulose

acetate membranes were investigated by SEM. Cellulose acetate hollow fibers were fabricated, effect of bore liquid on hollow fiber porosity were observed. By aiming recovery of solvents which are contaminated while they are functioning as cleaning agents or reaction medium, polymer filtration tests in aprotic solvents were performed with regenerated flat sheet cellulose membranes.

CHAPTER 2

EXPERIMENTAL METHODS

2.1. Materials

Cellulose (cotton linter from fibers, medium), cellulose acetate ($M_n \sim 50000$ Da by GPC), 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc, 95%), ethanol (99.9%), acetone (99%), hexane (95%), Bromothymol Blue (Neutral, 624 Da), sodium hydroxide (NaOH), were purchased from Sigma-Aldrich. N,N-dimethylformamide (DMF, 99.8%), N-methyl pyrrolidone (NMP, 99.5 %), dimethyl sulfoxide (DMSO, 99%) and acetic acid were purchased from Merck. Polyether sulfone (PES, Ultrason E6020P) was supplied by BASF. Choline hydroxide solutions 45wt% in methanol and 46% in water were supplied from Sigma-Aldrich.

Reverse osmosis water was used as non-solvent in coagulation medium and was used for membrane washing. Ultra-pure water (18.3 m Ω .cm) was used to prepare regeneration solution. All solvents and dye were used without any purification.

2.2. Solution Preparation

Before preparing solutions, cellulose was dried in oven at 80°C during 48 hours and cellulose acetate was dried under vacuum during 48 hours at room temperature. [EMIM]OAc was used to dissolve cellulose. Before using [EMIM]OAc to prepare cellulose solution, because impurities such as water reduce solubility of cellulose, they were removed by heating at 90°C for 1 hour and then at 70°C for three hours (Swatloski, 2002). Dimethyl sulfoxide and acetone were used without any pretreatment. In Table 2.1, polymers solutions and their concentrations are listed.

Table 2.1. *Polymer Solutions and Ingredients*

No	Polymer	Solvent	Co-solvent	Solvent/Co-solvent
C1	10.5% Cellulose	29.83% [EMIM]OAc	59.66 % DMSO	1:2
C2	12% Cellulose	63% [EMIM]OAc	25% Acetone	2.5:1
CA1	25% Cellulose Acetate	40% DMSO	35% Acetone	1.15:1
CA2	20% Cellulose Acetate	42.6% DMSO	37.3% Acetone	1.15:1
CA3	20% Cellulose Acetate	80% DMSO	-	-

2.3. Membrane Fabrication

Both flat sheet and hollow fiber membranes were produced by non-solvent induced phase inversion method.

2.3.1. Fabrication of Flat Sheet Membranes

Prepared membrane solution was poured on a clean glass plate and by using a casting bar, membrane was cast. For nanofiltration experiments casting thickness of membranes were 30 and 50 μm , for polymer filtration tests casting thickness was 250 μm . Membranes which were cast from solution containing acetone were put into evaporation bath under nitrogen flow for 30 minutes to remove acetone from cast membrane and to increase polymer-solvent ratio. Nitrogen in the evaporation bath had a flow rate of 0.6 L/min. This step was represented by Step 2 in the Figure 2.1. Then cast solution was immersed in a coagulation bath which contains water as non-solvent. After washing membrane with reverse osmosis water for 24 hours and getting rid of remaining solvent, membrane was transferred to a storage tank which contains ethanol. Membrane was used after drying with nitrogen. If there was no acetone in the membrane casting solution, Step 2 was skipped and cast solution was immediately immersed into coagulation bath. Then, other steps were applied with the same order.

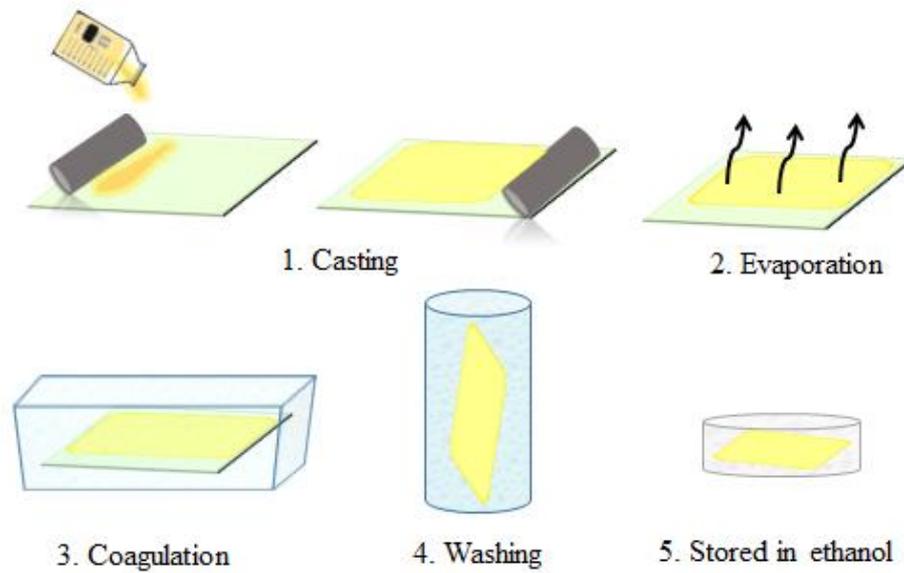


Figure 2.1. Schematic drawing of flat sheet membrane fabrication

2.3.1. Fabrication of Hollow Fibers Membranes

Hollow fiber membranes were produced by dry-wet spinning. A spinneret with 1.3 mm orifice diameter and 3 mm outer diameter was used. It was manufactured by FAYMER Makina, OSTİM, ANKARA. Spinning setup is shown in Figure 2.2. Polymer solution was poured into polymer solution tank one day before spinning to remove bubbles in the solution. At the spinning day, bore liquid tank and coagulation bath were filled. Flow rates of polymer solution and bore liquid were adjusted by separate gear pumps which were controlled with an electric panel. At target flow rates, polymer solution and bore were pumped to the spinneret and after a certain air gap, entered into coagulation bath which contains water as non-solvent. Air gap, polymer/bore liquid flow rate ratio and temperature of coagulation bath, compositions of polymer solution and bore liquid were changed and hollow fibers were fabricated at different conditions. After washing hollow fibers for 24 hours by changing water several times, they were stored in ethanol and they were dried before using in filtration tests.

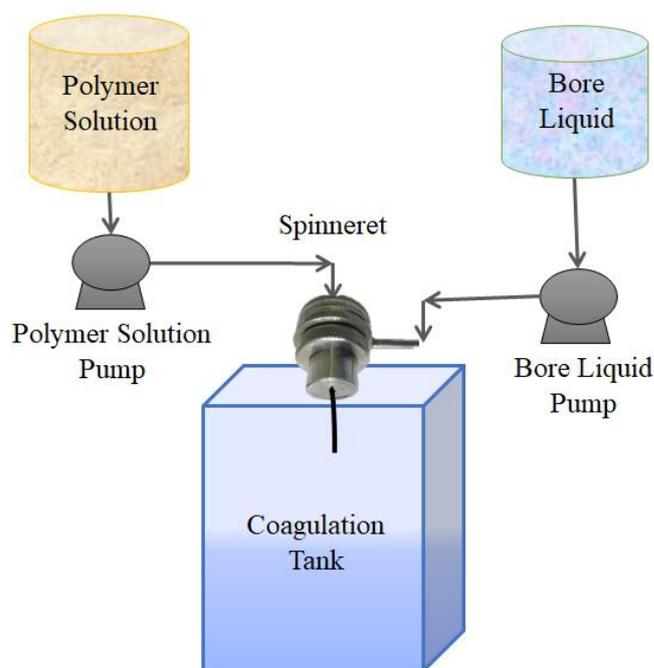


Figure 2.2. Spinning system schematic

Produced hollow fibers were classified into seven groups according to dope solutions, bore liquids and coagulation bath temperatures. Detailed spinning parameter such as air gap, polymer and bore solution flow rates and observations of fiber geometry are given in the appendix.

Table 2.2. Hollow fiber membrane groups

Group	Dope Solution	Bore Liquid	Coagulation Bath Temperature(°C)
A	C1	water	15
B	C1	%80 DMSO-water	15
C	C2	Emimac-DMSO;1:1	15
D	C1	water	50
E	C1	%80 DMSO-water	50
G	CA1	water	15
H	CA1	80% DMSO-water	15

2.4. Regeneration Procedure

In order to regenerate cellulose acetate membranes to cellulose, firstly, cellulose acetate membranes were produced either in flat sheet geometry or hollow fiber membrane geometry. After completing washing steps, cellulose acetate membrane was immersed in NaOH solution for certain time intervals. 0.05 M NaOH was dissolved in pure water or in 90% ethanol-water mixture. Then, the regenerated membrane was washed with reverse osmosis water for 24 hours. Produced regenerated cellulose membranes were stored in ethanol as all cellulose membranes, and they were dried before using. Fourier Transform Infrared Spectroscopy (FT-IR) (PerkinElmer UATR Two) measurements of cellulose acetate and regenerated cellulose membranes were done to verify regeneration was completed. Changing depending on decreasing acetyl groups and increasing hydroxyl groups was observed.

2.5. Annealing Procedure

Annealing of cellulose acetate membranes were done by two different procedures which are wet annealing and dry annealing. Wet annealing was done by immersing the membranes in hot water at 85°C for 3 hours. Wet annealing of cellulose acetate membranes were done at 85-90°C in the literature (Su, 2010; Han, 1995). After 3 hours, water bath taken out of heater and membranes were cooled in water at ambient conditions. Dry annealing was done in oven at 120°C for 6 hours. In the literature, dry annealing of cellulose acetate membranes were performed at 120 °C(Bhatt, 2015). Membranes firstly dried from ethanol and then dry annealing was done. After finishing dry annealing, membranes were cooled at ambient conditions. Different annealing and regeneration procedures were applied and nine different membranes were obtained. Produced membranes with different procedures and casting thickness are shown in Table 2.3.

Table 2.3. Membrane codes

Membrane Code	Casting Thickness	Wet Annealing (WA)	Dry Annealing (DA)	Regeneration Medium	Final membrane material
CA	50	-	-	not done	Cellulose Acetate
CA WA	50	+	-	not done	Cellulose Acetate
CA DA	50	-	+	not done	Cellulose Acetate
CA WA DA	50	+	+	not done	Cellulose acetate
CA RW	30	-	-	water	Cellulose
CA WA RW	50	+	-	water	Cellulose
CA DA RW	50	-	+	water	Cellulose
CA WA DA RW	50	+	+	water	Cellulose
CA RE	30	-	-	90% EtOH	Cellulose
CA WA RE	30	+	-	90% EtOH	Cellulose
CA DA RE	30	-	+	90% EtOH	Cellulose

2.6. Performance Tests

Filtration tests consist of pure solvent permeance and solute rejection tests.

2.6.1. Flat Sheet Membranes

Nanofiltration performance of flat sheet membranes were evaluated by dead end filtration of Bromothymol Blue (624 Da) solution in ethanol.

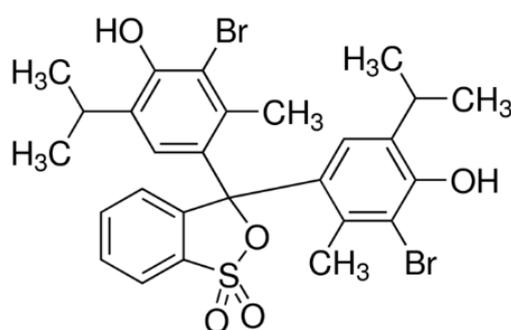


Figure 2.3. Chemical Structure of Bromothymol Blue

Amicon stirred cell of 10 ml or 50 ml volume were used with 250 rpm stirring to minimize concentration polarization during filtration. Stirred cell was pressurized by nitrogen and filtration experiments were performed at 4 bar. Schematic of dead end filtration cell is shown in Figure 2.4. Before the filtration experiment, pure solvent permeance of membrane was measured via solvent fluxes which were calculated in three different pressures. In the following equation PSP presents pure solvent permeance in L/ h.m². bar, J stands for solvent flux and transmembrane pressure is shown as TMP.

$$\text{Pure Solvent Permeance (L/hm}^2\text{bar)} = \left(\frac{J}{TMP} \right) \quad (1)$$

Concentration of permeate, feed and retentate samples were calculated by using absorbance data which were measured by UV-Vis Spectrophotometry (Schimadzu UV-1601) at 423 nm. Dye rejections were determined by following equation in which C_p , C_R and C_F represents concentration of permeate, retentate and feed respectively.

$$\text{Rejection \%} = \left(1 - \frac{C_p}{(C_F + C_R)/2} \right) \times 100 \quad (2)$$

Filtration experiments were continued until sorption of dye into membrane became zero and dye sorption were calculated by material balance which was given as;

$$\text{mmol dye sorbed in membrane} = C_F * V_F - \sum(C_P * V_P) - (C_R * V_R) \quad (3)$$

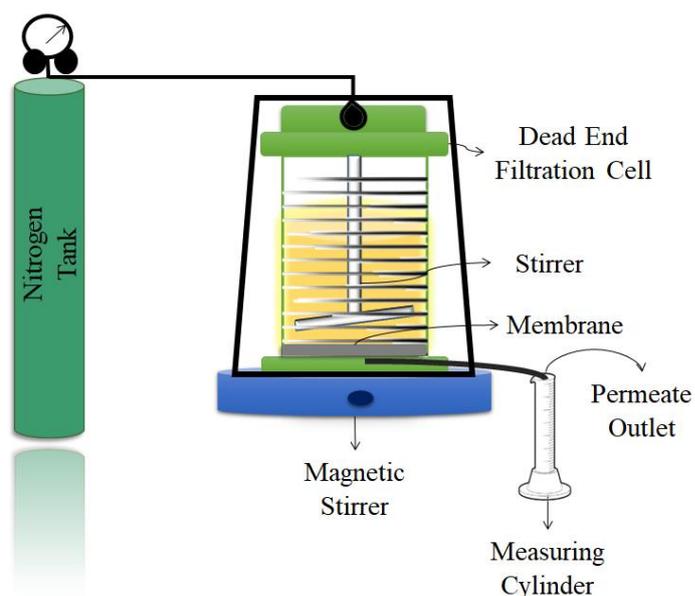


Figure 2.4. Schematic drawing of dead end filtration set-up

Experiments with aprotic solvents were performed by using HP4750 stirred cell of 300 ml volume in dead-end mode under stirring at 250 rpm. PES ($\bar{M}_w=55000$ Da) was used as solute which is rejected and three different solvent which are NMP, DMSO and DMF were used. Concentrations of permeates were calculated with the help of the UV-Vis Spectrophotometry. Measurements were done at different wavelengths for each solvent; 276 and 290 nm for NMP, 297 nm for DMSO and 276 nm for DMF.

2.6.1. Hollow Fiber Membranes

Nanofiltration experiments of hollow fiber membranes were performed by cross flow filtration of Bromothymol Blue (624 Da) solution in ethanol. Firstly hollow fiber membrane module was prepared by placing fiber in module. By using epoxy solution, ends of module were closed. Epoxy solution consists of REN HY 5160 and RENLAM CY 219 in 1:2 weight ratios. Epoxy solution dries after 24 hours approximately. One end of hollow fiber membrane module was cut open to collect permeate from this end. Then membrane module was placed in crossflow filtration

setup. As so for flat sheet membranes, the same procedure was applied for hollow fiber membranes. Firstly pure solvent permeance was measured, then filtration tests of hollow fiber membranes were done at 2 bar.

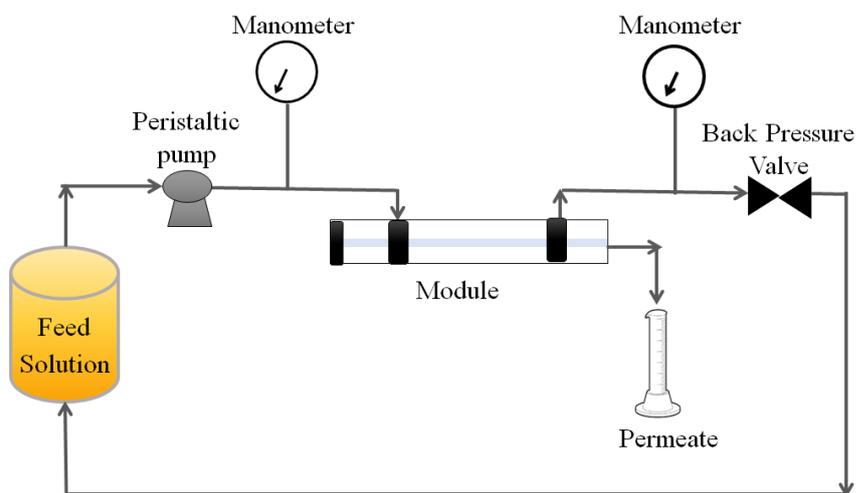


Figure 2.5. Schematic drawing of crossflow filtration set-up for hollow fiber membrane module

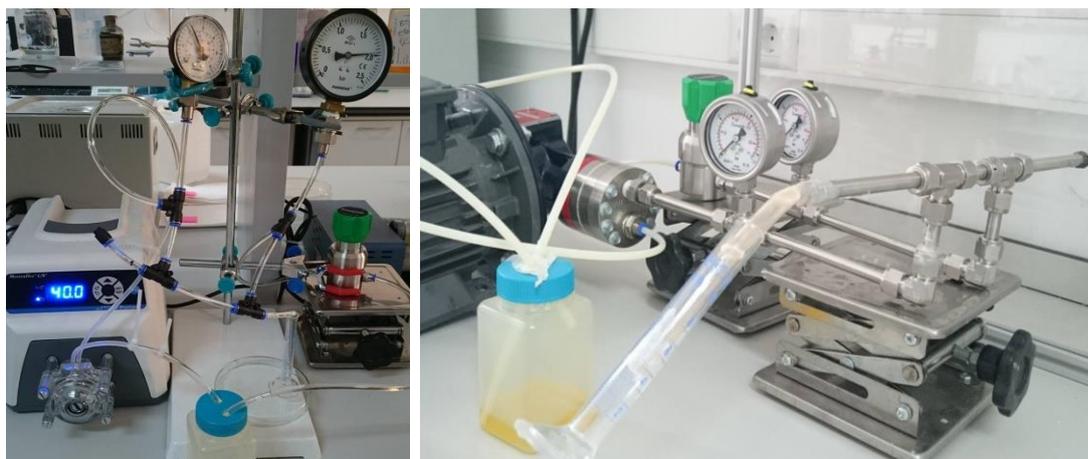


Figure 2.6. Crossflow filtration set-up for hollow fiber membrane module (a) Low pressure system, (b) high pressure and solvent resistant steel system

2.7. Swelling Tests

Membranes which were stored in ethanol were taken out of ethanol and they were cut in size of 2 cm × 3 cm. Firstly they were dried at ambient conditions. Then they were dried in vacuum in order to remove ethanol completely. The membranes were weighed in certain time intervals until their weights became constant. Complete drying of membrane lasted one week approximately. Dried membranes were placed into 20 ml of solvent. Their weights increased day by day as they became swollen. Membranes were taken from the solvent and excess solvent were gently wiped with a tissue paper. Weights of membranes were measured daily. When their weights reached a constant value, swelling test was completed. Swelling ratios were calculated by using the following equation.

$$\text{Swelling Ratio}\% = \left(\frac{W_{\text{wet membrane}} - W_{\text{dry membrane}}}{W_{\text{dry membrane}}} \right) \times 100 \quad (4)$$

2.7. Scanning Electron Microscopy (SEM)

The morphologies of membranes were analyzed by SEM. Analyses were done in METU Central Laboratory with QUANTA 400F Field Emission SEM and in METU Metallurgical and Materials Engineering Department with SEM, FEI Nanosem 430. In order to analyze cross section images, membranes were broken after freezing by using liquid nitrogen. Prepared samples were stored in vacuum. Before the analysis, samples were placed to holder with the help of the conductive tape and they were coated with gold-palladium.

CHAPTER 3

RESULTS

3.1. Cellulose Based Flat Sheet Membranes

Firstly, cellulose based flat sheet membranes were produced to observe the effect of fabrication parameters on membrane performance. Their morphology and separation performances were evaluated before producing cellulose hollow fiber membranes. As seen in the Figure 3.1, cellulose membranes(C-1), which were produced by using solution C1 with 250 μm casting thickness and dried from ethanol, have dense structure all through the membrane cross section.

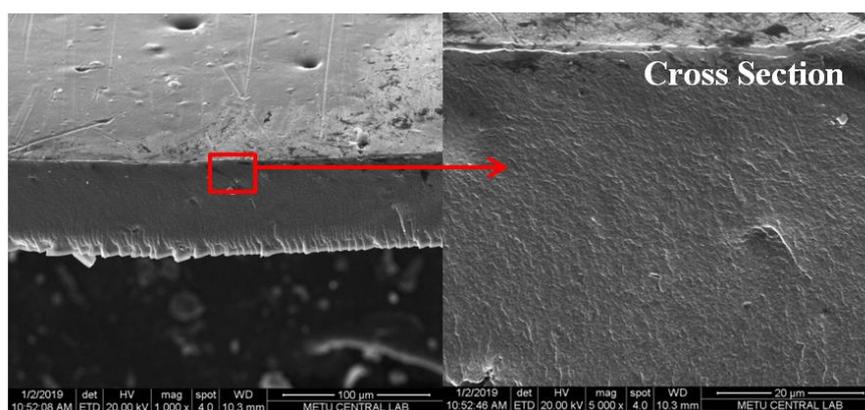


Figure 3.1. Cross section SEM images of flat sheet cellulose membrane(C-1). Scale bars are 100 μm (x1000) and 20 μm (5000x) from left to right

From previous studies (Sukma,2018; Konca, 2018) it is known that cellulose membranes have higher dye rejection when they are dried. However after immersing cellulose membranes into ethanol and drying, they become more brittle. They can be re-wetted to use in flat sheet membrane modules, however making hollow fiber membrane module by using dried cellulose membranes is difficult since modules need to be prepared dry and dried hollow fibers are broken easily when placing into membrane module. In order to solve this problem, drying conditions were changed

to improve mechanical properties of dry cellulose membranes. Jie et al. observed that elongation at break increases when cellulose hollow fiber membranes are dried after immersing firstly in ethanol and then hexane. If the elongation increases, the cellulose membranes may have a lower risk of breakage when placing them in the module (Jie, X., 2005). Before the dye filtration experiments, in order to observe effect of drying medium on membrane morphology, cellulose hollow membranes which were dried from ethanol and hexane were examined by scanning electron microscope (SEM). Membranes were cast from C1 solution. As seen in the Figure 3.2, cellulose hollow fiber membrane which was dried from hexane has more open pores and pore size was approximately 176 ± 36 nm. In the literature, pore sizes with similar order of magnitude were obtained. Cross-sections of cellulose hollow fibers which were fabricated by Falca et al. via cellulose and [EMIM]OAc solution were analyzed by Cyro-SEM. Due to wet analysis were carried out, membrane pores did not collapsed and open pores were clearly seen. Pore sizes of these hollow fibers were 100 ± 21 nm approximately (Falca, 2019). Separation performances of cellulose flat sheet membranes were evaluated by dead end filtration of Bromothymol Blue at 4 bar. Permeance of membrane dried from hexane(C-2) was higher and rejection was lower as expected because of larger pores (Figure 3.3). Additionally, there was no noticeable ease of treatment. As a result, all membranes were used by drying from ethanol throughout this study since drying form hexane did not provide any benefit.

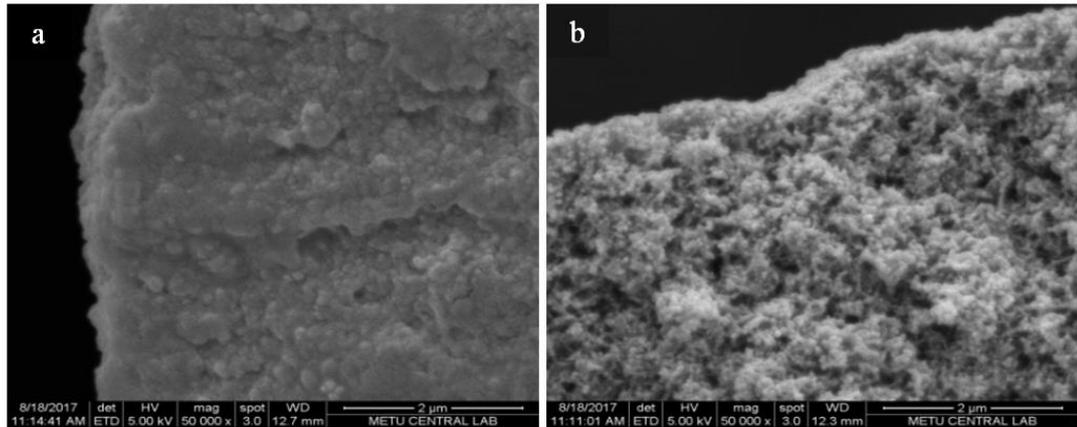


Figure 3.2. Cross section SEM images of hollow fiber cellulose membrane(bore sides) (a) dried from ethanol (b) dried from hexane. Scale bars are 2 μm (50 000x).

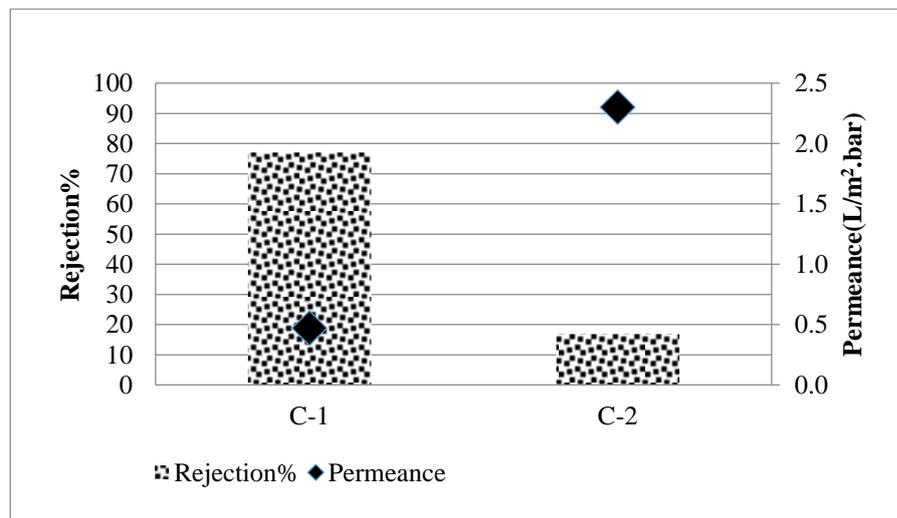


Figure 3.3. Dye retention and permeance for cellulose membrane dried from ethanol (C-1) and dried from hexane (C-2)

3.2. Hollow Fiber Cellulose Membranes

Cellulose hollow fiber membranes with different spinning parameters were produced and their morphologies were observed by SEM. Membrane morphology could be varied by changing spinning parameters such as bore liquid and polymer dope flow rate, polymer dope composition, bore liquid composition, air gap distance and temperature of external coagulant. In fabrication of cellulose hollow fiber membranes C1 and C2 polymer solutions were used as polymer dope. As bore liquid solution, water, 80% DMSO-water solution and 50% [Emim]OAc-DMSO solution were used in different compositions. Produced cellulose hollow fibers were evaluated in five different groups in terms of polymer dope, bore liquids and coagulation bath temperatures. Macroscopic properties and general observations of hollow fiber membranes are given in Appendix C. According to macroscopic properties from each group one membrane was chosen and was analyzed.

In production of cellulose hollow fiber membranes in group A (No:4, Table C.1.); solution C1 was used as dope liquid and water was used as bore liquid to produce dense skin layer in bore side. The presence of nonsolvent in the bore side accelerates phase inversion and results in dense bore side. It is observed in the SEM image of the bore side and shell side presented in Figure 3.4 that the hollow fiber has a dense structure along the entire cross-section. Due to dense structure of this membrane, ethanol permeance was found as $5.9 * 10^{-4} L / m^2 h$ which is too low to perform dye filtration experiment. In order to increase solvent permeance, bore liquid composition was changed to fabricate hollow fiber having a porous bore structure. The same polymer solution was used as polymer dope and 80% DMSO-water solution was used as bore liquid. By aiming for porous structure in the bore side, solvent was added in water. It is known that, if solvent content in the bore liquid increases, bore side of membrane becomes more porous (Koops, G. et al., 1994). Due to solvent in the bore liquid, concentration gradient between dope solution and bore liquid decreases and mass transfer rate of nonsolvent in the bore liquid towards dope solution decreases. During coagulation, polymer lean phase gains more time

for nucleation and growth. Therefore, polymer lean phase forms larger pores. The cellulose hollow fiber membrane in group B(No: 5,Table C.1.) is shown in Figure 3.5. In spite of increasing solvent content in bore liquid, there is no observable porosity difference between 4rd and 5th cellulose hollow fibers in terms of their bore side views. The second fiber also has a dense morphology all throughout the cross section.

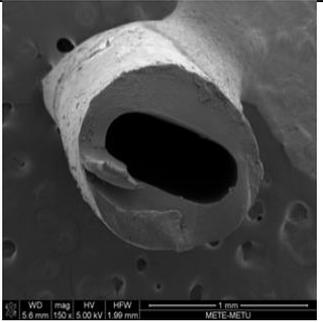
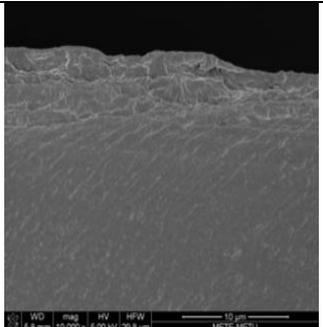
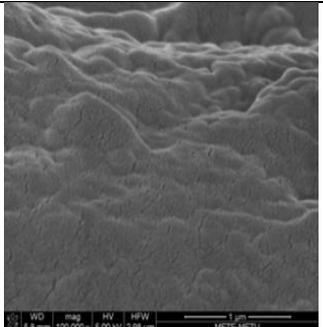
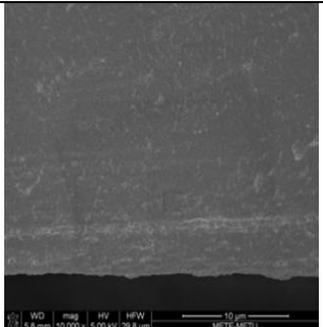
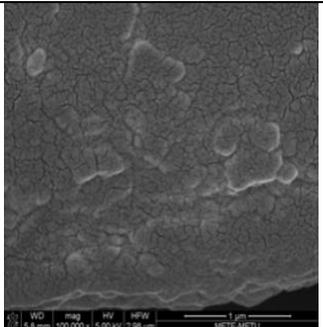
4	X100	
Cross Section	<div style="display: flex; align-items: center;">  <div style="margin-left: 20px;"> <p>Group :A Polymer Solution: C1 Bore Liquid: water Coagulation Bath Temperature: 15 °C</p> </div> </div>	
	x10000	x100000
Shell Side		
Bore Side		

Figure 3.4. Cross section SEM images of hollow fiber cellulose membrane 4. Scale bars are 1 mm(x150) for cross section images while 10 μm (10 000x) and 1 μm(x100000) for other magnifications

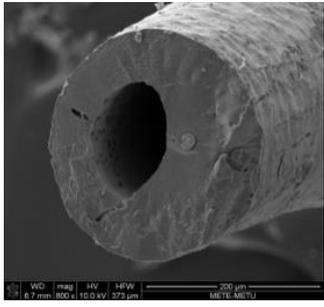
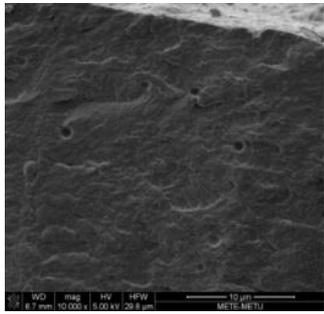
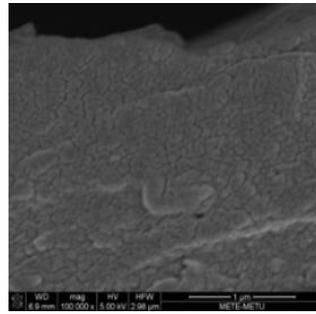
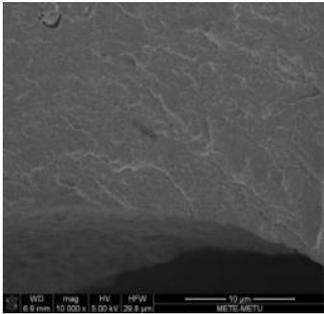
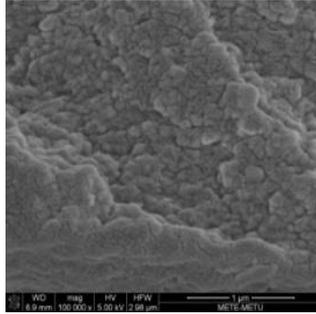
5	X100	
Cross Section	<div style="display: flex; align-items: center; justify-content: center;">  <div style="margin-left: 20px; text-align: left;"> <p>Group B Polymer Solution :C1 Bore Liquid : 80% DMSO-water Coagulation Bath Temperature: 15 °C</p> </div> </div>	
	x10000	x100000
Shell Side		
Bore Side		

Figure 3.5. Cross section SEM images of hollow fiber cellulose membrane 5. Scale bars are 200 μm (x800) for cross section images while 10 μm (10 000x) and 1 μm (x100000) for other magnifications

In the fabrication of hollow fibers in group C, both polymer solution and bore liquid were changed to obtain asymmetric membrane morphology and consequently increase solvent permeance. Dense shell side and porous bore side were aimed. To obtain dense skin layer in the shell side, C2 solution which contains volatile solvent was used. Due to volatile solvent removal, which is acetone evaporation, in polymer solution before phase inversion process, shell side of hollow fiber No: 15 (Table C.1.) in group C has dense structure as expected (Figure 3.6). [Emim]OAc-DMSO mixture was used as bore liquid in the production of hollow fiber No:15. Bore liquid consisted of a solvent mixture to obtain porous bore side structure. It was observed that this mixture dissolved cellulose (Durmaz, 2018). However, hollow fiber No:15 membrane has dense bore side. By comparing with shell side, bore side has more open pores but it does not have macroporous structure. As a result of dense structure in both sides, solvent permeance could not be measured.

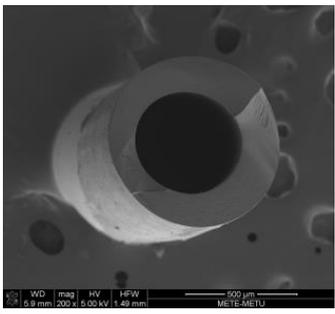
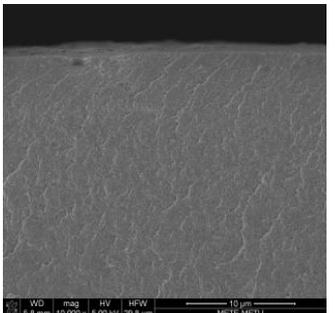
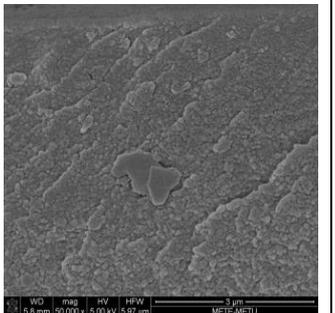
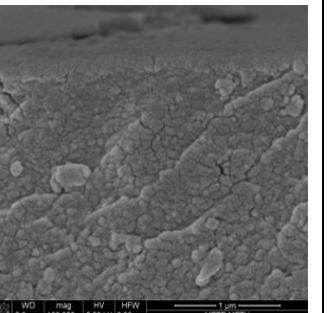
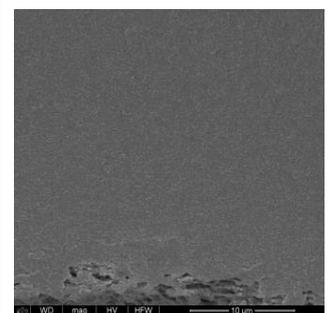
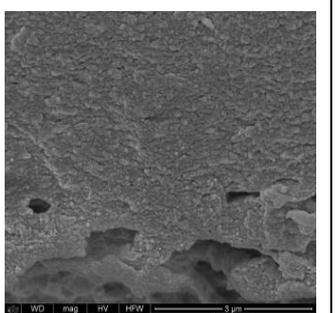
15	X100		
Cross Section	<p style="text-align: center;">Group C Polymer Solution :C2 Bore Liquid : [Emm]OAc-DMSO 1:1 Coagulation Bath Temperature: 15 °C</p> 		
	x10000	x50000	x100000
Shell Side			
	Bore Side		

Figure 3.6. Cross section SEM images of hollow fiber cellulose membrane 15. Scale bars are 500 μm (x200) for cross section images while 10 μm (10 000x), 3 μm (50 000) and 1 μm (x100000) for other magnifications)

Solvent permeance of these cellulose hollow fiber membranes was too low due to their dense structure. The reason of dense structure in the SEM image may be pore collapsing after drying. It was observed in previous studies that differences in the pore size may vanish due to pore collapsing (Durmaz, 2018). In nonsolvent induced phase inversion (NIPS) method, a dense skin layer forms in the nonsolvent side of membrane. However, if membrane outer layer is exposed with vapor of nonsolvent before immersing into coagulations bath, vapor induced phase separation (VIPS) is started and membrane with larger pores in the outer layer is obtained (US Patent 5906742, 1999) (US Patent 6045899, 2000). If precipitation rate decreases, time to progress nucleation and growth increases and polymer lean phase, which forms pores of membrane, finds an opportunity to progress further and generate larger pores. In order to decrease precipitation rate, nonsolvent vapor is introduced to shell side throughout the certain air gap and precipitation is started at a lower rate by nonsolvent vapor before reaching coagulation composition suddenly in coagulation tank (Ohya, 2009). In order to introduce nonsolvent vapor to the shell side of hollow fiber, hot water can be used as coagulant to generate vapor. For a spinning process, hollow fibers with varying pore size in the shell side can be obtained by changing parameters which effect exposure time to vapor, humidity and temperature of air. The exposure time increases with increasing air gap in between exit of spinneret and coagulation bath. The humidity and temperature of air are controlled by coagulation bath temperature (Khare, V., 2005; Yücel, 2018). Xu et al. produced flat sheet polysulfone (PSf) membrane and they observed that more porous structures were obtained after increasing coagulation bath temperature. As a result, pure water permeability of membrane increased while humic acid rejection decreased (Xu, J., 2014).

By using this approach, in order to produce membranes which have more porous outer layer and higher permeance, temperature of coagulation bath was increased. The coagulation bath temperatures in the production of hollow fibers in group D and group E were 50°C. Also, same polymer solution (C1) was used. In group D, water

was used as bore liquid to obtain dense bore side. However these membranes could not be fabricated in a regular cylindrical shape and bore side was not uniform as shown in the Figure 3.7. Then bore liquid was changed and 80% DMSO-water solution was used in group E. Hollow fiber in group E (No:27) is shown in Figure 3.8. Due to coagulation bath at 50°C, porous structure was obtained on the outside of hollow fiber. As bore liquid 80% DMSO-water solution was used, bore side has porous structure. Filtration experiment was performed at 2 bar. Solvent permeance was found as 0.15 L/h. m². bar and dye rejection is found as 40 %.

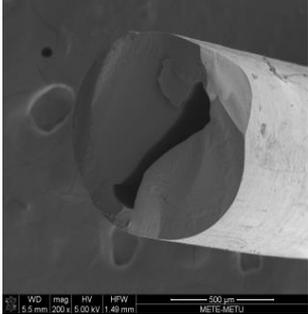
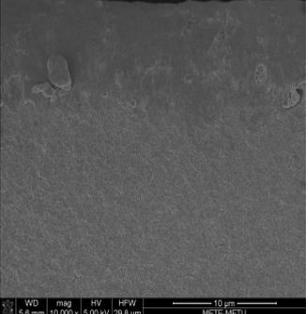
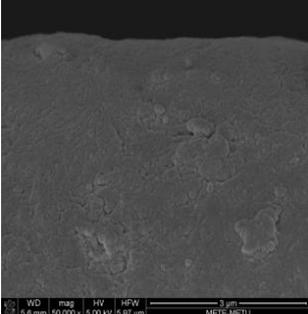
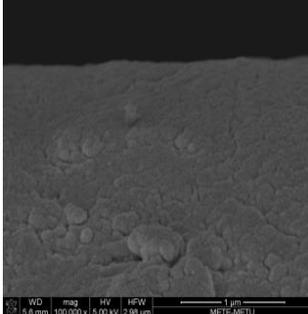
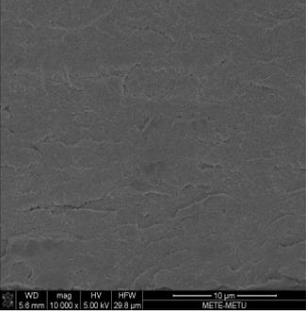
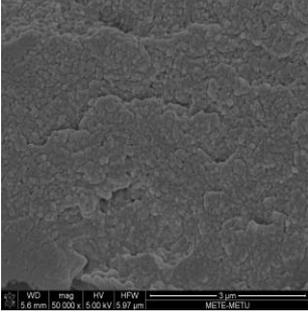
25	X100		
Cross Section			
	<p>Group D Polymer Solution :C1 Bore Liquid : water Coagulation Bath Temperature: 50 °C</p>		
	x10000	x50000	x100000
Shell Side			
	Bore Side		

Figure 3.7. Cross section SEM images of hollow fiber cellulose membrane 25. Scale bars are 200 μm(x500) for cross section images while 10 μm (10 000x), 2 μm(50 000) and 1 μm(x100000) for other magnifications

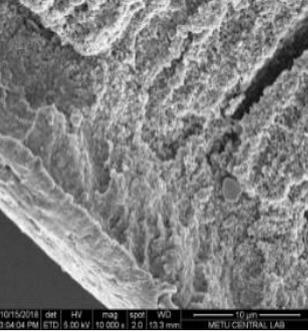
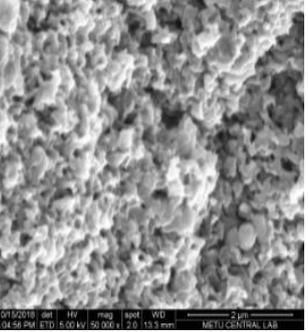
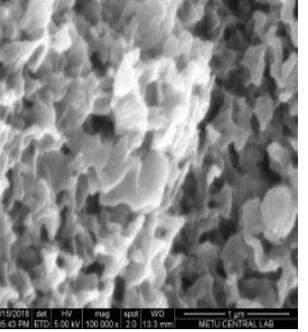
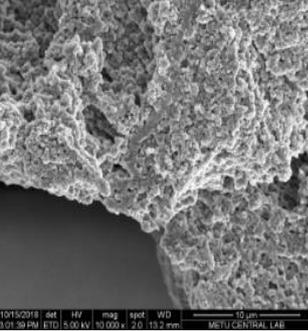
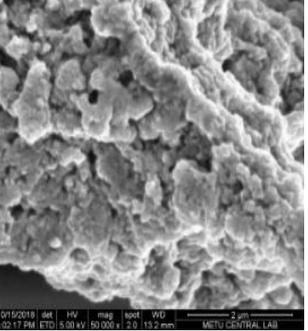
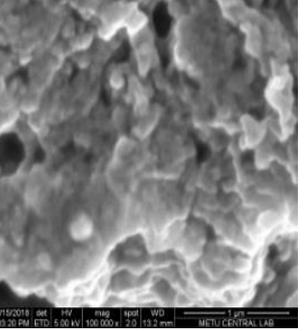
27	X100		
Cross Section	<p>Group E Polymer Solution :C1 Bore Liquid : 80 % DMSO-water Coagulation Bath Temperature: 50 °C</p> 		
	x10000	x50000	x100000
Shell Side			
Bore Side			

Figure 3.8. Cross section SEM images of hollow fiber cellulose membrane 27. Scale bars are 200 μm (x500) for cross section images while 10 μm (10 000x), 2 μm (50 000) and 1 μm (x100000) for other magnifications

3.3. Cellulose Membranes Fabricated from Alkaline Hydrolysis of Cellulose Acetate

After testing cellulose membranes, an alternative method was evaluated to produce robust and cost effective cellulose membranes. Due to high viscosity of ionic liquids, processing of cellulose solutions is difficult. Besides high viscosity, ionic liquids are relatively more expensive solvents. In fabrication of cellulose hollow fiber membranes, high amount of dope solution is needed. Therefore high amount of ionic liquid is required to prepare dope solution. Usage of ionic liquids in dope solution increases cost of membrane. Also, by using cellulose solution as dope liquid, performing a continuous spinning and membrane module preparation is difficult due to brittle structures of cellulose hollow fibers. As an alternative way, cellulose acetate membranes can be regenerated to cellulose membranes by alkaline hydrolysis. Cellulose acetate solutions are prepared without using ionic liquid within shorter time. Also, spinning of cellulose acetate hollow fiber membranes can be performed continuously more easily.

In the second part of this study, flat sheet and hollow fiber cellulose acetate membranes were regenerated to cellulose as described in experimental part. In this way cellulose membranes were obtained without using ionic liquids. Different annealing and regeneration procedures were applied to cellulose acetate membranes.

3.3.1. Regeneration of Cellulose Acetate Based Membrane

Regeneration of cellulose acetate membranes was verified by FTIR spectra. After regeneration of cellulose acetate to cellulose, acetyl groups (1736 cm^{-1}) disappeared and hydroxyl groups (3483 cm^{-1}) appeared (Figure 3.9). In Table 3.1 effect of regeneration duration and NaOH concentration on the ratio of acetyl groups to hydroxyl groups in the membrane is shown. As regeneration duration and concentration of NaOH solution increase, regeneration quality increases. Applied regeneration procedure in this study was chosen as 0.05 M NaOH-water solution during 24 hours, which was sufficient to convert all acetate groups to hydroxyl groups (Figure 3.9).

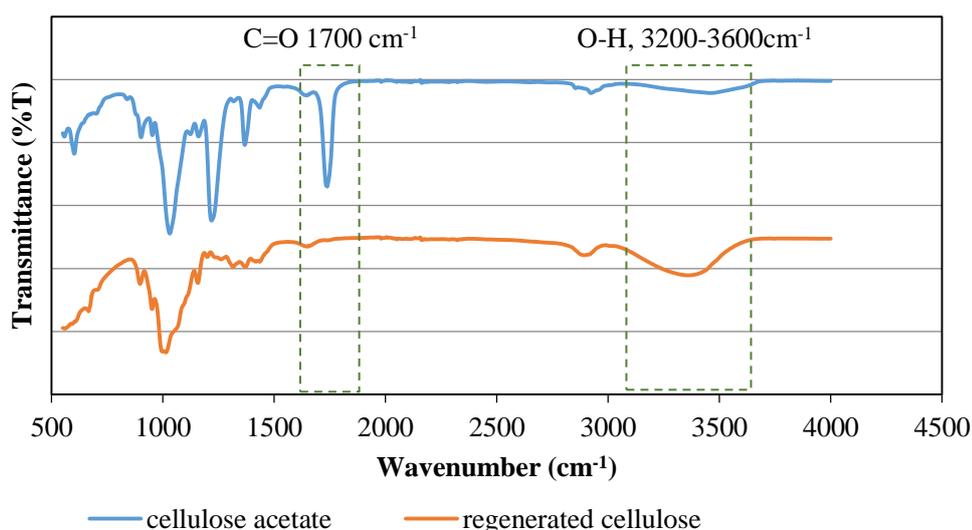


Figure 3.9. FTIR spectra of cellulose acetate and regenerated cellulose membranes in 0.05 M NaOH-water solution

Table 3.1. Changing C=O area/ O-H area ratios on the FTIR spectra with changing regeneration conditions

Duration (h)	C=O/O-H	C=O/O-H
	0.05 M	0.1 M
0.25	0.960	0.745
1	0.118	0.012
4	0.008	0.003
8	0.006	0.000
24	0.000	0.000

3.3.2. Effect of Annealing and Regeneration on Performance of Cellulose Acetate Based Membrane

In order to understand annealing and regeneration effect on separation performance of cellulose acetate membranes, different annealing and regeneration procedures were applied to flat sheet membranes which were prepared by using CA1 solution. Filtration tests were performed by using 0.5 mM Bromothymol Blue (BTB)-ethanol solution at 4 bar.

Thermal annealing was done to enhance separation performance of cellulose acetate membranes. Thermal annealing decreases pore size of membrane and reduces free volume between polymer chains (Swaidan, 2015). In order to improve dye rejection, cellulose acetate membranes were annealed. In Figure 3.10 annealing effect on bromothymol blue rejection of cellulose acetate membranes is shown. Firstly wet annealing 85°C was performed and it was observed that dye rejection increases after wet annealing. By comparison with wet annealed cellulose acetate membrane, dry annealed (120°C) membrane has higher dye rejection. Permeance of membrane decreased after both wet and dry annealing and there was no significant effect of annealing type on permeance of membrane. Temperature difference between two annealing procedures is effective parameter for degree of annealing. Dry annealing was done at 120°C while wet annealing was done at a lower temperature, 85°C . Then, these membranes were regenerated and their dye rejections were evaluated.

After regenerating annealed membranes, dye rejection values decreased as shown in Figure 3.11.

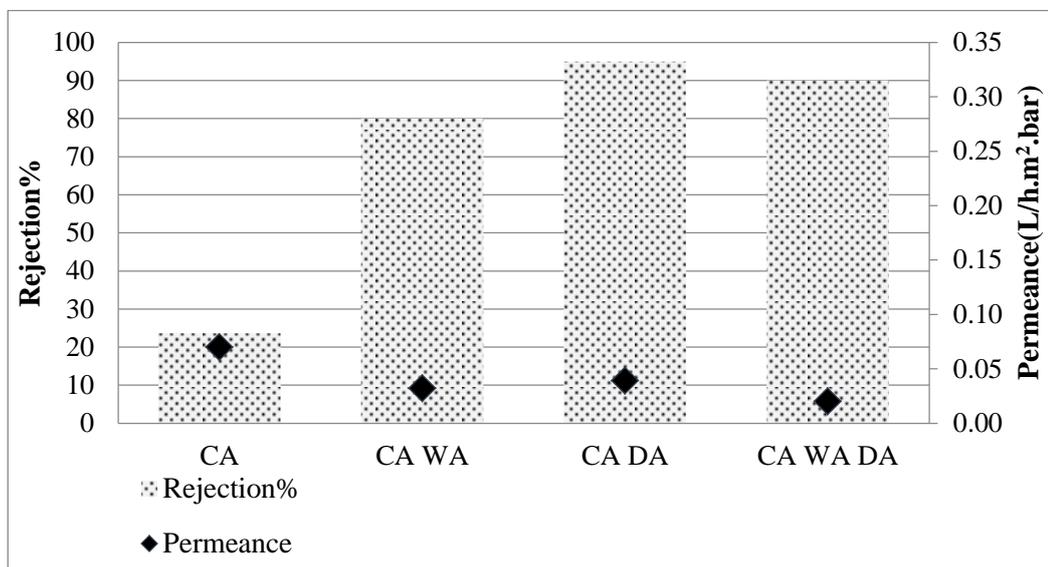


Figure 3.10. Bromothymol Blue Rejections of Non-Annealed and Annealed Cellulose Acetate Membranes

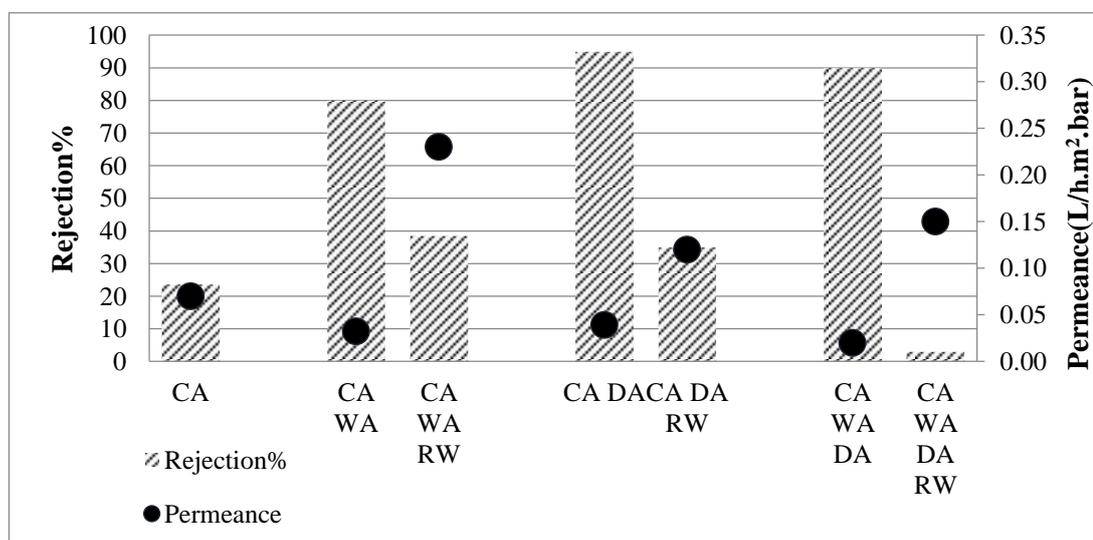


Figure 3.11. Bromothymol Blue Rejections of Annealed Cellulose Acetate and Annealed Regenerated Cellulose Membranes

Bromothymol Blue rejection of wet annealed membrane was 80% before the regeneration and this value reduced to 38% and ethanol permeance of this membrane

reached 0.23 L/h.m².bar by increasing 7 times after regeneration. Similarly, dye rejection of dry annealed membrane decreased to 35% from 95% and permeance which was 0.04 L/h.m².bar, increased approximately 3 times after regeneration. The reason of dye rejection decrease after regeneration was thought to be increasing porosity due to swelling of cellulose membranes in water during regeneration. While cellulose acetate membrane is regenerating, becomes more swollen as cellulose swells much more than cellulose acetate in water. Durmaz et al. found the swelling ratio of cellulose acetate dense film in water as 5% while cellulose dense film in water is 100% approximately (Durmaz, 2017).

Therefore, regenerated cellulose membrane could be in swollen form due to high water content of regeneration medium. It is shown in Figure 3.12 that cellulose membranes swell in water up almost two times of their weights. At the end of the regeneration, cellulose membranes with swollen form which have higher porosities were obtained.

In order to understand effect of regeneration medium on swelling of cellulose membranes, swelling ratios were measured for 3 different medium which are pure water, 90% ethanol-water solution and pure ethanol. As seen in the Figure 3.12, swelling ratio decreases as water compositions of regeneration solution decreases. It was hypothesized that if water content in regeneration solution is reduced by replacing a certain amount of it with ethanol, swelling could be prevented and cellulose membrane with a denser structure could be obtained at the end of the regeneration. Since 0.05 M NaOH solution prepared with pure ethanol did not completely dissolve, 90% ethanol-water solution with the same NaOH molarity was used as regeneration medium.

In swelling test, both membrane material and porosity of membrane have significant effect on swelling ratio. The swelling ratios of regenerated cellulose membranes and original cellulose membrane in water were illustrated in Figure 3.13. It was observed that original cellulose membrane has dense structure as seen in the SEM image of

C-1 membrane. Therefore there is a minor effect if at all of porosity on swelling ratio of original cellulose membrane. The swelling ratio of original cellulose membrane can be considered as minimum swelling ratio due to membrane material for regenerated cellulose membranes. Regenerated cellulose membrane in 0.05 M NaOH 90% ethanol-water solution (CA RE) has similar swelling ratio with original cellulose membrane. Consequently, it can be expected to have similar pore size and therefore same separation performance with this membrane. Membrane CA RW which was regenerated in 0.05 M NaOH-water solution has higher swelling ratio than both membrane C-1 and membrane CA RE. This implies that porosity of regenerated cellulose membranes increases after regeneration in water.

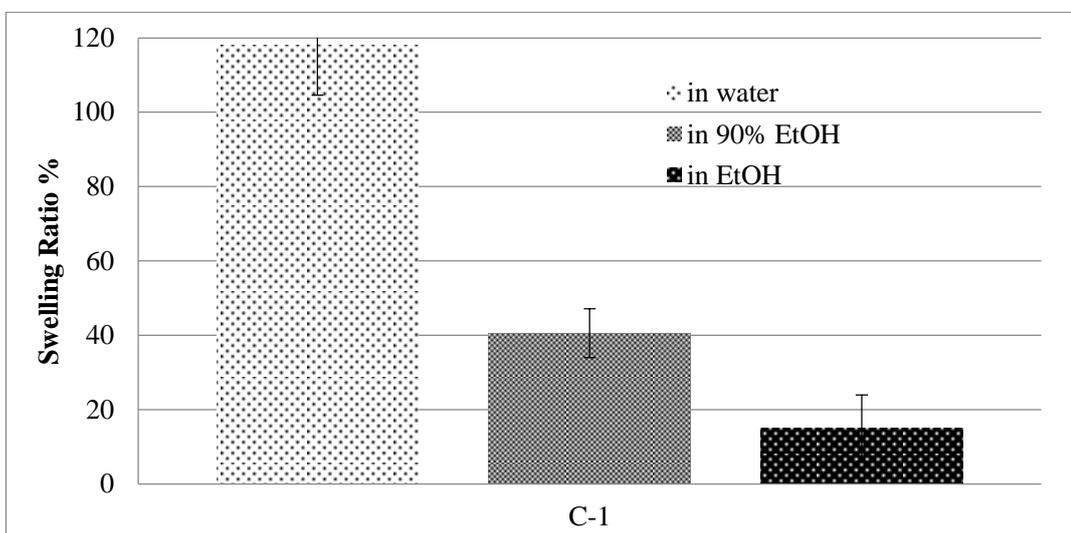


Figure 3.12. Swelling ratio of cellulose membrane (C1) in water, 90% ethanol-water and ethanol

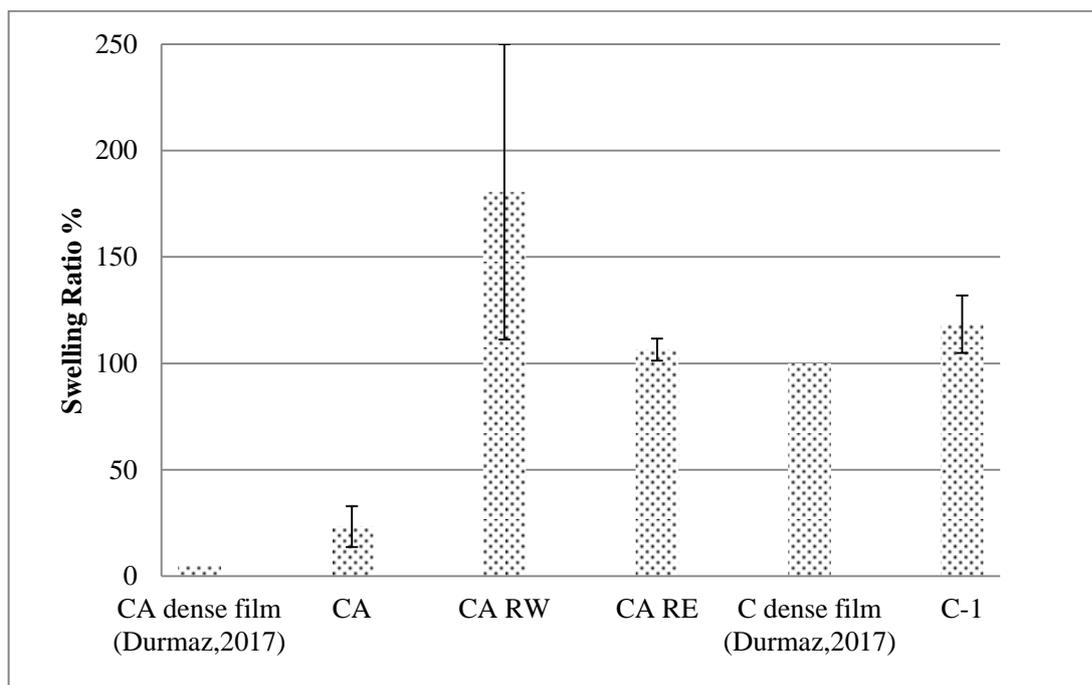


Figure 3.13. Swelling ratios of cellulose membrane, cellulose acetate membrane, regenerated cellulose membranes, cellulose dense film and cellulose acetate dense film in water

Filtration experiments were done with regenerated membranes in 90% ethanol-water mixture. Although dye rejection of non-annealed membrane increased from 30% to 55% after changing regeneration solution, there is no significant effect of regeneration medium on dye rejection of annealed cellulose acetate membranes as shown in the Figure 3.14. The dye rejection of the wet annealed and regenerated cellulose membrane remained approximately the same as 38% and 42%, respectively, after changing the regeneration medium. The dye rejection of dry annealed and regenerated membrane was also constant after changing regeneration medium from water to ethanol and it was 35% to 31%, respectively.

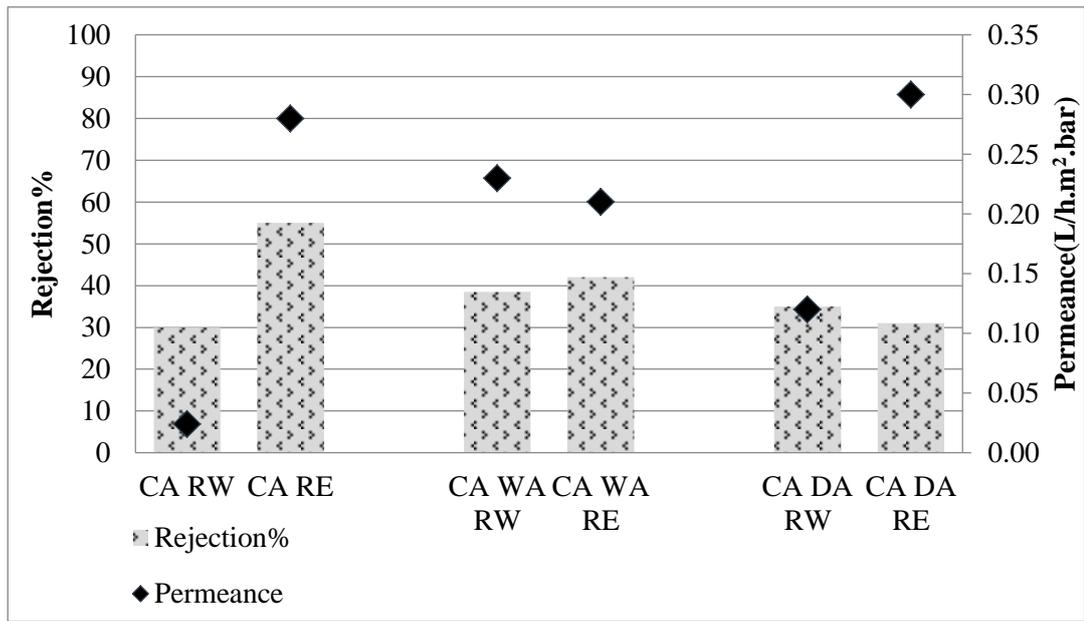


Figure 3.14. Dye Rejections of Regenerated Cellulose Membranes in Ethanol

3.3.3. Membrane Morphology

Scanning electron microscope images of cellulose acetate and regenerated cellulose membranes are given in Figure 3.15, Figure 3.16, respectively. In Table 2.3., detailed information about membrane codes were given. Membranes which were annealed with different procedures are also shown. All membranes were produced with a casting bar which provides 50 μm thicknesses and dried from ethanol before SEM analysis.

As seen from the SEM images, there is no noticeable porosity and structure difference between cellulose acetate and regenerated cellulose membranes. It was observed that annealing and regeneration affected membrane performance. Consequently it is expected that regeneration changes the membrane morphology. However, morphology of cellulose acetate and regenerated cellulose membranes appear similar. Due to collapsing of membrane pores because of drying, slight difference between morphologies of membranes could not be observed by SEM analysis (Durmaz, 2018).

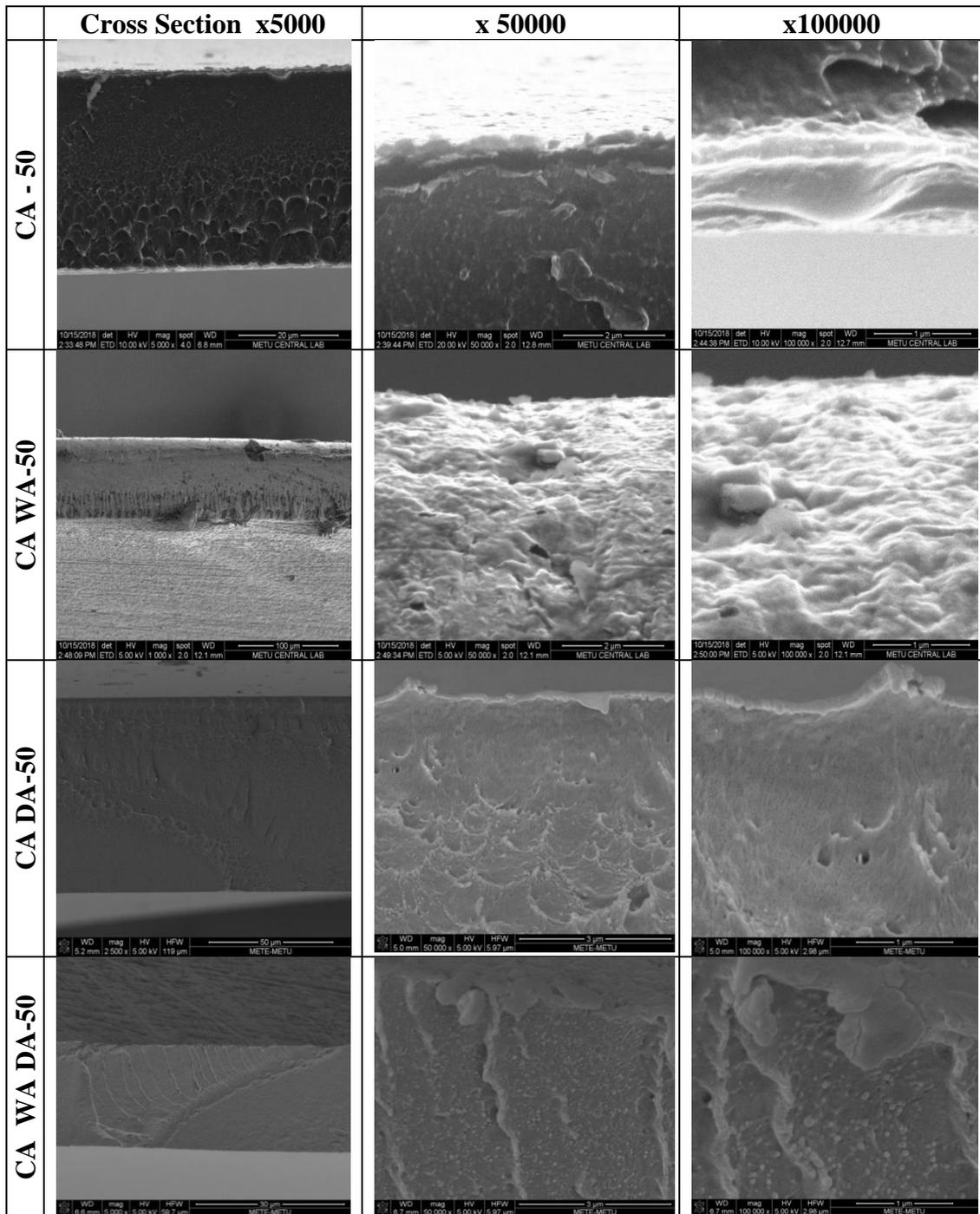


Figure 3.15. SEM images of flat sheet cellulose acetate membranes. Scale bars are 50 μm (x5000) for cross section images while 2 μm (50 000x) and 1 μm (x100000) for other magnifications.

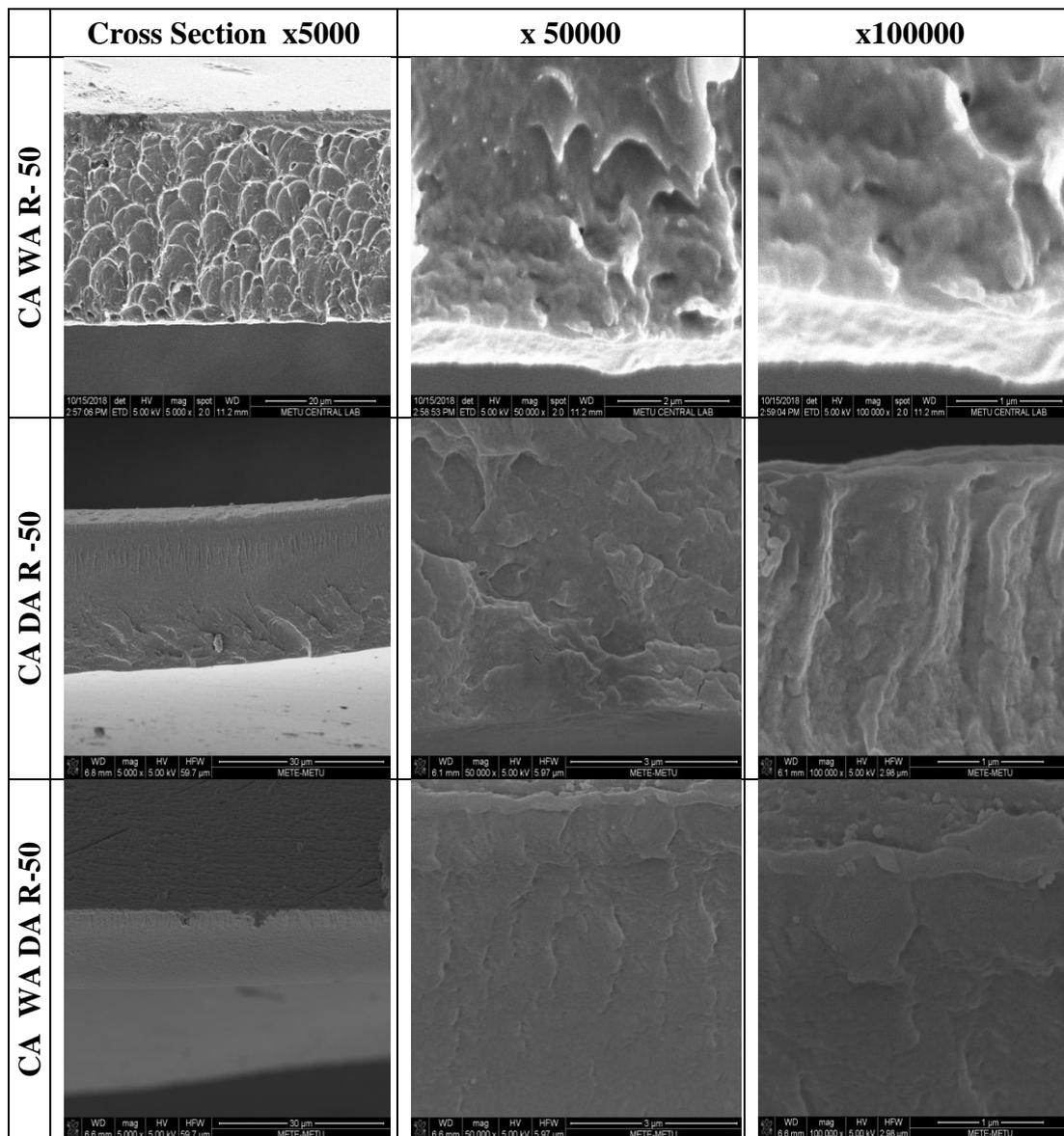


Figure 3.16. SEM images of flat sheet regenerated cellulose membranes. Scale bars are 30 μm (x5000) for cross section images while 3 μm (50 000x) and 1 μm (x100000) for other magnifications.

3.3.4. Cellulose Acetate Based Hollow Fiber Membranes

Cellulose acetate hollow fiber membranes were produced by using same polymer solution which was CA1 with cellulose acetate flat sheet membranes. In the production of cellulose acetate hollow fibers in group G and H, coagulation bath contained water as external coagulant to form dense skin layer in the shell side. Water was used as bore liquid by aiming to obtain a dense skin layer in the bore side in the fabrication of hollow fiber membranes in group G. In order to form more porous structure in the bore side, 80% DMSO-water mixture was used as bore liquid in the production of hollow fiber membranes in group H. Both cellulose acetate hollow fibers which are hollow fiber membrane No:31 in group G and hollow fiber membrane No:42 in group H, have macrovoids and sponge like structure in the bore sides. Hollow fiber No:42 was annealed at 120 °C for 6 hours and separation performance was evaluated at 10 bar by using 0.05 mM Bromothymol Blue-ethanol solution. Solvent permeance and dye rejection were found as 0.63 L/h.m².bar and 35% respectively (Table 3.2.). The flat sheet membrane which was produced with same polymer solution and annealed at same conditions had much higher solvent permeance, 0.039 L/h.m².bar and higher dye rejection, 95%. Depending on geometry of membrane, separation performance may be varied due to changing membrane morphology. When annealing time of cellulose acetate hollow fiber increases to 24 hours, dye rejection reached 45% (Table 3.2.). Then, this membrane was regenerated in 0.05 M NaOH-90% ethanol. As shown in the FTIR spectra (Figure 3.19), acetyl groups disappeared after regeneration with 0.05 M NaOH in both water and 90% ethanol-water solution which confirmed regeneration was completely accomplished. Solvent permeance of regenerated hollow fiber membrane No:42 was measured as 3 L/h.m².bar and membrane has no dye rejection as summarized in Table 3.2. As a result, regeneration of cellulose acetate membranes reduces separation performance independently of membrane geometry.

Table 3.2. Separation performance of cellulose acetate based hollow fibers

Hollow Fiber No	Annealing		Regeneration	Performance	
	Temperature °C	Duration(h)		Ethanol Permeance (L/h.m ² .bar)	BTB Rejection
42	120	6	-	0.63	35%
42	120	24	-	0.94	45%
42	-	-	+	3	-

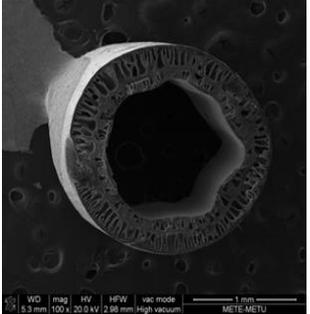
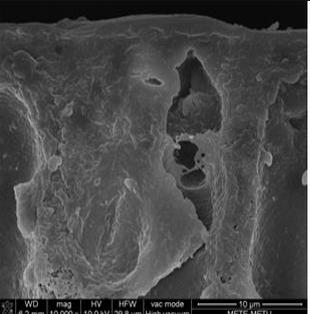
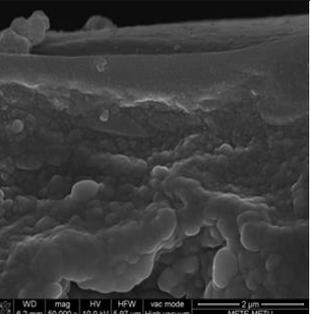
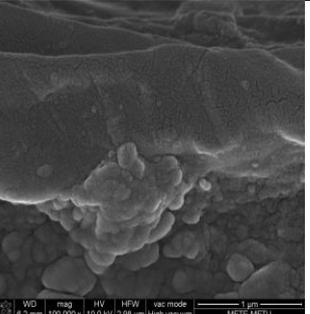
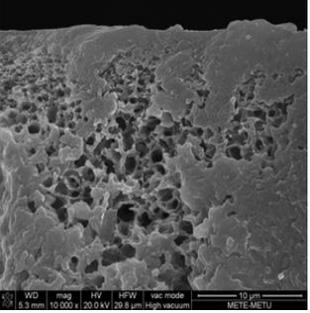
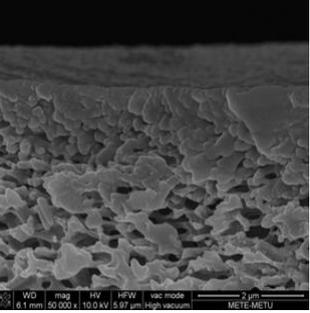
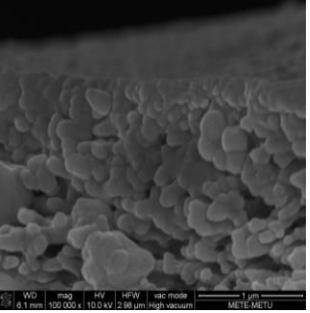
31	X100		
Cross Section	<div style="text-align: center;">  <p>Group G Polymer Solution :CA1 Bore Liquid : water Coagulation Bath Temperature: 15 °C</p> </div>		
	x10000	x50000	x100000
Shell Side			
Bore Side			

Figure 3.17. Cross section SEM images of hollow fiber cellulose acetate membrane 31. Scale bars are 1 mm(x100) for cross section images while 10 µm (10 000x), 2 µm(50 000) and 1 µm(x100000) for other magnifications

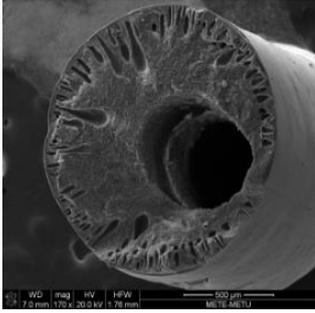
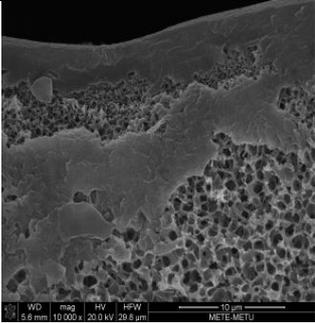
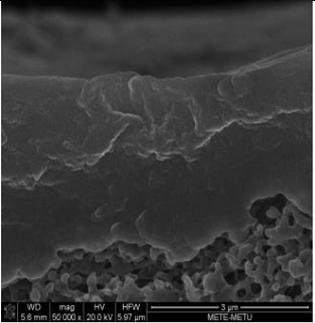
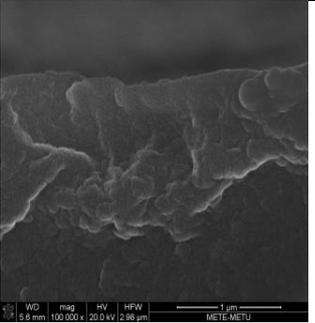
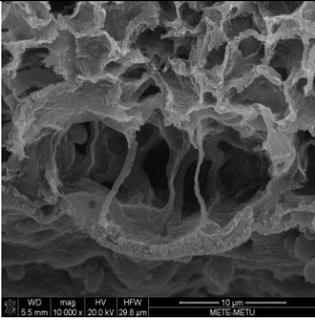
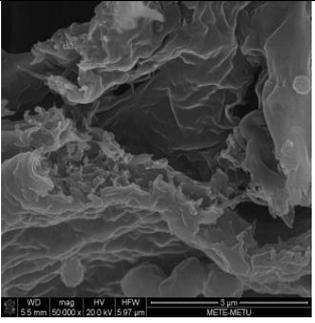
42	X100		
Cross Section			
	<p>Group H Polymer Solution :CA1 Bore Liquid: 80% DMSO-water Coagulation Bath Temperature: 15 °C</p>		
	x10000	x50000	x100000
Shell Side			
	Bore Side		

Figure 3.18. Cross section SEM images of hollow fiber cellulose acetate membrane 42. Scale bars are 200 μm(x500) for cross section images while 10 μm (10 000x), 2 μm(50 000) and 1 μm(x100000) for other magnifications

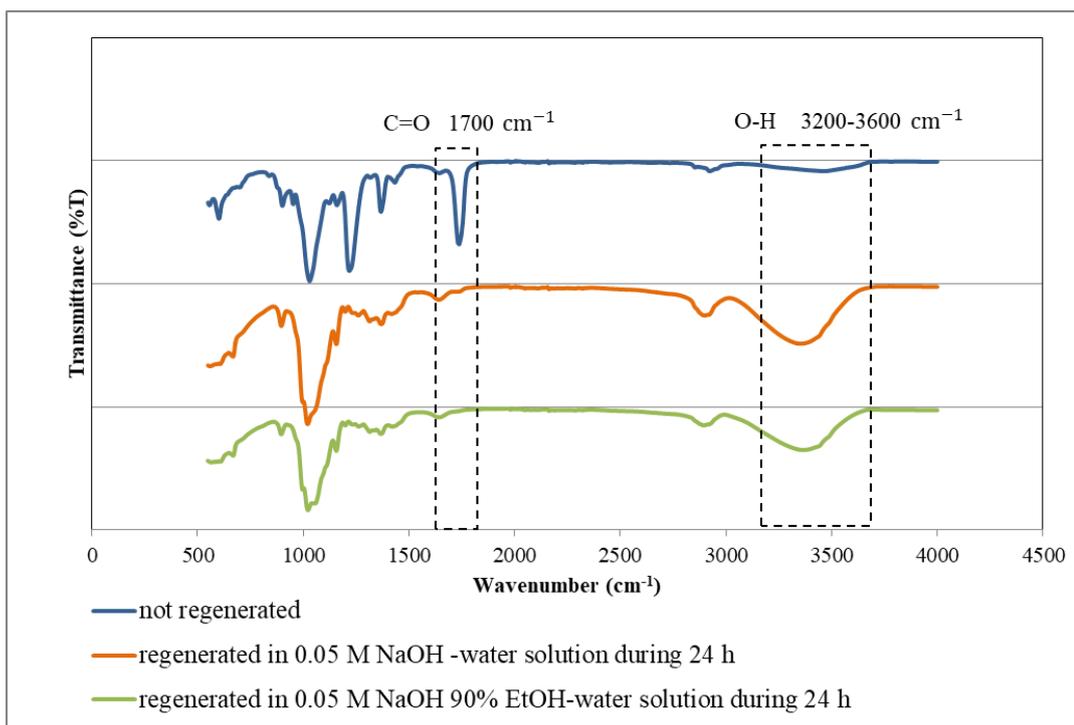


Figure 3.19. FTIR spectra of regenerated hollow fiber membranes

3.3.5. NaCl Rejection of Cellulose Acetate Membranes

Cellulose acetate was introduced as the first membrane material to produce high performance reverse osmosis membranes by Loeb and Sourirajan who invented asymmetric cellulose acetate membranes in 1960s (Loeb, 1963). Before the invention of thin film composite membranes by Cadotte (United States Patent No. US4277344A, 1981) and commercialization by FILMTEC Company, commercial cellulose acetate membranes were commonly used as reverse osmosis membranes. These cellulose acetate membranes have high salt rejection due to dense layer in their asymmetric structure which rejects salt (Shenvi, 2015). In order to get a dense regenerated cellulose membrane for our aimed application, firstly cellulose acetate membrane has to be dense. NaCl rejection of produced cellulose acetate membrane may provide an insight for aimed rejection in our study which is regenerated cellulose acetate membranes for OSN.

Firstly, by using dry annealed cellulose acetate (CA DA) membrane which has 95% dye rejection, NaCl filtration in water was performed and it was observed that salt rejection was 24%. Cellulose acetate solution contains 25% cellulose acetate and 35% acetone. As explained in experimental part, after casting membrane, evaporation is needed in order to remove acetone from membrane matrix. While acetone is evaporated, concentration of cellulose acetate in the cast membrane matrix increases. After coagulation, final membrane matrix is formed and due to higher polymer ratio, membranes are expected to have a denser structure. However if the evaporation time is not long enough to remove all acetone from the membrane matrix, membranes will form from a cellulose acetate, DMSO, acetone solution. The solvent in the system being a mixture of DMSO(strong solvent) and acetone(weak solvent) can affect membrane morphology. In order to understand interactions between polymer and two solvent, Hansen solubility parameter approach was used. (Hansen, 2007). Detailed calculations are given in the appendix B. RED value of DMSO-cellulose acetate interaction was calculated as 0.55 and RED value of acetone-cellulose acetate interaction was calculated as 0.93. According to RED values of solvent, DMSO is a good solvent and acetone is a weak solvent for cellulose acetate. Presenting small amount of weak solvent in polymer solution may lead to a looser skin layer. Especially for membranes which are cast by using polymer solutions with high polymer concentrations, all acetone may not be removed, lowering the acetone diffusion rate to the membrane surface and out of the solution due to high viscosity of polymer solution. To observe whether this has an effect on membrane, cellulose acetate in polymer solution was decreased to 20% from 25% and ratio of solvents which are acetone and DMSO kept constant. Produced membrane by using polymer solution which contains 20% cellulose acetate was tested at the same feed concentration and operation pressure. The salt rejection was found as 45%. Then these regenerated cellulose membranes which have low nanofiltration performances were used in ultrafiltration application.

3.3.6. The Recovery of Polymers via Regenerated Cellulose Membranes

Polymer-organic solvent solutions appear in many industrial processes such as polymer synthesis, coating removal by solvents and removal of photoresists after photolithography. Due to extensive solvent usage in the industry, solvent recovery and recycling have significant role in both of environmental and economic aspect (Cseri, 2018). Polar aprotic solvents such as DMSO, NMP and DMF are commonly used in polymerization reactions (Pan, 2019). After reaction takes place, reaction medium contains polymer, oligomers, unreacted monomers and solvent. A separation process is needed to obtain polymer after the reaction and to recover unreacted monomers and solvent. Another process in which polar aprotic solvents are used is photolithography. At the end of this process, organic solvents are contaminated with uncrosslinked polymers. By comparing with other separation techniques such as precipitation and centrifugation which are used for polymer recovery, membrane filtration has many advantages. After the precipitation of colloidal nanoparticles, they agglomerate and redispersion of particles completely is often not possible. Also, after the precipitation in nonsolvent, additional step is needed to remove nonsolvent. Centrifugation in the industrial scale is very expensive process. With the help of the ultrafiltration, organic solvent and polymers can be separated and the solvent can be recovered more effectively.

In order to separate polymer from organic solvents, regenerated cellulose membranes are good option due to their solvent resistant structure. In this part of the study, polyethersulfone(PES) and organic solvent mixtures were used as feed solution. PES rejection performances of regenerated cellulose membranes were tested in three different solvents which are dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone(NMP) and dimethylformamide(DMF). The same type of membrane which was annealed at 120°C and regenerated in water (CA DA RW) was used in filtrations. In order to understand interaction in between solvents and membranes, swelling tests were performed. From the literature (Fidale, L et al., 2008), it is

known that swelling ratio of cellulose in DMSO is higher than DMF and NMP. Similarly, as seen in Figure 3.20 annealed and regenerated cellulose membrane swells more in DMSO. Feed solutions were prepared as 1 gram of polymer per liter of solvent and operation pressure was kept as 10 bar during filtration. As seen in the Figure 3.21, all solvents were almost completely purified and regenerated cellulose membrane rejected the polymer which means membrane pores are smaller than the polymer chains in the solutions. The results of PES-DMSO and PES-NMP filtrations are presented by averaging two separate experiments. Also CA DA RW membrane exhibited great stability in all of solvents until at the end of filtration experiments over 10 days for DMSO and DMF and 25 day for NMP. Membranes used in the solvent filtration tests were undamaged at the end of the each experiment.

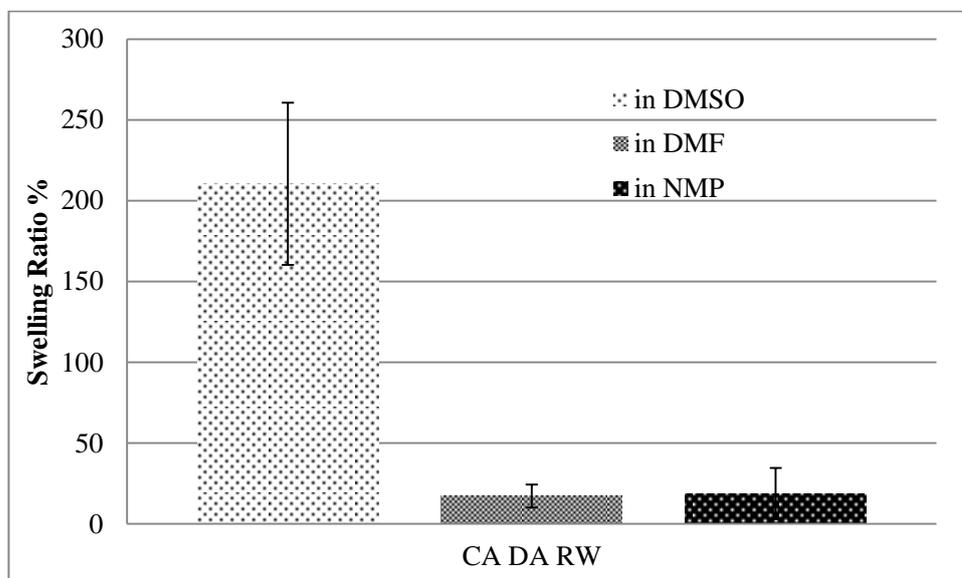


Figure 3.20. Swelling ratio of annealed and regenerated cellulose membrane in different solvents

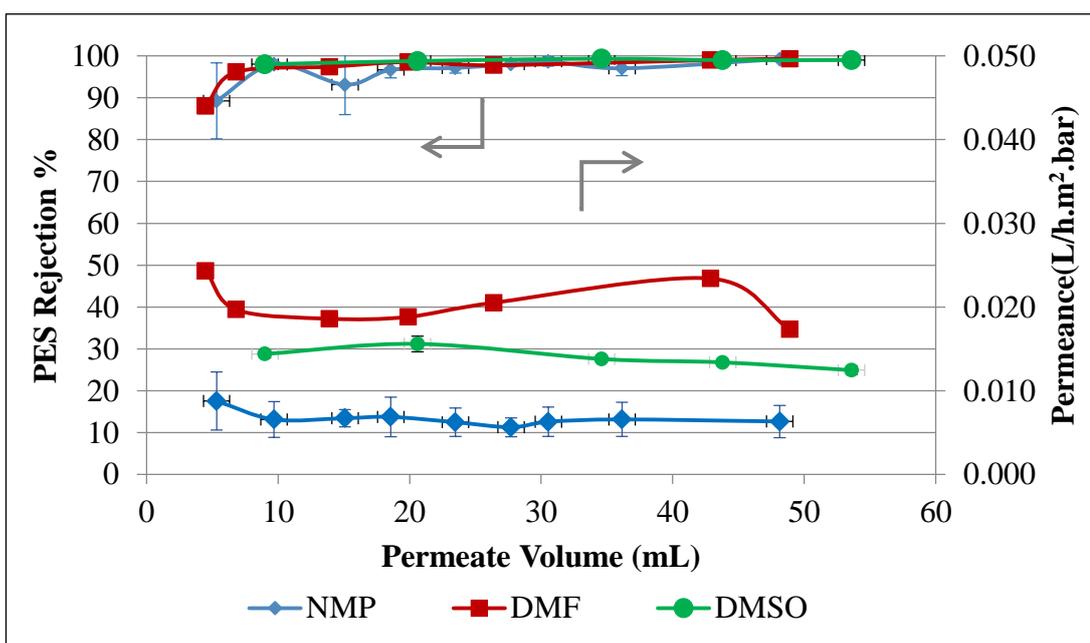


Figure 3.21. PES Rejection and permeance of CA DA RW membrane in different solvents. Filtration tests were performed at 10 bar with 1 g/L PES-NMP solution

In order to understand effect of transmembrane pressure and feed concentration, these parameters were changed and filtration tests were done by using the same type annealed and regenerated membrane, CA DA RW. Filtration experiment was done at 40 bar by using 1g/L PES-NMP solution as feed and it was observed that there was no decrease in PES rejection; it was remained constant at 99.9%. Then by keeping pressure at 10 bar, filtration experiment was performed with CA DA RW membrane by using 10 g/L PES-NMP solution. PES rejection was calculated as 99.8%. By taking these high separation performances of CA DA RW membrane in PES-NMP system into account same separation was tried with more porous membrane which has higher permeance may be used to perform PES separation at high quality. If more porous membrane will reject PES at sufficient ratio, there is no need to use dense membrane which produced by aiming nanofiltration in the beginning of the study. In order to produce a more porous membrane, polymer concentration in solution was changed. Polymer concentration was decreased and acetone was not

used as cosolvent. CA3 solution which contains 20% cellulose acetate and 80% DMSO were used to fabricate regenerated cellulose membrane (CA3 RW). This membrane was tested with 1 g/L PES-NMP solution at 10 bar. Pure solvent permeance was found as 1.23 L/h.m².bar which was much higher than previous membrane as intended. However PES rejection decreased to 91.5%. All of these results were concluded in Table 3.3.

Table 3.3. Results of PES-NMP filtration with varying membranes, feed concentrations and pressures

Membrane Code	PES-NMP concentration (g/L)	Operation pressure(bar)	Rejection%	Permeance (L/h.m².bar)
CA DA RW	1	10	99.9	0.007
CA DA RW	1	40	99.9	0.002
CA DA RW	10	10	99.8	0.003
CA3 RW	1	10	91.5	1.23

In summary, at 1 g/L and 10 g/L PES concentration at 10 bar and 40 bar over 99.8% polymer rejection was obtained in NMP. This is a quite promising result for ultrafiltration applications in polar aprotic solvents. Also, it was observed that as polymer concentration in the polymer solution decreases, rejection decreased.

CHAPTER 4

CONCLUSION

In this study, cellulose membranes and regenerated cellulose membranes via alkaline hydrolysis of cellulose acetate membranes were produced for filtration applications in organic solvents. Due to strong hydrogen bonds, cellulose is a resistant polymer to most of the solvents including polar aprotics. Ionic liquid, [EMIM]OAc, was used to prepare cellulose solutions for membrane fabrication via phase inversion. Firstly cellulose flat sheet membranes were produced and effect of drying medium on membrane morphology and separation performance was observed. From SEM images, it was shown that membrane dried from hexane has more open pores by comparing with the one dried from ethanol and separation performance of membrane dried from ethanol was better. Cellulose hollow fiber membranes were also fabricated by using two different polymer dope solutions. Bore liquid and coagulation bath temperature were varied to arrange the location of dense skin layer. Generally these hollow fibers had dense structures. When bore liquid was 80% DMSO-water mixture and coagulation bath temperature was 50 °C, hollow fibers which have porous structure were obtained. Bromothymol Blue (624 Da)- ethanol solution were used to test nanofiltration performance of these and dye rejection was found as 40% at 2 bar.

In the second part of the study, cellulose acetate membranes were produced by phase inversion process and regenerated to cellulose via alkaline hydrolysis. By this way cellulose membranes were produced without using ionic liquids which are viscous and expensive solvents. Deacetylation of cellulose acetate membranes were done by immersing in 0.05 M aqueous solution of NaOH for 24 hours. In order to evaluate the best deacetylation condition, regenerated membranes in different solution concentrations and durations were examined by FTIR spectra and deacetylation efficiencies were calculated by taking ratio of acetate group areas to hydroxyl group

areas. Firstly regenerated cellulose membranes are fabricated in flat sheet geometry. Effect of regeneration and annealing on separation performance is evaluated by dye filtration tests. By using 0.05 mM Bromothymol Blue (624 Da) - ethanol solution, filtration tests were done at 4 bar. Dye rejections of cellulose acetate membranes were improved from 24% to >80% after dry annealing at 120°C and wet annealing at 85°C. However, after deacetylation, the dye rejections of regenerated cellulose membranes decreased to 35-40%. Also cellulose acetate hollow fiber membranes were produced and annealed cellulose acetate hollow fibers have 35-45% dye rejection. After deacetylation to cellulose, no dye rejection was observed. Similarly with flat sheet membranes, deacetylation decreased separation performance.

In order to increase dye rejections of regenerated membranes, deacetylation medium was changed and ethanol-water mixture was used to decrease swelling during deacetylation but no significant difference occurred in separation performances. These regenerated membranes were used to recover different aprotic solvents which are DMSO, NMP and DMF from their 1 g/L and 10 g/L PES solutions. PES rejection of annealed and regenerated cellulose membranes were greater than 99% in all solvents at 10 bar and 40 bar. Regenerated membranes were stable all through the filtration during over 25 days in NMP and DMF and over 10 days for DMSO.

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APPENDICES

A. Calibration Curves

Calibration curves were used to calculate concentrations of permeates and retentate.

Bromothymol Blue-Ethanol

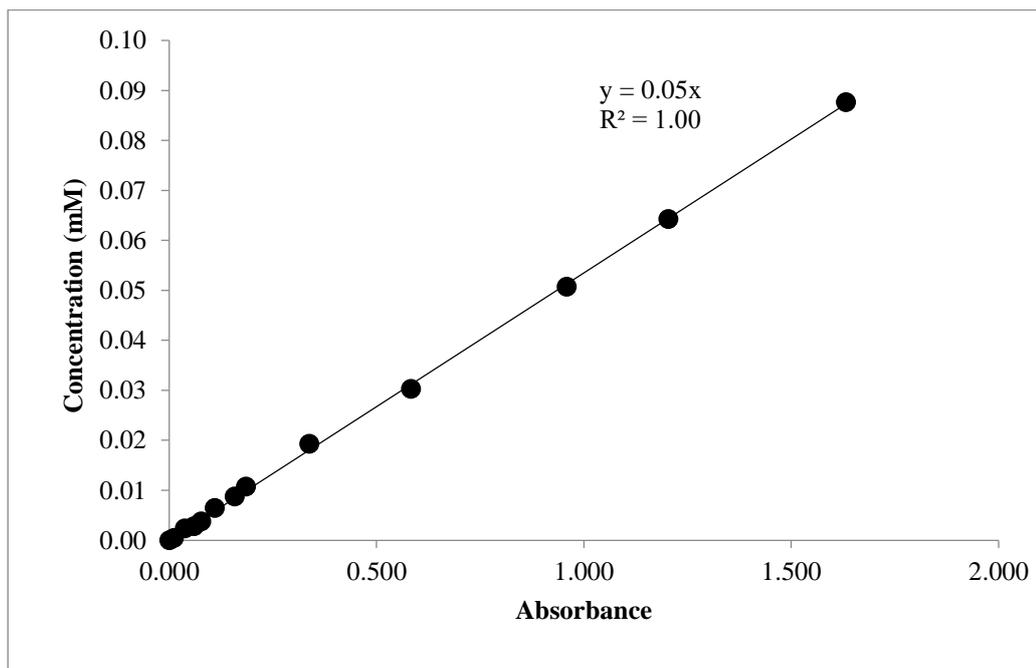


Figure A.1. Calibration curve of Bromothymol Blue-Ethanol solution at 423 nm(Konca, 2018)

PES- Aprotic Solvents

Uv visible spectra analysis of pure solvent and PES-solvent solutions in different concentrations were done to determine the optimum wavelength for absorbance measurements. The wavelength which gives maximum absorbance was chosen as calibration wavelength.

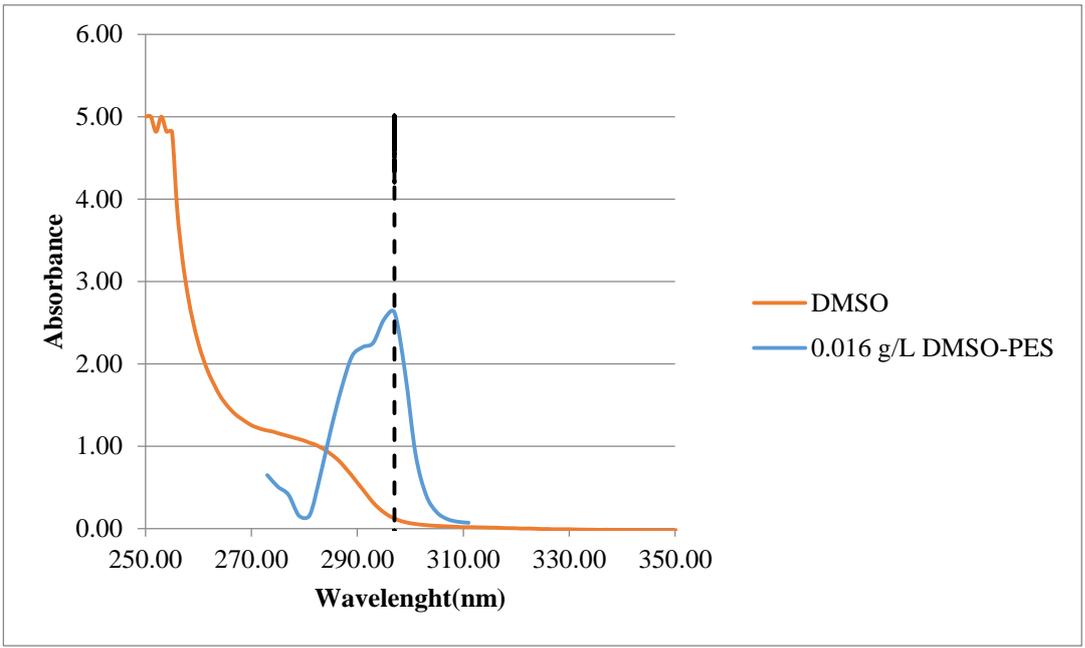


Figure A.2. UV visible spectra of PES-DMSO solution

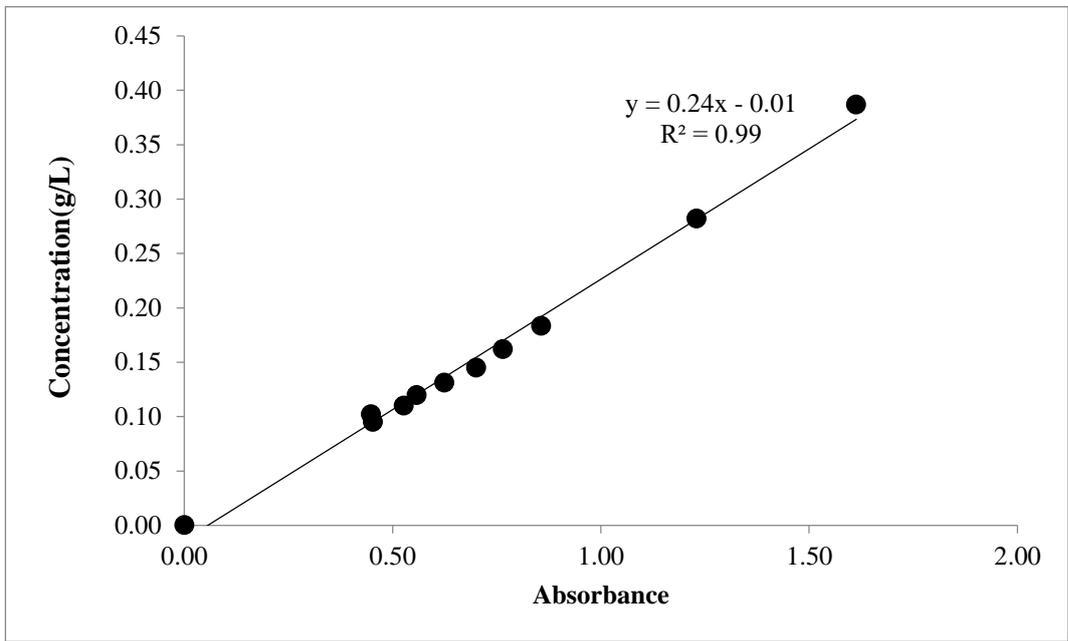


Figure A.3. Calibration curve of PES-DMSO solution at 297 nm

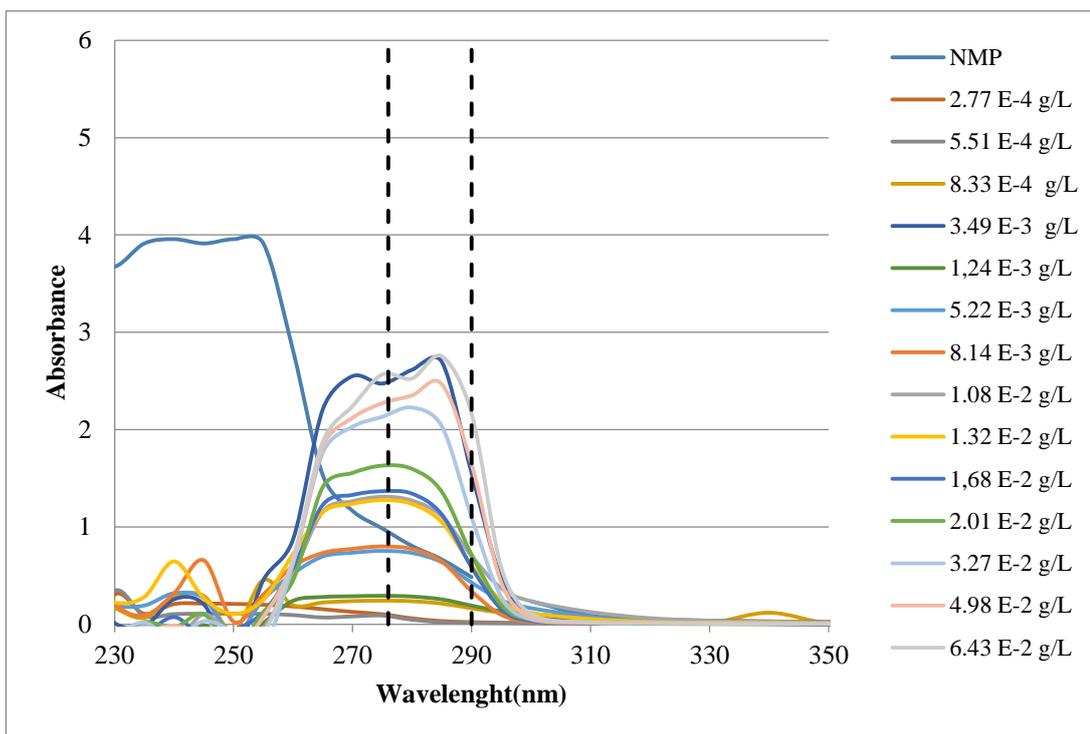


Figure A.4. UV visible spectra of PES-NMP solution

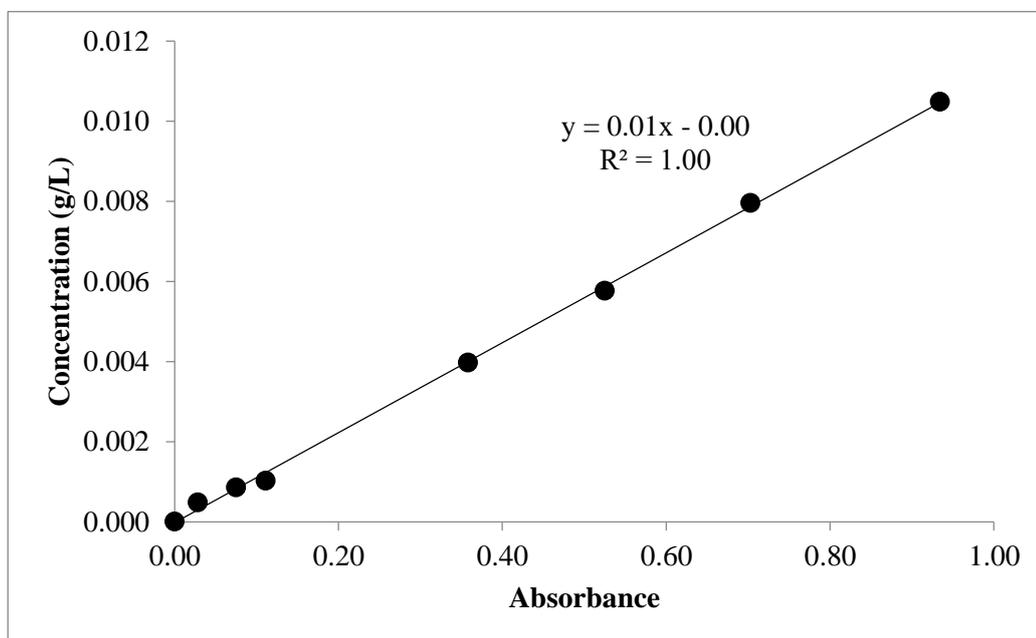


Figure A.5. Calibration curve of PES-NMP solution at 276 nm

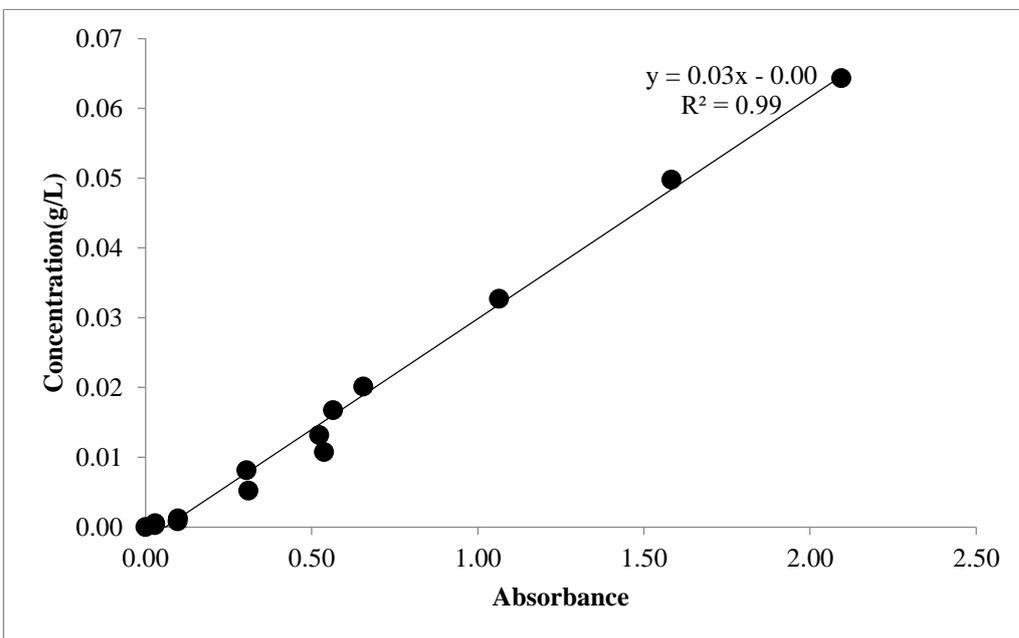


Figure A.6. Calibration curve of PES-NMP solution at 290 nm

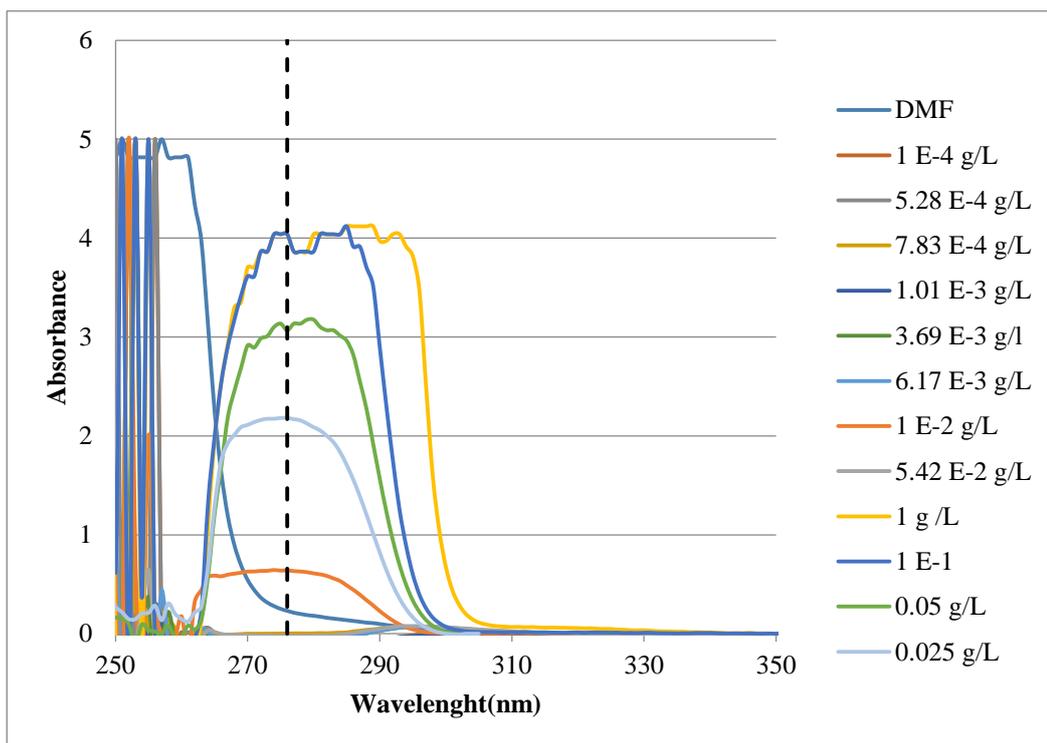


Figure A.7. UV visible spectra of PES-DMF solution

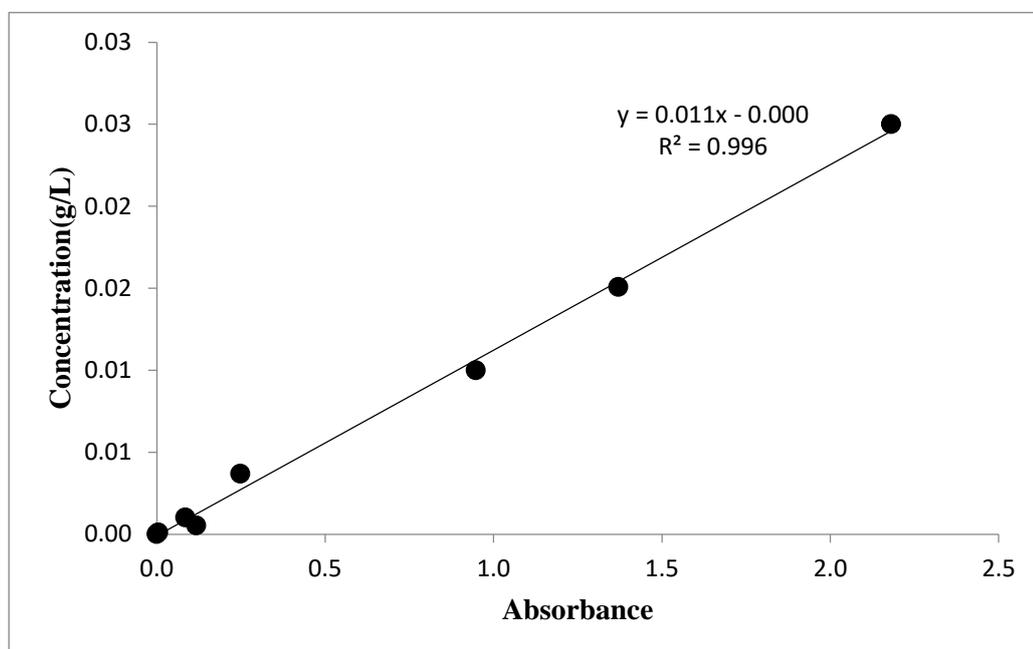


Figure A.8. Calibration curve of PES-DMF solution at 276 nm

NaCl-water solution

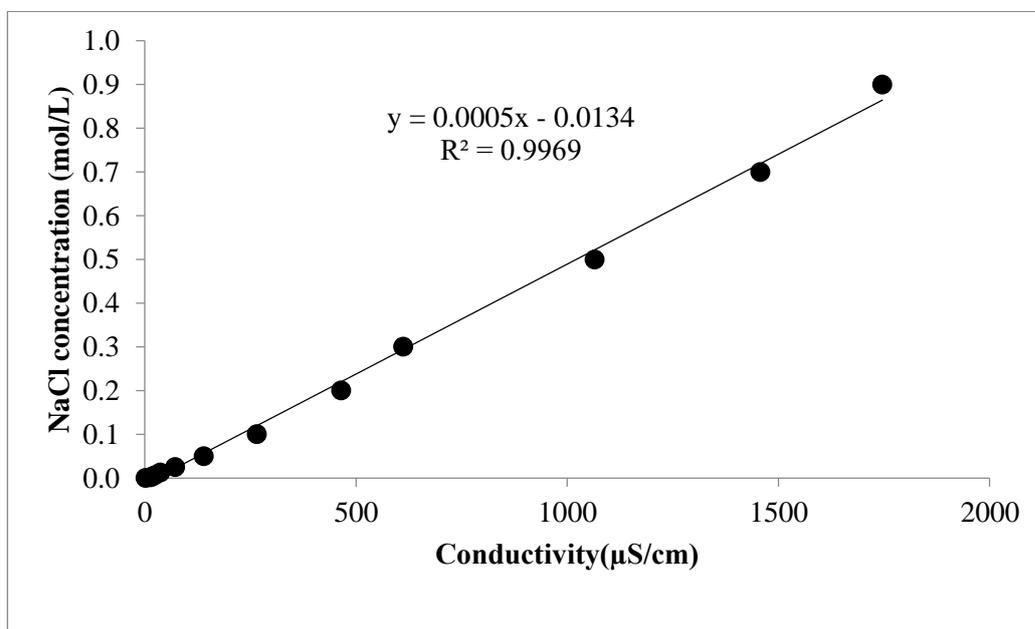


Figure A.9. Calibration curve for NaCl concentration and conductivity of solution at high conductivities

B. Solubility Parameters

Solubility parameters are used to predict solubility relation between solvent and polymers. “Like dissolves like“ principle is modified. If components have similar Hansen Solubility Parameters, their affinities to each other are high and consequently, they form a mixture spontaneously. By comparing solubility parameters of solvent with polymer, solvent and nonsolvent qualities can be determined.

Three different solubility parameter was used to represent three different types of molecular interactions which are permanent dipole-permanent dipole interactions (δ_p), dispersion interactions (δ_D) and hydrogen bonding(δ_H). By using these parameters Solubility Parameter Distance (Ra) is calculated by using following equation.

$$Ra^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2$$

The solubility area of the material is expressed in spheres, and the distance between the radii of the spheres of the two materials is expressed in R_a . The radius of the material to which the solvent should be compatible is also indicated as Radius of solubility sphere(R_o). If R_a is beyond R_o , interactions between two materials results in low affinity. In order to understand compatibility of two different components, Relative energy difference(RED) is calculated as;

$$RED = \frac{R_a}{R_o}$$

If RED value of solvent for a polymer is less than unity that means solvent is a good solvent for that polymer. As RED value diverges from zero, solvent quality decreases. As RED value approaches the unity, solvent may not dissolve polymer. If RED value is higher than unity, solvent affinity to polymer is very low. RED values of cellulose acetate-DMSO and cellulose acetate-acetone were calculated. Solubility parameters of components and radius of solubility sphere value of cellulose acetate were taken from Hansen Solubility Parameters (Hansen, 2007)

Table B.1. Solubility Parameters of cellulose acetate, DMSO and acetone

Chemical	δd (Mpa)^{1/2}	δp (Mpa)^{1/2}	δh (Mpa)^{1/2}
Cellulose Acetate	18.2	12.4	10.8
DMSO	18.4	16.4	10.2
Acetone	15.5	10.4	7

Table B.2. R_a and RED Values of Interactions between cellulose acetate-DMSO and cellulose acetate-acetone

Polymer-Solvent	Distance R_a	RED_{p-s}
Cellulose Acetate-DMSO	4.06	0.55
Cellulose Acetate-Acetone	6.90	0.93

C. Spinning Parameters of Hollow Fiber Membranes

Table C.1. Spinning parameters of cellulose hollow fibers

Group:	No	Flow rate(mL/min)	Flow rate(mL/min)	Air gap(cm)	Observation
A	1	5.7	1.7	2.5	Straight
	2	5.7	3.5	2.5	Straight
	3	11.5	3.5	2.5	Straight
	4	17.2	3.5	2.5	Straight
B	5	5.7	1.7	4	Straight
C	6	17.2	4.3	21	twisted, thin
	7	11.5	5.2	21	twisted, thin
	8	9.6	3.5	21	twisted
	9	11.5	5.2	9	straight, dense
	10	17.2	5.2	9	straight, dense
	11	17.2	3.5	9	straight, dense
	12	17.2	3.5	17	twisted
	13	17.2	3.5	13	twisted
	14	17.2	1.7	10	straight, boreless
	15	11.5	3.5	10	straight, dense
D	16	7.656	1.725	21	Straight, boreless
	17	7.656	3.45	21	Straight, boreless
	18	11.484	5.175	21	Straight, boreless
	19	11.484	3.45	4	Straight, thick
	20	11.484	3.45	20	Straight, thick
	21	5.742	1.725	20	Straight, thick
	22	5.742	3.45	20	Straight, thick
	23	17.226	5.175	20	Straight, thick
	24	11.484	8.634	11	
	25	15.314	11.513	15	thick
	26	11.484	8.634	15	
E	27	11.484	3.45	4	Straight, irregular
	28	17.226	5.175	4	Straight, irregular
	29	17.226	6.9	4	Straight, irregular
	30	11.484	5.175	4	Straight, irregular

Table C.2. *Spinning parameters of cellulose acetate hollow fibers*

Group:	No	Flow rate(mL/min)	Flow rate(mL/min)	Air gap(cm)	Observation
F	31	5.7	1.7	10	Straight
	32	5.7	1.7	18	Twisted
	33	11.5	3.5	16.3	Straight,thick
	34	11.5	3.5	4	Straight,thick
G	35	5.7	1.7	10	Twisted
	36	17.2	5.2	10	Twist
	37	5.7	1.7	4	Irregular
	38	11.5	3.5	4	Straight
	39	5.7	1.7	18	Twisted
	40	11.5	3.5	4	Straight
	41	11.5	1.7	4	Straight
	42	10.0	3.5	4	straight, porous
	43	10.0	1.7	4	straight
	44	6.0	1.7	4	straight

D. Choline Acetate Synthesis

Choline acetate which is a cheaper and biodegradable ionic liquid by comparing with [EMIM]OAc was synthesized by aiming preparation of cellulose solutions to membrane casting. Choline hydroxide solution in methanol and water were neutralized with acetic acid. As a result of this reaction, choline acetate was formed.

The amount of acetic acid should be added to complete the neutralization reaction and obtain choline acetate was calculated as;

Where ; ChOH: Choline Hydroxide

ChAc: Choline Acetate

AA: Acetic Acid

$$MW_{ChOH} = 121.18 \text{ g/mol}$$

$$MW_{ChAc} = 146.21 \text{ g/mol}$$

$$MW_{AA} = 60.05 \text{ g/mol}$$

In order to prepare 30 g ChAc solution ($30 \text{ g} * \frac{1}{MW_{ChAc}} = 0.205 \text{ mol ChAc}$) ; 12.31 g of AA ($0.205 \frac{\text{g}}{\text{mol}} AA * MW_{AA}$) 12.31 g was needed stoichiometrically.

ChOH solution which contains 0.205 mole of choline should be added.

- By using ChOH solution in water with wt 46%, 54 g of ChOH solution should be used.

$$\frac{0.205 \text{ mol ChOH} * 121 \frac{\text{g}}{\text{mol}} * 100 \text{ g solution}}{46 \text{ g ChOH}} = 54.004 \text{ g solution}$$

- By using ChOH solution in methanol with wt 45%, 55.2 g of ChOH solution should be used.

$$\frac{0.205 \text{ mol ChOH} * 121 \frac{\text{g}}{\text{mol}} * 100 \text{ g solution}}{45 \text{ g ChOH}} = 54.004 \text{ g solution}$$

AA was added drop by drop to the ChOH solutions. Then water and methanol was evaporated by using Rotary Evaporator(IKA RV 8) in Nanostructured Polymeric Materials Laboratory, METU-ChE . The solution which contains water was heated at 45°C for 40 min, at 70°C 45 min and solution which contains methanol was heated at 45°C for 45 min. Then synthesized mixtures were mixed at 90°C under vacuum.

In order to observed reaction progress and control whether reaction was completed or not, pH values were recorded as adding acetic acid into choline hydroxide solution 46 wt% in H₂O (Table D.1.). Totally 12.31 g acetic acid is added to 54.004 g choline hydroxide solution 46 wt% in H₂O.

Table D.1. *Added acetic acid amount and pH of ChOH-AA reaction mixture*

Added acetic acid amount (g)	Recorded pH
0	14.329
0.3	14.08
1	14.186
2	14.25
3	14.1
4.5	13.97
6	13.855
7.5	13.545
9	13.07
10.5	11.8
12.31	6.817

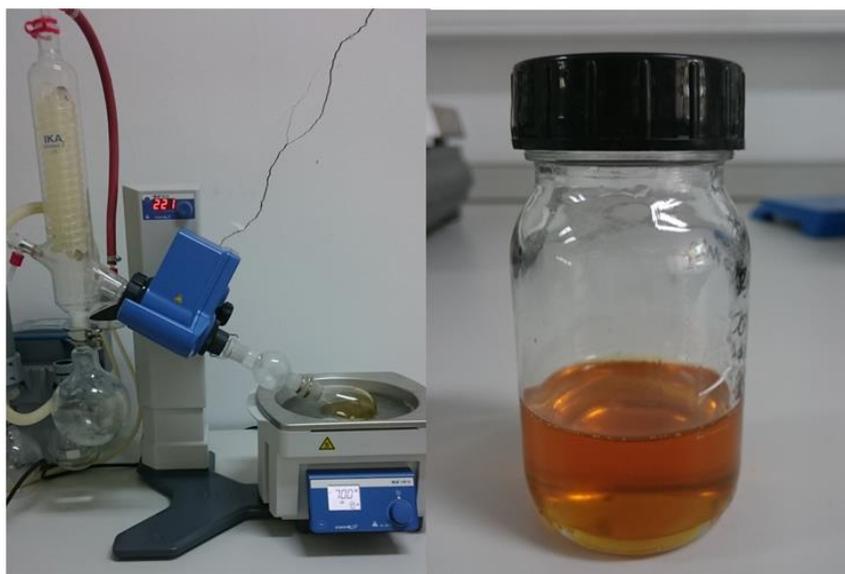


Figure D. 1. Solvent removal from choline acetate via Rotary Evaporator (left) and the produced choline acetate (right)

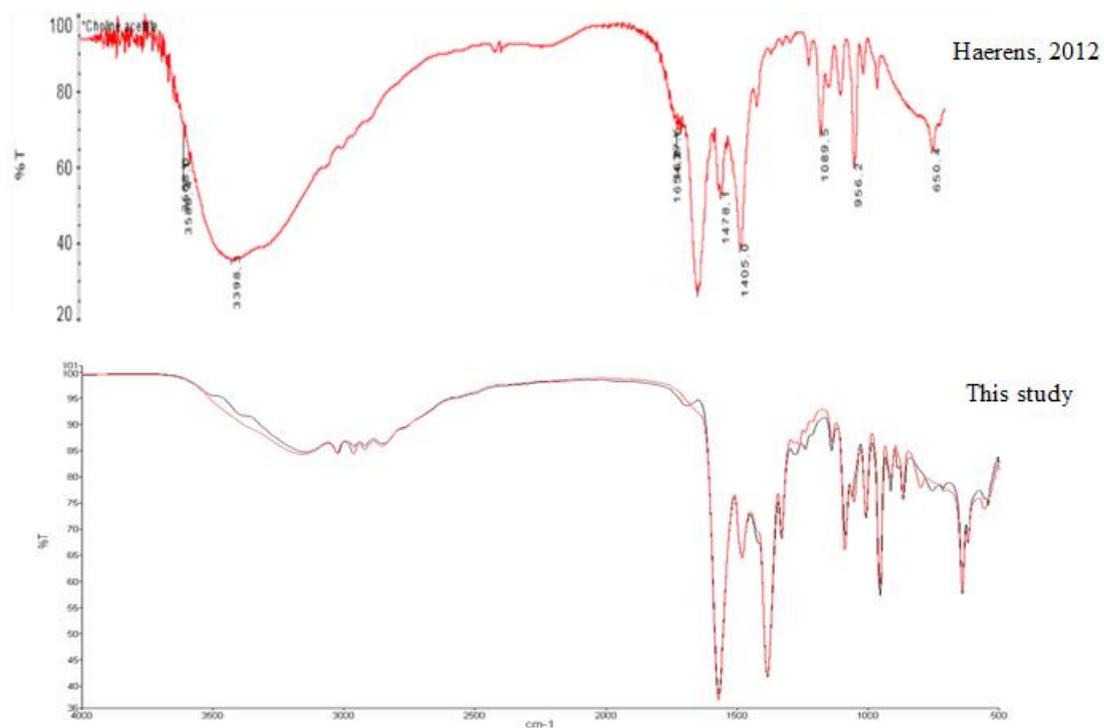


Figure D.2. FT-IR analysis of choline acetate in the literature (Haerens, 2012) (up), FT-IR analysis of produced choline acetate in this study (bottom)

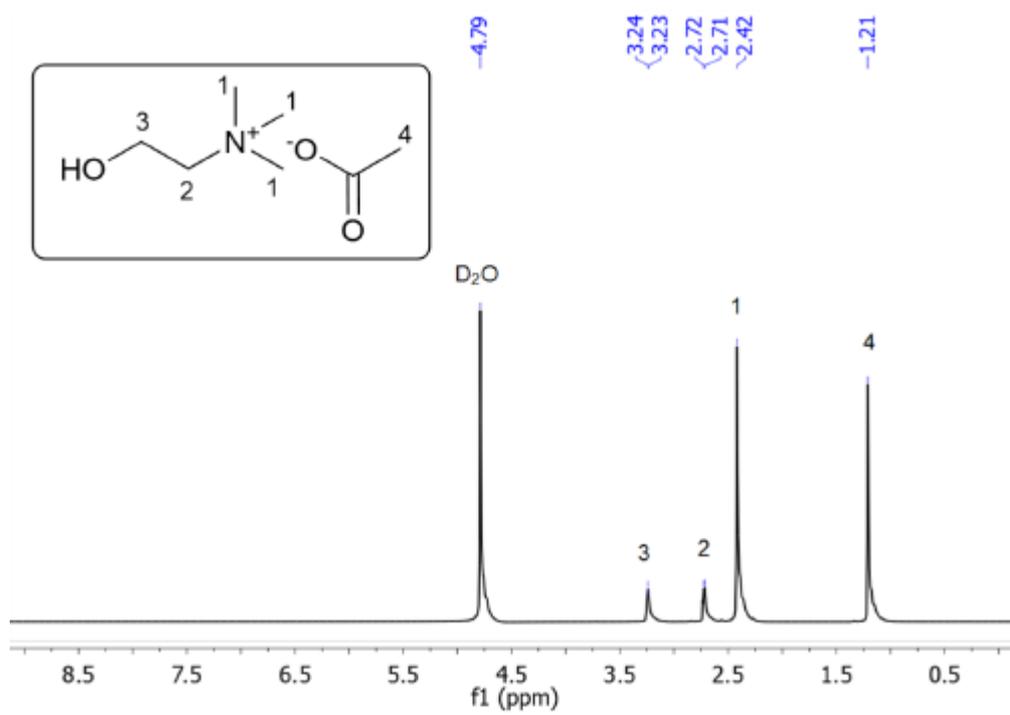


Figure D.3. NMR analysis of choline acetate in the literature (Sharma, 2015)

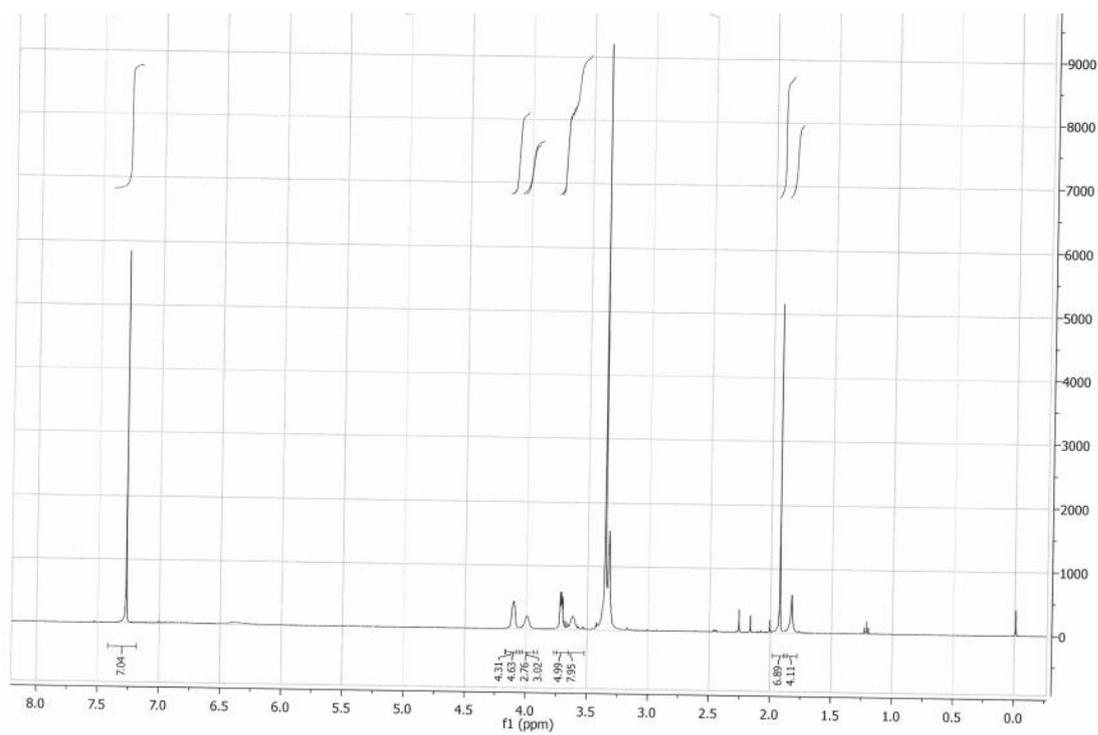


Figure D.4. NMR analysis of produced choline acetate

FT-IR and Nuclear Magnetic Resonance (NMR) analysis of produced choline acetate were done to verify synthesis completed and compared with literature.