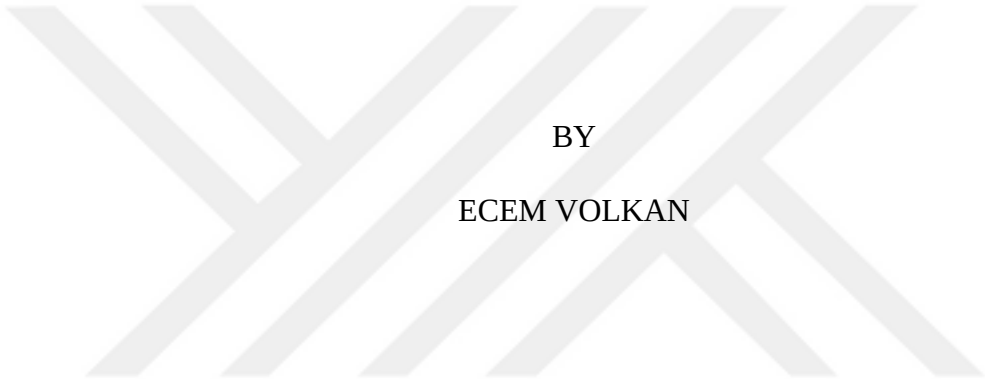


MEMBRANE FABRICATION USING NANOCRYSTALLINE CELLULOSE

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY



BY
ECEM VOLKAN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

SEPTEMBER 2020

Approval of the thesis:

**MEMBRANE FABRICATION USING NANOCRYSTALLINE
CELLULOSE**

submitted by **ECEM VOLKAN** in partial fulfillment of the requirements for the degree of **Master of Science in Chemical Engineering, Middle East Technical University** by,

Prof. Dr. Halil Kalıpçılar
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Pınar Çalık
Head of the Department, **Chemical Engineering**

Assoc. Prof. Dr. Zeynep Çulfaz Emecen
Supervisor, **Chemical Engineering, METU**

Examining Committee Members:

Prof. Dr. Halil Kalıpçılar
Chemical Engineering, METU

Assoc. Prof. Dr. Zeynep Çulfaz Emecen
Chemical Engineering, METU

Asst. Prof. Dr. Nazife Işık Haykır
Energy Engineering, Ankara University

Assoc. Prof. Dr. Erhan Bat
Chemical Engineering, METU

Asst. Prof. Dr. Emre Büküşoğlu
Chemical Engineering, METU

Date: 08.09.2020



I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name Last name : Ecem Volkan

Signature :

ABSTRACT

MEMBRANE FABRICATION USING NANOCRYSTALLINE CELLULOSE

Volkan, Ecem
Master of Science, Chemical Engineering
Supervisor : Assoc. Prof. Dr. Zeynep Çulfaz Emecen

September 2020, 185 Pages

Cellulose is a biopolymer which is resistant to many solvents due to inter- and intramolecular hydrogen bonds; also, it is hydrophilic and resistant to fouling, which makes cellulose attractive for membrane applications in aqueous and organic media.

Nanocrystalline cellulose (NCC) is a promising material due to high surface area, rod-like structure, good dispersion abilities, biodegradability and nanoscale. It is produced by acid hydrolysis using mineral acids to digest amorphous regions of the cellulose chain, yielding crystalline regions as discrete crystalline nanofibers.

In this study, the main aim is to fabricate membranes using nanocrystalline cellulose. The first procedure is to fabricate membranes via controlled precipitation of an NCC suspension on a support membrane to produce a selective membrane layer without using organic solvents, and these membranes' stability, morphology, and separation performance were examined. In other procedure, the all-cellulose nanocomposite membranes with improved crystallinity with the ultimate goal of increasing solute rejection were produced by either adding NCC into membrane casting solution or partial dissolution of cellulose by investigation membranes' crystallinity, morphology and separation performances.

Using 50 % aqueous H_2SO_4 solution, 10 ml/g acid to cellulose ratio and 30 minutes reaction time (NCC50 H_2SO_4 -cotton-30/10) NCC with ~ 250 nm length and ~ 30 nm width was produced and used in membrane fabrication by deposition.

For precipitating the stable colloids of NCC on the CA or PES support membrane, 200 mM AlCl_3 and 1 M NaOH were used. Different NCC deposition amounts on the CA support membrane were used to see the deposition thickness effect on the NCC membrane. Deposition of NCC on CA support membrane decreased the pure water permeance, proportional to the deposition amount, and increased the rejection of Blue Dextran (5 kDa) from 52 % to ~ 90 % for all deposition amounts. Besides, membranes with 0.24 mg/cm^2 deposit were stable in water for up to 1 week. Membranes fabricated by alkali desulfation of deposited NCC, on the other hand, did not form defect-free continuous deposits, possibly due to the effect of the high alkalinity used on the support membrane pores.

Membranes fabricated using polymer solutions containing NCC or partially dissolved cellulose did not show improved rejection due to aggregation, swelling or complete dissolution of crystalline regions of cellulose.

Keywords: Nanocrystalline cellulose, all-cellulose nanocomposite, colloid stability, ultrafiltration, membrane

ÖZ

NANOKRİSTAL SELÜLOZ KULLANILARAK MEMBRAN ÜRETİMİ

Volkan, Ecem
Yüksek Lisans, Kimya Mühendisliği
Tez Yöneticisi: Doç. Dr. Zeynep Çulfaz Emecen

Eylül 2020, 185 sayfa

Selüloz, moleküller içi ve moleküller arası hidrojen bağlarından dolayı birçok çözücüye dirençli bir hidrofilik biyopolimerdir ve kirlenmeye karşı dirençlidir, bu da selülozu sulu ve organik ortamlarda membran uygulamaları için çekici kılar.

Nanokristalin selüloz (NKS), yüksek yüzey alanı, çubuk benzeri yapısı, iyi dispersiyon yetenekleri, biyolojik olarak parçalanabilirlik ve nano boyutları nedeniyle gelecek vaat eden bir malzemedir. NKS, mineral asitler kullanılarak selülozun asit ile hidrolize edilip amorf bölgelerinin sindirilmesi ile elde edilir ve bu işlem sonucunda kristal nanolifler kalır.

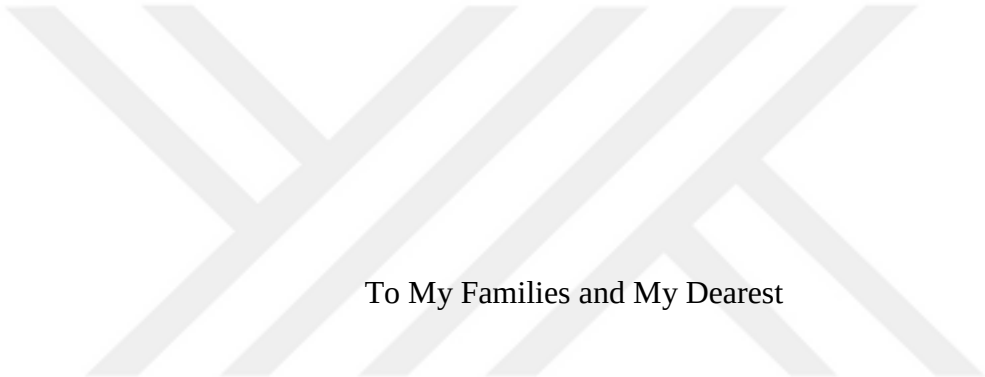
Bu çalışmada temel amaç nanokristalin selüloz kullanarak membran imalatı yapmaktır. İlk prosedür, seçici bir membran tabakası oluşturmak için bir destek membranı üzerinde bir NCC süspansiyonunun kontrollü çökeltilmesi yoluyla membranlar üretildi ve bu membranların stabilitesi, morfolojisi ve ayırma performansı incelendi. Diğer bir prosedürde ise çözünen madde reddini arttırma nihai amacı ile geliştirilmiş kristalliği olan tüm selüloz nanokompozit membranlar, ya NKS'nin membran döküm çözeltisine eklenmesi ya da selülozun kısmi çözünmesi ile üretildi.

% 50 sulu H₂SO₄ çözeltisi kullanılarak, 10 ml / g asit selüloz oranı ve 30 dakika reaksiyon süresi (NCC50H₂SO₄-pamuk-30/10) ile ~ 250 nm uzunluğunda ve ~ 30 nm genişliğinde NCC üretildi ve biriktirme yöntemi ile membran üretiminde kullanıldı.

NCC'nin stabil kolloidlerinin CA veya PES destek membranı üzerinde çökeltilmesi için 200 mM AlCl₃ ve 1 M NaOH kullanıldı. CA10 destek membranı üzerinde farklı NCC biriktirme miktarları, NCC membranı üzerindeki birikim kalınlığı etkisini görmek için kullanıldı. NCC'nin CA10 destek membranı üzerinde birikmesi, birikinti miktarıyla orantılı olarak saf su geçirgenliğini azalttı ve tüm biriktirme miktarları için Mavi Dekstranın (5 kDa) reddini % 52'den ~ % 90'a yükseltti. Ayrıca 0.24 mg / cm² birikimli membranlar suda 1 haftaya kadar stabil kalmıştır. Ek olarak, biriken NCC'nin alkali desülfasyonu ile üretilen membranlar, muhtemelen destek membran gözenekleri üzerindeki yüksek alkaliliğin etkisinden dolayı, gözeneksiz düzgün birikime sebep olmadı.

NCC veya kısmen çözünmüş selüloz içeren polimer çözeltileri kullanılarak imal edilen membranlar, selülozun kristalli bölgelerinin topaklaşması, şişmesi veya tamamen çözünmesi nedeniyle iyileştirilmiş reddetme değerleri elde edilemedi.

Anahtar Kelimeler: Selüloz nanokristal, tamamı selüloz nanokompozitler, kolloid stabilitesi, ultrafiltrasyon, membran



To My Families and My Dearest

ACKNOWLEDGMENTS

First of all, I would like to express my sincere gratitude to my advisor Assoc. Prof. Dr. Zeynep ulfaz Emecen for her patience, support, motivation, enthusiasm, and immense knowledge. Her guidance helped me to being a good researcher and writing of this thesis.

I would like to thank every new and old member of ulfaz-Emecen research group. Working in our lab was so much fun with their support, friendship, dancing, singing and nice conversations. Naneler who are Fatma, Zeynep, Canan and Begüm were always helped me in any problems when I started in our laboratory and even when they leave ODTU wherever they are in the world. Toprak who is the world's most entertaining travel and congress friend and the owner of the mouse tourism always supported me by saying that I will always be successful, and I would like to thank Aygen for her endless supports. They always encouraged me not only about my thesis but also in every problem.

I am very lucky girl in the world to have a family that supports me in every decision and my all education life. Their support, patience and love are more important to me than anything else in the world. My dear mom Nurhan, my dear dad Reşat and my little brother Efe who is sister's little sweet trouble and my companion always been with me. My brother born from another mother Kivan, I got to know you very late, but I'm glad to meet you. The support you gave us in every subject, especially the support you provided while writing my thesis, is very valuable for me. Atalay who is the love of my life, my peace, my joy, and my light; his endless support, endless patience, endless love and success of making me laugh in all conditions are priceless to me. You have such a big share in my every success that I am very lucky to be with me in any situation.

TABLE OF CONTENTS

ABSTRACT.....	v
ÖZ	vii
ACKNOWLEDGMENTS	x
TABLE OF CONTENTS.....	xi
LIST OF TABLES	xvi
LIST OF FIGURES	xviii
LIST OF ABBREVIATIONS	xxvi
LIST OF SYMBOLS	xxix
CHAPTERS	
1 INTRODUCTION	1
1.1 Membrane Preparation Techniques: Phase Separation Techniques.....	4
1.1.1 Non-solvent Induced Phase Separation (NIPS)	5
1.1.2 Solvents for Phase Separation Technique	7
1.2 Membrane Polymers: Cellulose	8
1.2.1 Cellulose and Its Derivatives	8
1.2.1.1 Cellulose	8
1.2.1.2 Nanocrystalline Cellulose (NCC)	11
1.3 Analysis of Particle Deposition on Membranes Using Resistances in Series Model with the Darcy's Law.....	17
1.4 The Kozeny-Carman Equation.....	18
1.5 The Aim of the Study	19
2 LITERATURE REVIEW	21

2.1	Effects of Production Conditions on Properties of NCC	21
2.2	Materials and Procedures to Affect Stability of NCC	23
2.3	Membranes/Films Production Using Nanoparticles	24
2.4	Cellulose Membranes	27
2.5	Fabrication of All-Cellulose Nanocomposite Films/Membranes by Partial Dissolution of Cellulose or Direct Addition of Nanocellulose into Membrane Matrix	31
3	EXPERIMENTAL PROCEDURES	37
3.1	Materials	37
3.2	Nanocrystalline Cellulose (NCC) Production.....	38
3.3	Membrane Production.....	42
3.3.1	Production of All-Cellulose Nanocomposite Membranes.....	42
3.3.1.1	Materials Used to Produce All-Cellulose Nanocomposite Membranes	42
3.3.1.2	Membrane Production Technique to Produce All-Cellulose Nanocomposite Membranes	43
3.3.2	Membrane Fabrication by Using Deposition of NCC on Support Membrane.....	47
3.3.2.1	Materials and Solutions to Produce Support Membrane.....	47
3.3.2.2	Used Techniques to Produce Support Membrane	48
3.3.2.3	Membrane Preparation Procedure by Deposition of NCC on Support Membrane	49
3.4	NCC Characterization.....	54
3.4.1	The Crystallinity Index Calculation	55
3.4.2	Sample Preparation for the DLS and Zeta Potential Measurement...	56
3.4.3	Sample Preparation for the TEM and SEM Analysis.....	57

3.5	Membrane Characterization	58
3.5.1	Sample Preparation for the SEM Analysis	58
3.5.2	Sample Preparation for the ATR-FTIR Analysis.....	58
3.6	Membrane Performance Tests.....	59
4	RESULTS AND DISCUSSIONS	63
4.1	Characterization of Nanocrystalline Cellulose (NCC).....	63
4.1.1	The NCC Made by HCl Hydrolysis (NCC-HCl).....	63
4.1.1.1	The X-Ray Diffraction (XRD) Analysis of NCC-HCl.....	63
4.1.1.2	The TEM Analysis of NCC-HCl	65
4.1.1.3	The DLS Analysis of NCC-HCl.....	67
4.1.2	The NCC Made by H ₂ SO ₄ Hydrolysis (NCC- H ₂ SO ₄)	67
4.1.2.1	The X-Ray Diffraction (XRD) Analysis of NCC- H ₂ SO ₄	67
4.1.2.2	The TEM and the SEM Analysis of NCC- H ₂ SO ₄	73
4.1.2.3	The DLS Analysis of NCC-H ₂ SO ₄	74
4.2	Membranes Fabricated via Controlled NCC Deposition	75
4.2.1	Precipitation of the NCC50H ₂ SO ₄ -cot-30/10 on the CA10 Support Membrane with AlCl ₃ and Different NCC Amounts to Produce the CA10D-P- S Membranes	75
4.2.1.1	The Zeta Potential Analysis of the NCC50H ₂ SO ₄ -cot-30/10 as a Function of AlCl ₃ Concentration	75
4.2.1.2	The ATR-FTIR Analysis of the CA10D-P-S Membranes	77
4.2.1.3	The SEM Analysis of the Support Membrane and the CA10D-P- S Membranes	79
4.2.1.4	The Separation Performance of the CA10D-P-S Membranes...	84

4.2.1.5	The BD5 Filtration Results of the CA10D-P-S Membranes Comparison with the Support Membrane.....	88
4.2.2	Precipitation of the Commercial NCC on the CA20 Support Membrane with AlCl_3	90
4.2.2.1	The Zeta Potential Analysis of the Commercial NCC as a Function of AlCl_3 Concentration.....	90
4.2.2.2	The ATR-FTIR Analysis of the CA20D-C-S Membranes	91
4.2.2.3	The SEM Analysis of the CA20D-C-S Membranes and the Support Membrane	92
4.2.2.4	The Separation Performance of the CA20D-C-S Membranes ...	94
4.2.2.5	The Solute Rejection Performance Analysis of the CA20D-C-S Membranes	96
4.2.3	Precipitation of the $\text{NCC50H}_2\text{SO}_4$ -cot-30/10 on the PES10PEG10-1MH Support Membrane with NaOH	97
4.2.3.1	The Zeta Potential Analysis of the $\text{NCC50H}_2\text{SO}_4$ -cot-30/10 as a Function of NaOH Concentration and Reaction Time	98
4.2.3.2	The ATR-FTIR Analysis of the PES10PEG10-1MH-D-P-NORMAL-B Membranes.....	100
4.2.3.3	The SEM Analysis of PES10PEG10-1MH-D-P-NORMAL-B Membranes and the Support Membrane.....	102
4.2.3.4	The Separation Performance of the PES10PEG10-1MH-D-P-NORMAL-B Membranes.....	105
4.2.3.5	The BD5 Rejection Performance Analysis of the PES10PEG10-1MH-D-P-NORMAL-B Membranes	106
4.3	All-Cellulose Nanocomposite Membranes	107
4.3.1	The XRD Analysis Results of Some of the All-Cellulose Nanocomposite Membranes	107

4.3.2	The Optic Microscope Images of Some of the All-Cellulose Nanocomposite Membranes.....	109
4.3.3	The Solute Rejection Performances of the All-Cellulose Nanocomposite Membranes.....	114
5	CONCLUSIONS.....	117
	REFERENCES	121
	APPENDICES	137
A.	Sample Deposition Thickness Calculation for Nonporous NCC Layer ...	137
B.	The Solute (Dye) Calibration Curves for UV-Vis Spectrophotometry	138
C.	The DLS Analysis Plots for Some of the NCC.....	141
D.	The ATR-FTIR Analysis Results of the NCC Membranes	142
E.	The Permeance and Average Resistance Results For the NCC Membranes During Deposition Procedure	147
F.	The Porosity and The Deposited Layer Thickness Calculation Using the Kozeny-Carman Equation for the CA10D-P-S Membranes.....	159
G.	The Precipitation of the Commercial NCC on the CA20 Support Membrane with HCl.....	162
H.	The Precipitation of the NCC-HCl on the KK2D Membrane Using Water and EtOH	172
I.	The Average Pore Size Calculation with Ferry-Renkin Equation	177
J.	The XRD Analysis Results of Some of Produced All-Cellulose Nanocomposite Membranes.....	178
K.	The SEM Images of Some of Produced All-Cellulose Nanocomposite Membranes.....	181
L.	The NCC Crystallinity Calculation from Calculated Yield Results	185

LIST OF TABLES

TABLES

Table 3.1 The Properties of Commercial NCC	37
Table 3.2 Different Preparation Condition of NCC	40
Table 3.3 Production Details of the NCC for Further Processes.....	41
Table 3.4 All-Cellulose Nanocomposite Membranes and Their Production Ways	44
Table 3.5 Produced Support Membranes Solutions and Their Precursor Solution Compositions.....	48
Table 3.6 Support Membranes with Production Technique(s).....	49
Table 3.7 Detailed Table of the Applied Procedures on the Support Membrane....	53
Table 3.8 Membranes and Their Used Filtration Solutions	60
Table 3.9 Summation of Material Properties of Solutes	61
Table 4.1 The Crystallinity Index (CI) Values of the Produced NCC-HCl	64
Table 4.2 The DLS Analysis Result for the NCC-HCl with Literature Comparison	67
Table 4.3 The Crystallinity Index (CI) Values of the Produced NCC-H ₂ SO ₄	70
Table 4.4 The DLS Analysis Result for the NCC-H ₂ SO ₄ with Literature Comparison.....	75
Table 4.5 The Absolute Value of Area under the Cellulose Peak / the Area under the CA Peak for Just After Deposition and the Normalized Values of Area under the Cellulose Peak / the Area under the CA Peak with Respect to Just after Deposition Values for Keeping the CA10D-P-S Membranes in Water for 24 Hours and 1 Week	79
Table 4.6 The Porosity and the Deposited NCC Layer Thickness Calculation Results Using Kozeny-Carman Equation for the CA10D-P-S.....	87
Table 4.7 The Absolute Value of Area under the Cellulose Peak / the Area under the CA Peak for Just After Deposition and the Normalized Values of Area under the Cellulose Peak / the Area under the CA Peak with Respect to Just after Deposition Values for Keeping the CA20D-C-NORMAL-S Membranes in Water for 24 Hours and 1 Week.....	91

Table 4.8 The Porosity and the Deposited NCC Layer Thickness Calculation Results Using Kozeny-Carman Equation for CA20C-P-NORMAL-S Membrane	96
Table 4.9 The Absolute Values of Area under the Cellulose Peak / the Area under the PES Peak for Just After Deposition and Keeping the PES10PEG10-1MH-D-P-NORMAL-B Membranes in Water for 24 Hours and 1 Week Using Different Measurements Place on the PES10/PEG10-1MH-D- P-NORMAL-B Membranes Surface Which Is Shown By Measurement Number	102
Table D.1 The Values of Area under the Cellulose Peak / the Area under the CA Peak for the CA10D-P-S Membranes	144
Table D.2 The Values of Area Under the Cellulose Peak / the Area Under the CA Peak for the CA20D-C-S Membranes	146
Table G.3 The Values of Area under the Cellulose Peak / the Area under the CA Peak for the NCC Membranes Prepared Using Different HCl Concentrations	165

LIST OF FIGURES

FIGURES

Figure 1.1. Schematic representation of membrane separation process.....	2
Figure 1.2. Classification of the pressure-driven membrane separation processes...	2
Figure 1.3. The ternary diagram of three components (solvent, polymer and non-solvent) of NIPS ¹⁹ with the qualitative representative path	5
Figure 1.4. Schematic representation of asymmetric and symmetric membranes	7
Figure 1.5. Structure of Cellulose ³³	9
Figure 1.6. Schematic representation of acid hydrolysis of cellulose ⁵⁹	12
Figure 1.7. Schematic representation of electrical double layer of the charged particle ⁷⁰	13
Figure 1.8. Schematic representation of zeta potential results	14
Figure 1.9. Schematic representation of stability changing of the NCC in the solution medium	15
Figure 1.10. The schematic representation of alkali desulfation of NCC ⁷⁷	16
Figure 2.1. The summation of production conditions of NCC effects on NCC properties	23
Figure 3.1. Schematic representation of NCC Production	39
Figure 3.2. The schematic representation of the membrane production steps for fabrication the all-cellulose nanocomposite membranes.....	43
Figure 3.3. Membrane production techniques by using VIPS before LIPS	49
Figure 3.4. Schematic representation of the NCC deposition on the support membrane	52
Figure 3.5. Schematic representation of XRD analysis with the peak positions.....	55
Figure 3.6. Schematic representation of alkali desulfation procedure	57
Figure 3.7. Schematic representation of dead end cell	59
Figure 4.1. The XRD results of the NCC produced from HCl.....	64
Figure 4.2. The TEM images of the produced NCC-HCl-avicel (a and b), the produced NCC-HCl-cotton (c) and literature TEM images of NCC produced via HCl (d ¹⁰⁸ at which the NCC was produced using 5 g cellulose pulp and 100 mL-3M	

HCl with 80 °C & 2 hours and e ¹⁰⁹ at which the NCC was produced using 100 g cellulose pulp and 500 mL-4N HCl with boiling conditions around 4 hours. Scale bars are respectively 500 nm for a and d and 500 for b, c and e.....	66
Figure 4.3. The XRD results of the NCC produced from MCC (Avicel) and 50 % H ₂ SO ₄	68
Figure 4.4. The XRD results of the NCC produced from MCC (Avicel) and 65 % H ₂ SO ₄	69
Figure 4.5. The XRD results of the NCC produced from Cotton Linter Cellulose and 50 % H ₂ SO ₄	69
Figure 4.6. The images of the NCC that was produced H ₂ SO ₄ hydrolysis using different cellulose sources.....	71
Figure 4.7. The TEM images of the produced NCC65H ₂ SO ₄ -8.75 (a), the NCC50H ₂ SO ₄ -cotton-30/10 (b) and the literature images of NCC that was produced with H ₂ SO ₄ (c ¹¹³ at which the NCC was produced 64-65 % (w/w) H ₂ SO ₄ and 10 ml acid/g cellulose pulp with 45 °C and 1.5 hours reaction time and d ¹¹² at which the NCC was produced using 64-65 % (w/w) H ₂ SO ₄ and 8.75 ml acid/g cellulose with 45 °C and 30 minutes reaction time. Scale bars are 200 nm.....	73
Figure 4.8. The SEM image of NCC50H ₂ SO ₄ -cotton-30/10 at 100000x magnification	74
Figure 4.9. The zeta potential analysis result of commercial NCC50H ₂ SO ₄ -cotton-30/10 in different AlCl ₃ concentrations	76
Figure 4.10. The ATR-FTIR analysis result for the CA10D-P-NORMAL-S	78
Figure 4.11. The surface SEM images of the CA10 and the CA10D-P-S membranes at different magnifications that are 1000x and 10000x for the CA10, the CA10D-P-THIN-S and the CA10D-P-NORMAL-S, and 1000x and 25000x for the CA10D-P-THICK-S.....	80
Figure 4.12. The cross section SEM images of the CA10 and the CA10D-P-S membranes at different magnifications that are 5000x and 25000x for the CA10 and 10000x and 25000x for the CA10D-P-THIN-S, the CA10D-P-NORMAL-S and the CA10D-P-THICK-S	82

Figure 4.13. The normalized permeance values with respect to PWP for all the CA10D-P-THIN-S membranes (Average of four membranes).....	84
Figure 4.14. The normalized permeance values with respect to PWP for all the CA10D-P-NORMAL-S membranes (Average of four membranes).....	85
Figure 4.15. The normalized permeance values with respect to PWP for all the CA10D-P-THICK-S membranes (Average of four membranes).....	85
Figure 4.16. The BD5 rejection and PWP (After deposition for NCC Membranes) results for the CA10D-P-S membranes with comparison the support membrane...	89
Figure 4.17. The zeta potential analysis result of the commercial NCC in different $AlCl_3$ concentrations.....	90
Figure 4.18. The surface SEM images of the CA20 and the CA20D-C-S membranes at different magnifications which are 1000x and 10000x for the CA20 and 2000x and 10000x for the CA20D-C-NORMAL-S	92
Figure 4.19. The cross section SEM images of the CA20 and the CA20D-C-NORMAL-S membranes at different magnifications which are 10000x and 25000x	93
Figure 4.20. The normalized permeance values with respect to PWP for all the CA20D-C-NORMAL-S membranes (Average of three membranes)	94
Figure 4.21. The solute rejection and solute permeance/EtOH permeance after deposition for deposited membranes results for the CA20D-C-NORMAL-S membranes.....	97
Figure 4.22. The zeta potential analysis results of the $NCC50H_2SO_4$ -cotton-30/10 at different NaOH concentration and reaction time	98
Figure 4.23. The images of some of the $NCC50H_2SO_4$ -cotton-30/10 after NaOH reaction with comparison the $NCC50H_2SO_4$ -cotton-30/10	99
Figure 4.24. The ATR-FTIR analysis result for the PES10PEG10-1MH-D-P-NORMAL-B.....	101
Figure 4.25. The surface SEM images of the PES10PEG10-1MH and the PES10PEG10-1MH-D-P-NORMAL-B membranes at different magnifications that	

are 50000x for the PES10PEG10-1MH-D-P-NORMAL-B and the PES10PEG10-1MH-membranes and 200000x for the PES10PEG10-1MH membrane	103
Figure 4.26. The cross section SEM images of the PES10PEG10-1MH and the PES10PEG10-1MH-D-P-NORMAL-B membranes at different magnifications which are 25000x and 50000x	104
Figure 4.27. The resistance values for all the PES10PEG10-1MH-D-P-NORMAL-B membranes during deposition process (Average of three membranes)	105
Figure 4.28. The BD5 rejection and PWP (After deposition for NCC membrane) results for the PES10PEG10-1MH-D-P-NORMAL-B membranes with comparison the support membrane	106
Figure 4.29. The XRD results of the EV18 membranes comparative results the NCC-HCl (Active (1) and inactive (2) surfaces of the membrane)	108
Figure 4.30. The XRD results of the EV19 membranes comparative results the NCC-HCl (Active (1) and inactive (2) surfaces of the membrane)	109
Figure 4.31. Optic microscope images of some of the all-cellulose nanocomposite membranes	110
Figure 4.32. The performance test results of the membranes that prepared using NCC-HCl, CA, Acetone and [EMIM]OAc.....	115
Figure B.1. The calibration curve of BTB/EtOH solution at 423 nm ¹²³	138
Figure B.2. The calibration curve of RB/EtOH solution at 560 nm ¹²³	138
Figure B.3. The calibration curve of CV/EtOH solution at 590 nm ¹²³	139
Figure B.4. UV Spectra of BD5/Water solution	139
Figure B.5. The calibration curve of BD5/Water solution at 591.5 nm.....	140
Figure C.6. The DLS analysis plot for NCC-HCl.....	141
Figure C.7. The DLS analysis plot for NCC50H ₂ SO ₄ -cotton-30/10	141
Figure D.8. The ATR-FTIR analysis result for the CA10D-P-THIN-S	142
Figure D.9. The ATR-FTIR analysis result for the CA10D-P-THIN-S-Rep.Exp.	142
Figure D.10. The ATR-FTIR analysis result for the CA10D-P-NORMAL-S-Rep.Exp.....	143
Figure D.11. The ATR-FTIR analysis result for the CA10D-P-THICK-S.....	143

Figure D.12. The ATR-FTIR analysis result for the CA10D-P-THICK-S-Rep.Exp.	144
Figure D.13. The ATR-FTIR analysis result for the CA20D-C-NORMAL-S.....	145
Figure D.14. The ATR-FTIR analysis result for the CA20D-C-NORMAL-S-Rep. Exp.....	145
Figure D.15. The ATR-FTIR analysis result for the PES10PEG10D-P-NORMAL- B-Rep.Exp.	146
Figure E.16. The permeance results for the CA10D-P-THIN-S during deposition procedure	147
Figure E.17. The permeance results for the CA10D-P-THIN-S-Rep.Exp.1 during deposition procedure	147
Figure E.18. The permeance results for the CA10D-P-THIN-S-Rep.Exp.2 during deposition procedure (Prepared for BD5 Filtration)	148
Figure E.19. The permeance results for the CA10D-P-THIN-S-Rep.Exp.3 during deposition procedure (Prepared for BD5 Filtration)	148
Figure E.20. The permeance results for the CA10D-P-NORMAL-S during deposition procedure	149
Figure E.21. The permeance results for the CA10D-P-NORMAL-S- Rep.Exp.during deposition procedure	149
Figure E.22. The permeance results for the CA10D-P-NORMAL-S-Rep.Exp.2 during deposition procedure (For BD5 Filtration)	150
Figure E.23. The permeance results for the CA10D-P-NORMAL-S-Rep.Exp.3 during deposition procedure (For BD5 Filtration)	150
Figure E.24. The permeance results for the CA10D-P-THICK-S during deposition procedure	151
Figure E.25. The permeance results for the CA10D-P-THICK-S-Rep.Exp. during deposition procedure	151
Figure E.26. The permeance results for the CA10D-P- THICK -S-Rep.Exp.2 during deposition procedure (For BD5 Filtration)	152

Figure E.27. The permeance results for the CA10D-P- THICK -S-Rep.Exp.3 during deposition procedure (For BD5 Filtration).....	152
Figure E.28. The resistance values for all the CA10D-P-THIN-S membranes during deposition process	153
Figure E.29. The resistance values for all the CA10D-P-NORMAL-S membranes during deposition process	153
Figure E.30. The resistance values for all the CA10D-P-THICK-S membranes during deposition process	154
Figure E.31. The permeance results for the CA20C-P-NORMAL-S during deposition procedure (For BTB Filtration)	154
Figure E.32. The permeance results for the CA20C-P-NORMAL-S during deposition procedure (For CV Filtration)	155
Figure E.33. The permeance results for the CA20C-P-NORMAL-S during deposition procedure (For RB Filtration).....	155
Figure E.34. The resistance values for all the CA20C-P-NORMAL-S membranes during deposition process	156
Figure E.35. The permeance results for the PES10PEG10-1MH-D-P-NORMAL-B during deposition procedure	156
Figure E.36. The permeance results for the PES10PEG10-1MH-D-P-NORMAL-B during deposition procedure-Rep.Exp.	157
Figure E.37. The permeance results for the PES10PEG10-1MH-D-P-NORMAL-B during deposition procedure-Rep.Exp.2	157
Figure E.38. The resistance values for all the PES10PEG10-1MH-D-P-NORMAL-B membranes during deposition process	158
Figure G.39. Schematic representation of HCl filtration on the commercial NCC deposited CA20 support membrane	163
Figure G.40. The ATR-FTIR analysis result for the CA20D-C-NORMAL-1 M HCl	163
Figure G.41. The ATR-FTIR analysis result for the CA20D-C-NORMAL-0.01 M HCl.....	164

Figure G.42. The ATR-FTIR analysis result for the CA20D-C-NORMAL-0.005 M HCl	164
Figure G.43. The surface SEM images of the CA20D-C-NORMAL-1 M HCl, the CA20D-C-NORMAL-0.01 M HCl and the CA20 membranes at different magnifications that are 1000x and 10000x for the CA20 and the CA20D-C-NORMAL-0.01 M HCl, and 2000x and 10000x for the CA20D-C-NORMAL-1 M HCl	166
Figure G.44. The cross section SEM images of the CA20D-C-NORMAL-1 M HCl, the CA20D-C-NORMAL-0.01 M HCl and the CA20 Membranes at different magnifications that are 10000x and 25000x.....	167
Figure G.45. The permeance results for the CA20C-P-NORMAL-1 M HCl during deposition procedure (TMP = 4 bar for PWP and during deposition)	169
Figure G.46. The permeance results for the CA20C-P-NORMAL-0.01 M HCl during deposition procedure (TMP = 4 bar for PWP and during deposition)	169
Figure G.47. The permeance results for the CA20C-P-NORMAL-0.005 M HCl during deposition procedure (TMP = 4 bar).....	170
Figure G.48. The CV rejection and dye permeance/ EtOH permeance after deposition for the CA20D-C-NORMAL- 0.005 M HCl membrane	171
Figure H.49. The schematic representation of deposition of the NCC-HCl with water or EtOH on the KK2D membrane	173
Figure H.50. The permeance results for the KK2D-Water membrane during deposition procedure	173
Figure H.51. The permeance results for the KK2D-EtOH membrane during deposition procedure	174
Figure H.52. The XRD analysis results for the KK2D-EtOH and the KK2D-Water with comparison NCC-HCl source.....	174
Figure H.53. The images of the KK2D deposited membranes to determine the NCC-HCl stability on the support membrane	175
Figure H.54. The SEM images of the KK2D-Water and the KK2D-EtOH membranes.....	176

Figure J.55. The XRD results of the EV7S, the EV7L, the EV8S and the EV8L membranes comparative results MCC	178
Figure J.56. The XRD results of the EV14 membranes comparative results MCC	179
Figure J.57. The XRD results of the EV16 membranes comparative results MCC	179
Figure J.58. The XRD results of the EV17 membranes comparative results MCC	180
Figure K.59. The cross section SEM images of the EV7L and the EV7S.....	181
Figure K.60. The cross section SEM images of the EV8L and the EV8S.....	183

LIST OF ABBREVIATIONS

ABBREVIATIONS

ATR-FTIR	Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy
AlCl ₃	Aluminum Chloride
BD5	Blue Dextran 5000 Da
BTB	Bromothymol Blue
BTCA	1,2,3,4-Butanetetracarboxylic Acid
CA	Cellulose Acetate
ClSO ₃ H	Chlorosulfonic Acid
CV	Crystal Violet
C _F	Feed Concentration
C _P	Permeate Concentration
C _R	Retentate Concentration
DMAc	Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
DLS	Dynamic Light Scattering
EtOH	Ethanol
HCl	Hydrochloric Acid
H ₂ SO ₄	Sulfuric Acid
ILs	Ionic Liquids

IPA	Isopropanol Alcohol
LiCl	Lithium Chloride
LIPS	Liquid Induced Phase Separation
MCC	Microcrystalline Cellulose
MgCl ₂	Magnesium Chloride
MH	Minute Humidity
MWCO	Molecular Weight Cut Off
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
NCC	Nanocrystalline Cellulose
NF	Nanofiltration
NFC	Nanofibrillated Cellulose
NIPS	Non-Solvent Induced Phase Separation
NMMO	N-Methylmorpholine-N-Oxide
NMP	N-Methyl-2-pyrrolidone
PDMS	Polydimethylsiloxane
PEC NPs	Polyelectrolyte Complex Nanoparticles
PEEK	Polyether Ether Ketone
PEG400	Polyethylene Glycol
PES	Polyethersulfone
PSP	Pure Solvent Permeance
PWF	Pure Water Flux

PWP	Pure Water Permeance
RB	Rose Bengal
Rep. Exp.	Repeat Experiment
RO	Reverse Osmosis
Rxn	Reaction
SEM	Scanning Electron Microscope
SH	Second Humidity
TBAF	Tetra-n-Butylammonium Fluoride
TCNC	Tunicate Cellulose Nanocrystal
TEM	Transmission Electron Microscope
TEP	Triethylphosphahate
THF	Tetrahydrofuran
TMP	Transmembrane Pressure Difference
UF	Ultrafiltration
UP	Pure Water
VIPS	Vapor Induced Phase Separation
XRD	X-Ray Diffraction
γ -BL	γ -Butyrolactone
[EMIM]OAC	1-Ethyl-3-Methylimidazolium Acetate
[AMIM]Cl	1-Allyl-3-Methylimidazolium Chloride

LIST OF SYMBOLS

SYMBOLS

A_{membrane}	Membrane area
D_p	Diameter of particle in the cake
m_{cake}	Mass of cake
R	Membrane resistance to flow
J	Membrane Flux
ξ	Zeta Potential
ε	Cake Porosity
ρ	Density of Particle
ϕ_s	Sphericity of Particle
η	Permeate Viscosity
δ	Cake thickness

CHAPTER 1

INTRODUCTION

Separation processes are important operations in many industrial areas such as the pharmaceutical and chemical industry since it arises the huge amount of both operational and capital costs in these industries. In addition, the commercial separation processes used in industry such as distillation, evaporation, adsorption and extraction are processes with high energy consumption ¹. Therefore, the more cost-effective, less energy-consuming and more effective separation processes are becoming essential day by day. At this point, membrane separation technologies become important in many specific areas of pharmaceutical and chemical industry such as wastewater treatment, food and beverage processing, gas separation and fuel cells since when this technology compares the conventional separation techniques, membrane separation techniques have several major advantages which are less energy-consuming, a system that takes up less space, the potential for replacing harder chemical processes and ease of scalability ². On the other hand, besides these advantages, the membrane separation processes have several disadvantages that can be low membrane permeance, membrane fouling, short lifetime, inconsistency with used chemicals and durability of the membrane. Due to all these drawbacks, the usage of membrane technology can be limited in many areas; but, these limitations are tried to be developed by using suitable membrane materials and additives and by optimization of membrane performance such as permeance and selectivity.

The membrane is a thin selective semi-permeable barrier to separate the components of a mixture depending on their size, charge, and relationship with the membrane under a driving force. In the membrane separation processes, as seen in Figure 1.1. , the feed separates into two streams which are called the retentate and

the permeate. During this process, while some species can easily pass through the membrane and collected at the permeate side of the membrane, some species are hindered by the membrane or pass through the membrane slower than other particles and concentrated at the retentate side of the membrane.

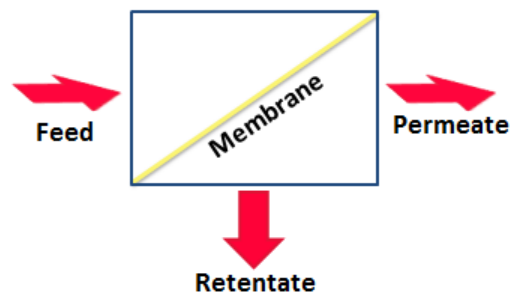


Figure 1.1. Schematic representation of membrane separation process

The pressure-driven membrane separation processes are divided into four sub-groups which are Reverse Osmosis (RO), Nanofiltration (NF), Microfiltration (MF) and Ultrafiltration (UF) with respect to pore size of membrane and size of rejected solute. The schematic illustrations of these membrane separation processes are given in Figure 1.2.

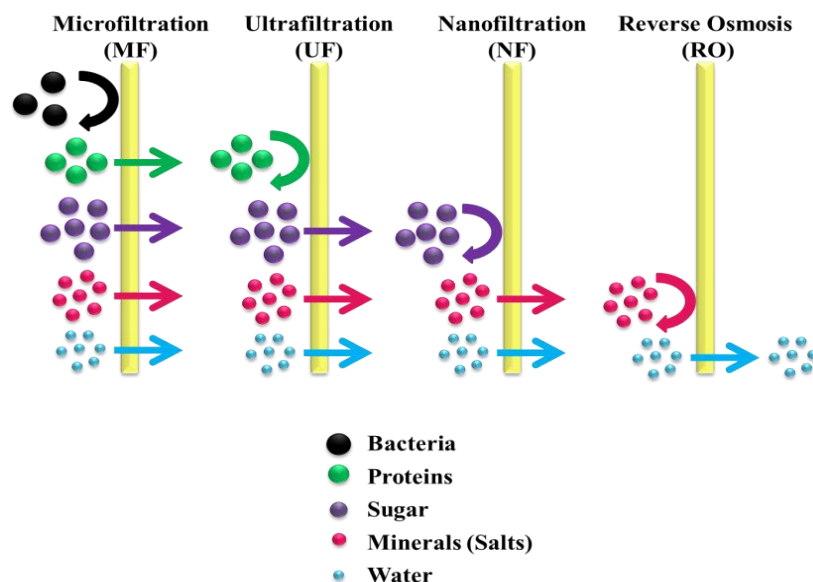


Figure 1.2. Classification of the pressure-driven membrane separation processes

As a detailed properties of these processes;

- Microfiltration (MF) membranes are porous membranes and used to separate suspended species in liquid whose sizes larger than 0.1 μm such as bacteria and blood cells.
- Ultrafiltration (UF) membranes whose molecular weight cut off (MWCO) is 5-100 kDa³ are finely porous membranes that are used to separate particles whose average sizes are larger than 0.001 μm such as colloids, proteins, viruses and polysaccharides from water and small particles. Moreover, polymeric materials such as polyether sulfone⁴, poly(vinyl chloride)⁵, polyamide⁶ and cellulose acetate⁷ can be used as well as ceramic materials⁸.
- Nanofiltration (NF) membranes are laying between ultrafiltration and reverse osmosis membranes. Nanofiltration membranes whose molecular weight cut off (MWCO) is 0.3- 0.5 kDa⁹ are used to separate mostly organic substances and particles whose sizes are a few nanometers such as dyes, sugars, drugs and multivalent salts. In addition to these, to produce nanofiltration membranes, polymeric materials such as polyether sulfone¹⁰, polyether ether ketone (PEEK)¹¹, polybenzimidazole (PBI)¹², polyimide¹³, polydimethylsiloxane (PDMS)¹⁴, poly (oxindolebiphenylenylene)¹⁵, poly (ether block amide)¹⁶ and cellulose¹⁷ can be used as well as ceramic materials¹⁸.
- Reverse osmosis (RO) membranes are non-porous membranes that are designed especially for the desalination process of seawater or groundwater. During this process, the reverse osmosis membranes are permeable to water, whereas they are impermeable to salt particles.

To determine pressure driven membrane processes' transport and separation mechanisms, there are two major models to be considered which are the pore flow model and the solution diffusion model. In the pore flow model, membrane separation occurs due to size differences between the membrane pore and the

particles. Particles whose sizes are smaller than the membrane pore size permeate through the membrane due to the pressure gradient across the membrane. However, particles whose sizes are larger than the membrane pore size are rejected (screen filtration) or captured (depth filtration) by the membrane. Microfiltration and ultrafiltration membranes' separation mechanisms are classified as the pore flow model. In the solution diffusion mechanism, the membrane separation occurs due to solubility and diffusion rate differences between particles. In this method, particles dissolve in the membrane material and then diffuse through the membrane due to concentration gradient across the membrane. Reverse osmosis membranes' separation mechanisms are classified as the solution diffusion mechanism. In the nanofiltration membranes, the transport and separation mechanisms are both the pore flow and the solution diffusion mechanisms. Thus, particles can pass through the membrane pores as in the pore flow mechanism or can dissolve in the membrane material and diffuse through membrane as in the solution diffusion mechanism¹⁹.

1.1 Membrane Preparation Techniques: Phase Separation Techniques

The Loeb - Sourirajan technique that is also called phase separation process or phase inversion process was developed by Loeb and Sourirajan in the early 1960s²⁰. This technique is the most common and versatile technique to produce various types of membrane morphologies. At this technique, membrane preparation can occur in three different ways; by solvent evaporation, by thermal precipitation (by decreasing temperature of casted solution) and by immersion of casted solution in a non-solvent environment (non-solvent induced phase separation). In all these techniques, the non-solvent induced phase separation (NIPS) is the most common process to produce RO, NF, UF and MF membranes². In the non-solvent induced phase separation technique, the used non-solvent can be vapor (vapor induced phase separation (VIPS)) or liquid (liquid induced phase separation (LIPS)). During the preparation of membranes with phase separation technique, the one-phase liquid casting solution turns into the two-phase liquid which is a polymer-

rich phase to form a solid part of the membrane and polymer lean phase to form membrane pores¹⁹.

1.1.1 Non-solvent Induced Phase Separation (NIPS)

Non-solvent induced phase separation occurs when the casting solution comes in contact with the non-solvent. There are three important components in this method which are the solvent, the polymer and the non-solvent. Moreover, the requirements of this process are that the polymer must be soluble in the solvent, and the solvent and the non-solvent have to be miscible with each other. When these requirements are met, flat sheet or hollow fiber membranes can be produced with this method either by exposing casting solution to vapor or immersing casting solution in liquid or first exposing casting solution to vapor then immersing in liquid. As a liquid non-solvent, water is usually used environmentally; also, some organic solvents such as Ethanol and Methanol or their mixture with water can be used rarely^{19,21–23}.

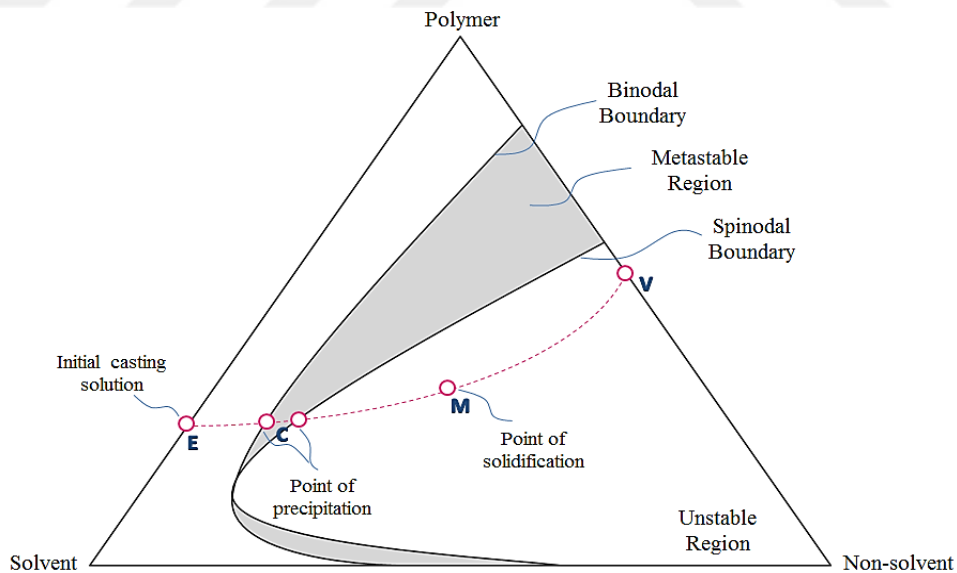


Figure 1.3. The ternary diagram of three components (solvent, polymer and non-solvent) of NIPS¹⁹ with the qualitative representative path

To prepare membranes by this technique, after dissolving a polymer in the solvent or solvent mixture, the casting solution is cast to the support layer. At the beginning of the non-solvent induced phase separation method, the initial casting solution is homogenous and thermodynamically stable (At point E). When this solution immersed in the non-solvent, the exchange between the solvent and the non-solvent starts at the interphase of the casting solution surface and the non-solvent. The casting solution loses its solvent and gains non-solvent. The casting solution moves from its initially stable region to a metastable two-phase region by crossing the binodal boundary (At point C); as a result of this, phase separation begins. When more non-solvent diffused into a casting solution, it moves from a metastable region to an unstable region by crossing the spinodal boundary to where the solidification starts because of increasing viscosity of the polymer-rich phase (At point M). At the final step of phase separation, two phases are in equilibrium (At point V), and the polymer-rich phase forms the membrane solid matrix, and the liquid solvent–non-solvent phase forms pores of the membrane. The all this path which represented by point of E,C,M and V was shown in Figure 1.3 ¹⁹.

Consequently, asymmetric (anisotropic) membranes can be prepared with this process since the phase separation occurs firstly and rapidly at the top of the casting solution due to come in contact with non-solvent, firstly. In this way, the thin-selective skin layer of a membrane which increases the flux of membrane is formed. However, this layer hinders and slows to pass the non-solvent from top to bottom (slow precipitation from top to bottom). By this way, thick-microporous layer of membrane which increases durability of membrane is formed ¹⁹. In addition to these, if the precipitation occurs much more slowly from top to bottom of membrane, a symmetric (isotropic) membranes without skin layer can be obtained by NIPS ²⁴. Their schematic representations are shown in Figure 1.4.

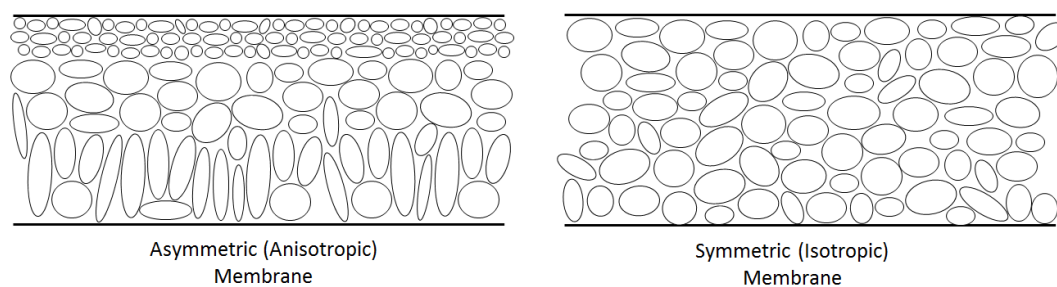


Figure 1.4. Schematic representation of asymmetric and symmetric membranes

Membranes having different morphologies e.g. different porosities, different thickness of selective layers and different pore sizes can be produced with the phase separation technique by changing some parameters which are polymer concentration of casting solution, type of polymer, type of solvent, type of the non-solvent, temperature of the non-solvent and adding additives to the casting solution^{19,21}.

1.1.2 Solvents for Phase Separation Technique

Solvent choice for the phase separation technique is important to obtain desired membrane with respect to porosity and membrane shape which are directly related with membrane performance¹⁹. There are several main parameters for solvent choice ; boiling temperature, melting temperature, solubility parameter, molecular weight, safety issues, cost, toxicity and environmental issues²⁵.

To produce membranes with phase separation technique, polar aprotic solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc) and N-Methyl-2-pyrrolidone (NMP) which can dissolve lots of type of polymer to form porous and anisotropic membranes are usually used¹⁹ along with other types of organic solvents like tetrahydrofuran (THF)²⁶, acetone²⁶, 1,4-Dioxane²⁶, phthalate esters²⁷ and morpholine²² ; however, these solvents are hazardous chemicals for human health and environment and limits safe working. Nonetheless, when the increasing awareness of environmental issues today is taking into consideration, new solvents

that are non-hazardous to human health and environment, and can be replaced with common solvents should be used. As alternative solvents to common solvents, the solvents given below can be used;

- Dimethyl sulfoxide (DMSO) ²⁶ is non-toxic organic solvent.
- Methyl lactate ²⁶ is biodegradable solvent.
- Ethyl lactate ²⁶ is biodegradable and noncorrosive solvent.
- Triethylphosphate (TEP) ²⁶ is low toxic solvent for human health.
- γ -Butyrolactone (γ -BL) ²⁶ is non-toxic solvent.
- Ionic liquids (ILs) ²⁶ are harmless solvents with low vapor pressure.
- Citroflex solvents ²⁷ is biodegradable plant based solvent.
- PolarClean®(methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate) ²⁸ is biodegradable synthetic organic solvent.

In addition to these alternative solvents, as a very new approach called Aqueous Phase Separation, water can be used for both the solvent and the non-solvent to produce membranes with desired structures from nanofiltration to microfiltration and excellent membrane performances by using polyelectrolytes and special pH and salinity conditions for both coagulation bath and casting solution ^{29,30}.

1.2 Membrane Polymers: Cellulose

1.2.1 Cellulose and Its Derivatives

1.2.1.1 Cellulose

Cellulose is the most abundant polymer in nature with 1.5 trillion tons of the totally annual biomass production, and it is biodegradable and non-toxic. Cellulose can be produced from natural cellulose-based materials such as trees, cotton and crop wastes as well as bacteria and algae ³¹.

As seen in Figure 1.5, cellulose is a high molecular weight linear polymer with two glycosidic bonds which gives the hydrophobic property of molecule linked to the first and fourth carbon atom. The repeating unit of cellulose is called cellobiose which consists of two glucose attached by 180° rotation to each other that eases to link each cellobiose unit to another. The amount of cellobiose (repeating unit of cellulose) can be from several hundreds to over ten thousand. Moreover, the cellulose molecule has lots of inter- and intramolecular hydrogen bonds (the blue lines in Figure 1.5) which give the hydrophilic property to the molecule^{32–34}.

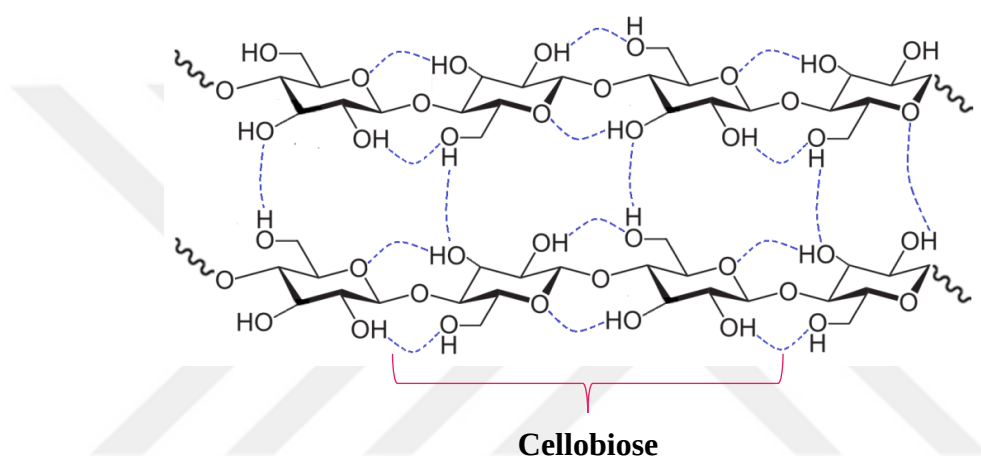


Figure 1.5. Structure of Cellulose³³

There are several types of cellulose with respect to its dimensions from the highest dimension to the lowest dimensions that are cotton linter cellulose (natural cellulose / microfibrils structure), microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC). With combination of different treatments like mechanical, chemical and enzymatic, the native cellulose is turned into microcrystalline or nanocrystalline cellulose and microcrystalline cellulose is turned into nanocrystalline cellulose³⁵. The MCC which is also called as micro-sized crystalline cellulose is obtained with partial hydrolysis of several cellulose sources such as native cellulose³⁶, cotton linter cellulose, flux fibres³⁷ and kraft wood pulp³⁸ by using mineral acid with 10 to 50 μm in diameter and several thousand μm in length³⁸. Moreover, the NCC is produced with strong acid hydrolysis (chemical treatment) from different cellulose sources like MCC³⁹,

wood pulp⁴⁰ and natural cellulose⁴¹ by controlling temperature, time and stirring conditions by removing the amorphous part of the cellulose with yielding highly crystalline nano-sized cellulose with 3 to 50 nm in width and 70 nm to several hundreds of micrometers in length^{35,42}. Unlike the NCC, the micro fibrillated cellulose (MFC) which is also called nano fibrillated cellulose is obtained by mechanical treatment such as homogenization⁴³, micro-fluidization⁴⁴, granulation⁴⁵, blade agitation⁴⁶ and sonication⁴⁷ either by using chemical or enzymatic pre-treatment or not from different cellulose suspensions such as kraft pulp⁴⁸ and cotton linter cellulose⁴⁹ suspensions. Besides, unlike NCC, the MFC contains both crystalline and amorphous regions, and has stronger structure than NCC with 20 to 60 nm in width and several hundreds of micrometers in length⁴².

In addition, there are four types of the crystalline lattice of cellulose depending on the inter- and the intramolecular interactions and molecular orientations; cellulose I - IV. All natural cellulose materials consist of cellulose I which is a composite of two crystallines that are I α and I β . Cellulose II is obtained by either dissolving cellulose I in a solvent and regeneration of cellulose or treating cellulose with a concentrated alkaline swelling agent and washing with water. Cellulose II is more stable than cellulose I, and conversion from cellulose I to cellulose II is an irreversible process. By exposing of cellulose I or II with amines or liquid ammonia, cellulose III is formed, and when cellulose III is heated with glycerol, cellulose IV is formed. When suitable conditions set like humid environment and high temperature, these two forms (cellulose III and IV) can be turned in to its original structure which is either cellulose I or cellulose II^{32,34}.

Cellulose is prevalently used in many different industries and areas as membrane, tissue, paper, paints and medicines. However, cellulose is resistant to many solvents due to high crystallinity and the strong inter- and intramolecular hydrogen bonds; therefore, it is difficult to dissolve cellulose into common organic solvents and water. To dissolve the cellulose, the solvents such as N-methylmorpholine-N-oxide (NMMO) that has low thermal stability and require high dissolution temperatures can be used as well as aprotic solvents which are supplemented with

salts (like; dimethylacetamide (DMAC) / lithium chloride (LiCl), dimethyl sulfoxide (DMSO)/ Tetra-n-butylammonium fluoride (TBAF)) or ionic liquids (ILs) with high chemical and thermal stability, low volatility, dissolution at room temperature and non-flammable can be used ^{50,51}. Ionic liquids are molten organic salt groups comprising anions and cations that are usually ammonium, imidazolium or pyridinium ions, and show liquid properties below 100 ° C. Due to their ionic structure, they are able to dissolve polymers that cannot be easily dissolved by other organic solvents ^{32,52}.

1.2.1.2 Nanocrystalline Cellulose (NCC)

Nanocrystalline cellulose (or cellulose nanowhiskers, cellulose nanocrystal) is produced by acid hydrolysis from different types of cellulose sources such as cotton linter cellulose ⁵³, microcrystalline cellulose (MCC) ⁵⁴ and cellulose obtained from different sources like bacteria ⁵⁵. For this reaction, harsh acids (H_2SO_4 ³⁶ and HCl ⁵⁴) can be used as well as some mild acids (Formic Acid) ⁵⁶, heteropoly acids (phosphotungstic acid) ⁵⁷ and other mineral acids. During acid hydrolysis, the acids firstly infiltrate to the more easily reachable glycosidic bonds in the amorphous part and hydrolyze them. After hydrolysis of these glycosidic bonds, the rest of the reaction takes place slower than the amorphous part since it is difficult the hydrolysis of the surface of the crystalline region and end of the cellulose molecule.⁵⁸ As a result of this reaction, the disordered amorphous regions of cellulose are hydrolyzed and removed; however, the highly ordered crystalline regions of cellulose remain unaffected from acid hydrolysis and form the nanocrystalline cellulose ³⁵. This reaction is shown schematically in Figure 1.6.

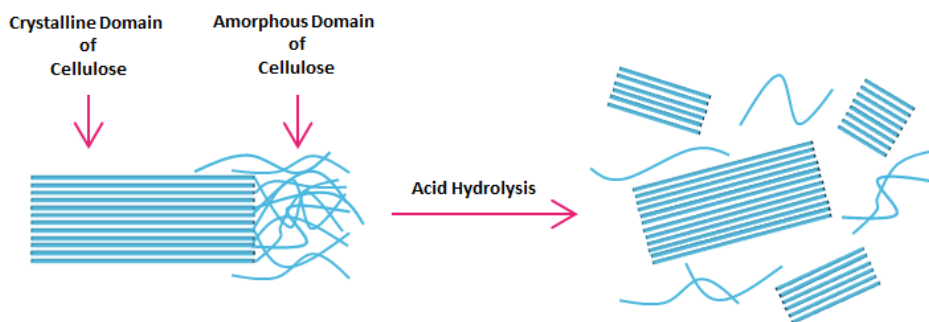


Figure 1.6. Schematic representation of acid hydrolysis of cellulose⁵⁹

The obtained nanocrystalline cellulose has nanoscale dimensions that are between tens of nanometers to several micrometers as length and 3 to 70 nm as width³⁴. Moreover, it has a high surface area, rod-like structure, good dispersion abilities, excellent mechanical properties and biodegradability⁶⁰. Due to these excellent properties, it is finding in many different applications and areas like a reinforcing agent⁶¹, packaging material⁶², rheology modifier⁶³, drug delivery⁶⁴ and biosensors⁶⁵. In addition, acid type, acid concentration, acid/cellulose ratio, reaction temperature, and reaction duration affect the properties of NCC and reaction results. When the reaction time, acid/cellulose ratio, reaction temperature and acid concentration increase, the size of NCC and reaction yield decrease with darkened the color of NCC; but, the optimum value of crystallinity of cellulose has to be found^{39,54,58,66–68}. Moreover, the type of acid that used for hydrolysis of cellulose affects the surface charge and dispersion stability of cellulose. The NCC produced using HCl has dimensions typically between 5-25 nm in width and 100-420 nm in length, and it is difficult to disperse and tends to precipitate in suspension^{35,36}. However, the NCC produced using H₂SO₄ has dimensions typically between 3-50 nm in width and 70 nm to several hundreds of micrometers in length, and it has charged surface since during the hydrolysis reaction, the hydroxyl groups on cellulose surface change with sulfate ester groups. This charged surface facilitates the dispersion of NCC in suspension while decreasing NCC's thermal stability^{34,35,69}.

- **Zeta Potential of Nanocrystalline Cellulose**

The zeta potential (ξ) of a colloid is an indication of the surface charge of the particle.

As seen in Figure 1.7, when the particle surface has a net negative or positive charge, the charged particle surface attracts the oppositely charged particles in the colloidal solution by the electrostatic force. As a result of this, the net charge around the particle surface forms that affects the distribution of charged ions around the particle. By this way, a layer called an electrical double layer around the particle which is electrically neutral forms. An electrical double layer has two different parts;

- Stern layer:** It is a layer in which oppositely charged particles cover the particle surface by the electrostatic force (immobile layer).
- Diffuse layer:** It is a layer in which a part of the solution medium adjoins to the particle. This layer contains a higher amount of opposite charged free particles affected by the electrostatic force of the particle surface.

The imaginary boundary layer that is called a Slipping Plane separates the solution medium that attached to the surface and the bulk solution medium. The zeta potential of particle measures at the slipping plane⁷⁰.

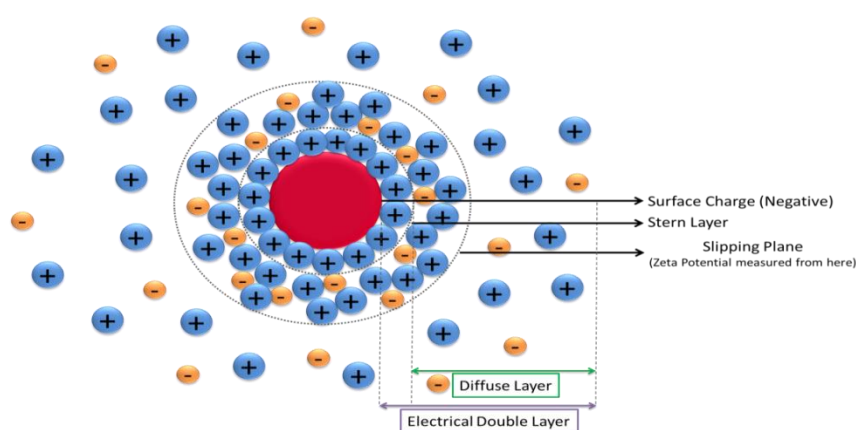


Figure 1.7. Schematic representation of electrical double layer of the charged particle⁷⁰

Zeta potential of the particle is generally used to determine the physical (colloidal) stability of the solution medium. As seen in Figure 1.8, when zeta potential value is higher than +30 and lower than -30, this means that the suspension is stable i.e. particles do not precipitate due to electrostatic repulsion between particles. However, if zeta potential value is close to zero, the suspension is unstable i.e. particles in solution medium agglomerate and precipitate due to the van der Waals forces between particles ⁷¹. Also, the zeta potential of the particles affects from pH, ionic strength and temperature of medium and the concentration of any additive to medium ⁷².

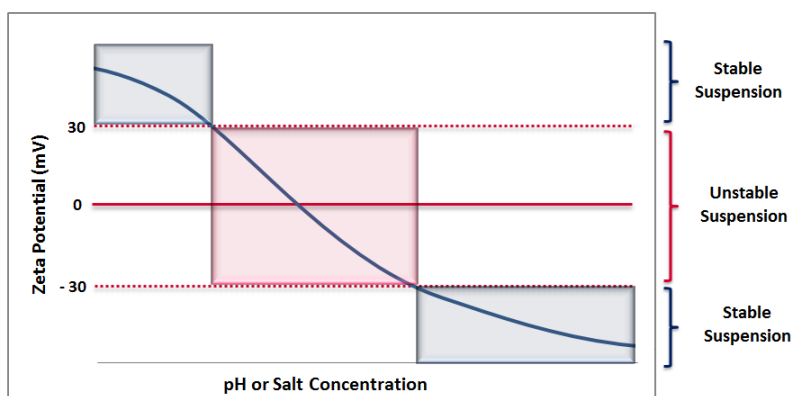


Figure 1.8. Schematic representation of zeta potential results

The colloidal stability in the solution medium and the surface charge properties of NCC change depending on the acid type used for the reaction. Although the NCC produced by using hydrochloric acid (HCl) are inclined to aggregation in solution medium due to lack of surface charge, the NCC that produced by using sulfuric acid (H_2SO_4) has good dispersion stability in solution medium due to electrical repulsion force between particles. During the hydrolysis reaction with sulfuric acid (H_2SO_4), esterification occurs with hydroxyl groups, and hydroxyl groups and sulfate groups displace. As a result of this, the produced NCC has negatively charged surfaces that give the colloidal stability ^{54,73}.

To change the colloidal stability of the NCC produced using sulfuric acid (H_2SO_4), the pH or/and ionic strength of solution medium can be changed by adding acid or

base for pH and salt for ionic strength of the solution. When the ionic strength of solution increases by increasing salt concentration or/and electrical charge of the salt, the zeta potential of the NCC goes to zero since the adsorption of free ions and ion pairs to NCC's surface increases. However, the changing zeta potential of the NCC by changing the pH of the solution medium is more complicated than the ionic strength change. If the pH of the solution medium stays between 2 to 10, the pH change has little effect on zeta potential of the NCC since the dissociation state of sulfate ester groups does not change and stays as $-O-SO_3^-$. However, if the pH of solution medium becomes lower than 2, the pH change has a considerable effect on zeta potential of the NCC since protonation of sulfate groups start at lower pH (the pKa value of sulfate ester groups are nearly 2) to make sulfate groups as $-O-SO_3H$ i.e. the NCC's zeta potential value approaches to zero. In other words, at low pH values, the NCC become less stable and tend to aggregation⁶⁹. The schematic representation of changing stability of the NCC is given in Figure 1.9.

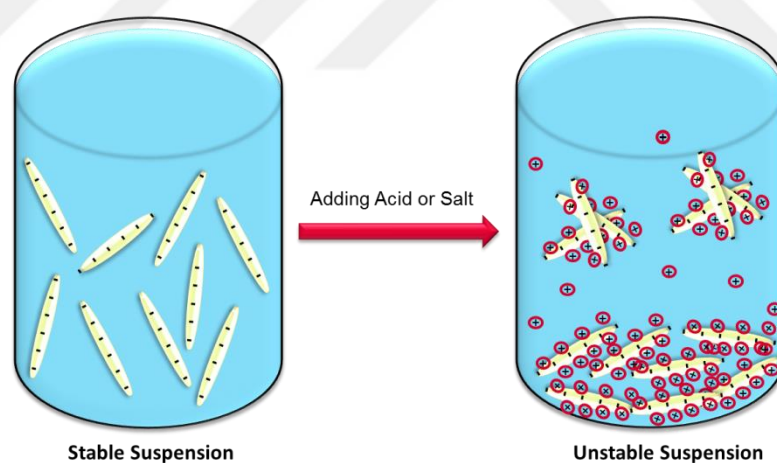


Figure 1.9. Schematic representation of stability changing of the NCC in the solution medium

Besides, the desulfation procedure to replace surface ester groups with hydroxyl groups can be used to change the surface charge of the NCC to decrease its colloidal stability in its medium. During the desulfation procedure, several methods

can be used that are acidic desulfation, solvolytic desulfation and alkali desulfation. During acidic desulfation, the hydrochloric acid (HCl) hydrolysis is used, but this process has to be repeated to remove all sulfate groups from the surface and can cause undesirable physical property change of the NCC. For the solvolytic desulfation procedure, pyridinium salt in polysaccharides is heated in DMSO with methanol, and in contrast to acidic desulfation, one step is enough to remove almost all sulfate groups from the surface. In the alkali desulfation procedure, sodium hydroxide (NaOH) is used at different NaOH concentrations and different reaction times via heating since using stronger NaOH solution and/or higher reaction times result in lower sulfate ester groups in the NCC surface, and this method needs lower energy than other desulfation procedures⁷⁴⁻⁷⁶. The schematic representation of alkali desulfation is given in Figure 1.10.

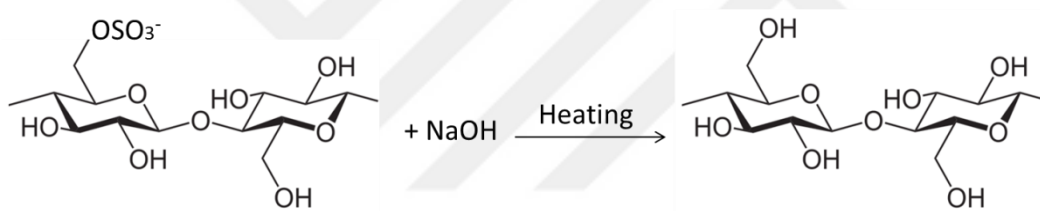


Figure 1.10. The schematic representation of alkali desulfation of NCC⁷⁷

- **All-Cellulose Nanocomposite Materials**

Composite materials are obtained by combination of usually different two or more substances that are called usually as matrix and reinforcement. As a result of mixing of substance features, the obtained material (composite) has new and unique properties^{78,79}. If the one or more substances in composite material have nano-scale dimensions, the composite is called nanocomposite material. However, since the composites are generally composed of two foreign materials that are chemically incompatible, an interface is formed between these two materials. This interface causes several important problems that are poor adhesion and moisture retention. Nonetheless, if the substances that are used as a matrix and reinforcement in composites have similar properties, the interface problem can be

eliminated, and composites with better properties such as better adhesion and easily recyclability can be produced. At this point, all-cellulose nanocomposite materials gain importance. In all-cellulose nanocomposite materials, both matrix and reinforcement are cellulosic materials, and crystalline cellulose regions in nanometer scale dimensions are found within an amorphous cellulose matrix. Because both are the same material, no incompatibility problems are expected^{79,80}. All-cellulose nanocomposite membranes/films are obtained either partial dissolution of cellulose in a solvent or direct addition of nanocrystalline cellulose to the generated cellulose matrix^{79,81}.

1.3 Analysis of Particle Deposition on Membranes Using Resistances in Series Model with the Darcy's Law

Darcy's law is a phenomenological equation which is applicable for pore flow model in the membrane and relates the resistance against flow of membrane to permeate flux and viscosity at constant pressure drop. In Darcy's law given in equation (1), the resistance against flow is proportional to transmembrane pressure difference and inversely proportional to permeate flux and viscosity.

$$R = \frac{\text{TMP}}{\eta J} \quad (1)$$

R = Resistance of membrane against flow

TMP = Transmembrane pressure difference

η = Permeate viscosity

J = Permeate flux

The membrane has a certain resistance value against the flow through in it due to its pore size, porosity, tortuosity and thickness. The membrane resistance against flow increases with decreasing pore size or increasing membrane thickness⁸².

However, during filtration, there can be additional resistances due to concentration polarization and fouling on the membrane resistance that called the cake resistance. The concentration polarization occurs when the rejected species concentration increases or decreases around the both side of the membrane due to difference transport rate, which causes the decrease in rejection of rejected species or membrane flux ¹⁹. In addition, membrane fouling occurs when the rejected species deposit on the membrane surface, which causes the decrease in permeate flux in time ¹⁹. By using the resistance-in-series model given in equation (2) and the Darcy's Law, the cake resistance can be calculated ⁸³.

$$R_{\text{Filtration}} = R_{\text{Membrane}} + R_{\text{Cake}} \quad (2)$$

In this study, the some membranes produced using the NCC deposition on a support layer method. In this method, the NCC forms the cake layer on the support membrane that affects the membrane resistances and membrane properties. The Darcy's law is used to determine this cake layer resistance.

1.4 The Kozeny-Carman Equation

The Kozeny-Carman equation given in equation (3) was developed by Kozeny in 1927, firstly by combining two different methodologies which are the Hagen-Poiseuille equation and the Darcy's law with tortuosity concept. Then, in 1937, this equation was developed by Carman and called the Kozeny-Carman equation ⁸⁴. This equation can be applicable for porous membranes in which during the filtration process, cake formation occurs, dead-end filtration mode and 100 % rejection ⁸⁵. By using this equation, the cake porosity can be calculated with known specific cake resistance and properties of cake such as mass of cake, particle size and density in cake and particle sphericity.

$$R_{\text{cake}} = \frac{m_{\text{cake}}}{\rho * (1 - \varepsilon) * A_{\text{membrane}}} * \frac{180 * (1 - \varepsilon)^2}{\varepsilon^3 * (\phi_s D_p)^2} \quad (3)$$

R_{cake} = Specific cake resistance

m_{cake} = Mass of cake

A_{membrane} = Area of membrane

ε = Cake porosity

ρ = Density of particle in cake

ϕ_s = Particle sphericity that represents how close the particle shape to sphere

D_p = Diameter of particle in cake (The diameter of the volume equivalent

spherical particle)⁸⁶

After calculating the cake porosity using the Kozeny-Carman equation, the equation (4) can be used to calculate the cake thickness.

$$\delta = \frac{m_{\text{cake}}}{\rho * (1 - \varepsilon) * A_{\text{membrane}}} \quad (4)$$

1.5 The Aim of the Study

The main aim of this study is to fabricate membranes using nanocellulose. To achieve the aim, firstly, nanocrystalline cellulose (NCC) was produced by acid hydrolysis via using different acids and cellulose sources and different production conditions such as different reaction times, different acid concentrations and different adding orders of materials to determine the best production conditions of the NCC. The nanocrystalline cellulose (NCC) is used for this study since it has nanoscale dimensions, high crystallinity, low cost, and it is solvent resistant and abundant in nature. Then, as a first method, the membranes were produced via controlled precipitation of an NCC suspension on a support membrane to produce a selective membrane layer for ultrafiltration or nanofiltration processes without using any solvent other than water. The original aspect of this method is forming a deposit from the aqueous suspension of a precisely defined building block (NCC)

and stabilizing the deposited NCC layer by changing the surface charge to obtain a long-lasting membrane. During this method, after the deposition of the NCC on the support membrane, different solutions were filtered through the deposited NCC layer to decrease its colloidal stability by bringing zeta potential close to zero to obtain a stable deposited NCC layer on the support membrane. In addition to using different solutions, different support membranes depending on the durability of the support membrane in different solutions and different NCC deposition amounts to obtain different deposited NCC layer thickness were used. After making permeance and resistance calculations during the deposition procedure to see the deposition effect on the membrane, the ATR-FTIR analysis to determine the stability of the deposited NCC layer on the support membrane and the SEM analysis to determine the morphology of the NCC membranes were used. As a final part of this method, the NCC membranes were tested by using different solute/solvent solutions to determine the NCC deposition effect on membranes separation performances.

In the second method, all-cellulose nanocomposite membranes were produced using the direct addition of nanocrystalline cellulose into generated cellulose matrix or partial dissolution of cellulose. Then, to produce all-cellulose nanocomposite membranes, different dissolution times, different types of cellulose sources, different type of co-solvents, heating solvent at different temperatures and different adding order of materials to the membrane casting solution was used to see their effects on the membrane crystallinity and the membrane solute rejection for partial dissolution of cellulose method. Also, in direct addition of the NCC into the generated cellulose matrix method, the produced NCC was added to the cellulose acetate membrane casting solution. Then, these membranes were regenerated via the alkaline hydrolysis to turn these cellulose acetate membranes into cellulose membrane. Then, these all-cellulose nanocomposite membranes' crystallinity and membrane separation performances using different solute/EtOH solutions were examined.

CHAPTER 2

LITERATURE REVIEW

In this study, there are three main topics to be investigated which are NCC production, all-cellulose nanocomposite membrane production and membrane production using NCC precipitation. In this literature review, the general point of view about these topics tried to be given by referring studies in the literature.

2.1 Effects of Production Conditions on Properties of NCC

The main properties of NCC are determined depending on production conditions during acid hydrolysis such as reaction temperature, reaction time, acid/cellulose ratio and acid type.

Araki et al.³⁶ produced NCC by using both 5 g cellulose, 4N & 175 mL of HCl at 80 °C for 225 minutes and 65 % (w/w) H₂SO₄, 10 ml acid / g cellulose ratio at 70 °C for 10 minutes. They observed that while the NCC-H₂SO₄ and the NCC-HCl have similar morphologies and XRD patterns, their rheological structures differ from each other. Although the suspension prepared with the NCC-H₂SO₄ showed no time dependency on viscosity, the suspension prepared with the NCC-HCl showed either thixotropic or rheopectic behaviors depending on the suspension concentration. Also, another study⁵⁴ showed that the reaction yield of the HCl hydrolysis is higher than the reaction yield of the H₂SO₄ hydrolysis. The reason is that HCl is less aggressive acid than H₂SO₄ towards the MCC which causes less hydrolysis of crystalline domains. In the same study, they produced NCC by using 6 M HCl, different reaction times between 2 to 3 hours, different reaction temperatures from 100 to 120 °C and different acid to cellulose ratios changing between 40 to 60. They showed that as the acid/cellulose ratio and reaction time

increase, the color of the NCC becomes darker due to excessive degradation of cellulose while the length of the NCC and the reaction yield decrease.

Dong et al.⁵⁸ showed that when the different reaction conditions which are reaction temperatures ranging between 26 and 65 °C, reaction times ranging from 1 to 18 h , 64% (w/v) H₂SO₄ and 8.75 ml acid / g cellulose ratio are used, the NCC becomes darker while the yield of the reaction and the length of obtained NCC decrease with increasing reaction temperature and time. In addition to this, Musa et al.⁶⁰ have shown that the length of the NCC that was produced by using 64% H₂SO₄, 10 ml acid / g cellulose ratio and 45 °C at different reaction times ranging from 30 to 60 minutes decreases with increasing reaction time due to removal of not only amorphous regions of cellulose but also incomplete loss of the crystalline region of cellulose. Moreover, another study⁶⁸ showed that the NCC that obtained using different reaction conditions which are different H₂SO₄ concentrations ranging between 16 and 64, reaction temperatures ranging from 45 to 85 °C, 25 minutes reaction time and 8.75 ml acid / g cellulose ratio shows different properties depending on the reaction temperature and acid concentration. When the acid concentration and the reaction temperature increase, the reaction yield and the length of the produced NCC decrease. The crystallinity index values of the produced NCC increase with reaction temperature for lower acid concentrations (16 and 45 wt %); however, decrease with reaction temperature for higher acid concentrations (64 wt %). In addition to these, for 64 wt% acid concentration, the crystallinity index values of the produced NCC first decrease and then increase with time which means that optimum reaction time should be determined depending on the reaction conditions.

The summary of these information are given in Figure 2.1.

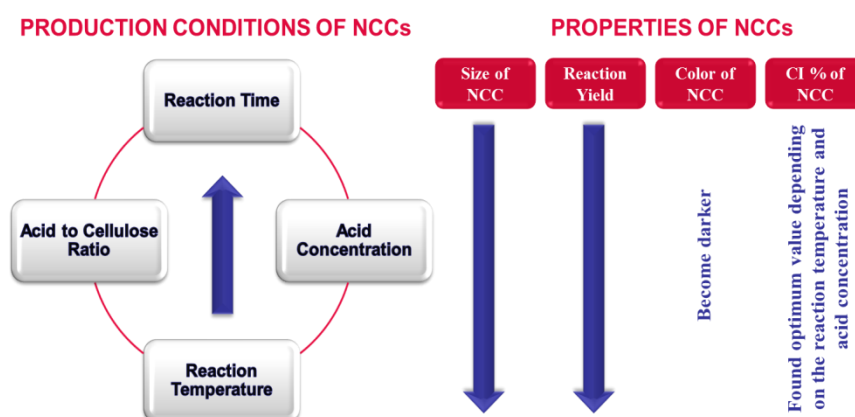


Figure 2.1. The summation of production conditions of NCC effects on NCC properties

2.2 Materials and Procedures to Affect Stability of NCC

Studies have been carried out to decrease or increase the stability of NCC in liquid solutions by changing surface charge of NCC.

Prathapan et al.⁶⁹ investigated the NCC stability at different pH values by adding hydrochloric acid (HCl) and sodium hydroxide (NaOH) to the liquid solutions of NCC after production of NCC by using ~47 % H_2SO_4 , 22 mL acid / g cellulose ratio, 45 °C and 2 hour as a reaction conditions. Their studies showed that the stability of NCC decreases at very low (pH <2) pH and very high (pH >10) pH values; however, in between these pH values, the pH change has little effect on the NCC's zeta potential. Also, in the same study, they showed that by changing ionic electrolytes in the NCC liquid solution by adding NaCl or CaCl_2 , the stability of NCC decreases as the salt concentration or the ionic strength of solution increases. In a similar study⁸⁷, after production of NCC by using 64 wt% H_2SO_4 , 10 ml acid / g cellulose ratio, 45 °C and 2 hour as a reaction conditions, the NCC stability was investigated with the similar methods with Prathapan et al. study, and they concluded the similar results with respect to the zeta potential change of the NCC with pH and salt concentration.

After production the NCC using 64 wt % H_2SO_4 , 20 ml acid / g cellulose ratio, 45 °C and 60 mins as reaction conditions, Dufresne et al.⁸⁸ worked on postsulfation of the NCC using chlorosulfonic acid (ClSO_3H) and alkaline desulfation of the NCC by using sodium hydroxide (NaOH). During these procedures, different acid and base concentrations with different reaction times were used to see their effects on the surface properties of the NCC. As a result of their studies, while these conditions have nearly no effect on the crystallinity of the NCC due to not destroying or construction the innate crystalline structure of the NCC, the zeta potential of the NCC increases with postsulfation and decreases with desulfation with increasing time and concentration because of increasing (postsulfation) or decreasing (desulfation) amount of sulfate groups on the NCC's surface.

2.3 Membranes/Films Production Using Nanoparticles

There are several different studies to produce membranes or films using nanoparticle deposition on a support.

Mautner et al.^{89,90} used different types of nanocellulose which are bacterial cellulose, TEMPO-oxidized cellulose nanofibrils, wood derived nanocellulose and cellulose nanocrystals to produce cellulose nanopapers. In order to produce nanopapers during their studies, nanocellulose which was dispersed in water in certain concentrations has been turned into membranes by paper production method after filtering on cellulose filter paper by vacuum filtration method. However, during these processes, nanocellulose which has very small length and high surface charge created problems since nanocellulose was able to pass through the filter paper easily. In order to solve this problem, the surface charge of nanocellulose was changed by adding aluminum chloride (AlCl_3) or magnesium chloride (MgCl_2) at different concentrations into the solution, so that nanocellulose zeta potential value reached zero; therefore, nanocellulose collapsed and clumped more easily. As a result of this, nanocellulose remained on the filter paper. Studies have shown that produced membranes' permeance and the rejection values can be

adjusted by size or type of the nanocellulose and the amount of filtrated nanocellulose.

Zhang et al.⁹¹ produced ultrathin nanoporous membranes by filtering cellulose nanofibers (NFC) whose length is smaller than 10 nm through alumina support using different filtration volumes from 0.8 ml/cm² to 4 ml/cm² at constant pressure. They prepared cellulose nanofibers by dissolving cellulose into N-methylmorpholine-N-oxide (NMMO) to obtain very dilute cellulose solution. Then, this solution was frozen in liquid nitrogen to turned NMMO molecules to its glassy state among the cellulose chains that stretched easily into the very dilute solution. Then, when the temperature raised from -196 to 4 °C in the fridge, cold crystallization of frozen NMMO molecules occurred to obtain cellulose nanofibers by removing them from the NMMO nanocrystals. Then, cellulose nanofibers were procured by extraction of these cellulose-NMMO solids in to water with ultrasonication. Then, ultrathin nanoporous membranes were produced by filtering these nanofibers on the alumina support. They stated that by adjusting filtration volume, they can easily adjust the thickness and porosity of the nanoporous membrane, and while the thickness of nanoporous membrane increases with increasing filtration volume, the flux of nanoporous membrane decreases with increasing filtration volume. Also, during filtration of cellulose nanofiber solution, the water flux decreased continuously until some point due to compaction of cellulose nanofiber membrane. In addition to these, when they worked on membrane filtration performance, the rejection values of gold nanoparticles and ferritin molecules increase with nanoporous membrane thickness. Moreover, the produced nanoporous membrane showed high flux value for organic solvent filtration. As a result of the experiments, they concluded that these ultrathin nanoporous membranes offer a wide range of application to separation of both nanoparticles and macromolecules and have huge potential for solutions that contains organic solvents.

Cheng et al.⁹² produced superhydrophilic and superoleophobic membranes using tunicate cellulose nanocrystal (TCNC) via vacuum filtration on the nylon filter

membrane using different TCNC amounts to separate oil/water mixtures. During their experiments, after obtaining tunicate cellulose, the tunicate nanocrystalline cellulose was produced using sulfuric acid hydrolysis of tunicate cellulose. Then, by using different TCNC amounts, the TCNC was filtered through a nylon filter membrane. Then, they analyzed these membranes' morphology, performance, durability and stability. When the SEM images were investigated, the obtained membranes have fibrous like homogenous surface. Moreover, they stated that while the TCNC deposition amount increases, the membrane flux decreases and the membrane thickness increases. The main issues of these membranes are stability and durability in extreme conditions such as high/low pH, temperature changes, alkaline conditions and mechanical scratch. Therefore, they tested these membranes reusability by applying the same membrane performance test in several cycles by controlling water permeance and oil rejection values. As a result of this test, they did not observe any change for water permeance and oil rejection values. Then, the stability of the membranes in NaCl, HCl and NaOH was tested via contact angle measurements. Finally, they concluded that reusable, having pH and temperature resistance, having excellent mechanical properties, super hydrophilic and superoleophobic membranes using TCNC were produced successfully with high oil rejection ($\sim 100\%$) and permeance values ($> 1700 \text{ L/m}^2\text{hbar}$) using cheap, easy and environmentally friendly method.

In another work⁹³, cellulose nanofiber (CNF) based cellulose nanopaper membrane separators for lithium-ion batteries were produced using the vacuum filtration method. To produce these membranes, CNF was produced via high-pressure homogenizer in IPA-water mixtures. After preparing and dispersing CNF in the IPA-water mixture, they filtered this solution on to filter paper in the Buchner funnel via vacuum filtration. Then, using the papermaking technique, they produced cellulose nanopaper membranes. During this process, they used different IPA-water ratios to see their effects on membrane morphology. They said that when the IPA amount increases, the porosity of membrane increases because of the decrease in attractive forces between CNF particles. Besides, these membranes'

mechanical properties were tested concerning the IPA-water ratio, and the mechanical properties like tensile strength and tensile modulus are directly related to it due to changing porous structure. Also, when the performances of these membranes were compared with traditional membrane separators for lithium-ion batteries, it can be concluded that these membranes show excellent cell performances when the concentration balance of water-IPA is established and promising material for future lithium-ion batteries.

2.4 Cellulose Membranes

Durmaz et al.⁹⁴ produced membranes by using 8 % cellulose as a polymer, [EMIM]OAC as a solvent and DMSO as a co-solvent with phase inversion technique. After preparing membrane casting solutions and casting them on a glass support, the membranes were coagulated either in water or EtOH bath. They investigated these membranes in several different ways. As a result of their experiments, it can be said that the crystallinity of cellulose membranes is higher at the non-solvent side of the membrane due to the asymmetric structure of the membrane. The crystallinity of cellulose membranes increases with either increasing the solvent amount in the casting solution because of the regular arrangement of cellulose in the ionic liquids or decreasing co-solvent amount in the casting solution due to increasing pore size of the membrane. Also, the solute rejection (blue dextran 20kDa and BTB) of cellulose membranes increases with increasing the cellulose membrane crystallinity. In addition to these, the crystallinity of cellulose membranes is higher in water coagulated membranes than the EtOH coagulated membranes due to fast coagulation in water. And, they stated that these produced membranes can be used for NF or UF processes depending on the solvent amount in the casting solution. The NF cellulose membranes were produced using cotton linter cellulose, [EMIM]OAC as a solvent and acetone as a volatile co-solvent by using different polymers and solvent concentrations via phase inversion method in Sukma et al.¹⁷ study. After preparing the membrane

casting solutions, the membranes were cast on the glass support. Then, if the membrane casting solutions contained the acetone, firstly evaporation of acetone was done before putting the membrane into a water coagulation bath, but if the membrane casting solutions did not contain acetone, it was coagulated in water directly. Then, they tested these membranes by using different types of solute solution whose sizes and charges are different from each other. As a result of their works, they stated that when polymer concentration in the casting solution increases, the denser membrane can be obtain with higher neutral solute rejection and lower permeance; however, depending on the solute properties, it can be said that the relation between solute and the membrane is determining factor in solute rejection, and solutes with low sorption in the membrane are typically rejected to a high extent and vice versa. In addition to this, the addition of acetone in the casting solution with pre-evaporation of acetone before coagulation bath causes to increase the neutral solute rejection with decrease the membrane permeance due to increase of cellulose concentration in the membrane. The produced membranes are stable in organic solvents.

Konca et al ⁹⁵. produced cellulose acetate membranes using cotton linter cellulose, [EMIM]OAC as a solvent and acetone as a co-solvent via phase inversion and crosslinking with BTCA (1,2,3,4-Butanetetracarboxylic acid). After preparing membrane casting solutions and casting them on a glass support, the evaporation of acetone was done by using N₂ containing evaporation bath. Then, after the coagulation of the membranes in the coagulation bath, the membranes were put into BTCA/NaH₂PO₄ solution. Finally, the crosslinked membranes were obtained after the drying membranes in the oven and washing membranes with water and EtOH. Then, the crosslinked membranes were tested by using different solutes with similar sizes and differently charged which are bromothymol blue (BTB-neutral), crystal violet (CV-positive) and rose bengal (RB-negative) to show that the membrane rejection does not only depend on the size of the solute but also the affinity between the membrane and the solute. As a result of mechanical testing of the crosslinked membranes, it can be concluded that the mechanical properties

(elastic modulus and tensile strength) of the crosslinked membranes increase due to obtaining more stiff membranes after crosslinking. Moreover, when the crosslinked membranes were tested with EtOH and DMSO, although the membranes' EtOH permeance stays similar after crosslinking, the DMSO permeance of the membranes decreases since the membranes swell in the DMSO and become stiffer after crosslinking which causes decreasing pore size of membranes. In addition, after the crosslinking process, the surface of the membranes became negatively charged due to having free carboxyl groups which cause to decrease in CV rejection and increase in RB rejection. However, there is no effect of membrane crosslinking on BTB rejection. As a result of this study, the similar things with Sukma et al¹⁷. can be concluded that the membrane solute rejection is highly related to the relation between the membrane and the solute.

In another study ⁹⁶, the cellulose membranes were produced using wheat straw cellulose and [BMIM]Cl via phase inversion in the water coagulation bath. As results of ATR-FTIR analysis and XRD analysis that was used to see cellulose bonding structure and crystallinity before and after the dissolution of cellulose, they concluded that the cellulose I structure turns into cellulose II structure because the IL breaks both internal and external hydrogen bonds. This situation also causes a decrease in the thermal stability of the cellulose. In addition to these, when they investigated the permeability and mechanical properties of the cellulose membranes, it can be said that with respect to other cellulose membranes which prepare with other types of solvents like NMMO and NaOH, these cellulose membranes show better mechanical and separation performances with asymmetric membrane structure. Therefore, these cellulose membranes promise to be used for separation processes.

Anokhina et al. produced cellulose composite nanofiltration membranes using two different ways. In the first study⁹⁷, cellulose casting solutions were prepared by using cellulose, [EMIM]OAc as a solvent and DMSO as a co-solvent by using different DMSO and cellulose concentrations. After casting the cellulose solution on to polymer support, the composite membrane was put into water coagulation

bath. As a result of their observations, it can be said that when DMSO amount in the casting solution increases, the dissolution time of cellulose decreases until [EMIM]OAC:DMSO is equal to 1:1 ;however, after that point, the dissolution time of cellulose decreases since the dissolution of cellulose usually supplied with IL in the casting solution. In addition to these, when the composite membranes performances which contains different DMSO amounts by keeping cellulose amount constant were tested with DMF and two different dye solutions (Orange II and Remazol Brilliant Blue R), it can be said that although the DMF permeability stays nearly the same, dye rejection value increases with increasing IL amount due to obtaining the composite membrane with denser porous structure on the cellulose layer. Moreover, when the performance of the composite membranes which contain different cellulose amounts by keeping [EMIM]OAC:DMSO amount constant were tested with DMF and two different dye solutions (Orange II and Remazol Brilliant Blue R), they stated that when the cellulose amount increases, the dye rejection and DMF permeability of the composite membrane decreases due to having more denser cellulose layer on the composite membrane. As a result of these, it can be concluded that the ratio of solvent:co-solvent and the polymer amount in the casting solution are the determining factor for membrane rejection and permeability. In the second study⁹⁸, as similar in the first study, after preparing membrane casting solutions, they were cast the membrane solution on to polyester support; however, unlike the other study, they used NMMO instead of IL to dissolve cellulose. Finally, these membranes were coagulated firstly in a bath containing NMMO then in a water bath. Then, to determine the cellulose composite membranes' aprotic solvent stability and dye rejection, they were tested these membranes by using five different aprotic solvents (acetone, THF,DMF,NMP and DMSO) and two different dyes with different molecular weight (Orange II and Remazol Brilliant Blue R). As a result of their experiments, they stated that the cellulose composite membranes' performance depends more on the properties of the filtrated solvent regardless of the solute used. It can be said that when the filtrated solvent viscosity increases, the permeability decreases with increasing

solute rejection. This could be explained that the solute sorption and the solute affinity on the membrane highly depend on the solubility differences between solute and solvent. If the solute and the solvent have similar solubility, the sorption of solute does not occur on the membrane since the solute shows more affinity to the solvent or vice versa. They concluded that the produced cellulose membranes are stable in many different aprotic solvents and promising membrane for NF processes.

Li et al.⁹⁹ produced cellulose composite membranes via phase inversion method by using [AMIM]Cl. After casting the cellulose solution on to polymer support, the composite membrane was put into water coagulation bath. As a result of their investigation, it can be concluded that the composite membranes are produced successfully with stable, uniform and dense cellulose layers without macro voids which can be explained with having high viscosity of the casting solution that slows the phase separation time by eliminating macro void formation. In addition to these, the cellulose membranes are promising materials for NF applications with molecular weight cut-off smaller than 700 Da.

2.5 Fabrication of All-Cellulose Nanocomposite Films/Membranes by Partial Dissolution of Cellulose or Direct Addition of Nanocellulose into Membrane Matrix

Nishino et al.⁸⁰ who used all-cellulose composite term for the first time prepared all-cellulose composite by impregnation of cellulose fibers into cellulose matrix after activating the cellulose pulps. Before dissolving cellulose pulps into DMAc-LiCl, cellulose pulps had to be pre-treated. Therefore, after the pre-treatment of pulps with distilled water, acetone and DMAc, the pre-treated pulps were dissolved into DMAc-LiCl solution. Then, parallel aligned cellulose fibers were embedded to cellulose solution until obtaining gelation of solution at ambient conditions. Finally, to obtain all-cellulose composite, after putting this gel into methanol solution to remove DMAc-LiCl solution, it was dried both at room temperature and

the vacuum conditions, separately. After preparing all-cellulose composites, they tested all-cellulose composite's mechanical, structural and thermal properties. They stated that fibers are surrounded by the cellulose matrix which proves that all-cellulose composite obtained successfully. Also, it can be concluded that although the cellulose fibers maintains their crystallinity in all-cellulose composite and stayed with no damage, the celluloses into the cellulose matrix lose their crystallinity due to dissolution. In addition to these, when the mechanical tests of the only cellulose fibers and all-cellulose composite were done, they stated that despite all-cellulose composite decreases their tensile strength and Young's modulus with respect to the only cellulose fiber which can be caused due to loosing crystallinity of cellulose pulps, all-cellulose composite still have higher mechanical properties than conventional glass-fiber-reinforced composites. As a thermal property, all-cellulose composite shows no thermal expansion or contraction with respect to the cellulose matrix. However, during structural analysis, they realized that there are cracks in the interphase of the fiber and the cellulose matrix. Therefore, to obtain a smooth interface and to ensure good adhesion of the two surfaces, they pretreated the cellulose fibers by using a similar way of the cellulose pulps with different time durations for impregnation of the cellulose fibers into the cellulose pulps. As a result of this, they concluded that by determining the optimum time for impregnation due to prevent over-dissolving of fibers, all-cellulose composite with good interphase properties and similar properties of non-pre-treated fiber can be produced.

Zhao et al.⁸¹ produced cellulose nanocomposite films by using direct addition of NFC to generated cellulose matrix. During their experiment, to produce NFC, they used both sonication and high shear homogenization. After putting cut cellulose pulps into distilled water, the cellulose solution was processed with ultra-sonication. Then, after diluting this cellulose solution with distilled water, they treated with homogenizer. As a final step, by drying some of the solution and then by applying centrifugation, the NFC was obtained. After producing NFC, they dispersed NFC in the DMAc solution at different concentrations. Then, after

activating MCC in distilled water, methanol and DMAc, they dissolve it in the LiCl/DMAc solution. Finally, they mixed these two solutions until obtaining homogenous mixture. This activation of the cellulose method was used also Nishino et al.⁸⁰. After obtaining the cellulose nanocomposite films by casting the film solution in the ambient conditions, they concluded that although the cellulose nanocomposite films have higher tensile strength, crystallinity and thermal stability with respect to only cellulose films, the amount of NFC in the film affects these properties of films.

In another study¹⁰⁰, all-cellulose nanocomposite films were produced by using cellulose nanofiber sheets by using partial dissolution process in a similar way Zhao et al.⁸¹ and Nishino et al.⁸⁰. After producing cellulose nanofiber sheets from bagasse, these sheets were activated in distilled water, acetone and DMAc. Then, activated cellulose nanofiber sheets were put into DMAc/LiCl solution by using different dissolution times. Finally, before drying rinsed sheets with hot press to obtain all-cellulose nanocomposite films, these sheets were washed with EtOH to rinse solvent residues. Then, they tested these films' structural, mechanical and thermal properties as well as water vapor permeability. As a result of their studies, it can be concluded that the crystallinity of cellulose and the crystallite size of cellulose in the composite decrease with increasing dissolution time since when dissolution time increases, the solvent has time to penetrate into cellulose amorphous regions to dissolve crystalline part of the cellulose. This situation also proves with broadening cellulose I peak in the XRD results when dissolution time increases. In addition, with decreasing crystallinity of the composite, the thermal properties of the all-cellulose nanocomposite affects negatively. Moreover, with increasing the dissolution time, the water vapor permeability increases since water vapor can easily permeate from the cellulose matrix. As a result of comparison of these films' water vapor permeability with other literature values, it can be concluded that these all-cellulose composite films can be used instead other biodegradable packaging materials. Also, although the mechanical strength of composites increases with increasing dissolution time until one point, after that

point, the tensile strength of material decreases with time due to degradation of cellulose at long dissolution times. As a result of these, they concluded that the all-cellulose nanocomposite films are produced successfully by using this method and bagasse, and these produced all-cellulose nanocomposite films can be used in food packaging industries.

Duchemin et al.¹⁰¹ produced all-cellulose composite materials by using partial dissolution of cellulosic paper in ionic liquid (1-Butyl-3-Methylimidazolium Chloride) at different dissolution times. To produce all-cellulose composite, after IL was distributed on the petri dish, the cellulosic paper was put to top of it. Then, this petri dish was put into oven at different time durations. Then, after stopping dissolution of cellulose paper by waiting samples into ambient conditions, the samples were washed to remove rest of the solvent or remaining solvents with water. After drying the samples, they tested samples' structural and mechanical properties. As a result of their study, when the dissolution time effect on the all-cellulose nanocomposite films' crystallinity and mechanical strength investigated, the similar things can be concluded with Ghaderi et al.¹⁰⁰. They concluded that this method prefers alternative the LiCl/DMAc system to prepare cellulose composite materials.

In a similar study ¹⁰², all-cellulose nanocomposite films were produced by using microfibrillated cellulose and IL which is [BMIM]Cl (1-Butyl-3-Methylimidazolium Chloride) via partial dissolution. To produce all-cellulose nanocomposite films, after preparing transparent solution with different MFC amounts and IL by stirring and heating through different dissolution times, the samples poured into petri dish, and cooled at room temperatures to stop dissolution of cellulose to obtain gel form. After washing IL remaining from the samples with distilled water, they dried all-cellulose nanocomposite films both at room conditions and at vacuum conditions, separately. They investigated all-cellulose nanocomposite films at several different ways to determine their structural, thermal and mechanical properties. As a result of XRD results, they concluded that the crystallinity of all-cellulose nanocomposites decreases with increasing the

dissolution of cellulose, but the dissolution of cellulose can be controlled with cellulose amount and dissolution time. The dissolution of cellulose increases with decreasing MFC amount or increasing dissolution time. Besides, all samples had lower crystallinity value than MFC source which can be attributed to reaching partial dissolution, successfully. However, the deterioration of XRD pattern of all-cellulose nanocomposite films is observed due to the dissolution of cellulose I structures by turning into cellulose II, and dissolution of cellulose II structures by turning into non-crystalline cellulose. While these non-crystalline parts form cellulose matrix, these undissolved parts show the cellulose I crystalline structure, in all-cellulose nanocomposite films. Also, the prepared all-cellulose nanocomposite films are transparent films which can be explained with good interphase adhesion and good bonding between matrix and crystalline part of the all-cellulose nanocomposite films. In addition to these, due to having more crystalline regions by decreasing dissolution of MFC, the thermal stability and the strength (storage modulus) of the all-cellulose nanocomposite films increase.

Zhang et al ³¹. produced all-cellulose nanocomposite materials by using MCC and [AMIM]Cl (1-Ally-3-Methylimidazolium Chloride) via partial dissolution technique. To prepare all-cellulose composites, different amounts of MCC were mixed with [AMIM]Cl at different dissolution temperatures and times until obtaining transparent solution. After casting this solution on to glass support, it was coagulated in the distilled water to get rid of solvent residues, and dried in vacuum. As a result of TEM images, they concluded that despite the solutions are transparent, the nanocrystals of cellulose are shown in the TEM images of the solution. In similar to the previous studies^{100,101}, they concluded a similar effect of dissolution time on the all-cellulose nanocomposites' crystallinity and mechanical properties. In addition, the dissolution temperature affects the crystallinity of all-cellulose nanocomposites and reaching maximum strength time since cellulose dissolution rate increases with increasing the dissolution temperature. Also, the obtained all-cellulose nanocomposite films are highly transparent due to having

good interphase and properly dispersed nanocrystalline cellulose as explained elsewhere¹⁰².



CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Materials

Sulfuric acid (H_2SO_4 , 95.0-97.0 %), sodium hydroxide (NaOH , 97.0 %) , 1-Ethyl-3-methylimidazolium acetate ([EMIM]OAC, 95.0 %), cellulose acetate (CA, 97.0 %), cotton linter (97 %), avicel (97 %), Blue Dextran 5000 MW (BD5), Bromtimol Blue (BTB, 95.0 %), Rose Bengal (RB, 95.0 %) and Poly(ethylene glycol) (PEG400) were purchased from *Sigma-Aldrich*. Dimethyl sulfoxide (DMSO, 99.0 %), N-Methyl-2-Pyrrolidone (NMP, 99.5 %), hydrochloric acid (HCl , 37.0 %), Dimethylformamide (DMF, 99.5%), acetone (99.5% purity) and Crystal violet (CV, 88% Dye content) was purchased from *Merck*. Ethanol (EtOH , 99.5% purity) was purchased from *J.T.Baker*, polyether sulfone (PES E6020P) was purchased from *BASF*, and Nanocrystalline Cellulose that prepared using H_2SO_4 was purchased from *CelluForce*. The properties of commercial NCC are given in Table 3.1.

Table 3.1 The Properties of Commercial NCC

Color of NCC	White
Particle Length (nm)	44-108
Particle Diameter (nm)	2.3-4.5
Hydrodynamic Diameter (nm)	70
Zeta Potential (mV)	-37

The reverse osmosis water (RO) that is used as a non-solvent phase in coagulation bath and ultra-pure water (UP) that is used as a solvent to test membrane

performances and in dialysis procedure were provided from chemical engineering department of METU.

3.2 Nanocrystalline Cellulose (NCC) Production

To produce nanocrystalline cellulose (NCC), different acid types (hydrochloric acid (HCl) or sulfuric acid (H_2SO_4)), different aqueous H_2SO_4 concentrations (50 and 65 wt %), different cellulose types (cotton linter cellulose and Avicel (MCC)), different acid to cellulose ratios, different acid, cellulose and water addition sequence, and different reaction times were used to see their effect on produced NCC's properties. However, as a general NCC production procedure, firstly, after preparing the acid in the desired concentration, it was heated to the desired temperature. Then, cellulose in the desired amount with respect to the cellulose/acid ratio was added to the top of the acid. After adding the desired amount cellulose into the acid, the reaction was continued through the desired time by mixing at 250 rpm, and to stop the reaction, threefold of pure water was added to the top of this NCC-acid mixture. As a final part of the NCC production, to purify the NCC-acid mixture from its acid, two different methods were used. In one method, just after the reaction, the NCC-acid mixture was purified from its acid with precipitation of cellulose by using centrifugation. In another method, either just after reaction or after centrifugation procedure (All the NCC-acid mixture cannot be totally purified by using centrifugation since cellulose is not precipitating after certain pH depending on the reaction conditions), the NCC-acid mixture was purified from its acid by using dialysis membranes. After these methods, some part of the NCC was dried for some analysis and to determine the NCC amount, and another part of the NCC was kept in a bottle as a dispersed phase in water in the fridge to prevent the formation of bacteria etc. to use in membrane production. The general NCC production method is shown in Figure 3.1 as a schematically.

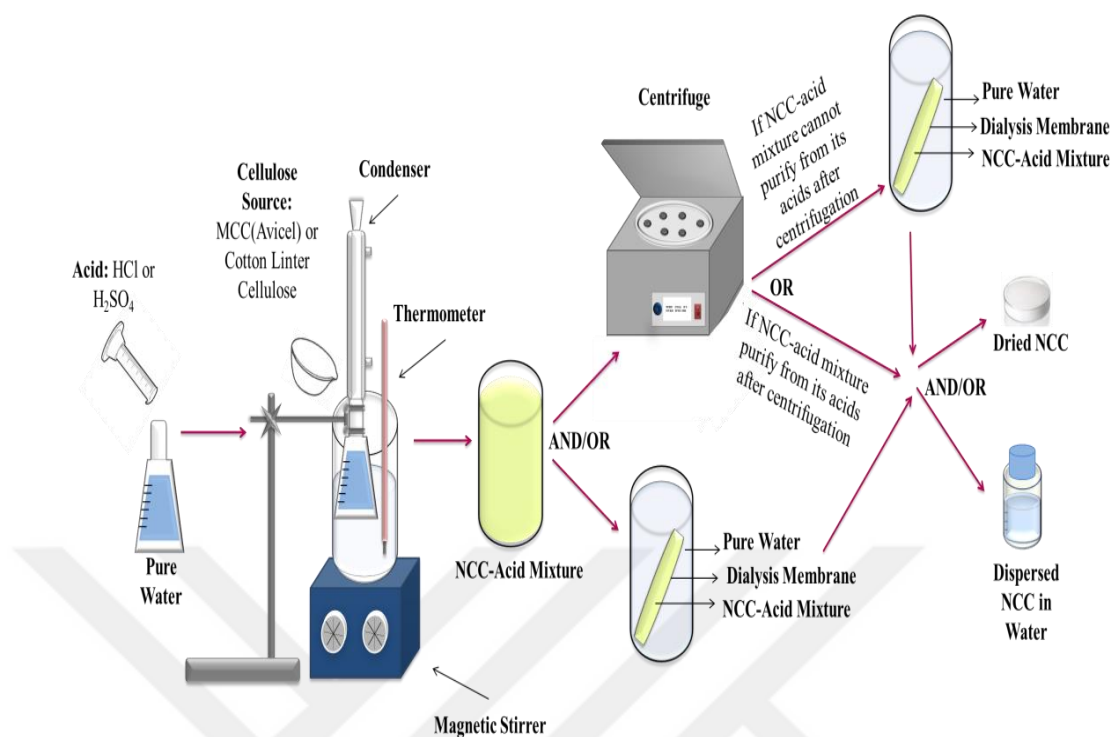


Figure 3.1. Schematic representation of NCC Production

The details of different preparation conditions of the NCC as mentioned using different acid types (hydrochloric (HCl) or sulfuric acid (H_2SO_4)) and different aqueous H_2SO_4 concentrations (50 and 65 wt %), different cellulose types (cotton linter cellulose or Avicel), different acid to cellulose ratios, different acid, cellulose and water addition sequence, different reaction times and temperatures is given in Table 3.2.

Table 3.2 Different Preparation Condition of NCC

NCC Codes	NCC-HCl	NCC65H ₂ SO ₄ - time/8.75	NCC65H ₂ SO ₄ - time/10	NCC50H ₂ SO ₄ - time/10	NCC50H ₂ SO ₄ - -time/8.75	NCC50H ₂ SO ₄ - -time/10
Cellulose Source	MCC (Avicel)/ Cotton Linter Cellulose	MCC (Avicel)	MCC (Avicel)	MCC (Avicel)	MCC (Avicel)	Cotton Linter Cellulose
Acid Type	HCl	H ₂ SO ₄	H ₂ SO ₄	H ₂ SO ₄	H ₂ SO ₄	H ₂ SO ₄
Acid and Cellulose Amount	5 g Avicel, 175 mL 4 N HCl	8.75 ml/ g acid/cellulose ratio, 65 wt% H ₂ SO ₄	10 ml/ g acid/cellulose ratio, 65 wt% H ₂ SO ₄	10 ml/ g acid/cellulose ratio, 50 wt% H ₂ SO ₄	8.75 ml/ g acid/cellulose ratio, 50 wt% H ₂ SO ₄	10 ml/ g acid/cellulose ratio 50 wt% H ₂ SO ₄
Reaction Temperature (°C)	80	45	45	45	45	45
Reaction Time (Minute)	225	60	60	60	60	60
Sample Taking Time (Minute)	225	60	30-45-60	15-45-60		15-30-60
Centrifugation Conditions	Centrifugation was done until reaching neutral pH at 7000 rpm/10 minutes and room conditions.		Centrifugation was done until reaching 2-3 pH value at 7000 rpm/10 minutes and room conditions.			
Other Processes	It was dried in a vacuum oven.		It was kept in a dialysis bag until the pH of the water around the dialysis bag stay constant. Then, it was dried in a vacuum oven.			
NCC Color After Reaction	White	Black	Reddish/Black	Beige		
Order of Materials Addition	Firstly, 4 N HCl was prepared. Then, depending on the acid/cellulose ratio, the desired amount of cellulose was added to the top of the acid solution. Reaction continued through 225 minutes at 80 °C.	Firstly, 65 % H ₂ SO ₄ was prepared. Then, depending on the acid/cellulose ratio, the desired amount of cellulose was added to the top of the acid solution. Reaction continued through 60 minutes at 45 °C.	Firstly, 65 % H ₂ SO ₄ was prepared. Then, depending on the acid/cellulose ratio, the desired amount of cellulose was added to the top of the acid solution. Reaction continued through 60 minutes at 45 °C by taking samples at 30, 45 and 60 minutes.	Firstly, 50 % H ₂ SO ₄ was prepared. Then, depending on the acid/cellulose ratio, the desired amount of cellulose was added to the top of the acid solution. Reaction continued through 60 minutes at 45 °C by taking samples at 15, 45 and 60 minutes.		Firstly, 200 ml of 96 % H ₂ SO ₄ was mixed with 150 ml of pure water. Then, it was heated to 45 °C. At the same time, 38.4- gram cotton linter cellulose was added to the top of the 34 mL pure water by mixing magnetic stirrer. Then, this cellulose-water mixture was added to the top of the acid solution at 45 °C. After adding all cellulose-water mixture to the top of the acid solution, the reaction continued through 60 minutes by stirring and taking samples at 15, 30 and 60 minutes.

As a result of these experiments and analyses that are given in the results and discussions parts, the best NCC production conditions are determined as 30 minutes reaction time, 50 wt % aqueous H₂SO₄ concentration, cotton linter cellulose as a cellulose source and 10 ml/g acid to cellulose ratio.. For this reason, the NCC that was used for NCC membrane production was produced using these conditions, and the details of this NCC is given in Table 3.3.

Table 3.3 Production Details of the NCC for Further Processes

NCC Codes	NCC50H ₂ SO ₄ -30/10
Cellulose Source	Cotton Linter Cellulose
Acid Type	H ₂ SO ₄
Acid and Cellulose Amount	10 ml acid / g cellulose ratio, 50 wt% H ₂ SO ₄
Reaction Temperature (°C)	45
Reaction Time (Minute)	30
Centrifugation Conditions	Centrifugation was done until reaching neutral pH at 7000 rpm/10 minutes and room conditions.(Half of the sample)
Other Processes	It was kept in a dialysis bag until the pH of the water around the dialysis bag stay neutral. Then, it was kept in the fridge.(Other half of the sample)
NCC Color After Reaction	Nearly white
Order of Materials Addition	Firstly, 150 ml of 96 % H ₂ SO ₄ was mixed with 80 ml pure water. Then, it was heated at 45 °C. At the same time, 28.8 gram cotton linter cellulose was added to top of the 58 mL pure water by mixing magnetic stirrer. Then, this cellulose-water mixture was added to top of acid solution at 45 °C as soon as possible. After adding all cellulose-water mixture to top of acid solution, the reaction was continued through 30 minutes by stirring.

After production of the NCC, the reaction yield of hydrolysis reaction was calculated by using equation (5).

$$\% \text{ Rxn. Yield} = \frac{\text{The Total NCC Amount After Hydrolysis Reaction (g)}}{\text{The Initial Cellulose Source Amount (g)}} * 100 \quad (5)$$

3.3 Membrane Production

3.3.1 Production of All-Cellulose Nanocomposite Membranes

3.3.1.1 Materials Used to Produce All-Cellulose Nanocomposite Membranes

To produce membranes by partial dissolution of cellulose or adding NCC into membrane casting solution, four different types of cellulose which are avicel (MCC), cotton linter cellulose, cellulose acetate and NCC were used. Before using Avicel and cotton linter cellulose, they were dried in an oven at 80 °C for 48 hours to get rid of moisture content in cellulose. Also, before using cellulose acetate, it was put into a vacuum oven for the same purpose of celluloses. In addition to this, 1-Ethyl-3-methylimidazolium acetate ([EMIM]OAC) was used as the cellulose solvent, and dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) was used as the co-solvent of cellulose. However, before using 1-Ethyl-3-methylimidazolium acetate ([EMIM]OAC), it was heated for an hour at 90 °C and three hours at 70 °C to get rid of moisture in it. Moreover, N-Methyl-2-pyrrolidone (NMP) was used to dissolve cellulose acetate, and acetone was used as the co-solvent of cellulose acetate. Other solvents and co-solvents other than mentioned above were used without pre-treatments.

3.3.1.2 Membrane Production Technique to Produce All-Cellulose Nanocomposite Membranes

During the production of the all-cellulose nanocomposite membranes, flat membranes were produced using the liquid induced phase separation (LIPS). During this method, after preparing a membrane solution, firstly, the membrane solution was poured on a clean glass support by using a casting bar whose thickness is 250 μm . After this step, if the membrane solution contained acetone, the casted membrane was put into an evaporation bath through 30 minutes under 0.6 L/min nitrogen flow to evaporate acetone from the casted membrane for increasing polymer-solvent ratio. Then, either just after membrane pouring or acetone evaporation, the casted membrane was placed in the coagulation bath for phase separation and solvent exchange. For washing the membrane, the water in the coagulation bath was changed several times in 24 hours. After finishing the washing step, the membrane was obtained and kept in technique ethanol until use. During non-solvent induced phase separation, RO water was used as a non-solvent. The membrane production steps for fabrication the all-cellulose nanocomposite membranes are shown schematically in the Figure 3.2.

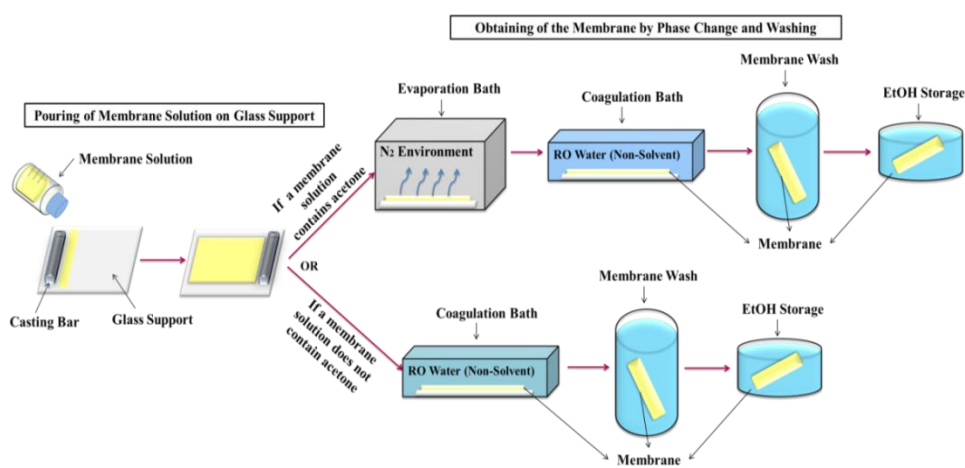


Figure 3.2. The schematic representation of the membrane production steps for fabrication the all-cellulose nanocomposite membranes

In addition to these steps, the membranes which contain cellulose acetate were regenerated by the alkali hydrolysis method to obtain cellulose membranes after the annealing procedure. Firstly, a membrane that contained cellulose acetate was removed from EtOH storage and dried in ambient conditions. After that, the membrane was put into an oven at 120 °C for 6 hours for dry annealing to increase the tightness of the membrane. After the membrane cooled at ambient conditions to finish annealing, the membrane was put into 2L - 0.05 M NaOH/EtOH solution for 24 hours to regenerate the cellulose acetate membrane to cellulose membrane. Then, the membrane was put into RO water to wash the membrane for 24 hours. After these steps, the membrane was put into technique EtOH storage until use.

While creating the membrane solutions, it was tried to obtain the all-cellulose nanocomposite membranes by changing the proportions of the ingredients, materials used as co-solvent, dissolution and mixing times, heating temperatures of the solvents and the order of addition of the substances by using materials in given part 3.3.1.1. Then, these membranes were obtained by using techniques in given part 3.3.1.2. The detailed explanations of the produced all-cellulose nanocomposite membranes are given in Table 3.4.

Table 3.4 All-Cellulose Nanocomposite Membranes and Their Production Ways

Preparation Method and Content of Membrane Solutions to Produce All-Cellulose Nanocomposite Membranes	
EV7S	After all MCC was mixed with DMF through 10 minutes, [EMIM]OAC was added to the top of this mixture. After 15 minutes mixing of membrane solution, the membrane was cast. (8.0 % MCC, 69.0 % DMF, 23.0 % [EMIM]OAC)
EV7L	After all MCC was mixed with DMF through 1 hour, [EMIM]OAC was added to the top of this mixture. After 1 night mixing of membrane solution, the membrane was cast. (8.0 % MCC, 69.0 % DMF, 23.0 % [EMIM]OAC)

Table 3.4 (cont'd) All-Cellulose Nanocomposite Membranes and Their Production Ways

EV8S	After all [EMIM]OAC was mixed with DMF through 15 minutes, MCC was added to the top of this mixture. After 15 minutes mixing of membrane solution, the membrane was cast. (8.0 % MCC, 69.0 % DMF, 23.0 % [EMIM]OAC)
EV8L	After all [EMIM]OAC was mixed with DMF through 1 hour, MCC was added to the top of this mixture. After 1 night mixing of membrane solution, the membrane was cast. (8.0 % MCC, 69.0 % DMF, 23.0 % [EMIM]OAC)
EV12	Firstly, half of the cotton linter cellulose to be added was mixed with DMSO for 4 hours, and the rest of the cotton linter was mixed with [EMIM]OAC until dissolving the cotton linter cellulose in it. After dissolving the cotton linter cellulose, the DMSO-cotton linter cellulose mixture was added to the top of this mixture at room temperature. After the membrane solution looked like a homogeneous mixture, the membrane was cast. Also, after dissolving all cellulose into solvent-co-solvent mixture, the membrane (EV12-d) was cast to compare EV12 membrane with dissolved one. (8.0 % Cotton Linter Cellulose, 61.3 % DMSO, 30.7 % [EMIM]OAC)
EV14	After all cotton linter cellulose was mixed with DMSO through 5 minutes, [EMIM]OAC was added to the top of this mixture. After the membrane solution looked like a homogeneous mixture, the membrane was cast at time equal to 3 minutes (EV14/3) and 15 minutes (EV14/15). Also, after dissolving all cellulose into solvent-co-solvent mixture, the membrane (EV14-d) was cast to compare EV14/3 and EV14/15 membranes with dissolved one. (4.0 % Cotton Linter Cellulose, 64.0 % DMSO, 32.0 % [EMIM]OAC)

Table 3.4 (cont'd) All-Cellulose Nanocomposite Membranes and Their Production Ways

EV16	After all cotton linter cellulose was mixed with DMSO through 30 minutes, [EMIM]OAC was added to the top of this mixture. After the membrane solution looked like a homogeneous mixture, the membrane was cast at time equal to 2 minutes (EV16/2) and 5 minutes (EV16/5). Also, after dissolving all cellulose into solvent-co-solvent mixture, the membrane (EV16-d) was cast to compare EV16/3 and EV16/15 membranes with dissolved one. <i>(8.0 % Cotton Linter Cellulose, 61.3 % DMSO, 30.7 % [EMIM]OAC)</i>
EV17	Firstly, half of the cotton linter cellulose to be added was mixed with DMSO for 3 hours, and the rest of the cotton linter was mixed with [EMIM]OAC until dissolving the cotton linter cellulose in it. After dissolving the cotton linter cellulose, the DMSO-cotton linter cellulose mixture was added to the top of this mixture at 70 °C. After the membrane solution looked like a homogeneous mixture, the membrane was cast at time equal to 1 minute (EV17/1). Also, after dissolving all cellulose into solvent-co-solvent mixture, the membrane (EV17-d) was cast to compare EV17/1 membrane. <i>(8.0 % Cotton Linter Cellulose, 61.3 % DMSO, 30.7 % [EMIM]OAC)</i>
EV18	Firstly, NCC-HCl was mixed with acetone, and cellulose acetate was mixed with NMP. Then. NCC-acetone mixture was added to the top of the cellulose acetate- NMP mixture by using an impeller mixer. After the membrane solution looked like a homogeneous mixture, the membrane was cast. Then, these membranes were annealed at 120 °C and/or regenerated. Annealed membranes were code with EV18-120, and annealed and regenerated membranes were code as EV18-120R. <i>(1.33 % NCC-HCl, 19.73 % Cellulose acetate, 36.83 % Acetone, 42.11 % NMP)</i>

Table 3.4 (cont'd) All-Cellulose Nanocomposite Membranes and Their Production Ways

EV19	Firstly, cellulose acetate, acetone and NMP were mixed until dissolving cellulose acetate. Then NCC-HCl was added to this solution by a quarter of the amount of cellulose acetate. This solution was mixed with magnetic and waited in a roller mixer until the solution looked like homogenous. Then, it was put into the ultrasonic bath for 10 minutes. After that, it was put into again roller mixer through 30 minute and ultrasonic bath for 10 minutes. Finally, the membrane was cast. Then, these membranes were annealed at 120 °C and/or regenerated. Annealed and regenerated membranes were code as EV19-120R. (2.44 % NCC-HCl, 9.76 % Cellulose acetate , 46.83 % Acetone , 40.98 % NMP)
------	--

Some of these produced membranes were tested with pure solvent (ethanol) before the filtration test which is done by using Bromothymol Blue either after drying of membrane or not. (For details, see 3.6 Membrane Performance Tests).

3.3.2 Membrane Fabrication by Using Deposition of NCC on Support Membrane

3.3.2.1 Materials and Solutions to Produce Support Membrane

To produce support membranes for using controlled precipitation of the NCC, cellulose acetate and PES was used as a polymer for the support membranes. Before using cellulose acetate, it was put into a vacuum oven to get rid of moisture content in cellulose acetate. Also, before using PES, it was dried in an oven at 80 °C for 48 hours for the same purpose of cellulose acetate. In addition to this, DMSO was used as the solvent for cellulose acetate and PES, and PEG400 was

used as an additive for PES membranes. The produced membranes solutions and their contents are given in Table 3.5.

Table 3.5 Produced Support Membranes Solutions and Their Precursor Solution Compositions

Membranes Code	Polymer	Solvent	Additive
CA10	10 % Cellulose Acetate	90 % DMSO	-
CA20	20 % Cellulose Acetate	80 % DMSO	-
PES10/PEG10	10 % Polyether Sulfone	80 % DMSO	10 % PEG400

3.3.2.2 Used Techniques to Produce Support Membrane

During the production of the support membranes, flat membranes were produced using either only the liquid induced phase separation (LIPS) that explained in part 3.3.1.1 in detailed or vapor induced phase separation (VIPS) and the liquid induce phase separation (LIPS) together. In VIPS, the membranes were put into a humid air environment that used as a vapor phase to increase the porosity of the membrane. During VIPS, the air was pumped into a gas washing bottle that has the pure water in it by aquarium pump using to make bubbles through filter disc. These bubbles help to increase the relative humidity of the air. The gas washing bottle was placed in a hot water bath at 50 °C. The exit of the gas washing bottle was connected to a box where the humid air collects, and after casting the membrane solution, the casted membranes were put into this box to exposure them to humid air for the desired time. The relative humidity values of air in the box were measured 80 ± 15 % by hygrometer. After the desired time, the membranes were put into RO water to continue LIPS procedure. The schematic representation of the VIPS procedure is given in Figure 3.3.

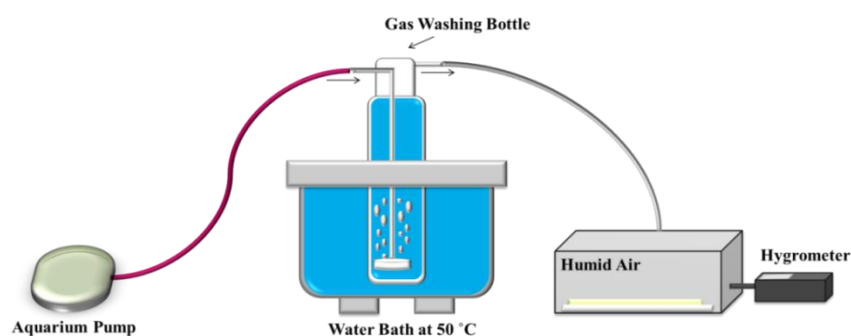


Figure 3.3. Membrane production techniques by using VIPS before LIPS

The support membranes are given in Table 3.6 with respect to production technique.

Table 3.6 Support Membranes with Production Technique(s)

Code of Membrane	LIPS	VIPS+LIPS	Humid Air Exposure Time
CA10	+	-	-
CA20	+	-	-
PES10/PEG10	+	+	1 minute (1MH)

3.3.2.3 Membrane Preparation Procedure by Deposition of NCC on Support Membrane

To produce membranes by using precipitation of NCC on a support membrane method, two types of nanocrystalline cellulose which are NCC50H₂SO₄-cot-30/10 and commercial NCC and three type of support membrane those are CA10, CA20 and PES10/PEG10-1MH were used. Moreover, dead end filtration method was used with 10 mL and 50 mL Amicon stirred cell for the CA support membranes and 300 mL HP4750 stirred cell for the PES support membranes at 0.5 bars for the CA10 and PES membranes, but 4 bar for CA20 membranes due to permeance of

membranes since the CA10 and PES membranes permeance is higher than the CA20 membranes. Firstly, the support membrane was tested by using pure water until reaching stable permeance value. Then, the nanocrystalline cellulose was dispersed completely into water using a magnetic stirrer and ultrasonic bath for the commercial NCC and ultrasonic probe for the NCC50H₂SO₄-cot-30/10 at 74 W by keeping mg/ml cellulose amount constant during ultrasonication (Step 1). To prevent over heating during the NCC dispersion in water by ultra-sonication procedure, the ice bath was used. While determining the amount of NCC, it was decided by determining how much material is required to cover the membrane surface. Accordingly, it was determined as 3.4 mg for the membrane with a surface area of 13.4 cm² and 1 mg for the membrane with a surface area of 4.1 cm² for the commercial NCC, and 1.7, 3.4 and 6.8 mg for the membrane with a surface area of 13.4 cm² and 0.5, 1 and 2 mg for the membrane with a surface area of 4.1 cm² for the NCC50H₂SO₄-cot-30/10 to see the deposition thickness effect on NCC membrane properties. These different thicknesses refer to 0.75, 1.5 and 3 µm deposition thickness if dense layers were to form. (The sample calculations of these thicknesses are given in the Appendix A). After dispersing the NCC into water, the nanocrystalline cellulose was filtered through the membrane surface (Step 2). To understand whether the NCC stayed on the membrane surface or not, the turbidity of feed and the turbidity of permeate were controlled before and after the deposition procedure. Depending on the nanocrystalline cellulose type, the commercial NCC was filtered on the CA20 membrane and the NCC50H₂SO₄-cot-30/10 was filtered on the CA10 and the PES10/PEG10-1MH. After that, to decrease the NCC's stability and increase the NCC membrane stability i.e. to change the zeta potential of NCC on the support membrane surface, 200 mM AlCl₃ (0.02 mg NCC/ ml salt) , was filtered through the commercial NCC deposited CA20 membrane , 200 mM AlCl₃ (0.02 mg NCC/ ml salt) was filtered through the NCC50H₂SO₄-cot-30/10 deposited CA10 membrane, and 1 M NaOH (For 30 minute at 60 °C) was filtered through the NCC50H₂SO₄-cot-30/10 deposited PES10/PEG10-1MH membrane . Filtration of AlCl₃ and NaOH were done in dead

end cell and steel cell, respectively. Before NaOH filtration on the NCC deposited PES10/PEG10-1MH membrane, after preparing 1 M NaOH, it was heated to 60 °C before putting it into steel cell. Then, after putting heated NaOH into steel cell, it was waited in steel cell for 10 minutes to obtain stable conditions (Step 3). As a final step of deposition procedure, to wash NCC membrane from salt/base remaining, pure water was filtered through NCC membrane (Step 4). The permeance of each step was recorded to see effects of these steps on support membrane and NCC membrane. Also, deposited support membranes is named with 'D' and the deposited CA10, CA20 and PES10/PEG10-1MH support membranes are called as CA10D, CA20D and PES10/PEG10-1MH-D , respectively. Depending on the NCC type, the deposited membranes are named with C for the commercial NCC and P for the produced NCC. In addition to these, with respect to the NCC deposition amount (different NCC thickness), deposited membranes are named with thin, normal or thick. Depending on the material that used for changing stability of the NCC membrane and the NCC, the deposited membranes are named with salt or base. The schematic representation and the detailed table of these steps and the naming of NCC membranes are given in Figure 3.4 and Table 3.7, respectively.

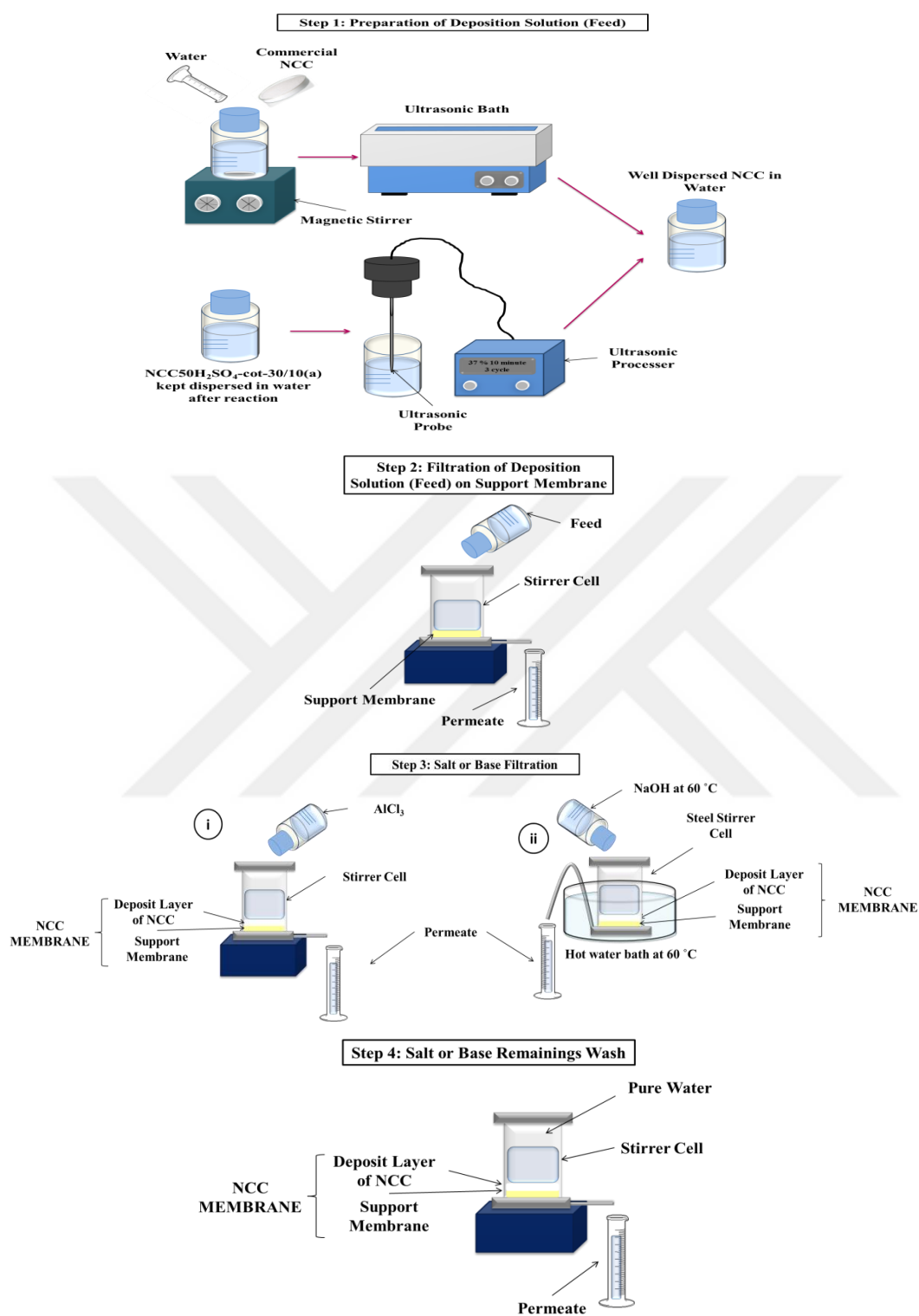


Figure 3.4. Schematic representation of the NCC deposition on the support membrane

Table 3.7 Detailed Table of the Applied Procedures on the Support Membrane

		NCC Membranes				
Applied Procedures During Deposition		CA10D-P-THIN-S	CA10D-P-NORMAL-S	CA10D-P-THICK-S	CA20D-C-NORMAL-S	PES10/PEG10-1MH-D-P-NORMAL-B
Support Membrane	CA10	+	+	+	-	-
	CA20	-	-	-	+	-
	PES10/PEG10-1MH	-	-	-	-	+
Type Of Cellulose	Commercial NCC (C)	-	-	-	+	-
	NCC50H ₂ SO ₄ -cot-30/10 (P)	+	+	+	-	+
NCC Amount	0.12 mg/cm ² (THIN)	+	-	-	-	-
	0.24 mg/cm ² (NORMAL)	-	+	-	+	+
	0.48 mg/cm ² (THICK)	-	-	+	-	-
Type Of Material To Effect The Zeta Potential Of NCC	200 mM AlCl ₃ (SALT-S)	+	+	+	+	-
	1 M NaOH (BASE-B)	-	-	-	-	+

To determine the resistances in each step of deposition procedure, the Darcy's law which is given in equation (6) was used.

$$R_{\text{membrane}} = \frac{\text{TMP}}{\eta J_{\text{pw}}} \quad (6)$$

During resistances calculations, R_{membrane} , $R_{\text{During Deposition}}$, $R_{\text{Salt Filtration}}$ and $R_{\text{Membrane After Deposition}}$ were calculated by using flux values at each step. After that, the resistance due to NCC deposition (cake resistance due to NCC deposition) was calculated using equation (7).

$$R_{\text{due to NCC Deposition}} = R_{\text{Membrane After Deposition}} - R_{\text{membrane}} \quad (7)$$

Then, by using these resistance values, deposited layer porosity and deposited layer thickness were calculated theoretically by using the Kozeny- Carman equation, and detailed calculation is given in the Appendix F.

These NCC membranes were washed with pure solvent/water after deposition procedure and tested with pure solvent/water before the filtration test which is done by using solute of different structures. (For details, see 3.6 Membrane Performance Tests).

3.4 NCC Characterization

The morphology of NCC was examined using Scanning Electron Microscope (QUANTA 400F Field Emission SEM, METU Central Laboratory) and Transmission Electron Microscope (FEI Tecnai G2 Spirit BioTwin CTEM, METU Central Laboratory). In addition to these, the crystallinity index (crystallinity) of NCC was analyzed using X-Ray Diffraction (XRD) Analysis (Rigaku Ultima-IV X-Ray Diffraction Device, METU Central Laboratory). The particle size analysis of NCC were done by using Dynamic Light Scattering (DLS) Analysis (MALVERN Zetasizer Ultra-Pro, METU Chemical Engineering Department), and

the surface charge of NCC in different AlCl_3 and NaOH concentrations were done by using Zeta-Potential and Mobility Measurement Device (MALVERN Nano ZS90, METU Central Laboratory and MALVERN Zetasizer Ultra-Pro, METU Chemical Engineering Department).

3.4.1 The Crystallinity Index Calculation

In order to calculate the crystallinity index of NCC, firstly, XRD analysis results are needed (Schematic representation of XRD analysis results is given in Figure 3.5). Then, there are two peak intensity values have to be found from these results; $2\theta = 22.5$ (maximum intensity, crystal intensity, I_{002}) and $2\theta = 18-18.4$ (minimum intensity, amorphous intensity, (minimum intensity, I_{am} between 101 and 002)).

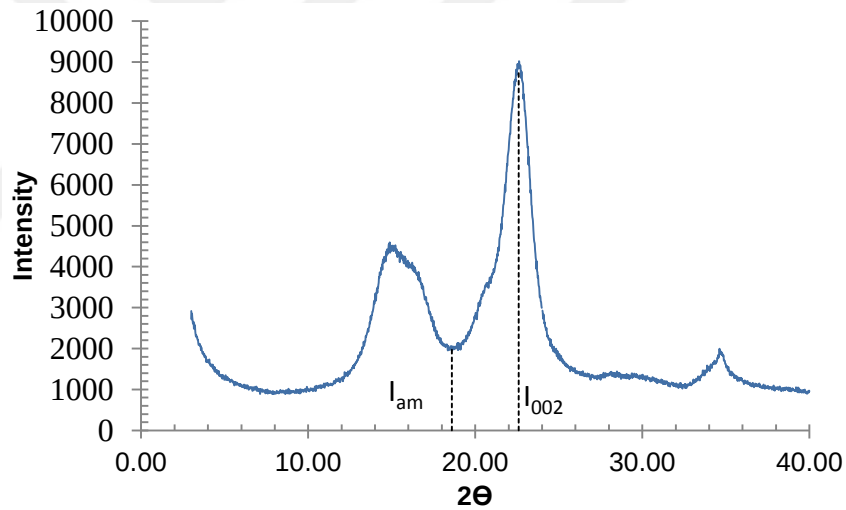


Figure 3.5. Schematic representation of XRD analysis with the peak positions

By using these peak intensity values, the crystallinity index values of NCC can be calculated by using equation (8). This method is called the SEGAL method¹⁰³.

$$CI(\%) = \frac{I_{002} - I_{am}}{I_{002}} * 100 \quad (8)$$

In addition to this, the crystallinity of cellulose can be defined as the ratio of crystalline cellulose to total amount of cellulose dry basis including both crystalline and amorphous parts in the cellulose. In other words, the crystallinity of cellulose can be represented with equation (9) ¹⁰⁴.

$$CI = \frac{\text{g crystalline cellulose}}{100 \text{ g total amount of cellulose}} \quad (9)$$

3.4.2 Sample Preparation for the DLS and Zeta Potential Measurement

- **DLS Measurement**

During Zeta Potential and DLS analyses, the samples have to look like nearly clear which correspond to 3.3 mg/mL for our samples; therefore, the dispersed NCC in water after reaction was directly used during these measurements. Firstly, the dispersed NCC in water after reaction was put into ultrasonic bath for 2 hours with ice and 10 minute for ultrasonic probe to disperse them properly in the water. After dispersing them completely, the DLS analysis was done.

- **Different AlCl₃ Concentrations**

Firstly, the dispersed NCC in water after reaction was put into ultrasonic bath for 2 hours with ice to disperse them properly in the water. Then, this NCC solution was put into bottles whose capacities are 4 mL. After that, determined different AlCl₃ amounts were put into these bottles to obtain different concentrations of AlCl₃ (0, 0.5, 5, 10, 20, 50, 100, 130, 145, 160, 200, 250, 300 and 1000 mM). To dissolve salts in the NCC solution, bottles were put into vortex mixture and ultrasonic bath for several hours. After dissolving them fairly good, the Zeta Potential analysis was done.

- **Different NaOH Concentrations (Alkaline Desulfation)**

Depending on the literature procedure ⁸⁸, several different NaOH molarities (0.005, 0.5, 1 and 2 M) and reaction times (30 minute, 1 and 3 hour) were decided,

firstly. Then, the desired amount NaOH to obtain desired molarity for 40 mL of total NCC-NaOH solution was put into 20 mL pure water to dissolve it completely. After the dispersed NCC in water after reaction was put into the ultrasonic bath for 2 hours with ice, 20 mL of this NCC solution was put into this NaOH solution to obtain 40 mL of the total NCC-NaOH solution. After mixing the total solution 1 or 2 minute with magnetic stirrer, the total NCC-NaOH solution was put into heater at 60 °C for desired reaction time by stirring at 250 rpm. To stop the reaction, the total NCC-NaOH solution was put into cold water bath. After cooling the solution, to wash NCC from NaOH, this solution was put into dialysis bag until reaching stable pH for pure water around the dialysis bag. After removing the NCC from dialysis bag, the Zeta Potential analysis was done. The schematic representation of this procedure is shown in Figure 3.6.

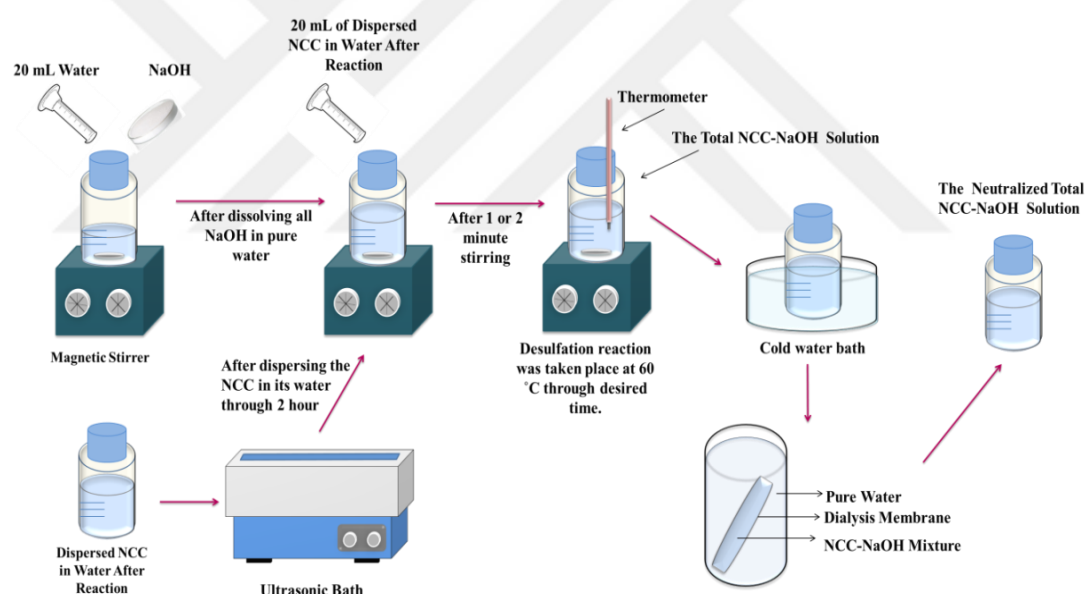


Figure 3.6. Schematic representation of alkali desulfation procedure

3.4.3 Sample Preparation for the TEM and SEM Analysis

Firstly, the dispersed NCC in water after reaction was put either into ultrasonic bath for 2 hours or into ultrasonic probe with ice to disperse them properly in the

water. Then, these samples were diluted to 10,100 and 1000 fold with pure water to obtain well dispersed images for samples without aggregation. After each dilution, the samples were put in to again ultrasonic bath for 5-10 minutes to disperse diluted samples into water. Then, the 10 μ l of each prepared samples was dropped on the TEM grid, and 1-5 ml was dropped on the SEM sample holder.

3.5 Membrane Characterization

Membrane morphology was investigated using Scanning Electron Microscope (QUANTA 400F Field Emission SEM, METU Central Laboratory) and optical microscope (Zeiss Axioscope A.1). In addition, the crystallinity index of the membranes was examined using X-Ray Diffraction (Rigaku Ultima-IV X-Ray Diffraction Device, METU Central Laboratory). Analysis of structural groups in membranes was done by using Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR, PerkinElmer UATR Two, METU Chemical Engineering Department).

3.5.1 Sample Preparation for the SEM Analysis

After drying membranes in fume hood and waited in vacuum oven at least one day, to analyze the cross section of the membranes, the membrane were broken after freezing by using liquid nitrogen. However, for analyzing the surface of the membrane, there was no extra process. After preparing the SEM samples, they were put into the vacuum oven at least one day until analysis time. Before analysis, the samples were placed to sample holder by using carbon tape, and the samples were coated with gold-palladium.

3.5.2 Sample Preparation for the ATR-FTIR Analysis

The membranes have to be dry completely before ATR-FTIR analysis since any humidity in the membrane affects the cellulose peaks in the membrane. Therefore,

firstly, to dry membranes completely, they were put into a fume hood after processes, and then, they were kept in a vacuum oven at least one day to get rid of any humidity in the membrane. After the drying membrane completely, the ATR-FTIR analysis was done.

3.6 Membrane Performance Tests

To make membrane performance tests, dead end filtration process was applied by using 10 mL and 50 mL Amicon stirred cell at 4.0 bar & 250 rpm for partially dissolved membranes and 10 mL and 50 mL Amicon stirred cell for the CA10 membranes and 300 mL HP4750 stirred cell for the PES10/PEG10D membranes at 0.5 bars & 250 rpm, and 10 mL and 50 mL Amicon stirred cell for the CA20 membranes at 4.0 bars & 250 rpm. The reason of stirring during membrane performance test is to decrease the concentration polarization of rejected material. The schematic representation of dead end cell is given in Figure 3.7.

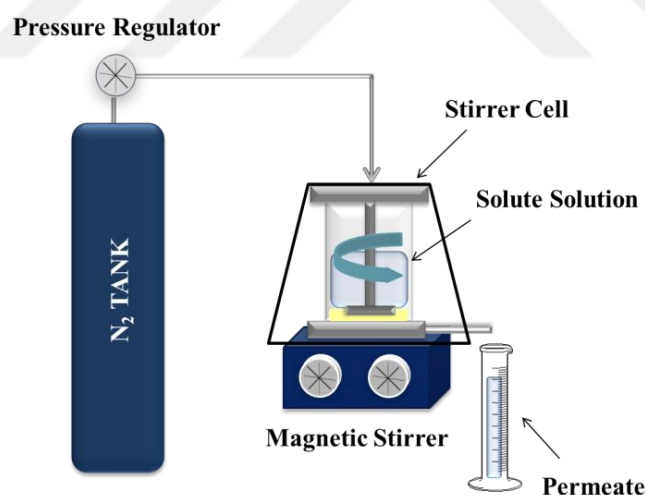


Figure 3.7. Schematic representation of dead end cell

Before the filtration experiment, the pure solvent or the pure water permeance of membrane (PSP or PWP) was measured by measuring the membrane fluxes at

three different pressures. Then, by using equation (10), the membrane flux values were turned into the membrane permeance values.

$$\text{PWP or PSP} \left(\frac{\text{L}}{\text{m}^2 \cdot \text{h} \cdot \text{bar}} \right) = \frac{\text{The Membrane Flux (J)}}{\text{Transmembrane Pressure Difference (TMP)}} \quad (10)$$

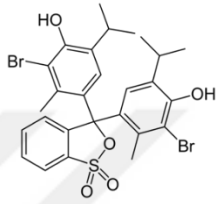
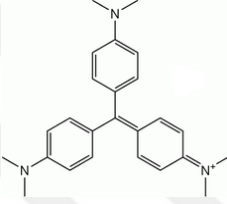
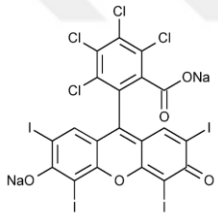
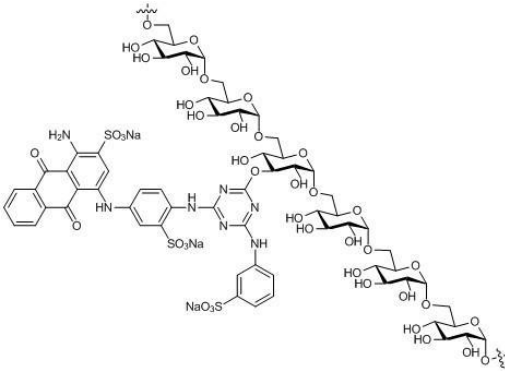
After finishing the membrane permeance measurement, the membrane filtration was done by using ethanol-Bromothymol Blue (BTB/EtOH) solution for all-cellulose nanocomposite membranes, ethanol-Bromothymol Blue (BTB/EtOH) solution, ethanol-Rose Bengal (RB/EtOH) solution and ethanol-Crystal Violet (CV/EtOH) solution for the CA20D membranes that deposited by using the commercial NCC, water-Blue Dextran 5000KDa (BD5/Water) for the CA10D and the PES10/PEG10D membranes. The detailed table of the membranes and the filtration solutions are given in Table 3.8.

Table 3.8 Membranes and Their Used Filtration Solutions

Membrane Name	Used Filtration Solutions			
	BTB/EtOH	RB/EtOH	CV/EtOH	BD5/Water
All-Cellulose Nanocomposite Membranes	+	-	-	-
CA20D-C/Salt	+	+	+	-
CA10D-P/Salt	-	-	-	+
PES10PEG10-P/NaOH	-	-	-	+

The solutions were prepared at a certain concentrations that are 0.05 mM for dye solutions and 0.16 mM for the BD5. The summations of material properties of solutes are given in Table 3.9.

Table 3.9 Summation of Material Properties of Solutes

Material Name	Charge	MW (Da)	Molecular Structure
Bromothymol Blue (BTB)	Neutral	624	
Crystal Violet (CV)	Positive	407	
Rose Bengal (RB)	Negative	1017	
Blue Dextran 5000 (BD5)	-	5000	

During filtration experiments, the permeate samples were taken from the solutions at certain time or mL intervals. At the end of filtration experiments, absorbance

values of feed, permeates and retentate were measured by using UV-Vis Spectrophotometry (Schimadzu UV-1601) at a specific wavelength of the solutions that are 423 nm for BTB, 560 nm for RB, 590 nm for CV, 591.5 for BD5, and these absorbance values was turned into concentration values by using calibration curves that give in the Appendix B. After that, the solutions rejection values were determined by using equation (11) in which C_F , C_P and C_R represents concentration of feed, permeate and retentate, respectively.

$$\text{Rejection \%} = \left(1 - \frac{C_P}{1 - \frac{C_P + C_R}{2}} \right) * 100 \quad (11)$$

The filtration experiments were continued until the solute sorption of membrane become zero which is calculated by using material balance in equation (12).

$$\text{mmol solution sorbed in membrane} = C_F * V_F - \sum (C_P * V_P) - C_R * V_R \quad (12)$$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Characterization of Nanocrystalline Cellulose (NCC)

4.1.1 The NCC Made by HCl Hydrolysis (NCC-HCl)

4.1.1.1 The X-Ray Diffraction (XRD) Analysis of NCC-HCl

The produced different nanocrystalline cellulose had been analyzed with X-Ray Diffraction (XRD) method to determine the crystallinity of NCC. During these analyzes, Cellulose I and Cellulose II structures in the NCC structure had been examined. The peaks seen at 14.8 °, 16.3 °, 21 °, 22.6 ° and 34.5 ° show the crystal structure of Cellulose I, while the peaks seen at 12.1 °, 19.8 ° and 22 ° show the crystal structure of Cellulose II^{105–107}. The XRD results of the NCC that had been produced from MCC (Avicel) and cotton linter cellulose via HCl hydrolysis are given in Figure 4.1.

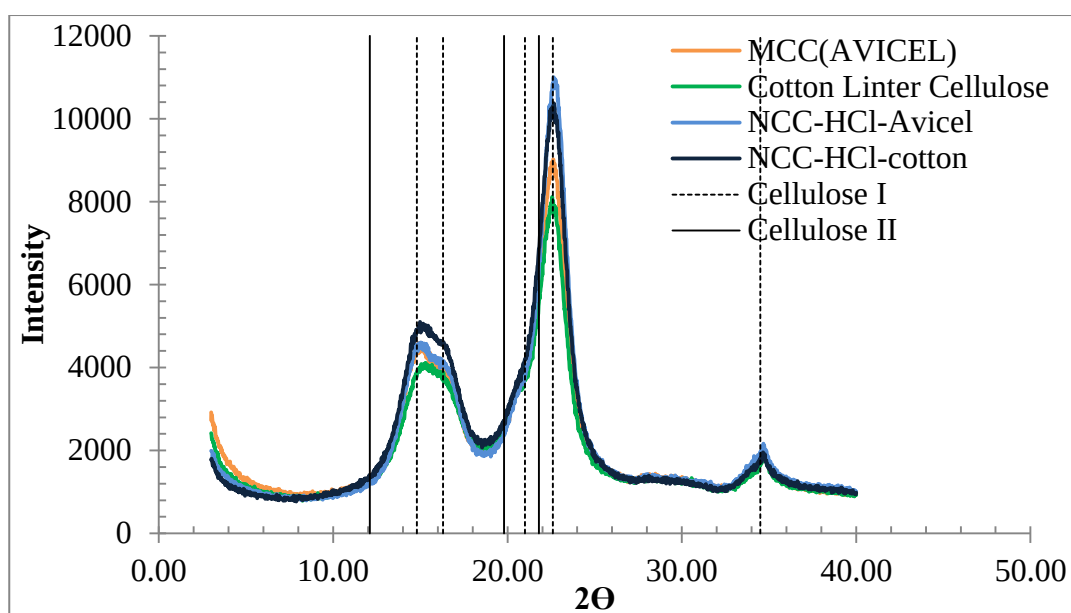


Figure 4.1. The XRD results of the NCC produced from HCl

Using Figure 4.1 and the equation (8), the crystallinity index values of the produced NCC-HCl had been calculated, and their results are given in Table 4.1.

Table 4.1 The Crystallinity Index (CI) Values of the Produced NCC-HCl

Sample Name	Crystallinity Index (CI) (%)
MCC(Avicel)	77
NCC-HCl-Avicel	82
Cotton Linter Cellulose	74
NCC-HCl-cotton	79

It can be concluded that the produced NCC-HCl using different cellulose sources has higher crystallinity than its cellulose source. In addition to the previous results, the reaction yields were calculated using equation (5) and based on the precipitated NCC amount, which is obtained by the centrifugation. These yield values are simply, as 91 % for NCC-HCl-avicel and 88 % for NCC-HCl-cotton. In addition,

when the calculated yield values were analyzed by using the equation (9) and the crystallinity index values of the cellulose source, it can be concluded that if all crystalline regions of the cellulose source remain during the hydrolysis reaction, the NCC-HCl-avicel and NCC-HCl-cotton crystallinities are calculated as ~85 % and ~84 %, respectively, which nearly correspond with the results obtained from the XRD analysis (Segal Method). The detail of the calculation is given in the Appendix L.

4.1.1.2 The TEM Analysis of NCC-HCl

The morphology and the dimension analyses of the NCC-HCl had been carried out using TEM analysis. TEM results of the NCC-HCl that was produced using different cellulose sources are shown in Figure 4.2.

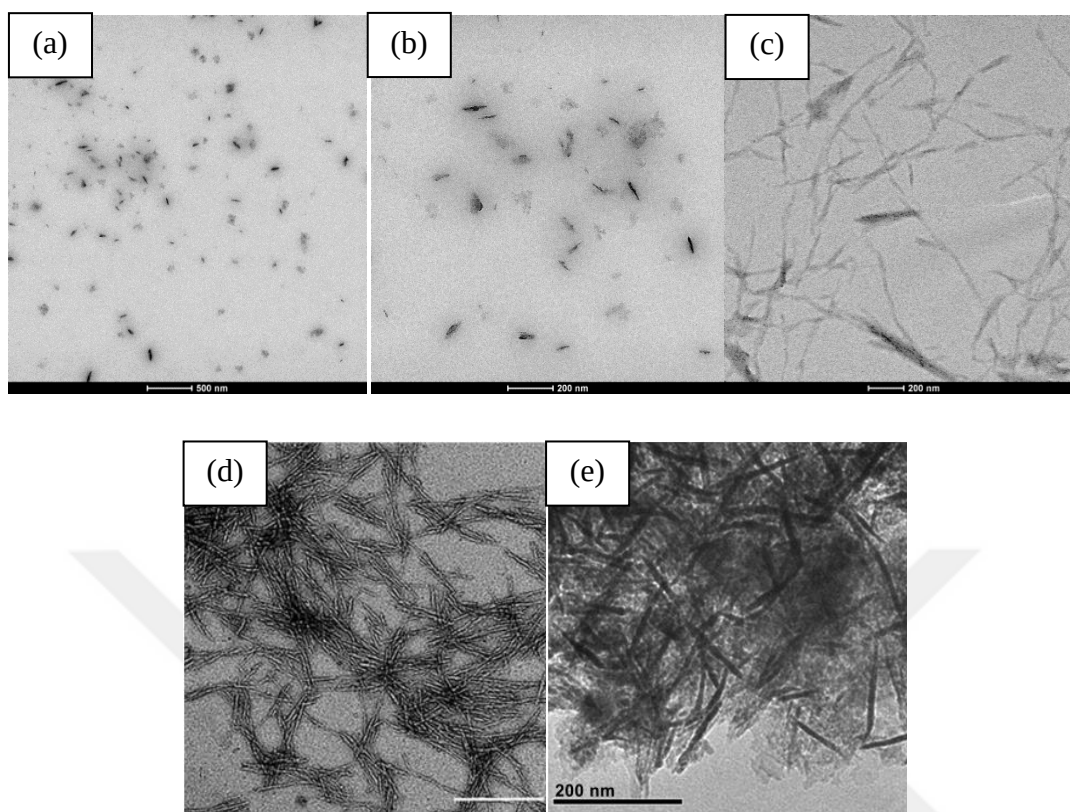


Figure 4.2. The TEM images of the produced NCC-HCl-avicel (a and b), the produced NCC-HCl-cotton (c) and literature TEM images of NCC produced via HCl (d¹⁰⁸ at which the NCC was produced using 5 g cellulose pulp and 100 mL-3M HCl with 80 °C & 2 hours and e¹⁰⁹ at which the NCC was produced using 100 g cellulose pulp and 500 mL-4N HCl with boiling conditions around 4 hours. Scale bars are respectively 500 nm for a and d and 500 for b, c and e

The results deduced from Figure 4.2 gave the followings:

- While the length of NCC-HCl-avicel was found around ~ 260 nm, the width of NCC-HCl was found around ~ 20 nm.
- While the length of NCC-HCl-cotton was found around ~ 350 nm, the width of NCC-HCl-cotton was found around ~ 35 nm.
- The TEM images of the NCC are quite similar to the ones in literature.

4.1.1.3 The DLS Analysis of NCC-HCl

In order to determine the particle size of the produced the NCC-HCl-avicel, the DLS analysis had been used. The hydrodynamic diameter which is defined as diameter of a perfect solid sphere that would exhibit the same diffusion coefficient of the particle⁸⁶ of NCC-HCl-avicel was found as 826 ± 195 nm. This result contradicts the previous results obtained from TEM analysis; therefore, this result is not comparable with TEM analysis. The DLS analysis plot is given in the Appendix C, and the DLS analysis result of the NCC-HCl-avicel is given in Table 4.2, along with a comparison to the literature results. The difference in the comparison is due to aggregation of the NCC-HCl, which is expected due to the little surface charge on NCC that was produced via HCl hydrolysis. Meanwhile, the aggregation of the NCC-HCl could have been seen with naked eye.

Table 4.2 The DLS Analysis Result for the NCC-HCl with Literature Comparison

Sample Name	Hydrodynamic Diameter of Sample
NCC-HCl-avicel	826 ± 195 nm
NCC-HCl in literature ¹¹⁰	329 ± 35 nm

4.1.2 The NCC Made by H₂SO₄ Hydrolysis (NCC- H₂SO₄)

4.1.2.1 The X-Ray Diffraction (XRD) Analysis of NCC- H₂SO₄

Following in a similar method with the NCC-HCl, the cellulose I and cellulose II structures of the produced NCC using H₂SO₄ hydrolysis were analyzed with XRD.

The XRD results of the produced NCC- H_2SO_4 have been analyzed in three different parts;

- The XRD results of the NCC produced from MCC (Avicel) and 50 % H_2SO_4 are given in Figure 4.3.
- The XRD results of the NCC produced from MCC (Avicel) and 65 % H_2SO_4 are given in Figure 4.4.
- The XRD results of the NCC produced from Cotton Linter Cellulose are given in Figure 4.5.

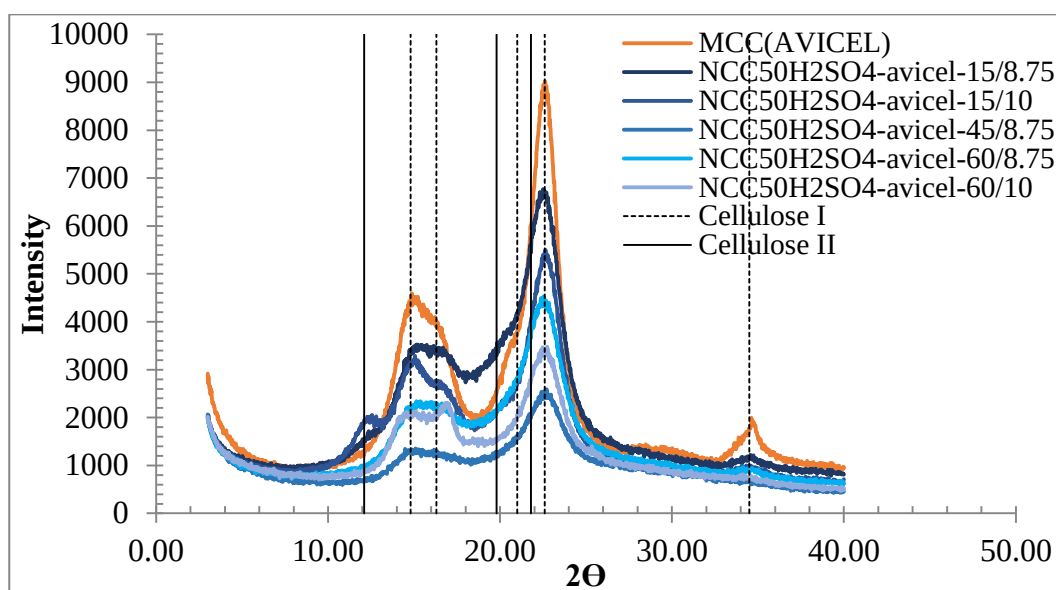


Figure 4.3. The XRD results of the NCC produced from MCC (Avicel) and 50 % H_2SO_4

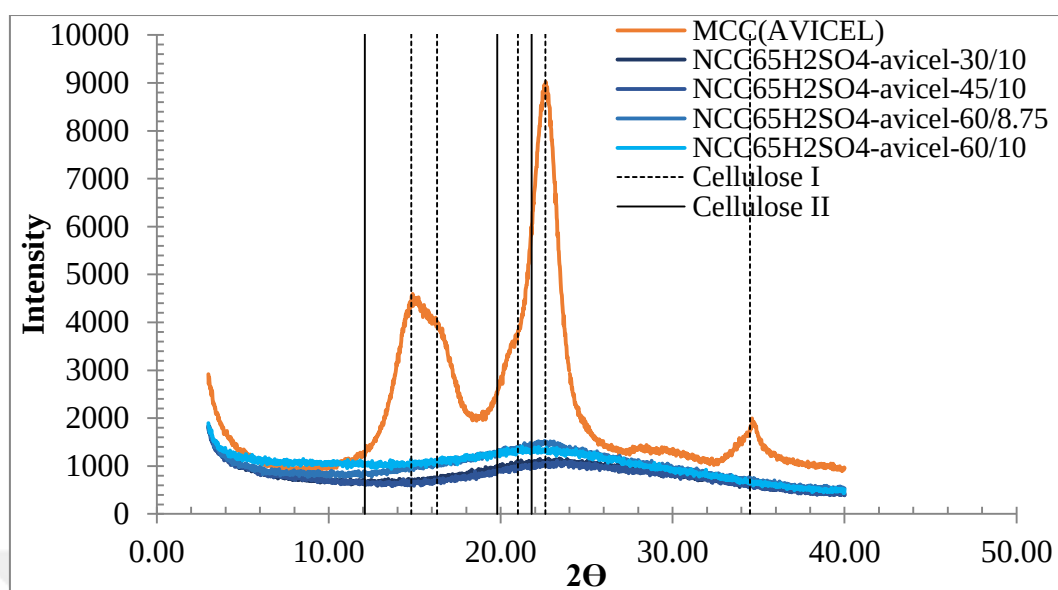


Figure 4.4. The XRD results of the NCC produced from MCC (Avicel) and 65 % H_2SO_4

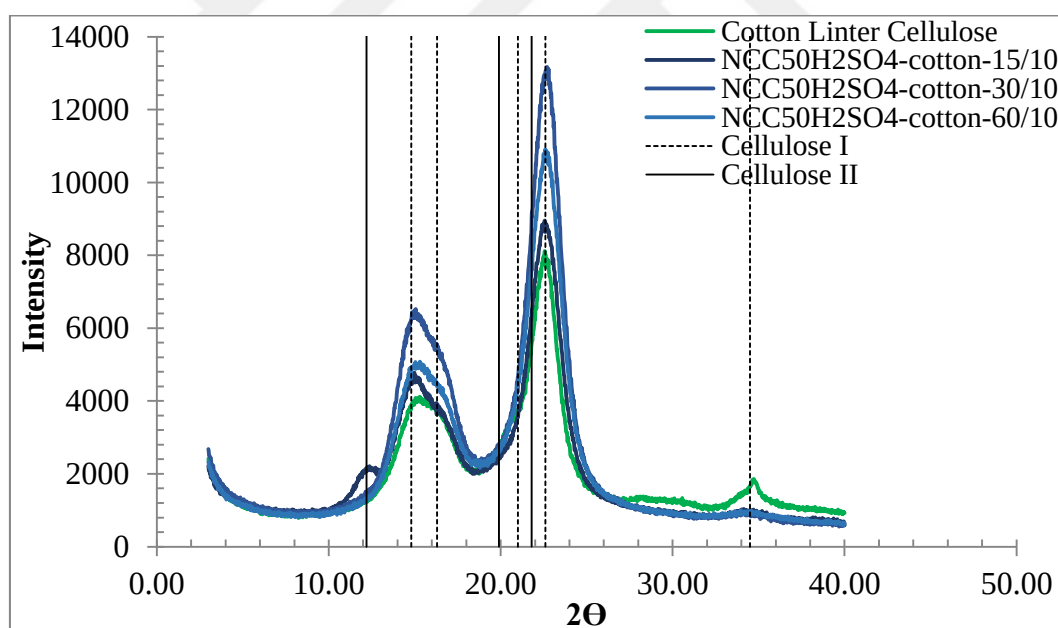


Figure 4.5. The XRD results of the NCC produced from Cotton Linter Cellulose and 50 % H_2SO_4

Using Figure 4.3, Figure 4.4 and Figure 4.5 and equation (8), the crystallinity index values of the produced NCC were calculated, and their results are given in Table 4.3.

Table 4.3 The Crystallinity Index (CI) Values of the Produced NCC-H₂SO₄

Sample Name	Crystallinity Index (CI) (%)	
MCC(Avicel)	77	
NCC50H ₂ SO ₄ -avicel-15/10	67	Produced using MCC
NCC50H ₂ SO ₄ -avicel-15/8.75	58	
NCC50H ₂ SO ₄ -avicel-45/8.75	59	
NCC50H ₂ SO ₄ -avicel-60/10	61	
NCC50H ₂ SO ₄ -avicel-60/8.75	59	
NCC65H ₂ SO ₄ -avicel	Amorphous	
Cotton Linter Cellulose	74	Produced using Cotton Linter Cellulose
NCC50H ₂ SO ₄ -cotton-15/10	77	
NCC50H ₂ SO ₄ -cotton-30/10	81	
NCC50H ₂ SO ₄ -cotton-60/10	78	

Since NCC cannot be settled completely during the centrifugation process after a specific pH scale i.e. supernatants still contain a significant portion of NCC, the true reaction yield could not be calculated. The yield values were calculated using precipitated NCC amount were 11.0 % for the NCC50H₂SO₄-avicel-10, 3.3 % for the NCC50H₂SO₄-avicel-8.75, 0.6 % for the NCC65H₂SO₄-avicel-10, 0.3 % for the NCC65H₂SO₄-avicel-8.75, 6.8 % for the NCC50H₂SO₄-cotton-10 and 11.4 % for the NCC50H₂SO₄-cotton-30/10. In addition, when the calculated yield value of

NCC50H₂SO₄-cotton-30/10 was analyzed by using the equation (9) and the crystallinity index value of the cellulose source, it can be concluded that the crystalline regions of cellulose is also hydrolyzed with the amorphous regions since the NCC50H₂SO₄-cotton-30/10 amount after hydrolysis reaction was much lower than initial crystallinity amount in the cellulose source. The detail of the calculation is given in the Appendix L.

The obtained NCC-H₂SO₄ had different colors which occurs as a matter of different production conditions. i.e The NCC50H₂SO₄ had yellowish/beige color whereas the NCC65H₂SO₄ had black color, and both can be seen clearly on Figure 4.6.

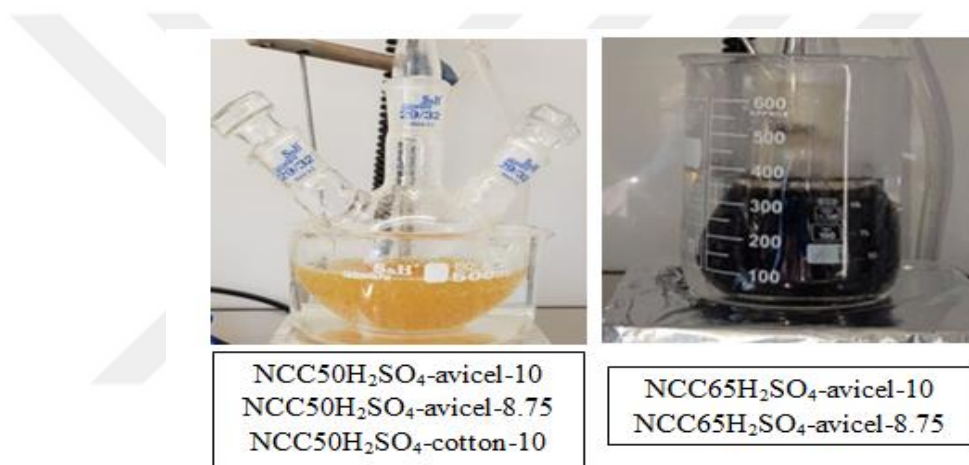


Figure 4.6. The images of the NCC that was produced H₂SO₄ hydrolysis using different cellulose sources

After washing these NCC's acid, it was observed that NCC65H₂SO₄ precipitated easily, whereas NCC50H₂SO₄ provided colloidal stability when dispersed in water.

As a result of these, it was observed that the NCC produced using MCC and HCl have higher crystalline index values and yields than those produced using MCC and H₂SO₄. The reason for such a difference can be explained by aggression of H₂SO₄ which attack to crystalline region of cellulose more than HCl that cause the change cellulose structure from cellulose I to cellulose II. Additionally, when the CI values, the reaction yield values and colors of NCC that was produced using 65

% H_2SO_4 and MCC was observed, it was seen that the cellulose was almost completely degraded, and the produced NCC becomes completely amorphous. Therefore, it can be concluded that the using a lower acid concentration gives better results in NCC production.

When the CI values of NCC that was produced by using cotton linter cellulose had been examined, it can be said that the NCC- H_2SO_4 has better CI values than the cellulose source. However, the CI value of the NCC50 H_2SO_4 -cotton-30/10 that was produced using 10 ml acid/g cellulose ratio and 30 minutes reaction time is determined to be the highest of all. The reason for the better crystallinity index can be explained that the cotton linter cellulose is more accessible to acid due to its amorphous regions in its structure compared to MCC.

When the effect of acid / cellulose ratios on NCC's percent crystallinity index is examined, it can be said that both 8.75 and 10 ml acid/ g cellulose values give approximately the same results.

When the effect of reaction times on the crystallinity index was investigated, it was observed that an optimum reaction time should be determined because during hydrolysis reaction, acid firstly diffuses into cellulose's amorphous regions to remove these regions by resulting crystallinity increase, and then into cellulose I structure to turn this structure to cellulose II structure. Due to this situation, when Figure 4.3 and Figure 4.5 were analyzed, there is cellulose II structure when hydrolysis reaction time is equal to 15 minutes. Then, as time goes by, the cellulose II structure turns to non-crystalline cellulose structure along with a decreasing behavior for crystallinity. Therefore, the optimum reaction time has to be specified to obtain high crystallinity^{35,102,111,112}.

4.1.2.2 The TEM and the SEM Analysis of NCC- H₂SO₄

The morphology and the dimension analyzes of the NCC-H₂SO₄ were performed using TEM and SEM analysis. The TEM and SEM results of the NCC-H₂SO₄ are shown in Figure 4.7 and Figure 4.8, respectively.

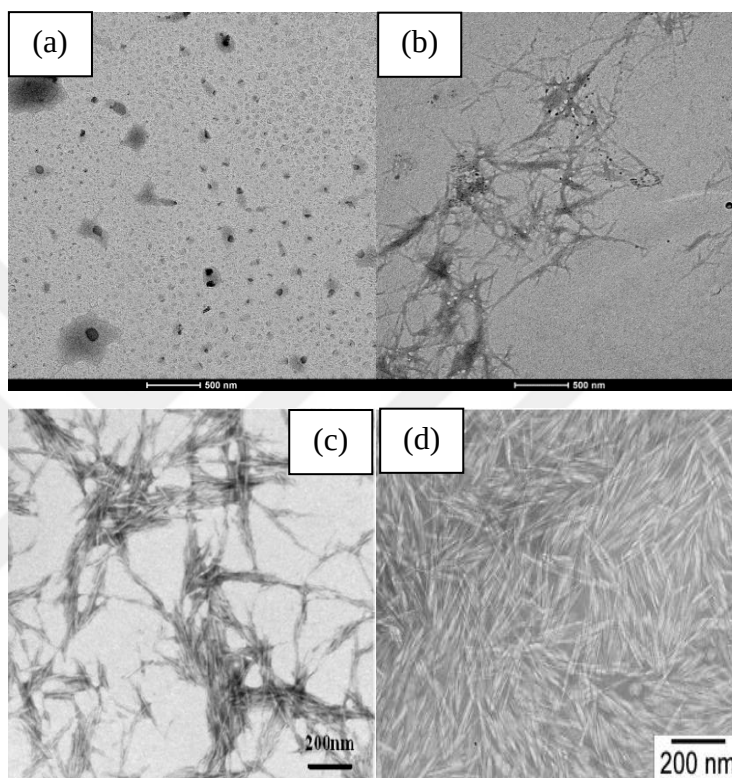


Figure 4.7. The TEM images of the produced NCC65H₂SO₄-8.75 (a), the NCC50H₂SO₄-cotton-30/10 (b) and the literature images of NCC that was produced with H₂SO₄ (c¹¹³ at which the NCC was produced 64-65 % (w/w) H₂SO₄ and 10 ml acid/g cellulose pulp with 45 °C and 1.5 hours reaction time and d¹¹² at which the NCC was produced using 64-65 % (w/w) H₂SO₄ and 8.75 ml acid/g cellulose with 45 °C and 30 minutes reaction time. Scale bars are 200 nm.

When the TEM images in Figure 4.7 were analyzed, the NCC65H₂SO₄-8.75 particles couldn't be observed in TEM due to complete degradation of cellulose. the NCC50H₂SO₄-cotton-30/10's dimensions could not be clearly observed in its TEM image. However, the SEM image of the NCC50H₂SO₄-cotton-30/10 clearly

shows distinct nanocrystals with the length of ~ 247 nm, and the width of ~ 27 nm (Figure 4.8). These values are corresponding with the literature values.

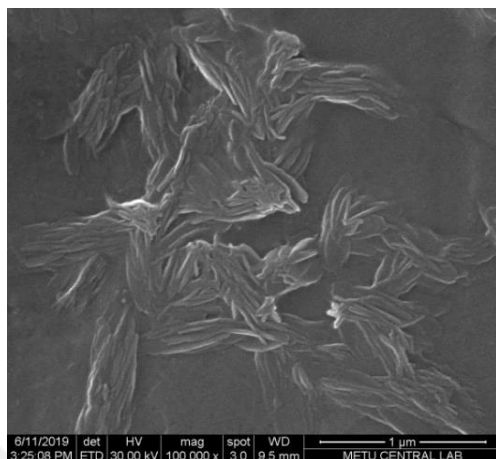


Figure 4.8. The SEM image of NCC50H₂SO₄-cotton-30/10 at 100000x magnification

4.1.2.3 The DLS Analysis of NCC-H₂SO₄

To determine the particle size of the produced NCC-H₂SO₄, the DLS analysis was used. The hydrodynamic diameter of the NCC50H₂SO₄-cotton-30/10 was found around 319 ± 48.0 nm. This result can be comparable with the results obtained from TEM and SEM analysis along with the results given in literature. The plot for one of produced NCC-H₂SO₄'s DLS analysis is given in the Appendix C. Furthermore, the one of produced NCC-H₂SO₄'s DLS analysis result is given in Table 4.4, along with its comparison with literature.

Table 4.4 The DLS Analysis Result for the NCC-H₂SO₄ with Literature Comparison

Sample Name	Hydrodynamic Diameter of Sample
NCC50H ₂ SO ₄ -cotton-30/10	319 ± 48.0 nm
NCC produced with 60 wt % H ₂ SO ₄ , 30 minute reaction time, 10 ml acid/g cellulose and 45 °C ¹¹⁴	~100 nm
NCC produced with 50 wt % H ₂ SO ₄ , 15 minute reaction time, 20 ml acid/g cellulose and 45 °C ¹¹⁵	~289.2 nm

4.2 Membranes Fabricated via Controlled NCC Deposition

4.2.1 Precipitation of the NCC50H₂SO₄-cot-30/10 on the CA10 Support Membrane with AlCl₃ and Different NCC Amounts to Produce the CA10D-P-S Membranes

Cellulose acetate membranes were used as a support membrane since they can easily be regenerated to cellulose membranes via alkali hydrolysis. Hence, this technique allows for cellulose membranes to be produced.

4.2.1.1 The Zeta Potential Analysis of the NCC50H₂SO₄-cot-30/10 as a Function of AlCl₃ Concentration

The zeta potential is a measure of the surface charge of the NCC, and this measure is proportional to ionic strength itself. For colloidal suspensions, in order to decrease the colloidal stability and the zeta potential of the NCC, multivalent ions proved more efficient than the monovalent ions ¹¹⁶. Therefore, different AlCl₃ concentrations were used for the zeta potential analysis of the NCC50H₂SO₄-

cotton-30/10 to determine the point at which zeta potential value of the material is zero and to determine point at which the NCC50H₂SO₄-cotton-30/10 reaches least stable point. The results obtained from the zeta potential analysis for the NCC50H₂SO₄-cotton-30/10 are given in Figure 4.9.

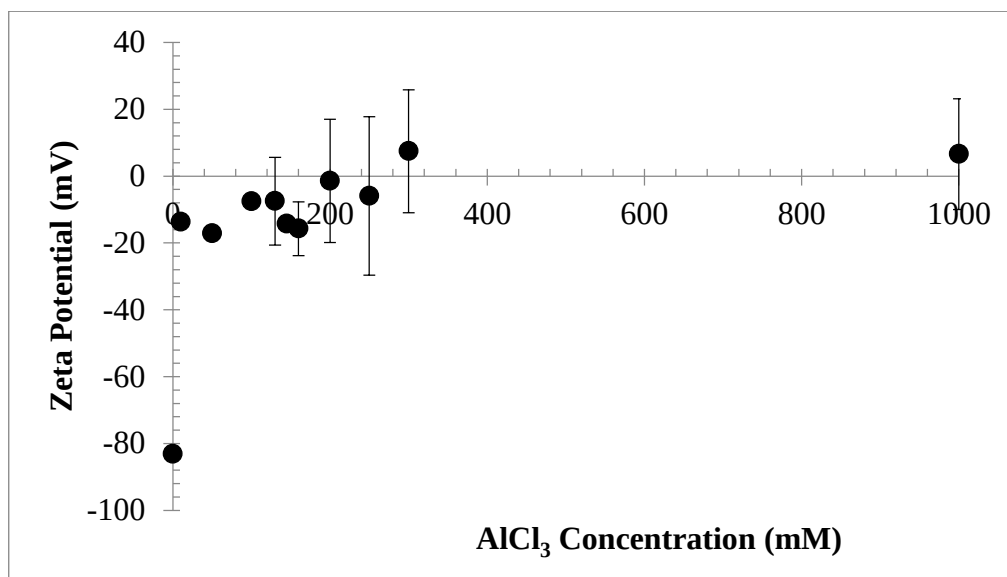


Figure 4.9. The zeta potential analysis result of commercial NCC50H₂SO₄-cotton-30/10 in different AlCl₃ concentrations

As a result of these analyses, it was observed that the stability of NCC changes with the salt concentration, and the NCC50H₂SO₄-cotton-30/10 reaches the least stable point around a concentration of 200 mM AlCl₃. This value was given in literature as 1mM for nanofibrillated cellulose with the initial surface charge -41 mV⁹⁰ and 2 mM for nanocrystalline cellulose with the initial surface charge -60 mV⁸⁹, and the zeta potential of these nanocelluloses change slightly with AlCl₃ concentration around zero zeta potential value, similar to the case in the NCC50H₂SO₄-cotton-30/10. However, when the NCC50H₂SO₄-cotton-30/10's results were compared with literature values with respect to salt concentration for obtaining the least stable point, the salt concentration for the NCC50H₂SO₄-cotton-30/10 was measured higher possibly because the initial zeta potential value of the NCC50H₂SO₄-cotton-30/10 is -83.1 ± 1.84 mV which is higher due to differences in production conditions of NCC.

4.2.1.2 The ATR-FTIR Analysis of the CA10D-P-S Membranes

After the deposition process, the NCC membranes had been analyzed with the ATR-FTIR to check whether there is deposition on the support membrane surface and to determine stability of deposited NCC layer on the support membrane,. The NCC membranes were kept in water for 24 hours and 1 week. After each of these processes, the membranes were dried under vacuum, and then their deposited and back sides were analyzed. During these analyzes, cellulose acetate and cellulose structures in the membrane surfaces were examined for the CA support membranes. The area under the cellulose peak / the area under the cellulose acetate peak was taken as an indication of cellulose presence in the surface of the membrane. The peak between 3700 cm^{-1} and 3200 cm^{-1} belongs to -OH groups (cellulose peak) and the peak between 1700 and 1550 cm^{-1} and the peak at 895 cm^{-1} belong to absorbed water molecules in the cellulose and C-O-C stretching on β -Glucosidic bond between the sugar units, respectively ¹¹⁷⁻¹²⁰.. In addition, the peak at nearly 1750 cm^{-1} belongs to -CO stretching (cellulose acetate peak)¹¹⁸. However, during analysis only -OH group peak is used since it is the characteristic cellulose peak that includes inter- and intramolecular hydrogen bonds in the cellulose, and the other peaks also shown in the CA structure.

One of the ATR-FTIR analysis results of the NCC membranes that was produced via precipitation of the NCC50H2SO4-cot-30/10 on the CA10 support membrane with AlCl_3 is given in Figure 4.10 to show the peak change and the peak positions. The remaining results of the ATR-FTIR analysis results are given in the Appendix D.

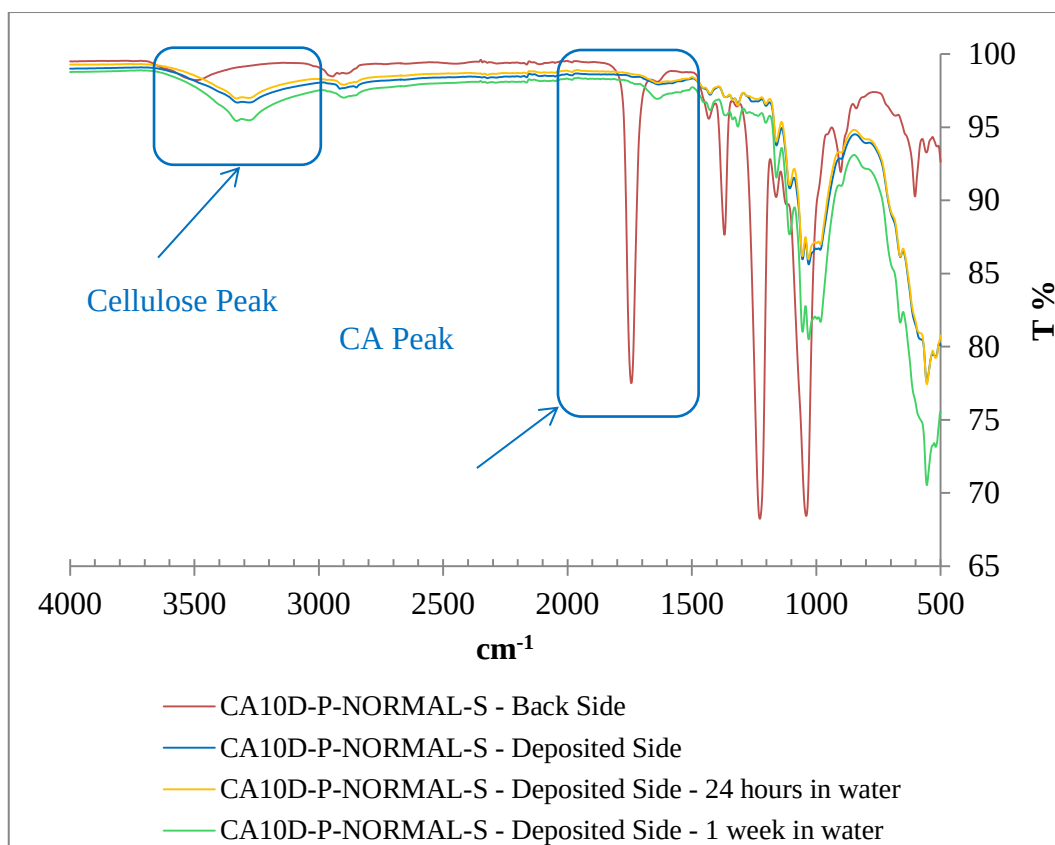


Figure 4.10. The ATR-FTIR analysis result for the CA10D-P-NORMAL-S

The normalized cellulose peak/cellulose acetate peak values with respect to just after deposition values are given in Table 4.5 for the CA10D-P-THIN-S, the CA10D-P-NORMAL-S and the CA10D-P-THICK-S membranes. Also, the cellulose peak/cellulose acetate peak values without normalization are given in the Appendix D for these NCC membranes.

Table 4.5 The Absolute Value of Area under the Cellulose Peak / the Area under the CA Peak for Just After Deposition and the Normalized Values of Area under the Cellulose Peak / the Area under the CA Peak with Respect to Just after Deposition Values for Keeping the CA10D-P-S Membranes in Water for 24 Hours and 1 Week

Name of NCC Membranes	Deposited Side		
	Just After Deposition Values	24 Hours in Water	1 Weeks in Water
CA10D-P-THIN-S	127.65 ± 53.35	0.895 ± 0.095	0.720 ± 0.050
CA10D-P-NORMAL-S	∞	1.0*	1.0*
CA10D-P-THICK-S	79.90 ± 27.10	0.925 ± 0.005	0.655 ± 0.055

*: These values were obtained from ∞/∞

When the CA10D-P-S membranes' ATR-FTIR analysis results are examined, the deposited NCC layers were observed on the NCC membrane surfaces. Although the normalized values of area under the cellulose peak / the area under the CA peak with respect to just after deposition values decrease at the CA10D-P-THIN-S and the CA10D-P-THICK-S, the CA10D-P-S membranes maintain their NCC stability up to a reasonable scale on the support membrane surface, especially for the CA10D-P- NORMAL-S membrane. This may be due to the fact that the NCC deposition amount of the CA10D-P-THICK-S may have come too high to obtain a tight deposited NCC layer whereas the CA10D-P-THIN-S may not be able to adhere sufficiently to the surface due to the low NCC deposition amount.

4.2.1.3 The SEM Analysis of the Support Membrane and the CA10D-P-S Membranes

The SEM images of the CA10D-P-S and the CA10 support membranes were investigated for determination of surface and cross section morphologies before

and after the deposition procedure. The surface SEM images of the CA10D-P-S and the CA10 membranes are given in Figure 4.11.

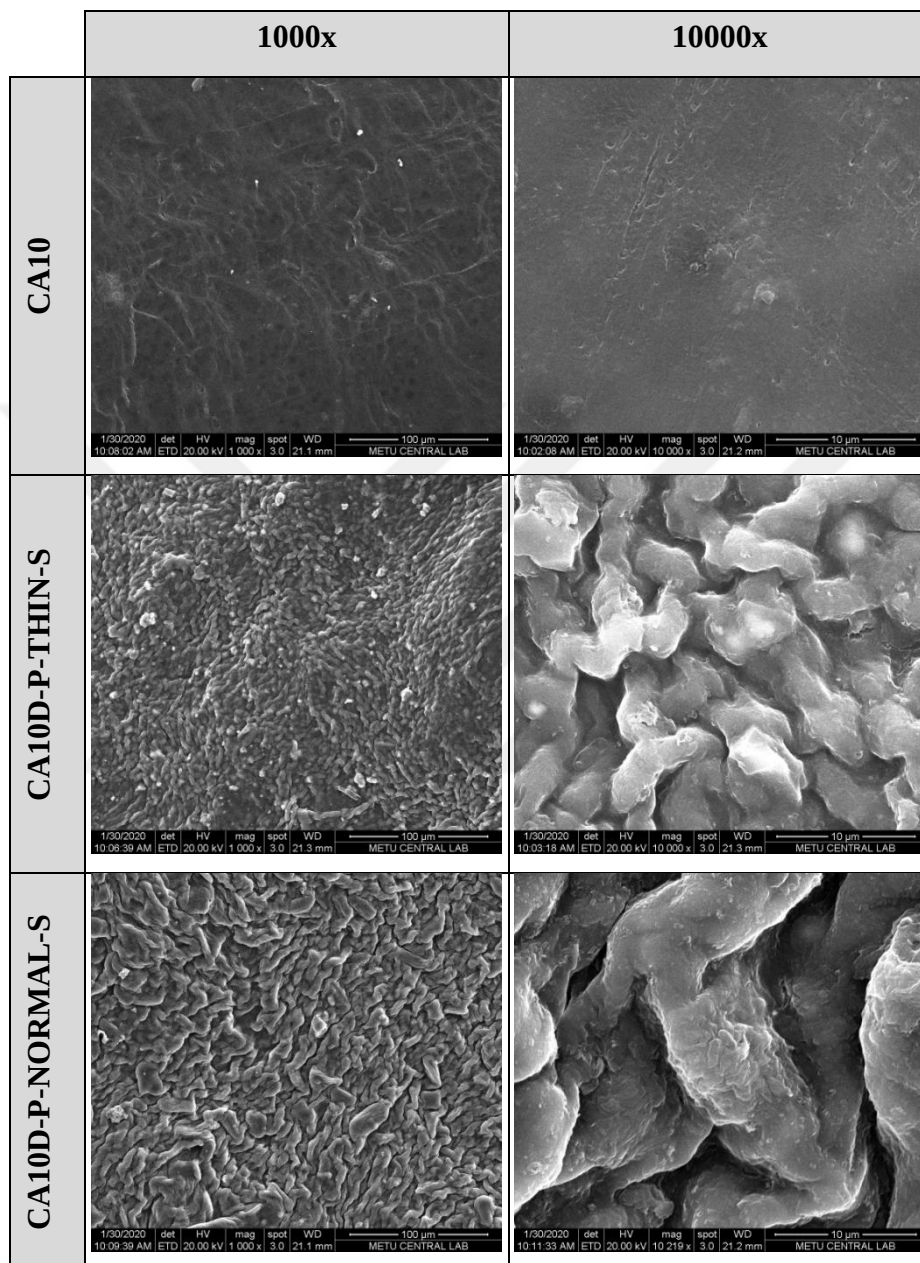


Figure 4.11. The surface SEM images of the CA10 and the CA10D-P-S membranes at different magnifications that are 1000x and 10000x for the CA10, the CA10D-P-THIN-S and the CA10D-P-NORMAL-S, and 1000x and 25000x for the CA10D-P-THICK-S

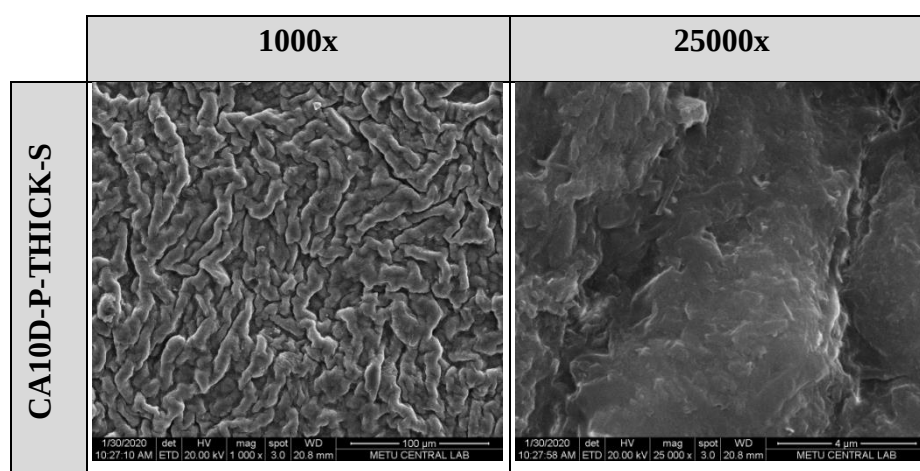


Figure 4.11. (cont'd) The surface SEM images of the CA10 and the CA10D-P-S membranes at different magnifications that are 1000x and 10000x for the CA10, the CA10D-P-THIN-S and the CA10D-P-NORMAL-S, and 1000x and 25000x for the CA10D-P-THICK-S

The CA10 support membrane has smooth surface. When the CA10D-P-S membranes' surfaces were examined, it clearly appears to have NCC deposition on the membranes' surfaces. The membranes' surfaces become curly during the drying of membrane since during deposition procedure, the rod-like NCC deposited randomly on the support membrane surface which causes these curls due to shrinking of the NCC. Moreover, the diameter of the curved bundles on the membranes' surface that were measured as $2.59 \pm 0.50 \mu\text{m}$, $5.13 \pm 1.36 \mu\text{m}$ and $9.26 \pm 1.80 \mu\text{m}$ for the CA10D-P-THIN-S, the CA10D-P-NORMAL-S and the CA10D-P-THICK-S membranes, respectively increases with increasing deposition thickness possibly due to the increase in the amount of NCC during the shrinking of the membranes. In addition to these, the cross section SEM images of the CA10 and the CA10D-P-S membranes are given in Figure 4.12.

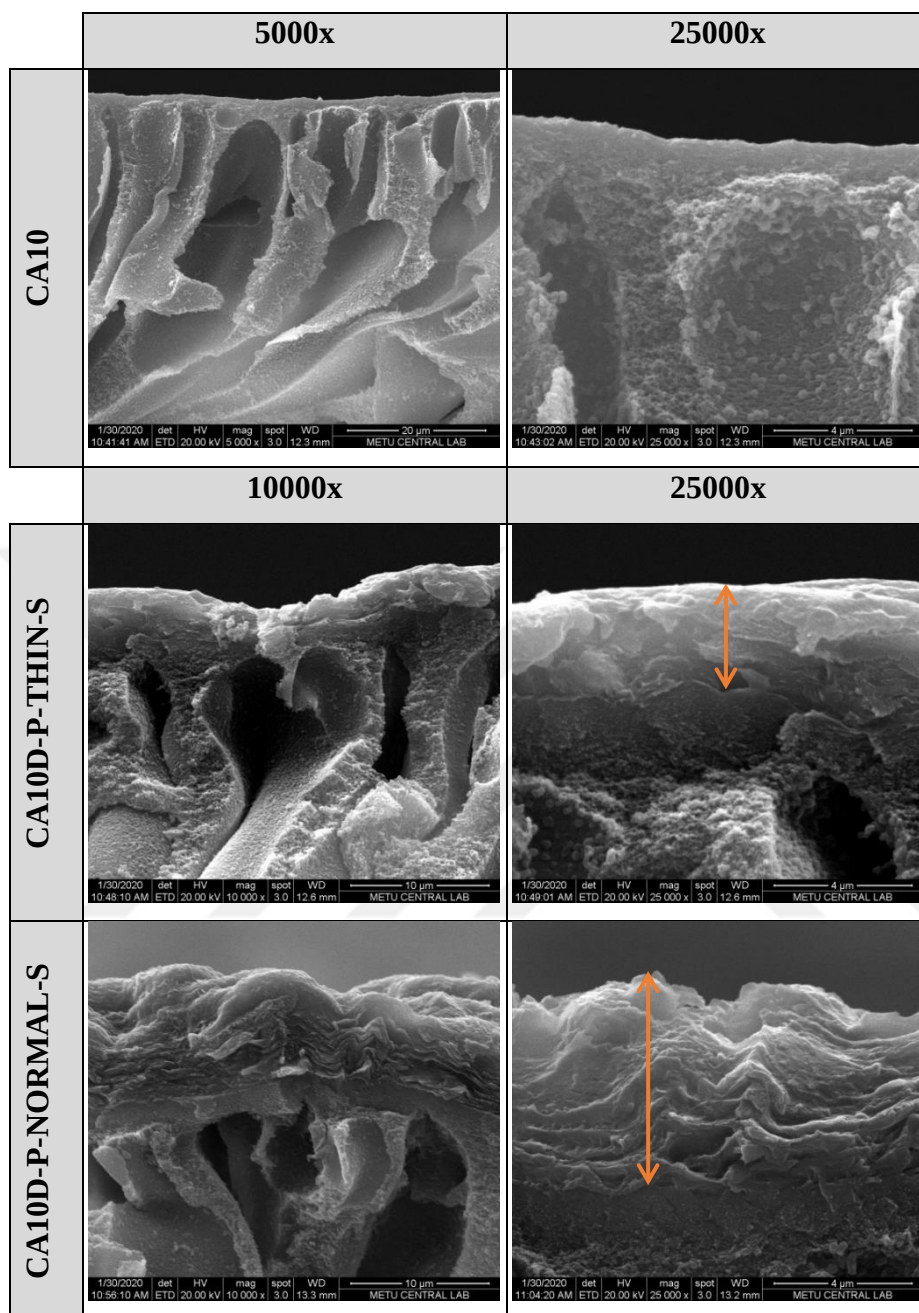


Figure 4.12. The cross section SEM images of the CA10 and the CA10D-P-S membranes at different magnifications that are 5000x and 25000x for the CA10 and 10000x and 25000x for the CA10D-P-THIN-S, the CA10D-P-NORMAL-S and the CA10D-P-THICK-S

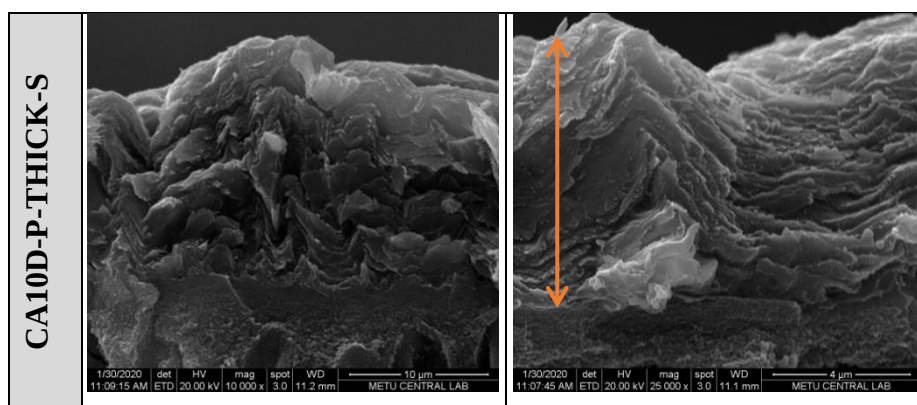


Figure 4.12. (cont'd) The cross section SEM images of the CA10 and the CA10D-P-S membranes at different magnifications that are 5000x and 25000x for the CA10 and 10000x and 25000x for the CA10D-P-THIN-S, the CA10D-P-NORMAL-S and the CA10D-P-THICK-S

As seen from Figure 4.12, the support membrane has asymmetric membrane structure with selective skin layer and porous support layer. To determine thickness of the deposited NCC layer, the support membrane which is the CA10 was used to compare the SEM images to understand where the support membrane is and where the deposited NCC layer is, and the deposited NCC layer's thicknesses were shown using orange double sided arrow. By this way, the thicknesses were determined as $3.40 \pm 0.50 \mu\text{m}$, $6.20 \pm 1.20 \mu\text{m}$ and $12.3 \pm 3.30 \mu\text{m}$ for the CA10D-P-THIN-S, the CA10D-P-NORMAL-S and the CA10D-P-THICK-S, respectively. As a result of these, the deposited NCC layer thickness increases with increasing deposition amount of NCC, proportionally. Besides, although there is no layer by layer accumulation image on the CA10D-P-THIN-S membrane due to low deposition amount, as the thickness of the deposited NCC seen in the cross-section increases, layer by layer accumulation is seen more. Therefore, the layered structure indicates that NCC was deposited horizontally on the surface.

4.2.1.4 The Separation Performance of the CA10D-P-S Membranes

In this chapter, the separation performances of the CA10D-P-S membranes that are normalized permeance results during deposition procedure and resistance calculations due to NCC deposition are given along with porosity and the deposited NCC layer thickness calculations by using the materials balance combined with the Kozeny-Carman equation.

Firstly, the averaged normalized permeance results for all experiments of the CA10D-P-S membranes were plotted with respect to PWP, and the results for THIN, NORMAL AND THICK NCC membranes are respectively given in Figure 4.13, Figure 4.14 and Figure 4.15 to understand membranes' permeance change during deposition procedure. Also, the permeance results (PWP, deposition permeance, salt filtration permeance and PWP after deposition) for the CA10D-P-S membranes are given in the Appendix E.

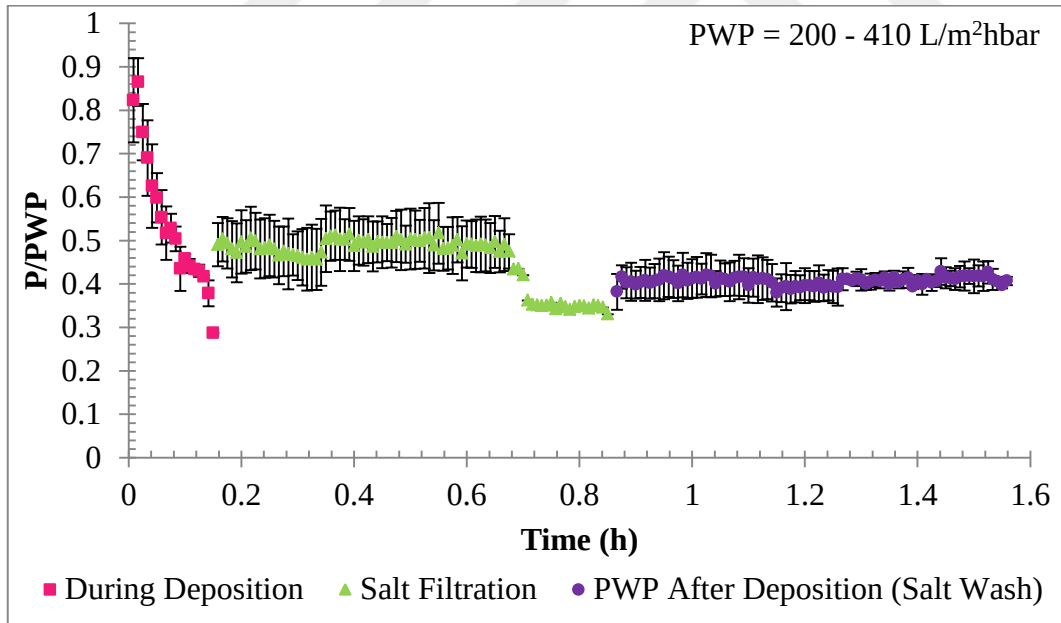


Figure 4.13. The normalized permeance values with respect to PWP for all the CA10D-P-THIN-S membranes (Average of four membranes)

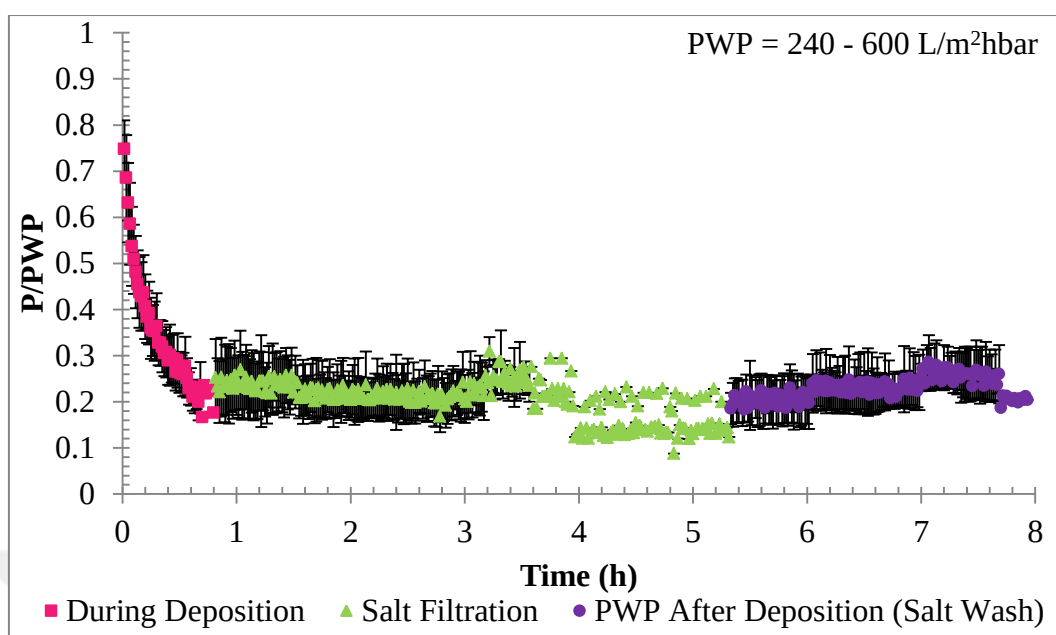


Figure 4.14. The normalized permeance values with respect to PWP for all the CA10D-P-NORMAL-S membranes (Average of four membranes)

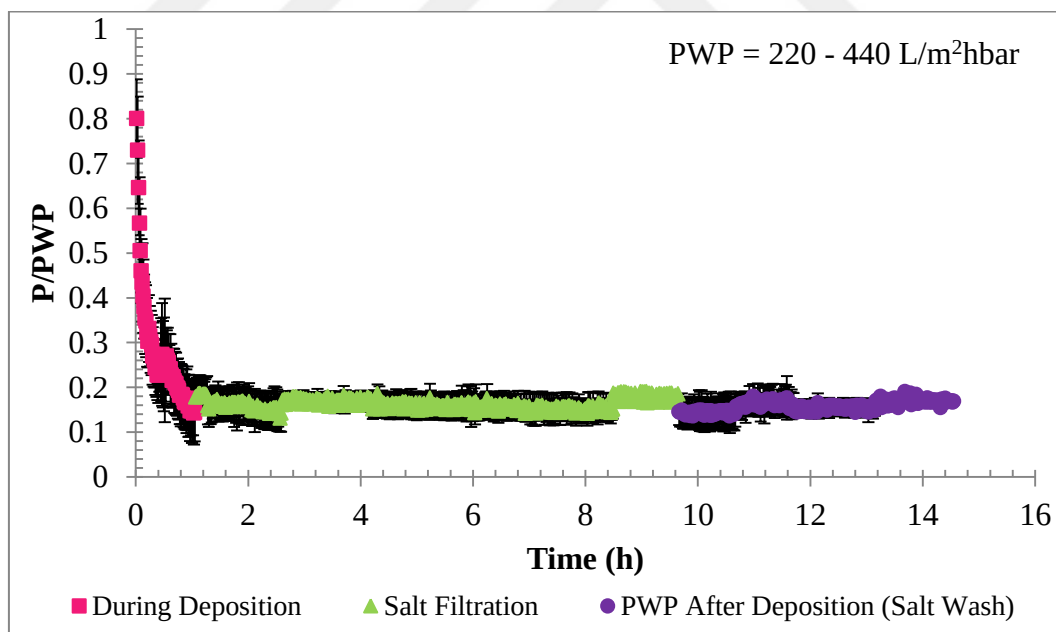


Figure 4.15. The normalized permeance values with respect to PWP for all the CA10D-P-THICK-S membranes (Average of four membranes)

As a results of Figure 4.13, Figure 4.14 and Figure 4.15, due to deposition procedure (forming the NCC membrane), the permeance value of the NCC membrane decreased due to the accumulation of NCC on the support membrane as expected. In addition to surface deposition, blocking or plugging of support membranes' pores may also have contributed to the permeance drop. After finishing deposition procedure, the permeance of the CA10D-P-S membranes remained nearly constant during salt filtration. Furthermore, when a decrease in P/PWP values during deposition for the CA10D-P-S membranes compared with respect to deposition amount, it can be easily seen that when the deposition amount of NCC increases, the P/PWP value during deposition decreases more.

Then, these NCC membranes resistances during deposition procedure and the resistance values due to NCC deposition were calculated using Darcy's law to see membranes' resistance change due to NCC deposition. The porosity and the thickness of the deposited NCC layer were estimated based on the calculated deposit resistance, assuming all this resistance is due to the deposition on the support surface by using the material balance combined with the Kozeny-Carman equation (Appendix F), and these results are given in Table 4.6 with resistance values due to NCC deposition.

Table 4.6 The Porosity and the Deposited NCC Layer Thickness Calculation
Results Using Kozeny-Carman Equation for the CA10D-P-S

	Name of The NCC Membrane		
	CA10D-P- THIN-S	CA10D-P- NORMAL-S	CA10D-P- THICK-S
Cake Resistance due to NCC Deposition (m^{-1}) * 10^{12}	1.68 $\pm$ 0.15	3.57 $\pm$ 0.82	6.09 $\pm$ 0.54
Calculated Porosity (ϵ)	0.33 $\pm$ 0.02	0.32 $\pm$ 0.04	0.33 $\pm$ 0.02
Calculated Thickness of Deposited NCC Layer (δ) (μm)	1.12 $\pm$ 0.04	2.21 $\pm$ 0.12	4.47 $\pm$ 0.12
Thickness of Deposited NCC Layer from SEM Analysis (μm)	3.40 $\pm$ 0.50	6.20 $\pm$ 1.20	12.3 $\pm$ 3.30
Calculated Porosity from Thicknesses Measured in SEM Analysis	0.78 $\pm$ 0.04	0.75 $\pm$ 0.05	0.74 $\pm$ 0.07

When Table 4.6 was investigated, the effect of NCC deposition amount is easily seen on cake resistance values due to NCC deposition and the thickness of deposited layer. As a result of these, while the calculated porosity values are nearly the same for different NCC deposition amounts, the cake resistance values due to NCC deposition increase which means that the thickness of the deposited NCC layer increases with increasing deposition amount as seen from the SEM analysis results. However, the calculated thickness of the deposited NCC layer and thickness of deposited layer from the SEM analysis have different values. This may be caused due to the entering of some of NCC to the pores of support membrane which increase the resistance of the support membrane and does not affect cake (deposited NCC layer) resistance. In that case, the calculated cake resistance due to NCC deposition would be lower than these values that were given in Table 4.6. If the calculated cake resistance due to NCC deposition is lower, the calculated thickness of the deposited NCC layer would be higher than these values given in Table 4.6 due to increase of the calculated porosity values. The calculated porosities using the deposited NCC thicknesses measured from the SEM images are given in the last row of Table 4.6. A loose NCC deposit may explain the absence of further permeance drop, or resistance increase with salt filtration. A loose and irregular deposit, while still having lowered colloidal stability due to the increase in ionic strength in the medium, may not be compressed to a measurable extent.

4.2.1.5 The BD5 Filtration Results of the CA10D-P-S Membranes Comparison with the Support Membrane

To test membrane rejection performances after deposition procedure, the CA10D-P-S membranes were tested with aqueous blue dextran (5 kDa) (BD5) solution and their results are given in Figure 4.16.

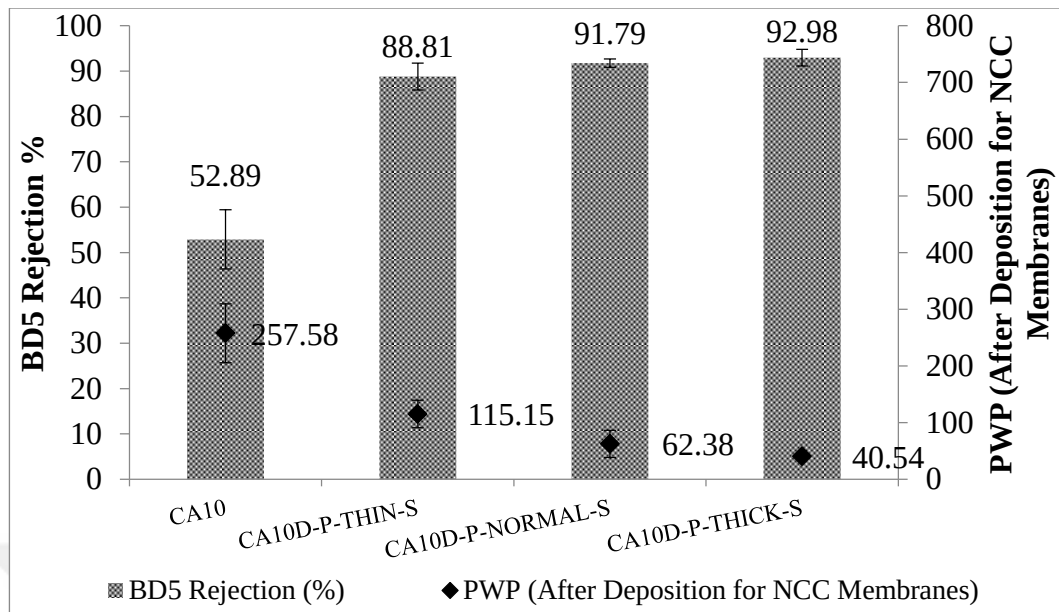


Figure 4.16. The BD5 rejection and PWP (After deposition for NCC Membranes) results for the CA10D-P-S membranes with comparison the support membrane

When Figure 4.16 was examined, although the support membrane also rejects the BD5 solution, the BD5 solution rejections of the CA10D-P-S membranes are much higher. When the NCC deposition amount increases, the rejection values of the CA10D-P-S membranes remain nearly the same. This is in accordance with the calculated porosity values in Table 4.6, which were nearly the same for the CA10D-P-S membranes. However, the PWP values of these membranes decrease with increasing deposition amount due to the increase of the NCC deposit layer thickness.

In addition to these, the BD5 solution permeance change in time and BD5 solution permeance/PWP values were calculated to determine whether there is fouling or concentration polarization on membrane. As a result of the BD5 solution permeance values calculations, it can be said that there is no fouling during BD5 solution filtration since there is nearly no change in BD5 solution permeance during filtration (Data not shown). Besides, the BD5 solution permeance/PWP values calculations which are 0.83 ± 0.1 , 0.76 ± 0.1 , 0.90 ± 0.1 , 0.83 ± 0.1 for CA10, CA10D-P-THIN-S, CA10D-P-NORMAL-S and CA10D-P-THICK-S,

respectively, imply that there is little concentration polarization during the filtration.

The effective pore diameter of the CA10D-P-S membranes with respect to these rejection values were roughly estimated using the Ferry-Renkin equation as ~4.4 nm, 4.2 nm and 4.2 nm for the CA10D-P-THIN-S, the CA10D-P-NORMAL-S and the CA10D-P-THICK-S membranes, respectively, based on a BD5 hydrodynamic radius of 1.68 nm, as calculated in the Appendix I.

4.2.2 Precipitation of the Commercial NCC on the CA20 Support Membrane with AlCl_3

4.2.2.1 The Zeta Potential Analysis of the Commercial NCC as a Function of AlCl_3 Concentration

The zeta potential of the commercial NCC as a function of AlCl_3 concentration is shown in Figure 4.17.

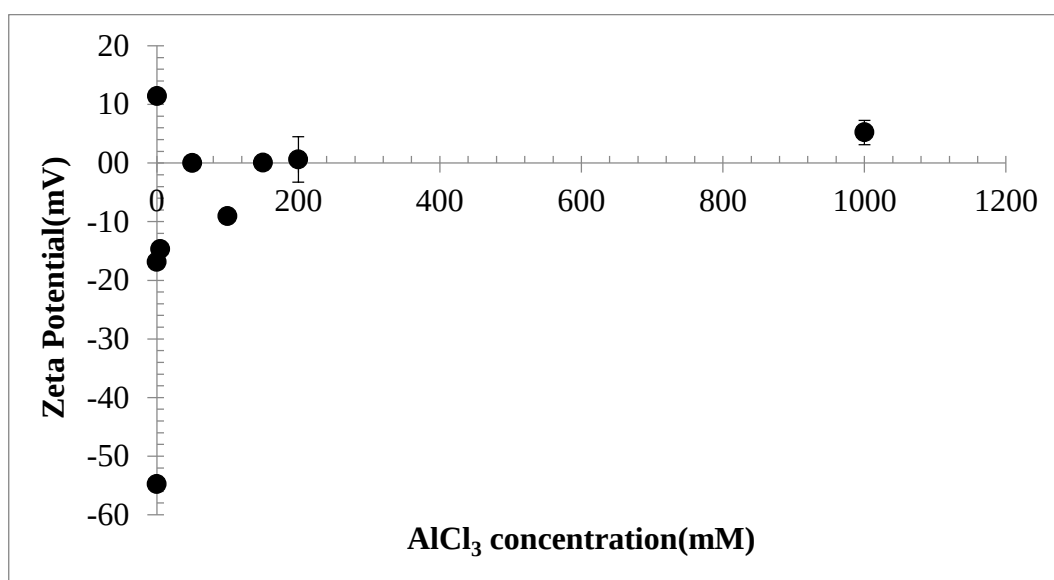


Figure 4.17. The zeta potential analysis result of the commercial NCC in different AlCl_3 concentrations

As a result of these analyzes, the stability of the commercial NCC changes with the salt concentration like the NCC50H₂SO₄-cotton-30/10, and the commercial NCC reaches the least stable point around a concentration of 200 mM AlCl₃ similar to the NCC50H₂SO₄-cotton-30/10.

4.2.2.2 The ATR-FTIR Analysis of the CA20D-C-S Membranes

The ATR-FTIR analysis results of the CA20D-C-S membranes were investigated using same peaks that explained and given in 4.2.1.2. The ATR-FTIR analysis results are given in the Appendix D. The normalized cellulose peak/cellulose acetate peak values with respect to just after deposition values are given in Table 4.7 for the CA20D-C-NORMAL-S membranes. Also, the cellulose peak/ cellulose acetate peak values without normalization are given in the Appendix D for these NCC membranes.

Table 4.7 The Absolute Value of Area under the Cellulose Peak / the Area under the CA Peak for Just After Deposition and the Normalized Values of Area under the Cellulose Peak / the Area under the CA Peak with Respect to Just after Deposition Values for Keeping the CA20D-C-NORMAL-S Membranes in Water for 24 Hours and 1 Week

Name of NCC Membrane	Deposited Side		
	Just After Deposition Values	24 Hours in Water	1 Weeks in Water
CA20D-C-NORMAL-S	56.05 ± 36.65	0.400 ± 0.140	0.115 ± 0.095

When the CA20D-C-NORMAL-S membranes were examined, the stability of deposited commercial NCC on the CA20 membrane surface is significantly less than CA10D-P-S membranes. As seen in Figure 4.19, the NCC layer has not penetrated much into the support membrane CA20, possibly due to the much

smaller pores of this membrane compared to the CA10. This could affect the stability of the deposited layer on the membrane.

4.2.2.3 The SEM Analysis of the CA20D-C-S Membranes and the Support Membrane

The SEM images of the CA20D-C-S and the CA20 support membranes were investigated to determine surface and cross section morphologies of NCC membranes. The surface SEM images of the CA20D-C-S and the CA20 membranes are given in Figure 4.18.

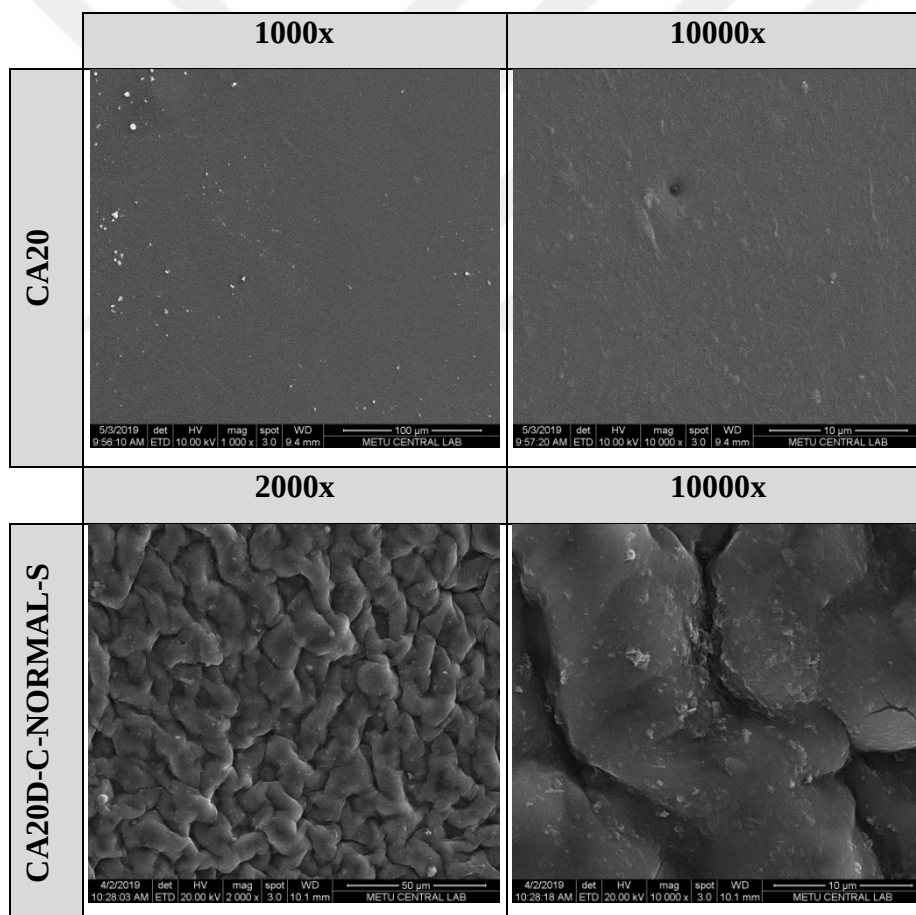


Figure 4.18. The surface SEM images of the CA20 and the CA20D-C-S membranes at different magnifications which are 1000x and 10000x for the CA20 and 2000x and 10000x for the CA20D-C-NORMAL-S

The CA20D-C-NORMAL-S surface is similar to the CA10D-P-S membranes. The cross section SEM images of the CA20D-C-S and the CA20 membranes are given in Figure 4.19.

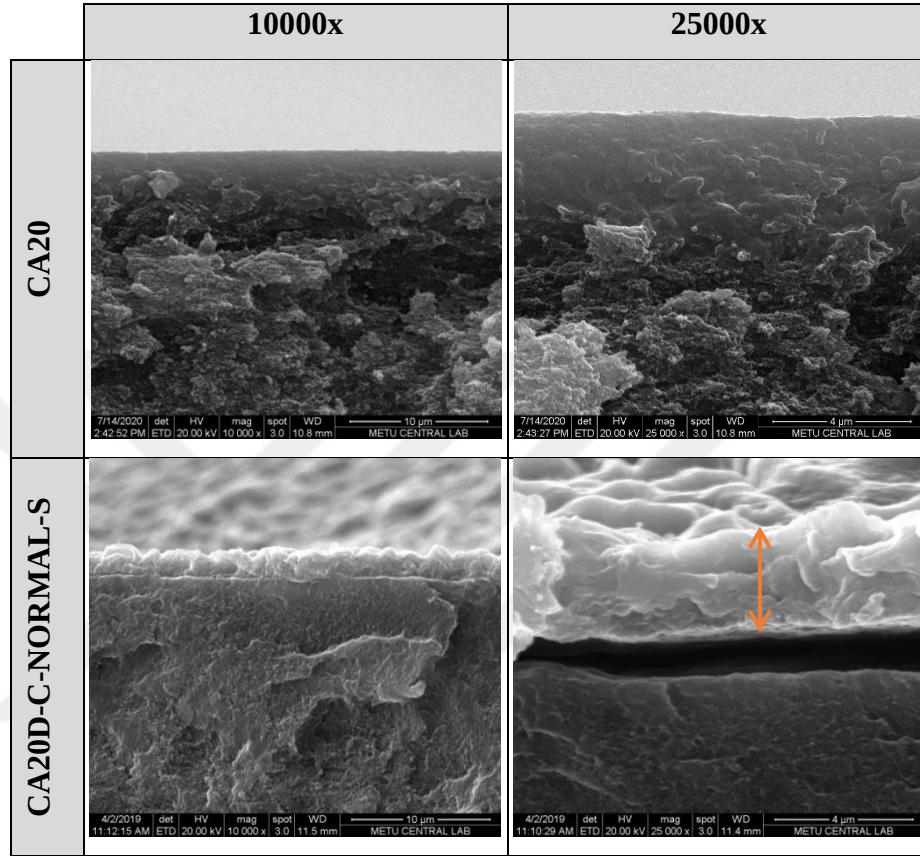


Figure 4.19. The cross section SEM images of the CA20 and the CA20D-C-NORMAL-S membranes at different magnifications which are 10000x and 25000x

As seen from Figure 4.19, the support membrane has asymmetric membrane structure with dense skin layer and looser support layer which is denser than the CA10 support membrane. To determine thickness of the deposited commercial NCC layer, the support membrane which is the CA20 was used to compare with the SEM images to understand where is the support membrane and where is the deposited layer (The deposited NCC layer's thicknesses were shown using orange double sided arrow), and there is a layer can be seen in the images of the CA20D-

C-NORMAL-S. As a result of the SEM images, the thickness of the deposited commercial NCC layer was determined as $2.47 \pm 0.36 \mu\text{m}$.

4.2.2.4 The Separation Performance of the CA20D-C-S Membranes

Average normalized permeance results for all the experiments of the CA20D-C-S membranes with respect to PWP are given in Figure 4.20. Also, the permeance results (PWP, deposition permeance, salt filtration permeance and PWP after deposition) of the CA20D-C-S membranes are given in the Appendix E.

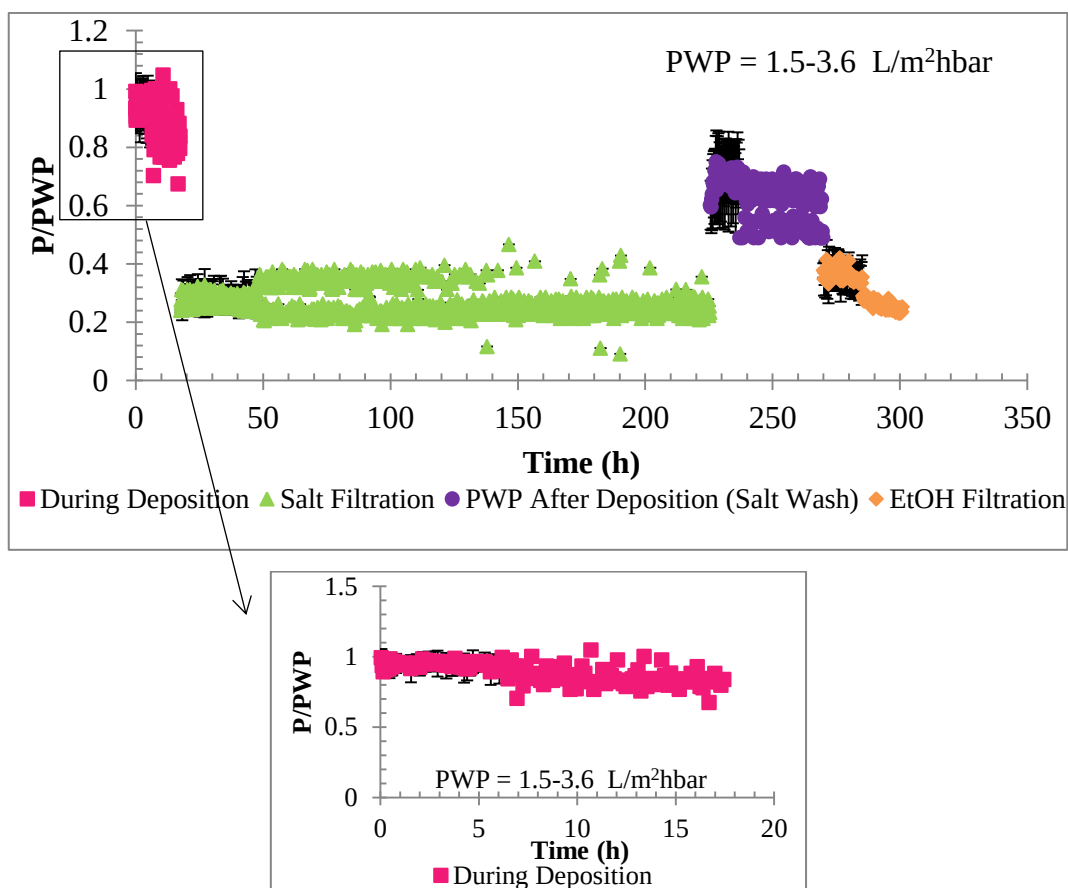


Figure 4.20. The normalized permeance values with respect to PWP for all the CA20D-C-NORMAL-S membranes (Average of three membranes)

As seen in Figure 4.20, similar to the CA10D-P-S membranes, the permeance values during deposition decreased in the CA20D-C-NORMAL-S membranes. During salt filtration, the NCC membrane permeance decreased, which can be attributed to compression of the deposited NCC layer due to compression of the electrical double layer with increasing salt concentration. This, however, was not observed on the CA10D-P-S membranes, which is possibly due to the higher porosity of the NCC layer, implying looser packing. The P/PWP for water and EtOH after deposition showed different behaviors. Such kind of behaviors can be explained by changing the compressibility of the NCC deposit layer due to the different relation of NCC to water and EtOH. Cellulose swells more in water and less in EtOH, which explains why the EtOH permeance is lower than the water permeance.

The cake resistance of the deposited NCC on the CA20D-C-NORMAL-S membranes, the calculated porosity, the calculated thickness of the deposited commercial NCC layer and the thickness of deposited commercial NCC layer measured in SEM are given in Table 4.8.

Table 4.8 The Porosity and the Deposited NCC Layer Thickness Calculation Results Using Kozeny-Carman Equation for CA20C-P-NORMAL-S Membrane

	Cake Resistance due to Commercial NCC Deposition (m^{-1}) * 10^{12}	Calculated Porosity (ϵ)	Calculated Thickness of Deposited NCC Layer (δ) (μm)	Thickness of Deposited NCC Layer from SEM Analysis (μm)
CA20D-C-NORMAL-S	99.52 $\pm$ 30.86	0.45 $\pm$ 0.09	2.82 $\pm$ 0.51	2.47 $\pm$ 0.36

The deposited NCC resistance on the CA20D-C-NORMAL-S is much higher than that on the CA10D-P-NORMAL-S. Deposition on the CA20 support membrane is done at 4 bars which compressed the deposit more, also reflected in the lower apparent porosity. The thickness and the porosity of the deposited NCC from the mass balance and the Kozeny-Carman equation and the SEM images are in agreement for this membrane, probably due to the lack of surface pore blocking by NCC.

4.2.2.5 The Solute Rejection Performance Analysis of the CA20D-C-S Membranes

To test membrane rejection performances after deposition procedure, the CA20D-C-NORMAL membranes were tested with different dye solutions in EtOH to test these membranes organic solvent nanofiltration performances (Figure 4.21).

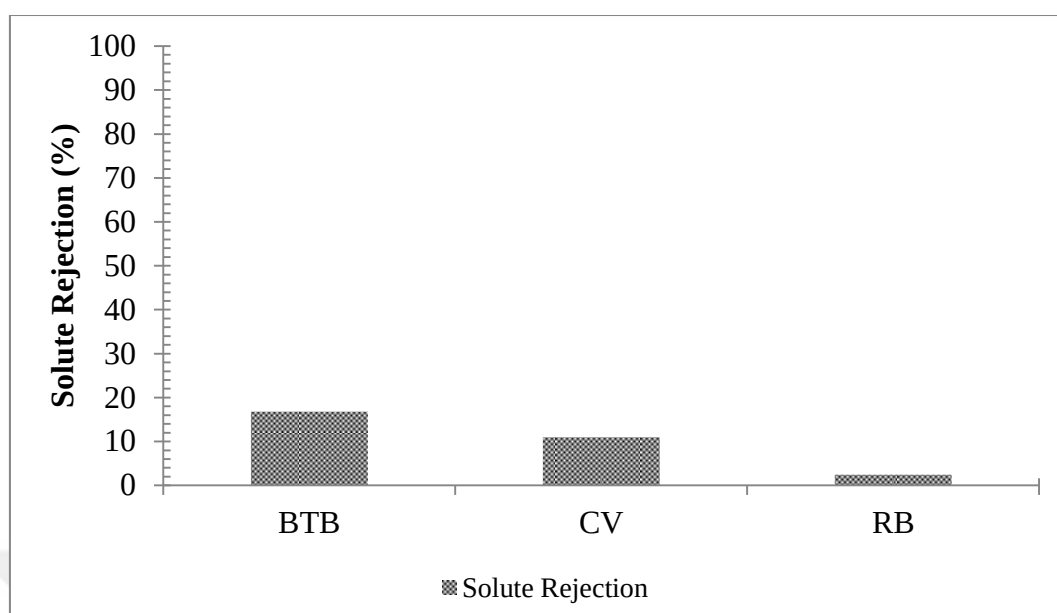


Figure 4.21. The solute rejection and solute permeance/EtOH permeance after deposition for deposited membranes results for the CA20D-C-NORMAL-S membranes

As a result of different solute/EtOH solution test on the CA20D-C-NORMAL membranes, all solutes showed similar behavior, and there is no effect on the NCC deposition on the NF membranes solute rejection.

4.2.3 Precipitation of the $\text{NCC50H}_2\text{SO}_4\text{-cot-30/10}$ on the PES10PEG10-1MH Support Membrane with NaOH

PES membranes were used as a support membrane because they are durable in very high pH values. Additionally, during deposition procedure of these membranes, 1 M NaOH solution was used for 30 minutes for alkali desulfation procedure to replace surface sulfate groups with hydroxyl groups.

4.2.3.1 The Zeta Potential Analysis of the NCC50H₂SO₄-cot-30/10 as a Function of NaOH Concentration and Reaction Time

The zeta potential of the NCC50H₂SO₄-cotton-30/10 was examined after treated with different NaOH concentrations and reaction times (Figure 4.22).

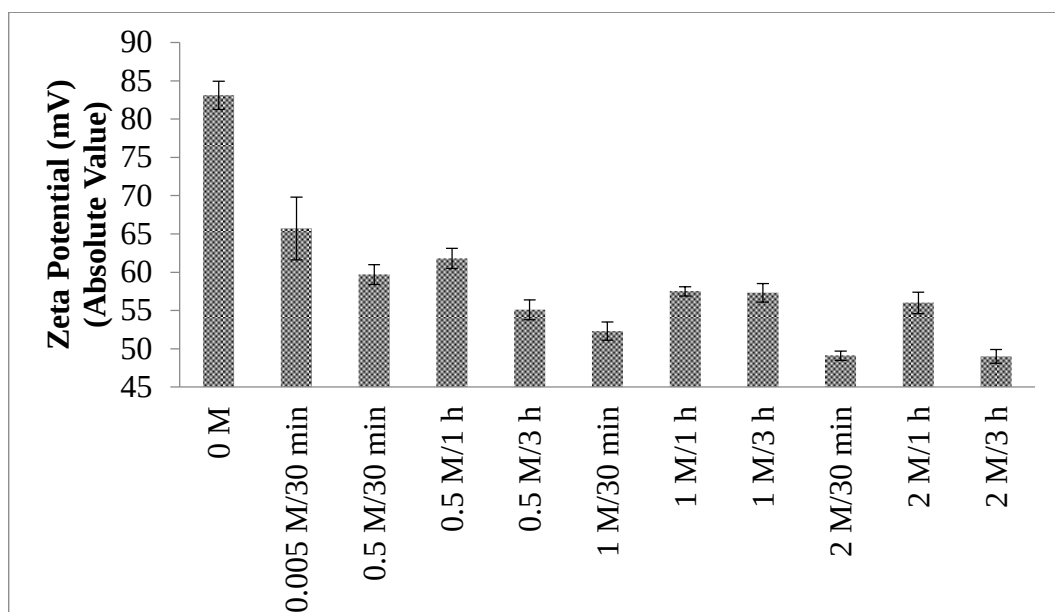


Figure 4.22. The zeta potential analysis results of the NCC50H₂SO₄-cotton-30/10 at different NaOH concentration and reaction time

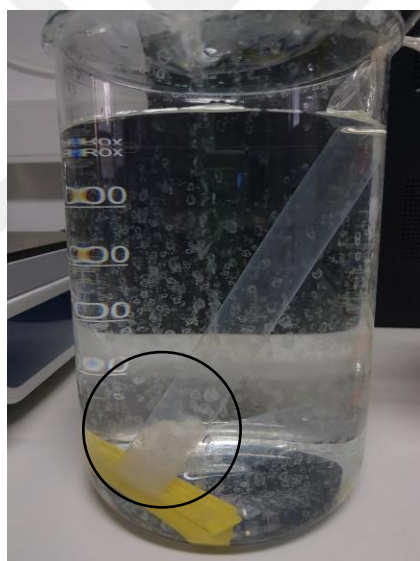
Furthermore, images of the NCC50H₂SO₄-cotton-30/10 are given in Figure 4.23 to show how the NCC50H₂SO₄-cotton-30/10 clumped and collapsed after the reaction due to zeta potential change.



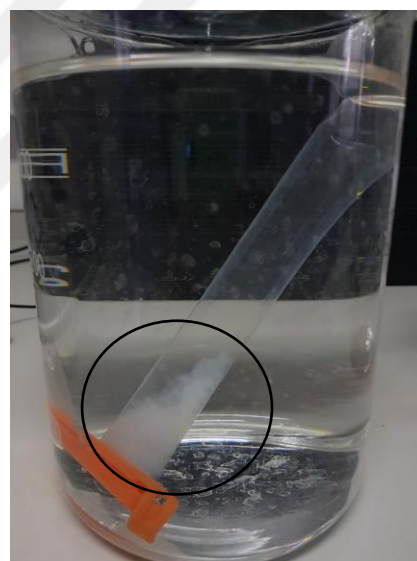
0 M



2 M/3 h



1 M/3 h



0.5 M/3 h

Figure 4.23. The images of some of the NCC50H₂SO₄-cotton-30/10 after NaOH reaction with comparison the NCC50H₂SO₄-cotton-30/10

As a consequence of these analyses, some of these results were compared with the literature values for 0.5 M/1h and 2M/3h to compare exact similar conditions. For 0.5M/1h reaction conditions, the decrease in NCC's absolute zeta potential is ~26

% where the absolute zeta potential value decreased from ~83 to ~61 mV which is compatible with the literature⁸⁸ where the absolute zeta potential value decreased from ~40 to ~32 mV. However, when the NCC's absolute zeta potential values were compared for 2M/3h, the decrease in the NCC's absolute zeta potential value is ~ 41 % where the absolute zeta potential value decreased from ~83 to ~49 mV where the absolute zeta potential value decreased from ~40 to ~7 mV in the study of Dufresne et al⁸⁸. However, as a general conclusion by comparing the literature values, the zeta potential value of the NaOH treated NCC50H₂SO₄-cotton-30/10 at different reaction conditions decreases with increasing NaOH concentration like in the literature due to alkali desulfation of sulfate groups on the NCC surface. In addition to these, when Figure 4.23 was investigated, it can be said that the NCC50H₂SO₄-cotton-30/10 flocculates and precipitates due to zeta potential change after reaction when compared with the original NCC50H₂SO₄-cotton-30/10. However, 1 M NaOH concentration and 30 minute reaction time was chosen to start deposition experiments as optimum working conditions since the used support membrane which is the PES10PEG10-1MH can be used at most pH 14.

4.2.3.2 The ATR-FTIR Analysis of the PES10PEG10-1MH-D-P-NORMAL-B Membranes

After deposition process, to analyze whether there is deposition on the support membrane surface and to determine the stability of the deposited NCC on the support membrane, the NCC membranes were analyzed with the ATR-FTIR analysis. The NCC membranes were kept in water for 24 hours and 1 week. After each of these processes, after the membranes were dried under vacuum, their deposited and back sides were analyzed by ATR-FTIR. Cellulose structure and PES structure in the membrane surfaces were examined for PES support membranes and the area under the cellulose peak / the area under the characteristic PES peak were calculated to estimate how much cellulose is present in the surface of the membrane. The peaks at 1580 cm⁻¹, 1488 cm⁻¹, 1244 cm⁻¹ and 1106 cm⁻¹

were attributed to PES structure¹²¹ and the peak at 1580 cm^{-1} (benzene ring stretching) was used during ATR-FTIR analysis.

One of the ATR-FTIR analysis results of the NCC membrane produced using 1 M NaOH is given in Figure 4.24 to show the peak change and the peak positions. The rest of the ATR-FTIR analysis results for these NCC membranes are given in the Appendix D.

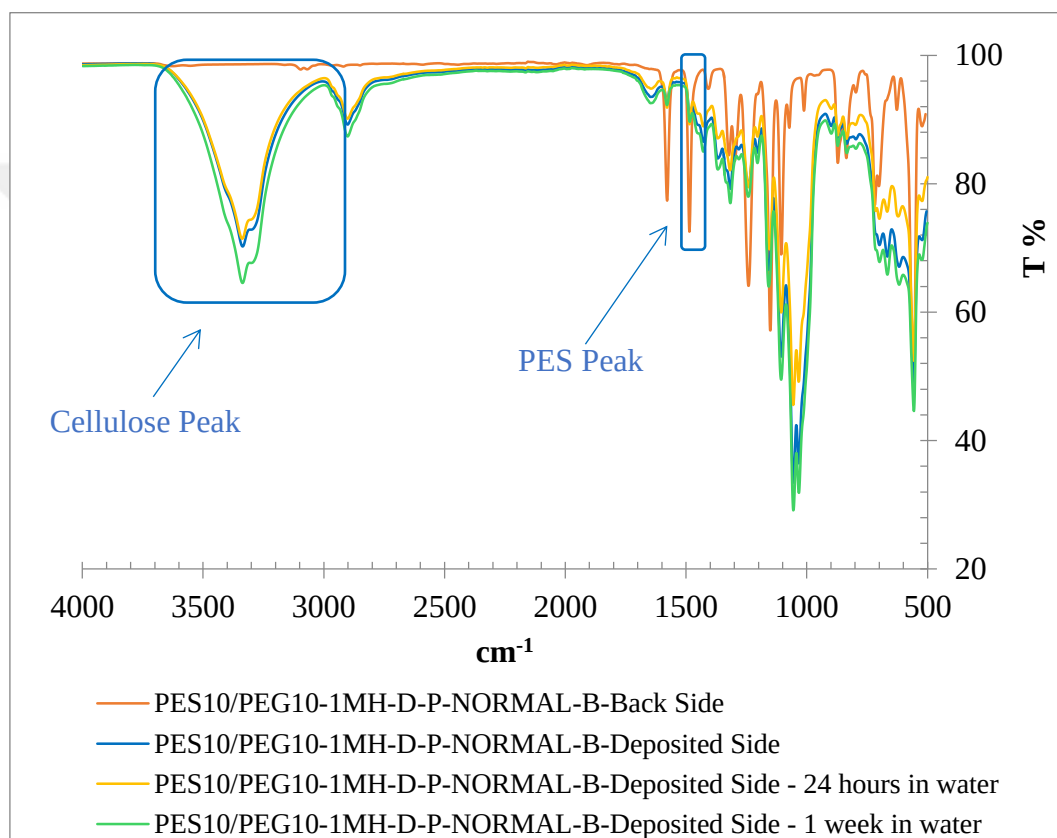


Figure 4.24. The ATR-FTIR analysis result for the PES10PEG10-1MH-D-P-NORMAL-B

Moreover, the cellulose peak/ PES peak values are given in Table 4.9 for the PES10PEG10-1MH-D-P-NORMAL-B membranes.

Table 4.9 The Absolute Values of Area under the Cellulose Peak / the Area under the PES Peak for Just After Deposition and Keeping the PES10PEG10-1MH-D-P-NORMAL-B Membranes in Water for 24 Hours and 1 Week Using Different Measurements Place on the PES10/PEG10-1MH-D- P-NORMAL-B Membranes Surface Which Is Shown By Measurement Number

Name of NCC Membrane	Measurement Number	Deposited Side		
		Just After Deposition	24 Hours in Water	1 Weeks in Water
PES10PEG10-1MH-D- P-NORMAL-B	First	163	117	80.5
	Second	77.6	33.1	188
	Third	-	191	29.5
PES10PEG10-1MH-D- P-NORMAL-B - Rep.Exp.	First	127	108	28.3
	Second	64.6	22.6	62.1
	Third	-	57.9	-

As seen from Table 4.9, the peak ratio changes between measurements since when the measurement was done at different place of the sample, the results came differently in contrast to other NCC membranes because the deposited NCC on the support membrane surface may not be have a homogeneous distribution on the surface. During NaOH filtration, the hot NaOH was put onto the NCC membrane surface at ambient conditions that may cause to temperature increase on the NCC membrane surface and move the deposited NCC layer. This situation may cause to have the non-homogenous NCC distribution on the NCC membrane surface.

4.2.3.3 The SEM Analysis of PES10PEG10-1MH-D-P-NORMAL-B Membranes and the Support Membrane

The SEM images of the PES10PEG10-1MH-D-P-NORMAL-B and the PES10PEG10-1MH support membranes were investigated to determine surface

and cross section morphologies before and after deposition procedures. The surface SEM images of the PES10PEG10-1MH-D-P-NORMAL-B and the PES10PEG10-1MH membranes are given in Figure 4.25.

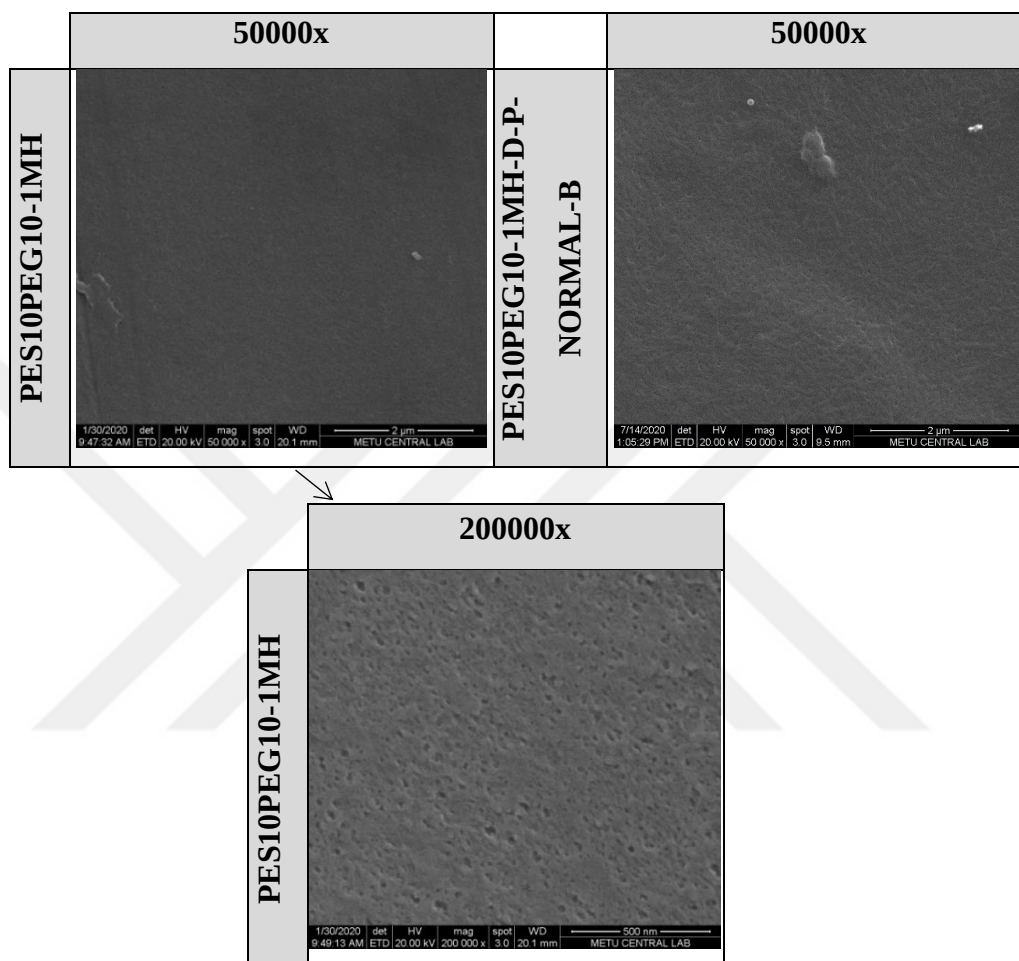


Figure 4.25. The surface SEM images of the PES10PEG10-1MH and the PES10PEG10-1MH-D-P-NORMAL-B membranes at different magnifications that are 50000x for the PES10PEG10-1MH-D-P-NORMAL-B and the PES10PEG10-1MH-membranes and 200000x for the PES10PEG10-1MH membrane

The PES10PEG10-1MH membrane has a porous surface due to having VIPS&LIPS membrane production techniques, and its pores were measured with a diameter 18.4 ± 7.5 nm on the surface. When the SEM images of the PES10PEG10-1MH support membrane and the PES10PEG10-1MH-D-P-NORMAL-B were compared to the deposited CA membranes, it can be concluded

that there is no deposited surface as distinct as the other deposited CA membranes. In the cross section SEM images of the PES10PEG10-1MH-D-P-NORMAL-B membranes (Figure 4.26) , there appears a layer structure, which may be attributed to NCC deposition, but the distinction between support and deposited layer is not very clear.

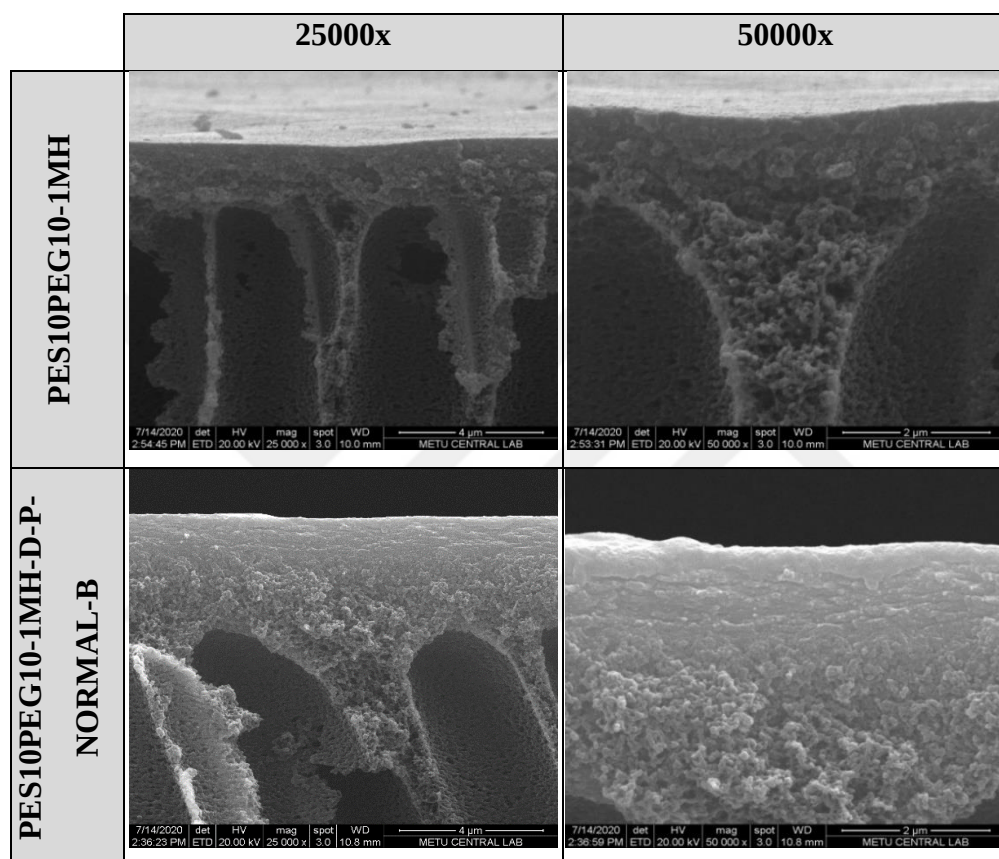


Figure 4.26. The cross section SEM images of the PES10PEG10-1MH and the PES10PEG10-1MH-D-P-NORMAL-B membranes at different magnifications which are 25000x and 50000x

The pores of the PES support are large enough to be partly blocked by NCC, but not as large as to completely permeate all NCC. The lack of a continuous deposit, as evident from ATR-FTIR analysis as well, can be due to enlarging of the pores at the high pH of NaOH.

4.2.3.4 The Separation Performance of the PES10PEG10-1MH-D-P-NORMAL-B Membranes

The averaged normalized permeance results for all experiments for the PES10PEG10-1MH-D-P-NORMAL-B membranes with respect to PWP are given in Figure 4.27. Also, the permeance results (PWP, deposition permeance, salt filtration permeance and PWP after deposition) of the PES10PEG10-1MH-D-P-NORMAL-B membranes are given in the Appendix E.

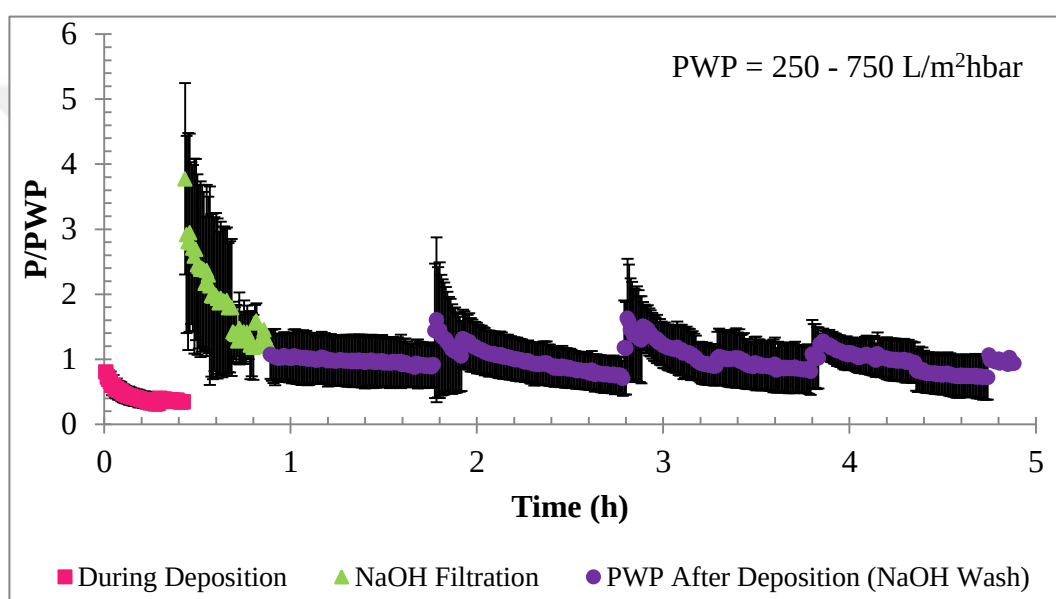


Figure 4.27. The resistance values for all the PES10PEG10-1MH-D-P-NORMAL-B membranes during deposition process (Average of three membranes)

During deposition of the NCC, permeance drop similar to the CA10D-P-S membranes is observed. However, when 1 M NaOH solution is filtered, the permeance increases to a value higher than the PWP. This situation can be explained with interaction of NaOH with PES by increasing the pore size of the support membrane¹²². This situation may cause several drawbacks. Due to pore enlargement, the permeance at the beginning of NaOH filtration increased drastically than PWP and after deposition permeance values, and then the deposited NCC layer may enter the expanding pores by removing from the NCC membrane

surface which causes to decrease in the NCC membrane permeance during NaOH filtration. This situation also explains the surface and cross-section SEM images, and the non-homogenous NCC deposit layer.

4.2.3.5 The BD5 Rejection Performance Analysis of the PES10PEG10-1MH-D-P-NORMAL-B Membranes

To test membrane rejection performance after deposition procedure, the PES10PEG10-1MH-D-P-NORMAL-B membrane was tested with aqueous BD5 solution, and its result is given in Figure 4.28.

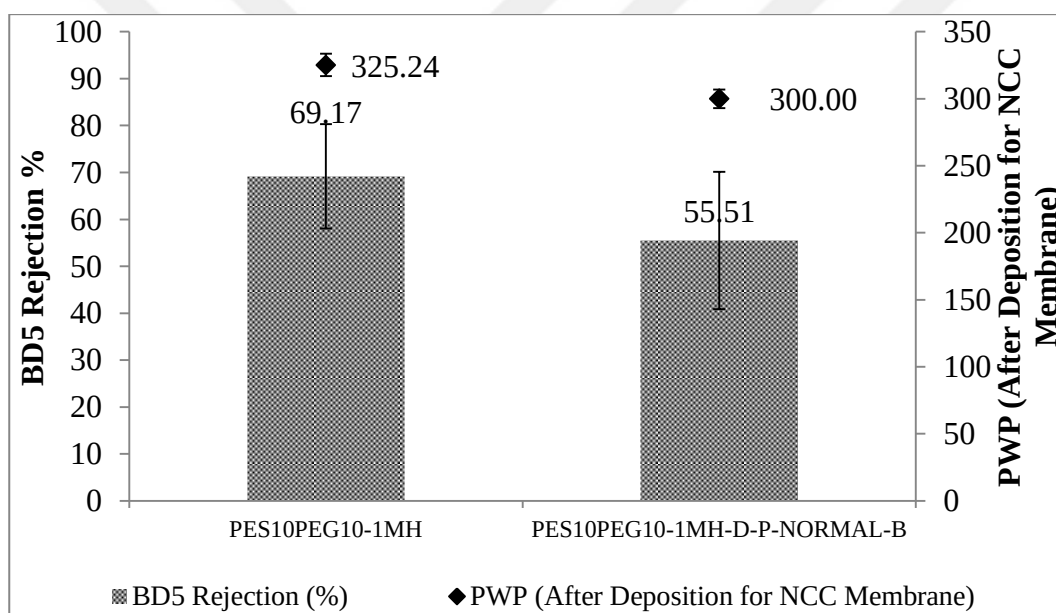


Figure 4.28. The BD5 rejection and PWP (After deposition for NCC membrane) results for the PES10PEG10-1MH-D-P-NORMAL-B membranes with comparison the support membrane

As seen from Figure 4.28, the BD5 rejection and permeance of the the PES10PEG10-1MH-D-P-NORMAL-B membrane is nearly same as the support membrane in the error range, which can be expected from previous analysis of the membranes in SEM and ATR-FTIR analysis.

4.3 All-Cellulose Nanocomposite Membranes

4.3.1 The XRD Analysis Results of Some of the All-Cellulose Nanocomposite Membranes

All-cellulose nanocomposite membranes were produced using two different methods which are the partial dissolution of cellulose and the direct NCC addition to the generated cellulose matrix.

In the first part of this chapter, the all-cellulose nanocomposite membranes that were produced using the partial dissolution of cellulose to obtain cellulose membranes with increased crystallinity to improve membrane rejection were analyzed with the XRD analysis to determine crystal structures of the membranes

When XRD analyses which are given in the Appendix J of these membranes were analyzed, the all-cellulose nanocomposite membranes produced via the partial dissolution of cellulose have amorphous structure. Thus, it can be said that the order of adding the membrane materials, using different types of cellulose or heating to the solvent during cellulose addition at different temperatures has no effect on the crystalline of the membrane, and the structures of these membranes produced are amorphous, and all celluloses are dissolved.

Due to obtaining amorphous structure in the all-cellulose nanocomposite membranes produced via the partial dissolution of cellulose, the approach to obtaining the all-cellulose nanocomposite membranes was changed to the direct addition of the NCC to the generated cellulose matrix since in this method, the NCC placed in the CA matrix cannot dissolve with the solvent used to dissolve CA, the NCC would be able to preserve their crystallinity, and then the cellulose membranes with increased crystallinity could be obtained from these membranes by alkali hydrolysis method.

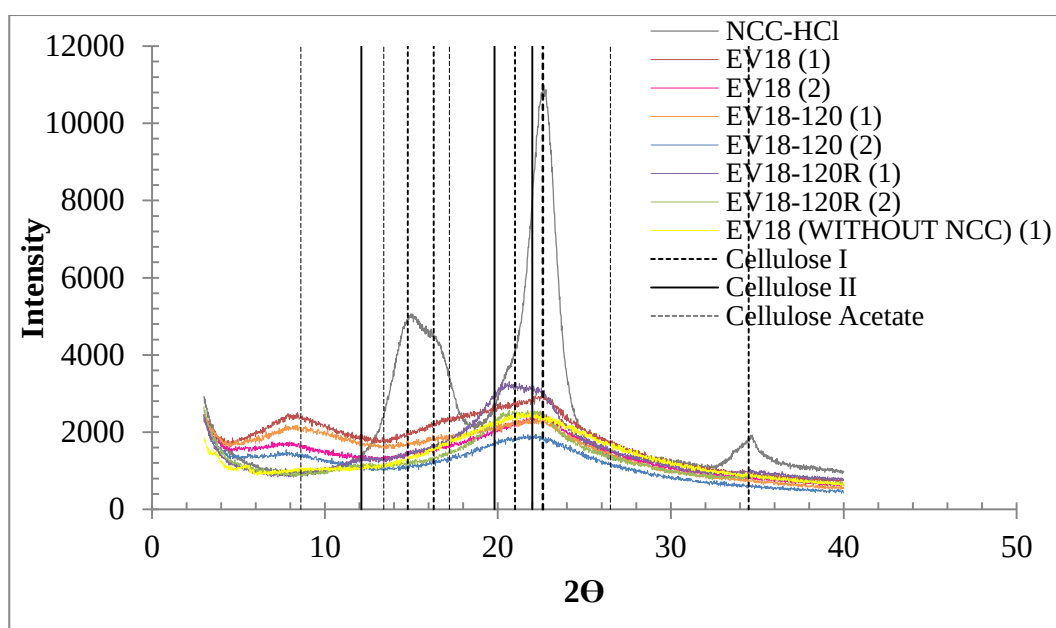


Figure 4.29. The XRD results of the EV18 membranes comparative results the NCC-HCl (Active (1) and inactive (2) surfaces of the membrane)

When Figure 4.29 is investigated, there is cellulose I structure in the EV18 membrane due to the NCC-HCl addition to cellulose acetate membrane which increase the membrane crystallinity slightly when compared with the EV18(WITHOUT NCC). In contrast to the EV18 membrane, the EV18-120R membrane has both cellulose I and cellulose II structure after annealing and alkaline hydrolysis of the EV18 membrane due to both the NCC-HCl (cellulose I) addition and cellulose II structure formation as a result of regeneration of cellulose acetate.

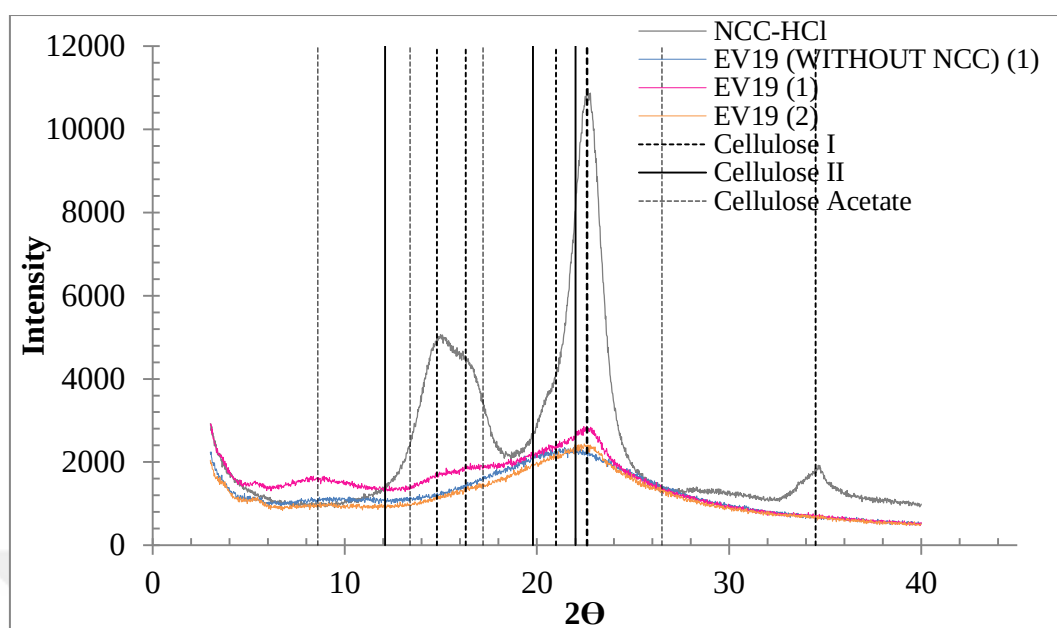


Figure 4.30. The XRD results of the EV19 membranes comparative results the NCC-HCl (Active (1) and inactive (2) surfaces of the membrane)

The EV19(1) membrane has cellulose I structure that increases the membrane crystallinity slightly as seen from Figure 4.30 when compared to the EV19(WITHOUT NCC) membrane.

As a result of these, it can be concluded that adding NCC-HCl to the membrane casting solution that prepared with cellulose acetate maintains its crystalline structure throughout the membrane formation process.

4.3.2 The Optic Microscope Images of Some of the All-Cellulose Nanocomposite Membranes

Some of the all-cellulose nanocomposite membranes were analyzed by optical microscope in order to observe the insoluble cellulose regions in the membranes, and their images are given in Figure 4.31.

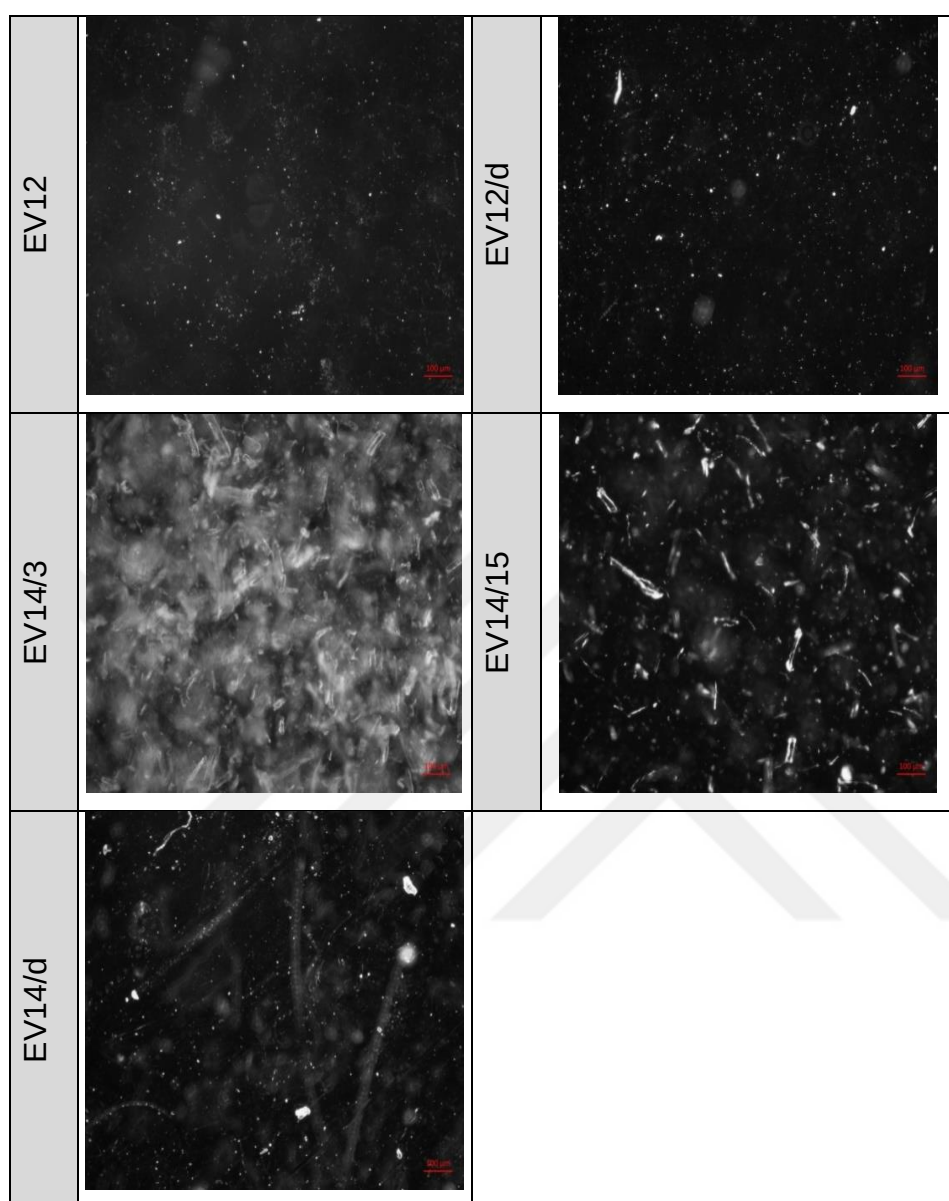


Figure 4.31. Optic microscope images of some of the all-cellulose nanocomposite membranes

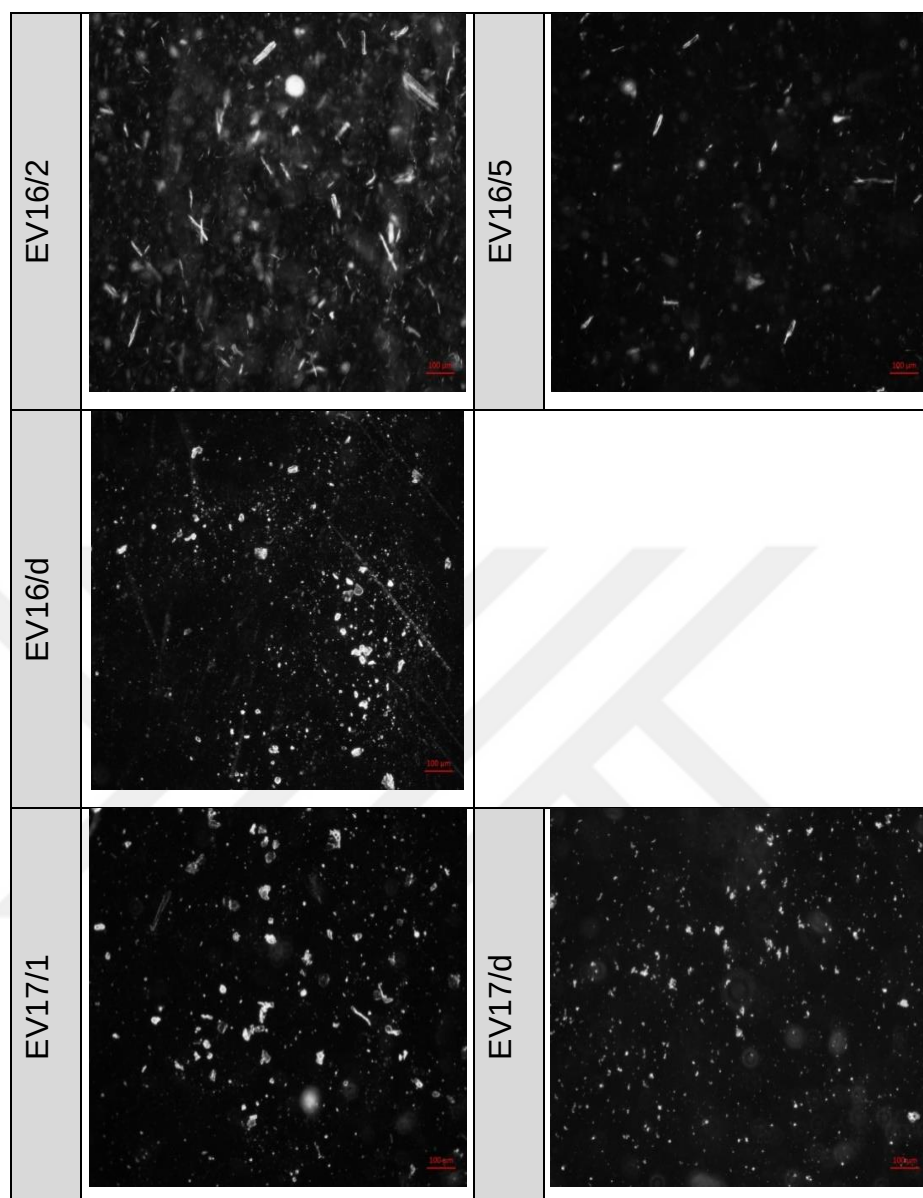


Figure 4.31. (cont'd) Optic microscope images of some of the all-cellulose nanocomposite membranes

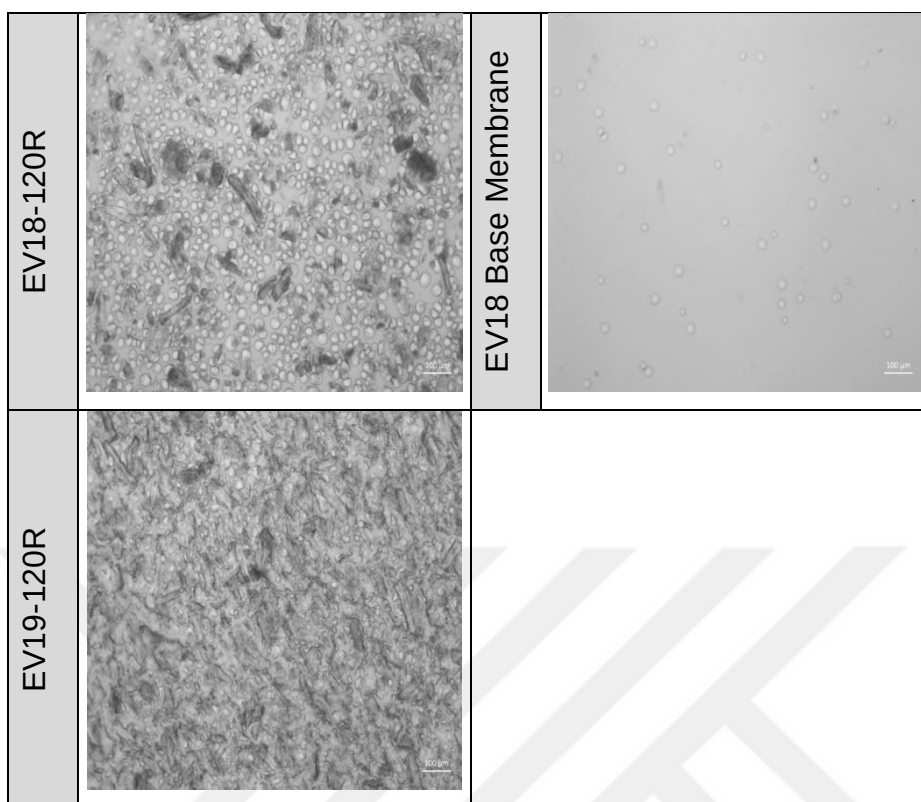


Figure 4.31. (cont'd) Optic microscope images of some of the all-cellulose nanocomposite membranes

When the optical microscope images were analyzed, the following results are reached;

- When the homogeneous membrane solution is casted at certain time intervals, the amount of undissolved cellulose fibers decreases in width and length as expected as time progressed, as observed.
- When the EV12 membrane that produced using 8.0 % cotton linter cellulose, 61.3 % DMSO and 30.7 % [EMIM]OAC by mixing half of cellulose with DMSO and half of cellulose with [EMIM]OAC at room temperature is examined, it was observed that there are no lumps in their structures implying complete dissolution, as no crystallinity was observed in the XRD analysis.

- When the EV14 membrane that produced using 4.0 % cotton linter cellulose, 64.0 % DMSO and 32.0 % [EMIM]OAC by mixing all of cellulose with DMSO at room temperature, undissolved cellulose fibers on the EV14/3 membrane were approximately 78.6 μm in length while their width was approximately 19.9 μm . However, the length and the width of the undissolved cellulose fibers on the EV14/15 membrane were slightly lower implying partial dissolution. The XRD pattern of this membrane, however, shows no crystallinity which implies that although cellulose does not fully dissolve, cellulose is largely swollen and has lost its crystalline structure. It was observed that there is no clumping in the EV14/d possibly due to complete dissolution.
- The similar observations with the EV14 membranes are shown in the EV16 membranes that produced using 8.0 % cotton linter cellulose, 61.3 % DMSO and 30.7 % [EMIM]OAC by mixing all of cellulose with DMSO at room temperature and EV17 membranes that produced using 8.0 % cotton linter cellulose, 61.3 % DMSO and 30.7 % [EMIM]OAC by mixing half of cellulose with DMSO and half of cellulose with [EMIM]OAC at 70°C.
- In the structure of the EV18-120R membranes that produced using 1.33 % NCC-HCl, 19.73 % CA, 36.83 % acetone and 42.11 % NMP, it was observed that there are aggregated cellulose nanocrystals (NCC-HCl) with length of $101.7 \pm 34.7 \mu\text{m}$, the width of $30.6 \pm 8.2 \mu\text{m}$.
- The similar observations with the EV18-120R membrane are shown in the EV19-120R membrane that produce using 2.44 % NCC-HCl, 9.76 % CA, 46.83 % acetone and 40.98 % NMP

As a result of these analyses for the all-cellulose nanocomposite membranes obtained via the partial dissolution of cellulose, although there are cellulose regions in the optic microscope images, there are no crystallinity in the membranes structure in the XRD analysis since partially dissolved cellulose regions swell and/or dissolved in solvent and lose their crystallinity. Therefore, the cellulose membranes with improved crystallinity could not be produced successfully.

Besides, when the all-cellulose nanocomposite membranes that were produced using the direct addition of the NCC to the generated cellulose matrix were investigated, the CA membrane crystallinity slightly increased with the NCC-HCl addition to the CA membrane casting solution as seen from the XRD analysis results.

4.3.3 The Solute Rejection Performances of the All-Cellulose Nanocomposite Membranes

The all-cellulose nanocomposite membranes were first tested with ethanol to determine PSP. Then, they were tested with Bromothymol blue (BTB) to see the solute (dye) rejection. Some of the membranes were tested after drying (DRY) and some of the membranes were tested just after removing EtOH storage box (WET).

When the EV7S(DRY) and the EV8S(DRY) membranes that produced with MCC, DMF and [EMIM]OAc and the EV14/15(WET), the EV16/2(WET), the EV16/5(WET) and the EV17/1(WET) membranes that produced with cotton linter cellulose, DMSO and [EMIM]OAc were examined, it can be concluded that there is no BTB rejection.

- The PSP and BTB Test Results of Membranes Produced with NCC-HCl, CA, Acetone and [EMIM]OAc;

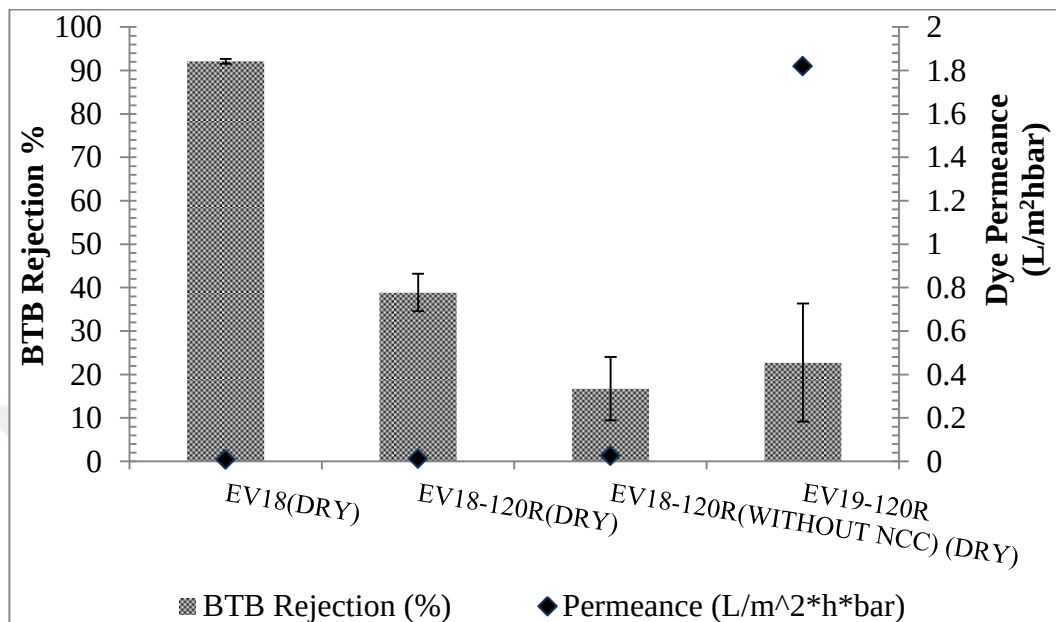


Figure 4.32. The performance test results of the membranes that prepared using NCC-HCl, CA, Acetone and [EMIM]OAc

When the effect of the NCC addition to the membrane structure on BTB rejection and permeance of membrane was compared between the EV18-120R and the EV18-120R (WITHOUT NCC) (Figure 4.32), it can be said that there is an increase in BTB rejection of membrane, but this effect is not as high as desired. Also, when the permeance and the BTB rejection of the EV18 compared with the EV18-120R, the BTB rejection of the non-regenerated membrane was very high ; however, after the alkaline regeneration process, it has been observed that the BTB rejection of the membrane decrease due to getting loose membranes structure.

CHAPTER 5

CONCLUSIONS

The main aim of this study is to produce membranes using nanocrystalline cellulose. To achieve this aim, after producing nanocrystalline cellulose (NCC), the membranes were produced using two different methods. In the first method, the membranes were produced using controlled precipitation of nanocrystalline cellulose on the support membrane by investigation membranes' stability, morphology and separation performances. In the second method, the all-cellulose nanocomposite membranes were produced by either adding NCC into membrane casting solution or partial dissolution of cellulose by investigation membranes' crystallinity, morphology and separation performances.

Nanocrystalline celluloses (NCC) were produced using acid hydrolysis. To produce NCC, different types of cellulose sources (MCC and cotton linter cellulose), different type of acids (HCl and H_2SO_4), different acid to cellulose ratios (8.75 or 10 ml acid/ g cellulose) during H_2SO_4 hydrolysis, different H_2SO_4 concentrations (50 or 65 wt%) and different reaction times during H_2SO_4 hydrolysis (15,30,45 and 60 minutes) were used to determine their effects on the NCC crystallinity, the color of NCC, the size of NCC and the reaction yield. From the XRD analysis results, when the cellulose source is the MCC, the crystallinity index values of the NCC produced using HCl is higher than the crystallinity index values of the NCC produced using H_2SO_4 . Also, when acid to cellulose ratio increases or H_2SO_4 concentration decreases, the crystallinity index value of NCC increases when the cellulose source is MCC. However, two different types of acid that are 50 wt% H_2SO_4 and HCl give similar crystalline index values when using cotton linter cellulose as a cellulose source for acid hydrolysis. The sizes of NCC-HCl obtained from TEM correspond with the literature values by changing from 260 nm to 350 nm in length and 20 to 35 nm in width. Besides, the sizes of $NCCH_2SO_4$ -cot-30/10

obtained from TEM, SEM and DLS analyzes correspond with the literature values by changing from 247 nm to 275 nm in length and 27 to 35 nm in width, however, the NCC produced with 65 wt % H_2SO_4 degraded completely as seen from its TEM image and XRD analysis. In addition, when the effect of reaction time on the NCC properties was examined, the optimum reaction time has to be determined. As a result of these experiments, the most suitable NCC is determined to continue for further experiments as the NCC50 H_2SO_4 -cotton-30/10 instead of the NCC-HCl or the NCC-HCl-cotton since the dispersibility of the NCC produced using H_2SO_4 is better with respect to the NCC-HCl, and in experiments with H_2SO_4 , this NCC50 H_2SO_4 -cotton-30/10 gave the best features. As a final step of the NCC characterization, the point of zero charge of the NCC was determined as a function of AlCl_3 concentration and NaOH molarities at different reaction times (alkali desulfation) to obtain the stable NCC membranes. As a result of zeta potential analysis, when the stability of the NCC in different salt concentration was examined, the both commercial and produced NCC reached nearly zero zeta potential value where the NCC are least stable and easily aggregates at 200 mM AlCl_3 concentration due to having similar initial zeta potential values and similar production conditions. In contrast to this, the zeta potential value of NCC decreases with increasing NaOH concentration like in the literature due to alkali desulfation of sulfate groups on the NCC surface.

In the second part of this study, the membranes were produced using deposition technique of the NCC/water solution on the support membrane with water and additional aqueous solutions to decrease the NCC colloidal stability on the support membrane to obtain the stable deposited NCC layers on the support membrane. The main aim of this part of the study is to produce selective membrane layers using water and the NCC. The produced membranes by this technique are called as the NCC membrane. To produce the NCC membranes, three different types of the support membranes (CA10, CA20 and PES10PEG10-1MH), different deposition amounts of the NCC on the support membrane (0.12, 0.24 and 0.48 mg/cm²) for the CA10 support membrane, different additional solutions (Salt- AlCl_3 for CA10

and the CA20 support membranes and Base-NaOH for the PES10PEG10-1MH support membrane) to change the surface charge of the NCC in deposited layer to obtain the more stable NCC layer and two different types of NCC (the commercial NCC for the CA20 support membrane and the NCC50H₂SO₄-cotton-30/10 for the CA10 and the PES10PEG10-1MH support membranes) were used. For the NCC membranes (CA10D-P-S) produced using 200 mM AlCl₃, the CA10 as a support membrane and the different amounts of the NCC50H₂SO₄-cotton-30/10, when the ATR-FTIR analysis results were investigated, CA10D-P-S membranes can remain stable for up to 1 week when 0.24 mg NCC/cm² was deposited. Therefore, 0.24 mg/cm² was determined as the optimum condition for deposition. Then, when the SEM analysis results of the CA10D-P-S membranes were analyzed, there are bundles on the NCC membranes' surfaces since during the deposition procedure, the NCC was deposited randomly on the support membrane surface, and this deposited NCC layer shrinks due to drying of the membrane. The thickness of the deposited NCC layer increases with increasing deposition amount. The permeance decreases due to the NCC deposition on the surface as expected and possibly partial pore blocking at the support membrane. Besides, the BD5 rejection of the support membrane is 53 % after deposition increases to ~ 90 % for all the three CA10D-P-S membranes.

For the NCC membranes produced using 200 mM AlCl₃, the CA20 as a support membrane and the commercial NCC, in contrast to the CA10D-P-S membranes, the NCC deposit layer is not a stable layer on the CA20D-C-NORMAL-S membranes with respect to the ATR-FTIR analysis; however, it is more compact because of deposition at 4 bars. These membranes tested for the OSN, but do not shown satisfactory performance.

As a final of this part, the NCC membranes produced using the PES10PEG10-1MH support membrane and the NCC50H₂SO₄-cotton-30/10 using alkali desulfation of the NCC via 1 M NaOH filtration on the deposited NCC layer for 30 minutes. As a result of the ATR-FTIR analysis, it can be concluded that these membranes have non-homogenous deposited layer possibly because during NaOH

filtration, the hot 1 M NaOH was put onto membrane surface, which cause temperature increase on the membrane surface. Besides, the 1 M NaOH can cause pore expanding, which can also be related to increasing permeance during NaOH filtration. Due to this pore expanding, the deposited NCC layer can enter the pores of the support membrane by removing from surface. This situation is also apparent in the SEM analysis results, and also causes to have the non-homogenous deposited layer. Thus, there is no any extra resistance on the support membrane caused by the NCC deposition. Besides, there is no effect of the NCC deposition on the membrane BD5 rejection values due to these reasons.

In the final part of this study, the cellulose membranes with increased crystallinity was tried to be produced either by the adding NCC in the membrane precursor solution or the partial dissolution of cellulose. Then, some of these membranes were tested using different solute/EtOH solutions to determine the membrane rejection performance. During the partial dissolution technique, different dissolution times, different types of cellulose sources (MCC and Cotton linter cellulose), different type of co-solvents (DMF and DMSO), heating solvent at different temperatures and different adding order of materials to the membrane casting solution was used to see their effects on the membrane crystallinity and the membrane solute rejection. When the XRD analysis results were examined, it can be concluded that there are no any effect of these on the membrane crystallinity and the solute rejections since celluloses either aggregated in the membrane structure or dissolved completely. In addition to these, although the adding NCC in the membrane casting solution has effect on the membrane crystallinity and the solute rejection, it is too low.

REFERENCES

1. Marchetti, P., Jimenez Solomon, M. F., Szekely, G. & Livingston, A. G. Molecular separation with organic solvent nanofiltration: A critical review. *Chemical Reviews* (2014). doi:10.1021/cr500006j
2. Nunes, S. P. *et al.* Thinking the future of membranes: Perspectives for advanced and new membrane materials and manufacturing processes. *Journal of Membrane Science* (2020). doi:10.1016/j.memsci.2019.117761
3. Boerlage, S. F. E., Kennedy, M. D., Dickson, M. R., El-Hodali, D. E. Y. & Schippers, J. C. The modified fouling index using ultrafiltration membranes (MFI-UF): Characterisation, filtration mechanisms and proposed reference membrane. *J. Memb. Sci.* (2002). doi:10.1016/S0376-7388(01)00618-4
4. Aksoy, C., Kaner, P., Asatekin, A. & Çulfaz-Emecen, P. Z. Co-Deposition of Stimuli-Responsive Microgels with Foulants during Ultrafiltration as a Fouling Removal Strategy. *ACS Appl. Mater. Interfaces* (2019). doi:10.1021/acsami.9b03217
5. Xu, J. & Xu, Z. L. Poly(vinyl chloride) (PVC) hollow fiber ultrafiltration membranes prepared from PVC/additives/solvent. *J. Memb. Sci.* (2002). doi:10.1016/S0376-7388(02)00261-2
6. Hosch, J. & Staude, E. Preparation and investigation of chemically modified porous polyamide ultrafiltration membranes. *J. Memb. Sci.* (1996). doi:10.1016/0376-7388(96)00166-4
7. Arthanareeswaran, G., Sriyamuna Devi, T. K. & Raajenthiren, M. Effect of silica particles on cellulose acetate blend ultrafiltration membranes: Part I. *Sep. Purif. Technol.* (2008). doi:10.1016/j.seppur.2008.08.010
8. Ciston, S., Lueptow, R. M. & Gray, K. A. Bacterial attachment on reactive ceramic ultrafiltration membranes. *J. Memb. Sci.* (2008).

doi:10.1016/j.memsci.2008.03.065

9. Mohammad, A. W. *et al.* Nanofiltration membranes review: Recent advances and future prospects. *Desalination* (2015). doi:10.1016/j.desal.2014.10.043
10. Ernst, M., Bismarck, A., Springer, J. & Jekel, M. Zeta-potential and rejection rates of a polyethersulfone nanofiltration membrane in single salt solutions. *J. Memb. Sci.* (2000). doi:10.1016/S0376-7388(99)00238-0
11. da Silva Burgal, J., Peeva, L. G., Kumbharkar, S. & Livingston, A. Organic solvent resistant poly(ether-ether-ketone) nanofiltration membranes. *J. Memb. Sci.* (2015). doi:10.1016/j.memsci.2014.12.035
12. Valtcheva, I. B., Kumbharkar, S. C., Kim, J. F., Bhole, Y. & Livingston, A. G. Beyond polyimide: Crosslinked polybenzimidazole membranes for organic solvent nanofiltration (OSN) in harsh environments. *J. Memb. Sci.* (2014). doi:10.1016/j.memsci.2013.12.069
13. Soroko, I. & Livingston, A. Impact of TiO₂ nanoparticles on morphology and performance of crosslinked polyimide organic solvent nanofiltration (OSN) membranes. *J. Memb. Sci.* (2009). doi:10.1016/j.memsci.2009.07.026
14. Zeidler, S., Kätzel, U. & Kreis, P. Systematic investigation on the influence of solutes on the separation behavior of a PDMS membrane in organic solvent nanofiltration. *J. Memb. Sci.* (2013). doi:10.1016/j.memsci.2012.11.056
15. Pulido, B. A., Waldron, C., Zolotukhin, M. G. & Nunes, S. P. Porous polymeric membranes with thermal and solvent resistance. *J. Memb. Sci.* (2017). doi:10.1016/j.memsci.2017.05.070
16. Aburabie, J. & Peinemann, K. V. Crosslinked poly(ether block amide) composite membranes for organic solvent nanofiltration applications. *J. Memb. Sci.* (2017). doi:10.1016/j.memsci.2016.09.027

17. Sukma, F. M. & Çulfaz-Emecen, P. Z. Cellulose membranes for organic solvent nanofiltration. *J. Memb. Sci.* (2018). doi:10.1016/j.memsci.2017.09.080
18. Rezaei Hosseinabadi, S. *et al.* Organic solvent nanofiltration with Grignard functionalised ceramic nanofiltration membranes. *J. Memb. Sci.* (2014). doi:10.1016/j.memsci.2013.12.032
19. Baker, R. W. *Membrane Technology and Applications.* (2004). doi:10.1002/0470020393
20. LOEB, S. & SOURIRAJAN, S. Sea Water Demineralization by Means of an Osmotic Membrane. in (1963). doi:10.1021/ba-1963-0038.ch009
21. Mulder, M. *Basic Principles of Membrane Technology. Second edition.* Kluwer Academic Publishers (1997).
22. Guillen, G. R., Pan, Y., Li, M. & Hoek, E. M. V. Preparation and characterization of membranes formed by nonsolvent induced phase separation: A review. *Ind. Eng. Chem. Res.* (2011). doi:10.1021/ie101928r
23. Deshmukh, S. P. & Li, K. Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fibre membranes. *J. Memb. Sci.* (1998). doi:10.1016/S0376-7388(98)00196-3
24. Strathmann, H. & Kock, K. The formation mechanism of phase inversion membranes. *Desalination* (1977). doi:10.1016/S0011-9164(00)88244-2
25. Kim, J. F., Jung, J. T., Wang, H., Drioli, E. & Lee, Y. M. 1.15 Effect of Solvents on Membrane Fabrication via Thermally Induced Phase Separation (TIPS): Thermodynamic and Kinetic Perspectives. in *Comprehensive Membrane Science and Engineering* (2017). doi:10.1016/b978-0-12-409547-2.12690-3
26. Figoli, A. *et al.* Towards non-toxic solvents for membrane preparation: A review. *Green Chemistry* (2014). doi:10.1039/c4gc00613e

27. Sawada, S. ichi *et al.* Effect of citrate-based non-toxic solvents on poly(vinylidene fluoride) membrane preparation via thermally induced phase separation. *J. Memb. Sci.* (2015). doi:10.1016/j.memsci.2015.07.003
28. Hassankiadeh, N. T. *et al.* Microporous poly(vinylidene fluoride) hollow fiber membranes fabricated with PolarClean as water-soluble green diluent and additives. *J. Memb. Sci.* (2015). doi:10.1016/j.memsci.2015.01.031
29. Durmaz, E. N., Baig, M. I., Willott, J. D. & de Vos, W. M. Polyelectrolyte Complex Membranes via Salinity Change Induced Aqueous Phase Separation. *ACS Appl. Polym. Mater.* (2020). doi:10.1021/acsapm.0c00255
30. Baig, M. I., Durmaz, E. N., Willott, J. D. & de Vos, W. M. Sustainable Membrane Production through Polyelectrolyte Complexation Induced Aqueous Phase Separation. *Adv. Funct. Mater.* (2020). doi:10.1002/adfm.201907344
31. Zhang, J. *et al.* All-Cellulose Nanocomposites Reinforced with in Situ Retained Cellulose Nanocrystals during Selective Dissolution of Cellulose in an Ionic Liquid. *ACS Sustain. Chem. Eng.* (2016). doi:10.1021/acssuschemeng.6b01034
32. Wertz, J. L., Bédué, O. & Mercier, J. P. *Cellulose science and technology. Cellulose Science and Technology* (2010). doi:10.1201/b16496
33. Wang, H., Gurau, G. & Rogers, R. D. Ionic liquid processing of cellulose. *Chemical Society Reviews* (2012). doi:10.1039/c2cs15311d
34. Habibi, Y., Lucia, L. A. & Rojas, O. J. Cellulose nanocrystals: Chemistry, self-assembly, and applications. *Chem. Rev.* (2010). doi:10.1021/cr900339w
35. George, J. & Sabapathi, S. N. Cellulose nanocrystals: Synthesis, functional properties, and applications. *Nanotechnol. Sci. Appl.* (2015). doi:10.2147/NSA.S64386
36. Araki, J., Wada, M., Kuga, S. & Okano, T. Flow properties of

- microcrystalline cellulose suspension prepared by acid treatment of native cellulose. *Colloids Surfaces A Physicochem. Eng. Asp.* (1998). doi:10.1016/S0927-7757(98)00404-X
37. Leppänen, K. *et al.* Structure of cellulose and microcrystalline cellulose from various wood species, cotton and flax studied by X-ray scattering. *Cellulose* (2009). doi:10.1007/s10570-009-9298-9
 38. Kian, L. K., Jawaid, M., Ariffin, H. & Alothman, O. Y. Isolation and characterization of microcrystalline cellulose from roselle fibers. *Int. J. Biol. Macromol.* (2017). doi:10.1016/j.ijbiomac.2017.05.135
 39. Bondeson, D., Mathew, A. & Oksman, K. Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. *Cellulose* (2006). doi:10.1007/s10570-006-9061-4
 40. Boluk, Y., Lahiji, R., Zhao, L. & McDermott, M. T. Suspension viscosities and shape parameter of cellulose nanocrystals (CNC). *Colloids Surfaces A Physicochem. Eng. Asp.* (2011). doi:10.1016/j.colsurfa.2011.01.003
 41. Revol, J. F., Godbout, L., Dong, X. M. & Gray, D. G. *Chiral nematic suspensions of cellulose. Use of Minerals in Papermaking* (1998). doi:10.1533/9781845698539.5.371
 42. Lavoine, N., Desloges, I., Dufresne, A. & Bras, J. Microfibrillated cellulose - Its barrier properties and applications in cellulosic materials: A review. *Carbohydrate Polymers* (2012). doi:10.1016/j.carbpol.2012.05.026
 43. Turbak, A. F., Snyder, F. W. & Sandberg, K. R. Microfibrillated Cellulose. US 4374702. 9 (1983).
 44. Siqueira, G., Bras, J. & Dufresne, A. Cellulosic bionanocomposites: A review of preparation, properties and applications. *Polymers (Basel)*. **2**, 728–765 (2010).
 45. Iwamoto, S., Abe, K. & Yano, H. The effect of hemicelluloses on wood pulp

- nanofibrillation and nanofiber network characteristics. *Biomacromolecules* (2008). doi:10.1021/bm701157n
46. Saito, T., Nishiyama, Y., Putaux, J. L., Vignon, M. & Isogai, A. Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules* (2006). doi:10.1021/bm060154s
 47. Li, Z., Renneckar, S. & Barone, J. R. Nanocomposites prepared by in situ enzymatic polymerization of phenol with TEMPO-oxidized nanocellulose. *Cellulose* (2010). doi:10.1007/s10570-009-9363-4
 48. Taipale, T., Österberg, M., Nykänen, A., Ruokolainen, J. & Laine, J. Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength. *Cellulose* (2010). doi:10.1007/s10570-010-9431-9
 49. Abdullah-Al-Mamun, M. *et al.* A Morphological Study of Microfibrillated Cellulose Prepared from Waste Cotton Linter. *Am. Chem. Sci. J.* (2016). doi:10.9734/acsj/2016/27903
 50. Xu, A., Wang, J. & Wang, H. Effects of anionic structure and lithium salts addition on the dissolution of cellulose in 1-butyl-3-methylimidazolium-based ionic liquid solvent systems. *Green Chem.* (2010). doi:10.1039/b916882f
 51. Zhao, Y., Liu, X., Wang, J. & Zhang, S. Insight into the cosolvent effect of cellulose dissolution in imidazolium-based ionic liquid systems. *J. Phys. Chem. B* (2013). doi:10.1021/jp4038039
 52. Zhu, S. *et al.* Dissolution of cellulose with ionic liquids and its application: A mini-review. *Green Chemistry* (2006). doi:10.1039/b601395c
 53. Morais, J. P. S. *et al.* Extraction and characterization of nanocellulose structures from raw cotton linter. *Carbohydr. Polym.* (2013).

doi:10.1016/j.carbpol.2012.08.010

54. Yu, H. *et al.* Facile extraction of thermally stable cellulose nanocrystals with a high yield of 93% through hydrochloric acid hydrolysis under hydrothermal conditions. *J. Mater. Chem. A* (2013). doi:10.1039/c3ta01150j
55. Gatenholm, P. & Klemm, D. Bacterial nanocellulose as a renewable material for biomedical applications. *MRS Bull.* (2010). doi:10.1557/mrs2010.653
56. Liu, C. *et al.* Properties of nanocellulose isolated from corncob residue using sulfuric acid, formic acid, oxidative and mechanical methods. *Carbohydr. Polym.* (2016). doi:10.1016/j.carbpol.2016.06.025
57. Liu, Y. *et al.* A novel approach for the preparation of nanocrystalline cellulose by using phosphotungstic acid. *Carbohydr. Polym.* (2014). doi:10.1016/j.carbpol.2014.04.040
58. Dong, X. M., Revol, J. F. & Gray, D. G. Effect of microcrystallite preparation conditions on the formation of colloid crystals of cellulose. *Cellulose* (1998). doi:10.1023/A:1009260511939
59. Ehmann, H. M. A. *et al.* Design of anticoagulant surfaces based on cellulose nanocrystals. *Chem. Commun.* (2014). doi:10.1039/c4cc05254d
60. Aminu, M. Acid Hydrolysis-Mediated preparation of Nanocrystalline Cellulose from Rice Straw. *Int. J. Nanomater. Nanotechnol. Nanomedicine* (2017). doi:10.17352/2455-3492.000021
61. Lee, S. Y. *et al.* Nanocellulose reinforced PVA composite films: Effects of acid treatment and filler loading. *Fibers Polym.* (2009). doi:10.1007/s12221-009-0077-x
62. Dhar, P., Bhardwaj, U., Kumar, A. & Katiyar, V. Poly (3-hydroxybutyrate)/cellulose nanocrystal films for food packaging applications: Barrier and migration studies. *Polym. Eng. Sci.* (2015). doi:10.1002/pen.24127

63. Yang, X. & Cranston, E. D. Chemically cross-linked cellulose nanocrystal aerogels with shape recovery and superabsorbent properties. *Chem. Mater.* (2014). doi:10.1021/cm502873c
64. Akhlaghi, S. P., Berry, R. C. & Tam, K. C. Surface modification of cellulose nanocrystal with chitosan oligosaccharide for drug delivery applications. *Cellulose* (2013). doi:10.1007/s10570-013-9954-y
65. Schyrr, B. *et al.* Biosensors based on porous cellulose nanocrystal-poly(vinyl alcohol) scaffolds. *ACS Appl. Mater. Interfaces* (2014). doi:10.1021/am502670u
66. Börjesson, M. & Westman, G. Crystalline Nanocellulose — Preparation, Modification, and Properties. in *Cellulose - Fundamental Aspects and Current Trends* (2015). doi:10.5772/61899
67. Yu, M. *et al.* Preparation and characterization of bamboo nanocrystalline cellulose. *BioResources* (2012). doi:10.15376/biores.7.2.1802-1812
68. Hamad, W. Y. & Hu, T. Q. Structure-process-yield interrelations in nanocrystalline cellulose extraction. *Can. J. Chem. Eng.* (2010). doi:10.1002/cjce.20298
69. Prathapan, R., Thapa, R., Garnier, G. & Tabor, R. F. Modulating the zeta potential of cellulose nanocrystals using salts and surfactants. *Colloids Surfaces A Physicochem. Eng. Asp.* (2016). doi:10.1016/j.colsurfa.2016.08.075
70. Park, S. J. & Seo, M. K. *Intermolecular Force. Interface Science and Technology* (2011). doi:10.1016/B978-0-12-375049-5.00001-3
71. Joseph, E. & Singhvi, G. Multifunctional nanocrystals for cancer therapy: a potential nanocarrier. in *Nanomaterials for Drug Delivery and Therapy* (2019). doi:10.1016/b978-0-12-816505-8.00007-2
72. Lu, G. W. & Gao, P. Emulsions and Microemulsions for Topical and

Transdermal Drug Delivery. in *Handbook of Non-Invasive Drug Delivery Systems* (2010). doi:10.1016/b978-0-8155-2025-2.10003-4

73. Jasmani, L. & Adnan, S. Preparation and characterization of nanocrystalline cellulose from Acacia mangium and its reinforcement potential. *Carbohydr. Polym.* (2017). doi:10.1016/j.carbpol.2016.12.061
74. Beck, S. & Bouchard, J. Auto-catalyzed acidic desulfation of cellulose nanocrystals. *Nord. Pulp Pap. Res. J.* (2014). doi:10.3183/npprj-2014-29-01-p006-014
75. Lokanathan, A. R., Uddin, K. M. A., Rojas, O. J. & Laine, J. Cellulose nanocrystal-mediated synthesis of silver nanoparticles: Role of sulfate groups in nucleation phenomena. *Biomacromolecules* (2014). doi:10.1021/bm401613h
76. Jordan, J. H., Easson, M. W. & Condon, B. D. Alkali hydrolysis of sulfated cellulose nanocrystals: Optimization of reaction conditions and tailored surface charge. *Nanomaterials* (2019). doi:10.3390/nano9091232
77. Kloser, E. & Gray, D. G. Surface grafting of cellulose nanocrystals with poly(ethylene oxide) in aqueous media. *Langmuir* (2010). doi:10.1021/la101795s
78. Sinaga, M. Z. E., Gea, S., Panindia, N. & Sihombing, Y. A. The preparation of cellulose nanocomposite film from isolated cellulose of corncobs as food packaging. *Orient. J. Chem.* (2018). doi:10.13005/ojc/340166
79. Gindl-Altmutter, W. *et al.* All-cellulose composites prepared from flax and lyocell fibres compared to epoxy-matrix composites. *Compos. Sci. Technol.* (2012). doi:10.1016/j.compscitech.2012.05.011
80. Nishino, T., Matsuda, I. & Hirao, K. All-cellulose composite. *Macromolecules* (2004). doi:10.1021/ma049300h
81. Zhao, J. *et al.* Reinforcement of all-cellulose nanocomposite films using

- native cellulose nanofibrils. *Carbohydr. Polym.* (2014). doi:10.1016/j.carbpol.2014.01.007
82. Davis, R. H. & Grant, D. C. Theory for Deadend Microfiltration. in *Membrane Handbook* (1992). doi:10.1007/978-1-4615-3548-5_32
 83. Ch . E . 420 Chemical Engineering Laboratory III Laboratory Booklet. (2020).
 84. Ozgumus, T., Mobedi, M. & Ozkol, U. Determination of kozeny constant based on porosity and pore to throat size ratio in porous medium with rectangular rods. *Eng. Appl. Comput. Fluid Mech.* (2014). doi:10.1080/19942060.2014.11015516
 85. Kruczek, B. Encyclopedia of Membranes. *Encycl. Membr.* 10–12 (2015). doi:10.1007/978-3-642-40872-4
 86. McCabe, W. L., C.Smith, J. & Harriot, P. Unit Operations of Chemical Engineering. 188–189 (2005).
 87. Zhong, L., Fu, S., Peng, X., Zhan, H. & Sun, R. Colloidal stability of negatively charged cellulose nanocrystalline in aqueous systems. *Carbohydr. Polym.* (2012). doi:10.1016/j.carbpol.2012.05.091
 88. Lin, N. & Dufresne, A. Surface chemistry, morphological analysis and properties of cellulose nanocrystals with gradiented sulfation degrees. *Nanoscale* (2014). doi:10.1039/c3nr06761k
 89. Mautner, A. *et al.* Cellulose nanopapers as tight aqueous ultra-filtration membranes. *React. Funct. Polym.* (2015). doi:10.1016/j.reactfunctpolym.2014.09.014
 90. Mautner, A. *et al.* Nanopapers for organic solvent nanofiltration. *Chem. Commun.* (2014). doi:10.1039/c4cc00467a
 91. Zhang, Q. G., Deng, C., Soyekwo, F., Liu, Q. L. & Zhu, A. M. Sub-10 nm

- wide cellulose nanofibers for ultrathin nanoporous membranes with high organic permeation. *Adv. Funct. Mater.* (2016). doi:10.1002/adfm.201503858
92. Cheng, Q., Ye, D., Chang, C. & Zhang, L. Facile fabrication of superhydrophilic membranes consisted of fibrous tunicate cellulose nanocrystals for highly efficient oil/water separation. *J. Memb. Sci.* (2017). doi:10.1016/j.memsci.2016.11.084
 93. Chun, S. J. *et al.* Eco-friendly cellulose nanofiber paper-derived separator membranes featuring tunable nanoporous network channels for lithium-ion batteries. *J. Mater. Chem.* (2012). doi:10.1039/c2jm32415f
 94. Durmaz, E. N. & Zeynep Çulfaz-Emecen, P. Cellulose-based membranes via phase inversion using [EMIM]OAc-DMSO mixtures as solvent. *Chem. Eng. Sci.* (2018). doi:10.1016/j.ces.2017.12.020
 95. Konca, K. & Çulfaz-Emecen, P. Z. Effect of carboxylic acid crosslinking of cellulose membranes on nanofiltration performance in ethanol and dimethylsulfoxide. *J. Memb. Sci.* (2019). doi:10.1016/j.memsci.2019.117175
 96. Chen, H. Z., Wang, N. & Liu, L. Y. Regenerated cellulose membrane prepared with ionic liquid 1-butyl-3-methylimidazolium chloride as solvent using wheat straw. *J. Chem. Technol. Biotechnol.* (2012). doi:10.1002/jctb.3802
 97. Anokhina, T. S., Pleshivtseva, T. S., Ignatenko, V. Y., Antonov, S. V. & Volkov, A. V. Fabrication of composite nanofiltration membranes from cellulose solutions in an [Emim]OAc–DMSO mixture. *Pet. Chem.* (2017). doi:10.1134/S0965544117060020
 98. Anokhina, T. S. *et al.* Cellulose composite membranes for nanofiltration of aprotic solvents. *Pet. Chem.* (2016). doi:10.1134/S0965544116110025
 99. Li, X., Zhu, L.-P., Zhu, B.-K. & Xu, Y. High-flux and anti-fouling cellulose

nanofiltration membranes prepared via phase inversion with ionic liquid as solvent. *Sep. Purif. Technol.* **83**, 66–73 (2011).

100. Ghaderi, M., Mousavi, M., Yousefi, H. & Labbafi, M. All-cellulose nanocomposite film made from bagasse cellulose nanofibers for food packaging application. *Carbohydr. Polym.* (2014). doi:10.1016/j.carbpol.2014.01.013
101. Duchemin, B. J. C., Mathew, A. P. & Oksman, K. All-cellulose composites by partial dissolution in the ionic liquid 1-butyl-3-methylimidazolium chloride. *Compos. Part A Appl. Sci. Manuf.* (2009). doi:10.1016/j.compositesa.2009.09.013
102. Shakeri, A., Mathew, A. P. & Oksman, K. Self-reinforced nanocomposite by partial dissolution of cellulose microfibrils in ionic liquid. *J. Compos. Mater.* (2012). doi:10.1177/0021998311418017
103. Segal, L., Creely, J. J., Martin, A. E. & Conrad, C. M. An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer. *Text. Res. J.* (1959). doi:10.1177/004051755902901003
104. Thygesen, A., Oddershede, J., Lilholt, H., Thomsen, A. B. & Ståhl, K. On the determination of crystallinity and cellulose content in plant fibres. *Cellulose* (2005). doi:10.1007/s10570-005-9001-8
105. Qi, H., Cai, J., Zhang, L. & Kuga, S. Properties of films composed of cellulose nanowhiskers and a cellulose matrix regenerated from alkali/urea solution. *Biomacromolecules* (2009). doi:10.1021/bm9001975
106. Siqueira, G., Bras, J. & Dufresne, A. New process of chemical grafting of cellulose nanoparticles with a long chain isocyanate. *Langmuir* (2010). doi:10.1021/la9028595
107. Asempour, F., Emadzadeh, D., Matsuura, T. & Kruczek, B. Synthesis and characterization of novel Cellulose Nanocrystals-based Thin Film

- Nanocomposite membranes for reverse osmosis applications. *Desalination* (2018). doi:10.1016/j.desal.2018.04.009
108. Hastuti, N., Kanomata, K. & Kitaoka, T. Hydrochloric Acid Hydrolysis of Pulps from Oil Palm Empty Fruit Bunches to Produce Cellulose Nanocrystals. *J. Polym. Environ.* **26**, 3698–3709 (2018).
 109. George, J. & Siddaramaiah. High performance edible nanocomposite films containing bacterial cellulose nanocrystals. *Carbohydr. Polym.* (2012). doi:10.1016/j.carbpol.2011.10.019
 110. Jiang, F., Esker, A. R. & Roman, M. Acid-catalyzed and solvolytic desulfation of H₂SO₄-hydrolyzed cellulose nanocrystals. *Langmuir* **26**, 17919–17925 (2010).
 111. Kargarzadeh, H. *et al.* Effects of hydrolysis conditions on the morphology, crystallinity, and thermal stability of cellulose nanocrystals extracted from kenaf bast fibers. *Cellulose* **19**, 855–866 (2012).
 112. Lu, P. & Hsieh, Y. Lo. Preparation and characterization of cellulose nanocrystals from rice straw. *Carbohydr. Polym.* **87**, 564–573 (2012).
 113. Li, W., Wang, R. & Liu, S. Nanocrystalline cellulose prepared from softwood kraft pulp via ultrasonic-assisted acid hydrolysis. *BioResources* (2011). doi:10.15376/biores.6.4.4271-4281
 114. Mendes, C. A. D. C., Ferreira, N. M. S., Furtado, C. R. G. & De Sousa, A. M. F. Isolation and characterization of nanocrystalline cellulose from corn husk. *Mater. Lett.* (2015). doi:10.1016/j.matlet.2015.02.047
 115. Chang, C. P., Wang, I. C., Hung, K. J. & Perng, Y. S. Preparation and characterization of nanocrystalline cellulose by acid hydrolysis of cotton linter. *Taiwan J. For. Sci.* **25**, 251–264 (2010).
 116. Phan-Xuan, T. *et al.* Aggregation behavior of aqueous cellulose nanocrystals: the effect of inorganic salts. *Cellulose* (2016).

doi:10.1007/s10570-016-1080-1

117. Hospodarova, V., Singovszka, E. & Stevulova, N. Characterization of Cellulosic Fibers by FTIR Spectroscopy for Their Further Implementation to Building Materials. *Am. J. Anal. Chem.* (2018). doi:10.4236/ajac.2018.96023
118. Gulec, H. A., Topacli, A., Topacli, C., Albayrak, N. & Mutlu, M. Modification of cellulose acetate membrane via low-pressure plasma polymerization for sugar separation applications: Part I. Membrane development and characterization. *J. Memb. Sci.* (2010). doi:10.1016/j.memsci.2010.01.006
119. Poletto, M., Pistor, V., Zeni, M. & Zattera, A. J. Crystalline properties and decomposition kinetics of cellulose fibers in wood pulp obtained by two pulping processes. *Polym. Degrad. Stab.* (2011). doi:10.1016/j.polymdegradstab.2010.12.007
120. Viera, R. G. P. *et al.* Synthesis and characterization of methylcellulose from sugar cane bagasse cellulose. *Carbohydr. Polym.* (2007). doi:10.1016/j.carbpol.2006.05.007
121. Zhu, S. *et al.* Preparation and characterization of a polyethersulfone/polyaniline nanocomposite membrane for ultrafiltration and as a substrate for a gas separation membrane. *RSC Adv.* (2015). doi:10.1039/c4ra16951d
122. Ji, M. *et al.* Commercial polysulfone membranes pretreated with ethanol and NaOH: Effects on permeability, selectivity and antifouling properties. *Sep. Purif. Technol.* (2019). doi:10.1016/j.seppur.2019.03.020
123. Konca, K. Effect of Crosslinking on Organic Solvent Nanofiltration Performance of Cellulose Membranes. *METU Thesis* (2018).
124. Moon, R. J., Beck, S. & Rudie, A. Cellulose Nanocrystals - A Material with

Unique Properties and Many Potential Applications. *Prod. Appl. Cellul. Nanomater.* (2013).

125. Zeman, L. J. & Zydney, A. L. *Microfiltration and ultrafiltration: Principles and applications. Microfiltration and Ultrafiltration: Principles and Applications* (2017). doi:10.1201/9780203747223
126. Granath, K. A. & Kvist, B. E. Molecular weight distribution analysis by gel chromatography on sephadex. *J. Chromatogr. A* (1967). doi:10.1016/s0021-9673(01)85930-6



APPENDICES

A. Sample Deposition Thickness Calculation for Nonporous NCC Layer

- $0.24 \frac{\text{mg NCC amount}}{\text{cm}^2 \text{ membrane area}} = 0.00024 \frac{\text{g NCC amount}}{\text{cm}^2 \text{ membrane area}}$
- $\rho_{\text{nanocrystalline cellulose}} = 1.6 \text{ g/cm}^3$

Assumptions:

1. Homogenous membrane
2. Homogenous deposition on membrane
3. Neglect any forces

Without porosity

$$\text{NCC Volume} = \frac{\text{NCC amount}}{\rho_{\text{nanocrystalline cellulose}}}$$

$$\text{Thickness of deposited layer} = \frac{\text{NCC volume}}{\text{membrane area}} \rightarrow$$

$$\text{Thickness of deposited layer} = \frac{\text{NCC amount}}{\text{membrane area} * \rho_{\text{nanocrystalline cellulose}}}$$

$$\begin{aligned} \text{Thickness of deposited layer} &= 0.00024 \frac{\text{g NCC amount}}{\text{cm}^2 \text{ membrane area}} * \frac{1}{1.6 \frac{\text{g}}{\text{cm}^3}} \\ &= 1.5 * 10^{-4} \text{ cm} = 1.5 \mu\text{m} \end{aligned}$$

B. The Solute (Dye) Calibration Curves for UV-Vis Spectrophotometry

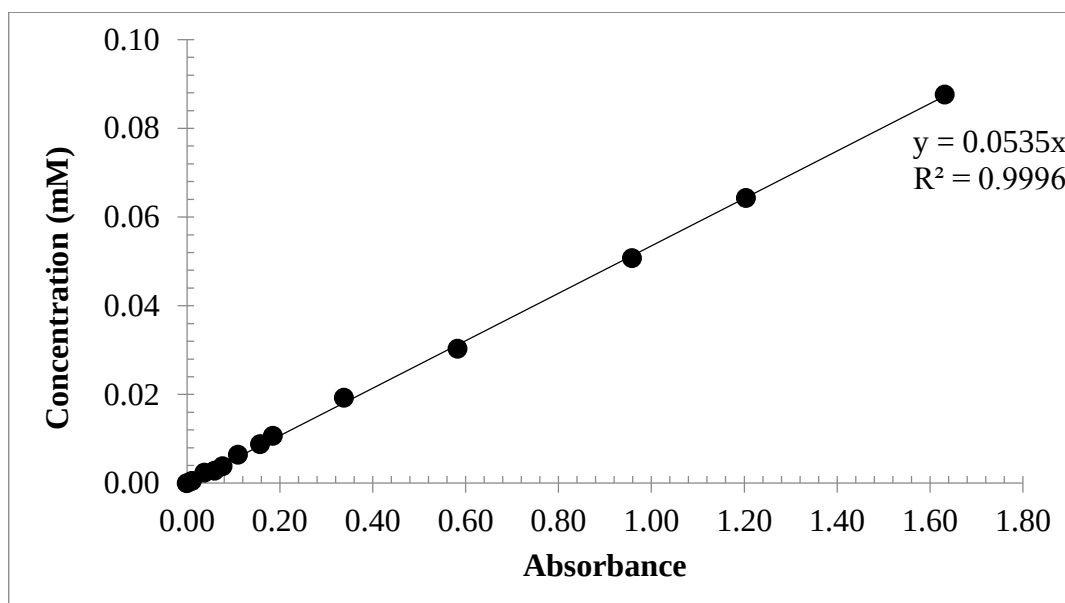


Figure B.1. The calibration curve of BTB/EtOH solution at 423 nm¹²³

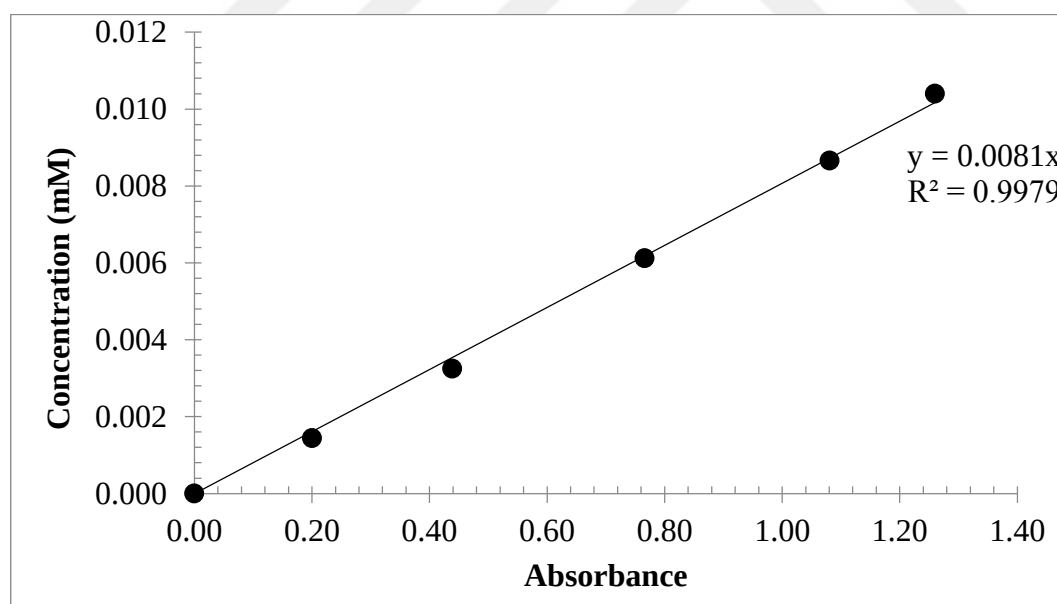


Figure B.2. The calibration curve of RB/EtOH solution at 560 nm¹²³

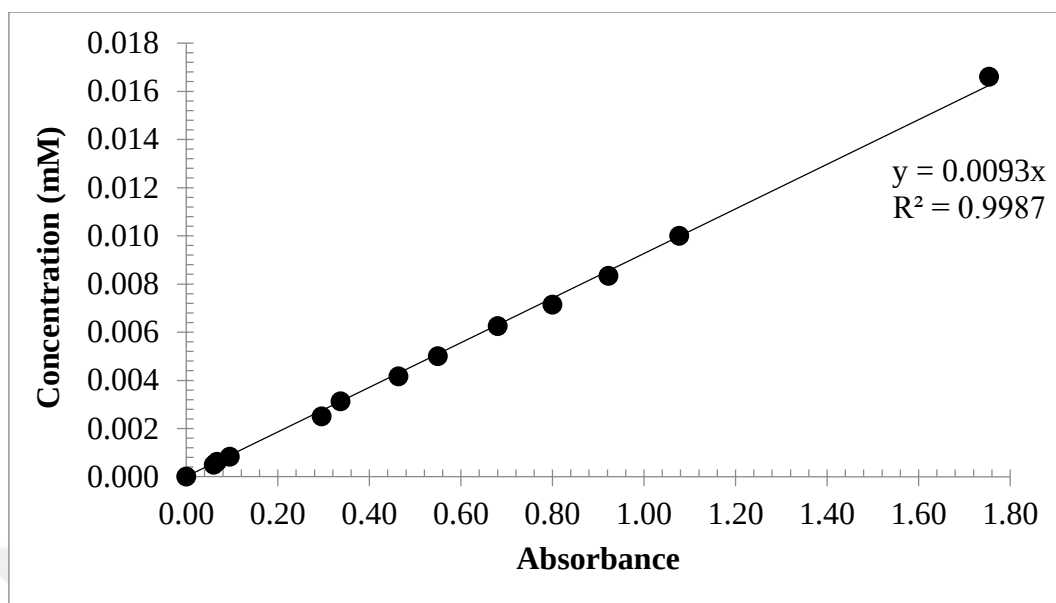


Figure B.3. The calibration curve of CV/EtOH solution at 590 nm¹²³

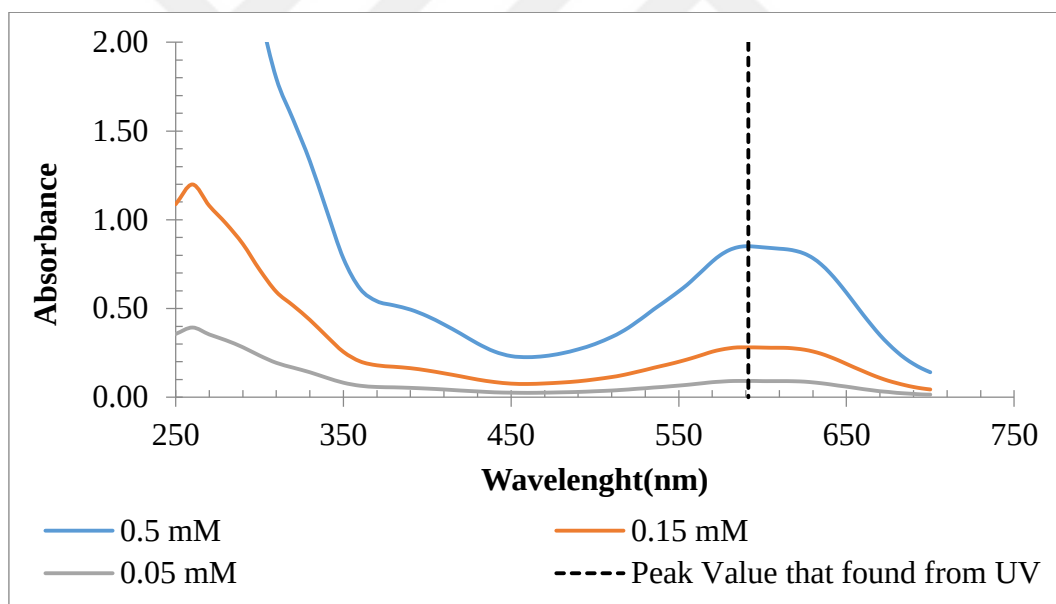


Figure B.4. UV Spectra of BD5/Water solution

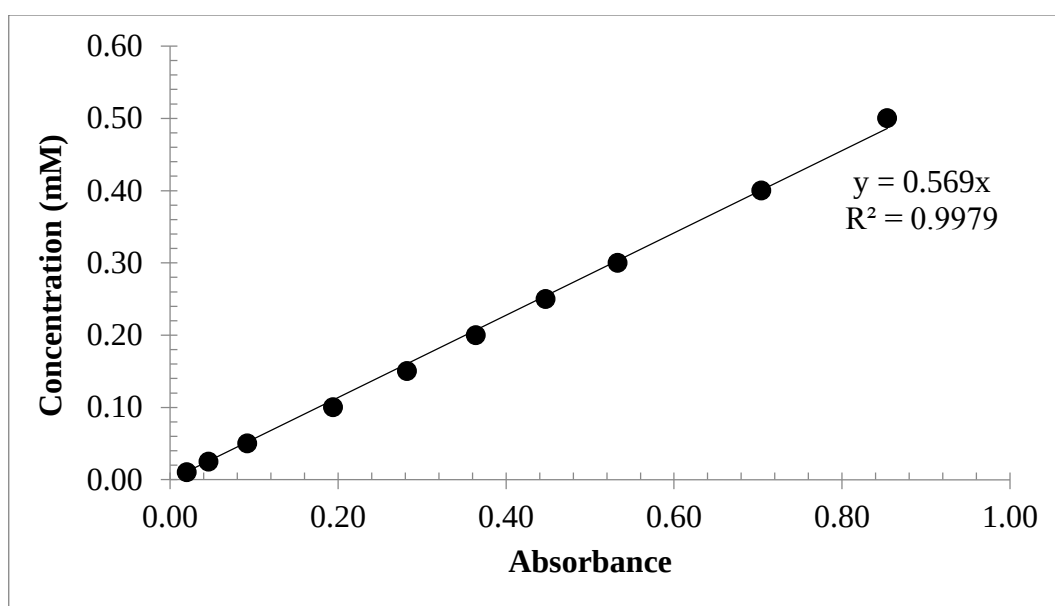


Figure B.5. The calibration curve of BD5/Water solution at 591.5 nm

C. The DLS Analysis Plots for Some of the NCC

The DLS analysis results of some of produced NCC are given in this chapter.

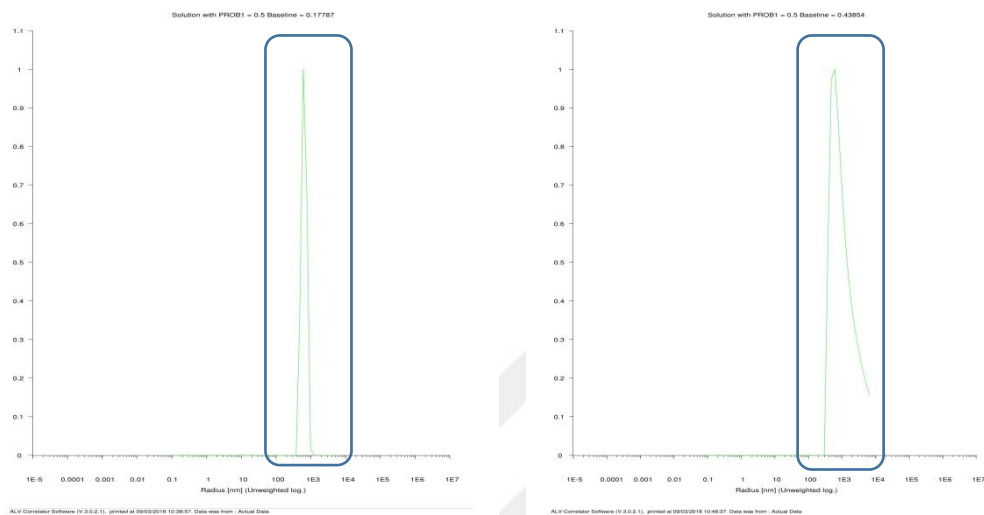


Figure C.6. The DLS analysis plot for NCC-HCl

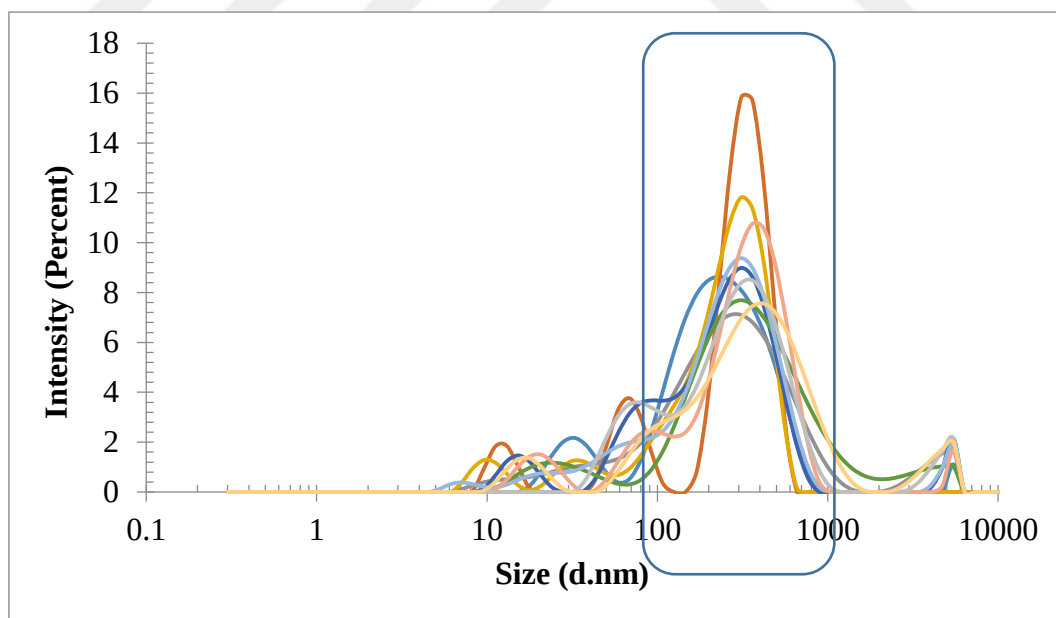


Figure C.7. The DLS analysis plot for NCC50H₂SO₄-cotton-30/10

D. The ATR-FTIR Analysis Results of the NCC Membranes

- The ATR-FTIR Analysis Results of the CA10D-P-S Membranes

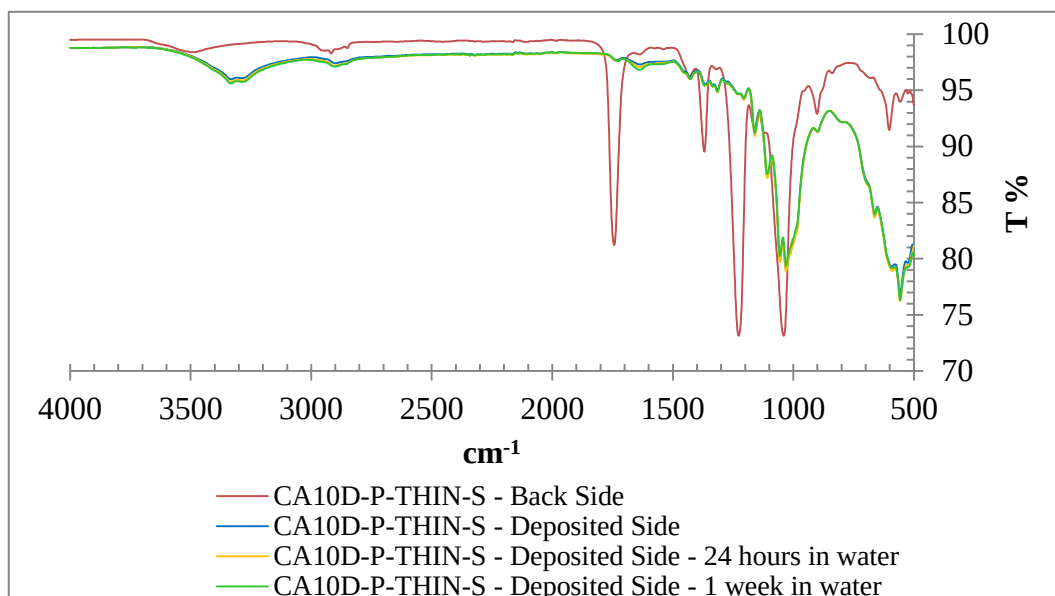


Figure D.8. The ATR-FTIR analysis result for the CA10D-P-THIN-S

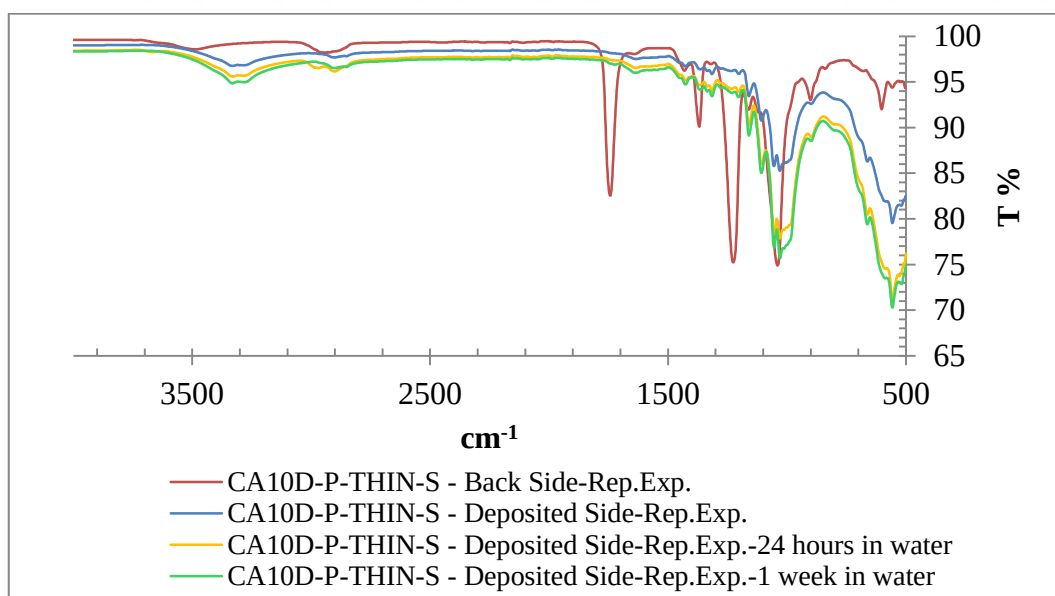


Figure D.9. The ATR-FTIR analysis result for the CA10D-P-THIN-S-Rep.Exp.

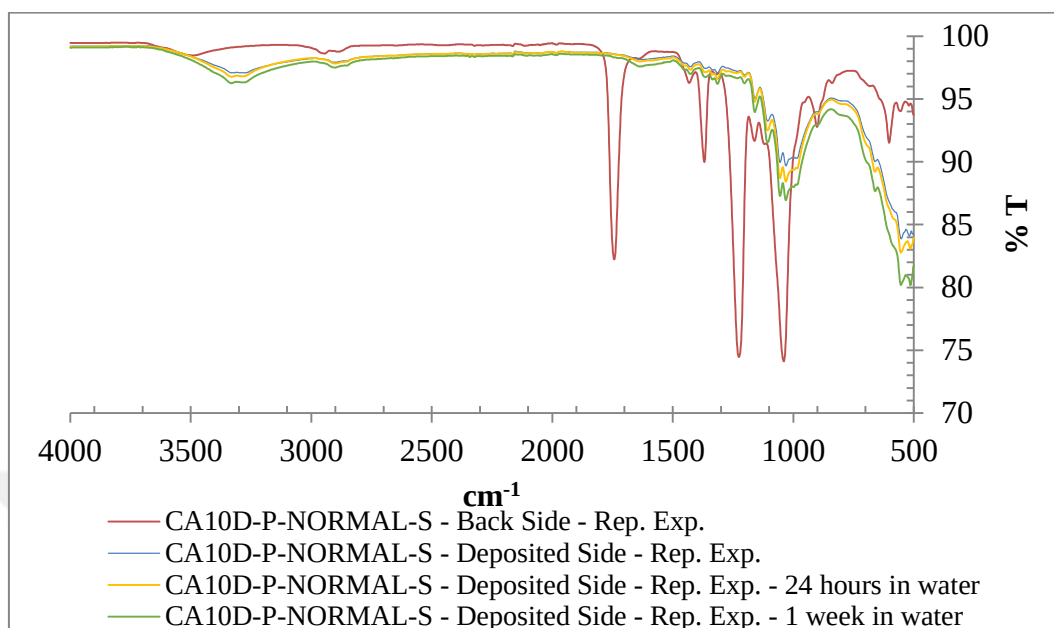


Figure D.10. The ATR-FTIR analysis result for the CA10D-P-NORMAL-S-Rep.Exp.

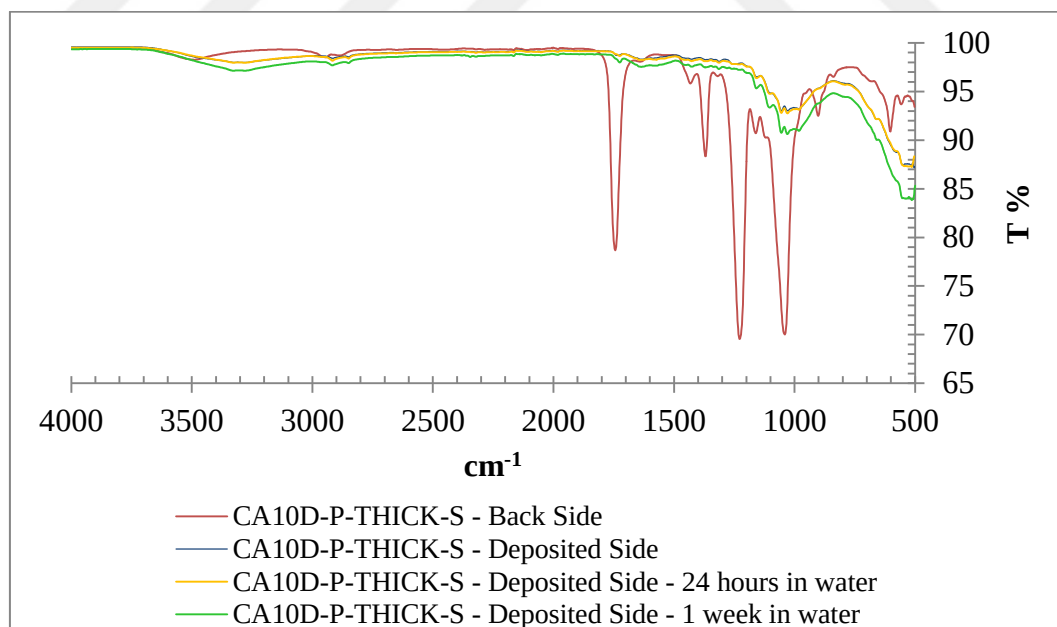


Figure D.11. The ATR-FTIR analysis result for the CA10D-P-THICK-S

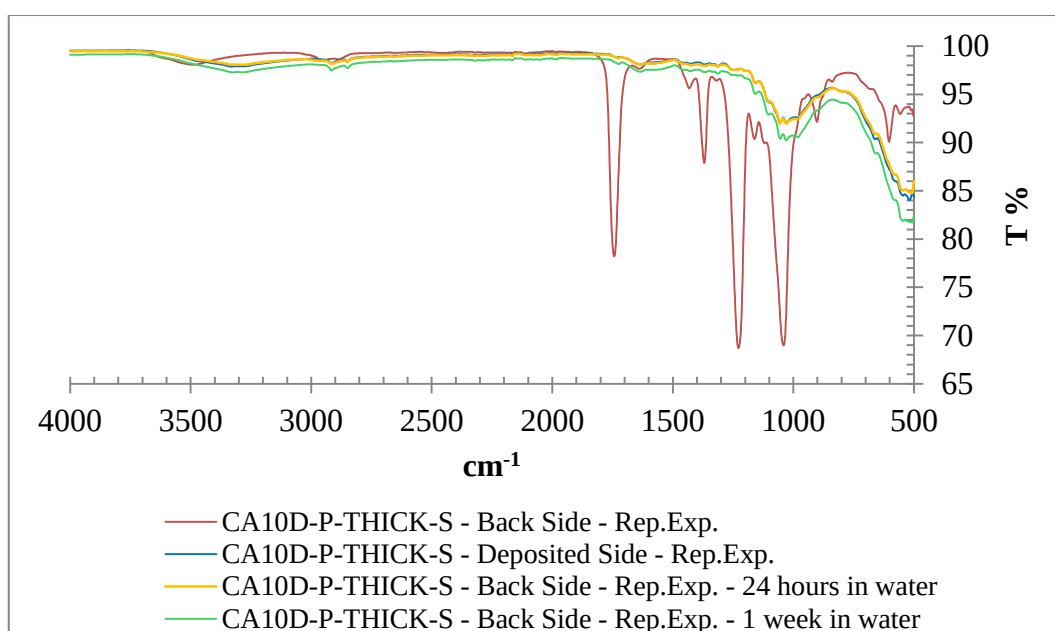


Figure D.12. The ATR-FTIR analysis result for the CA10D-P-THICK-S-Rep.Exp.

Table D.1 The Values of Area under the Cellulose Peak / the Area under the CA Peak for the CA10D-P-S Membranes

Sample Name (NCC Membranes)	Deposited Side		
	Just After Deposition	24 Hours in Water	1 Weeks in Water
CA10D-P-THIN-S	74.3	59.1	57.0
CA10D-P-THIN-S-Rep. Exp.	181	179	121
CA10D-P-NORMAL-S- Rep.	∞	∞	∞
CA10D-P-NORMAL-S- Rep. Exp.	∞	∞	∞
CA10D-P-THICK-S	52.8	48.4	37.5
CA10D-P- THICK –S- Rep. Exp.	107	100	64.0

- **The ATR-FTIR Analysis Results of the CA20D-C-S Membranes**

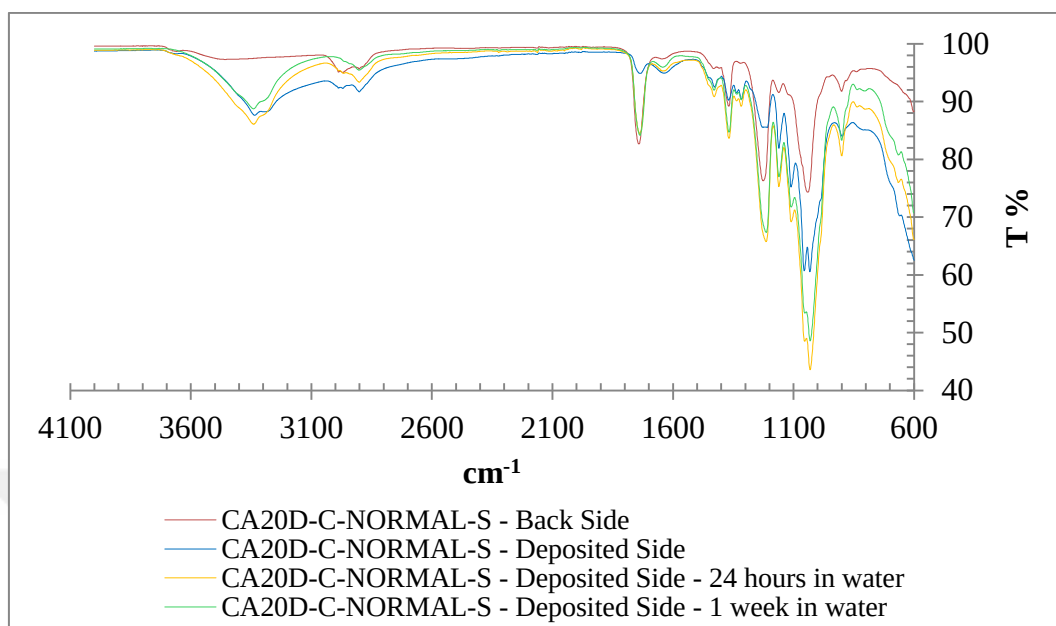


Figure D.13. The ATR-FTIR analysis result for the CA20D-C-NORMAL-S

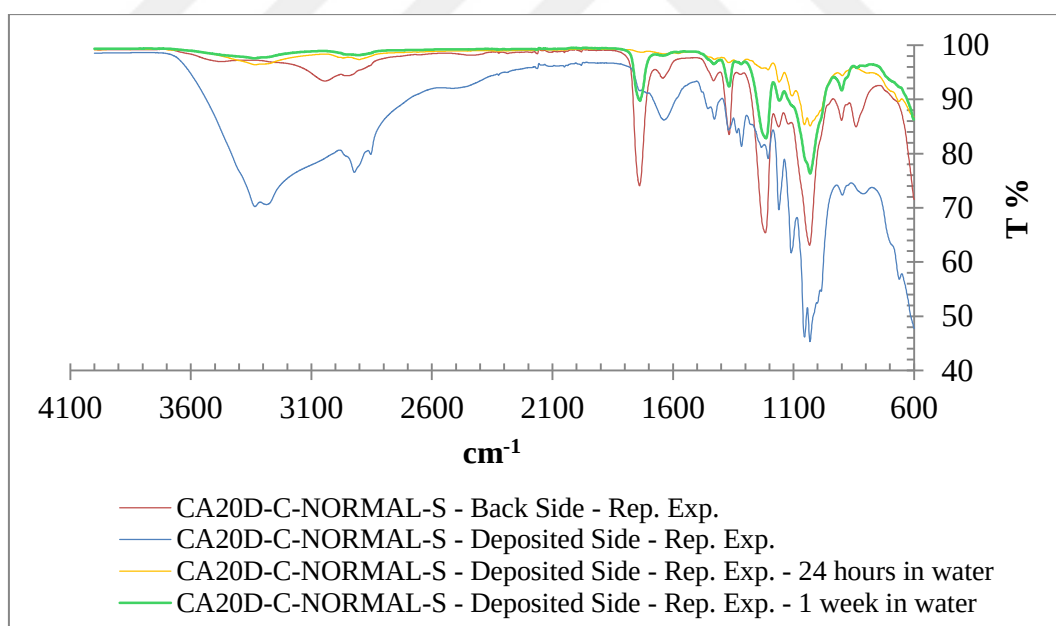


Figure D.14. The ATR-FTIR analysis result for the CA20D-C-NORMAL-S-Rep.
Exp.

Table D.2 The Values of Area Under the Cellulose Peak / the Area Under the CA Peak for the CA20D-C-S Membranes

Sample Name (NCC Membranes)	Deposited Side		
	Just After Deposition	24 Hours in Water	1 Weeks in Water
CA20D-C-NORMAL-S	19.4	5.02	4.02
CA20D-C-NORMAL-S- Rep. Exp.	92.7	49.9	1.16

- **The Fourier Transformation (ATR-FTIR) Analysis Result of the NCC Membrane Prepared By 1 M NaOH**

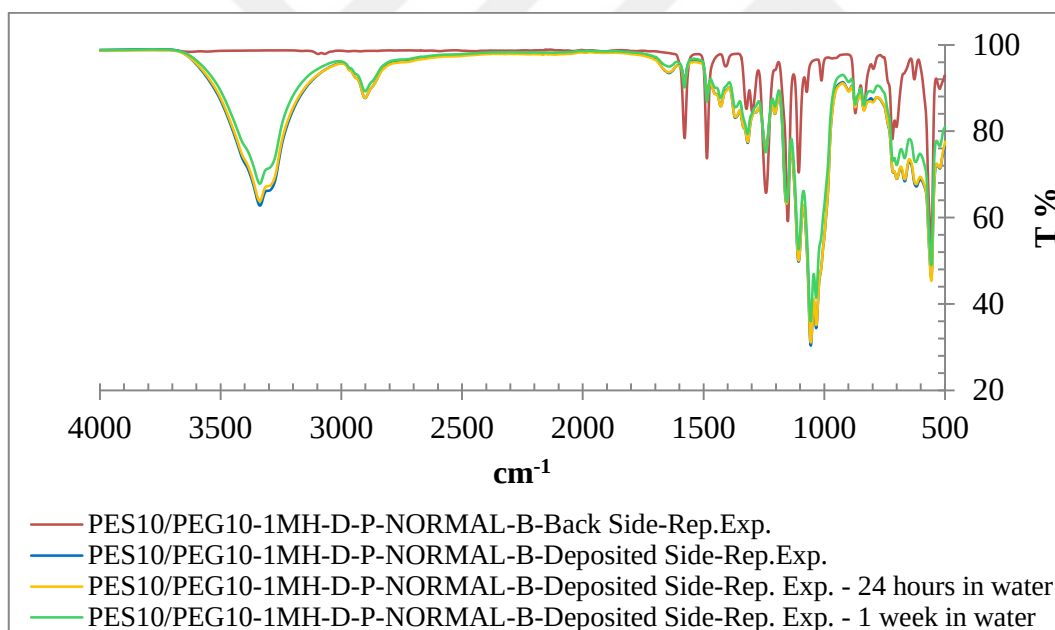


Figure D.15. The ATR-FTIR analysis result for the PES10/PEG10-1MH-D-P-NORMAL-B-Rep.Exp.

E. The Permeance and Average Resistance Results For the NCC Membranes During Deposition Procedure

- The Permeance Results of the CA10D-P-S Membranes

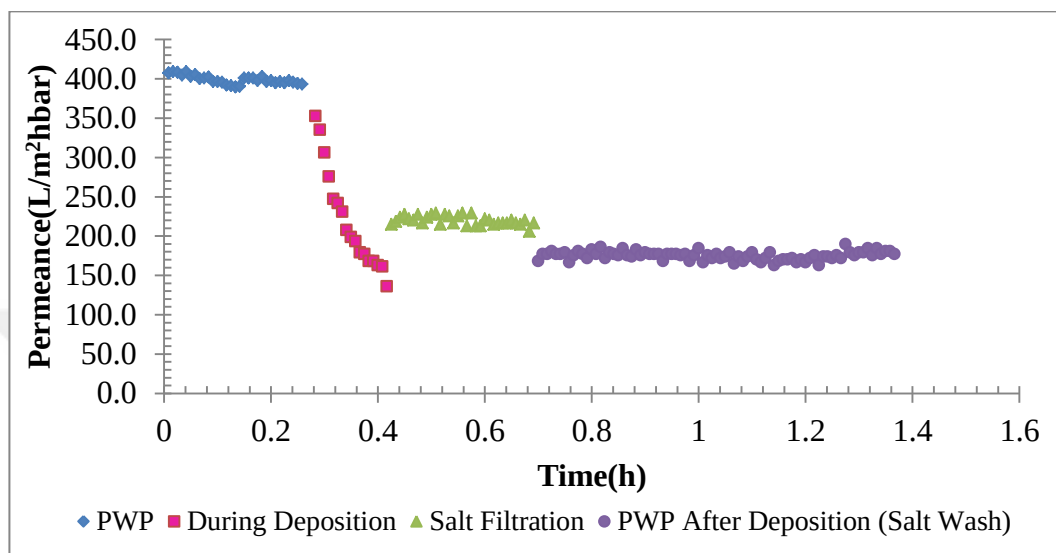


Figure E.16. The permeance results for the CA10D-P-THIN-S during deposition procedure

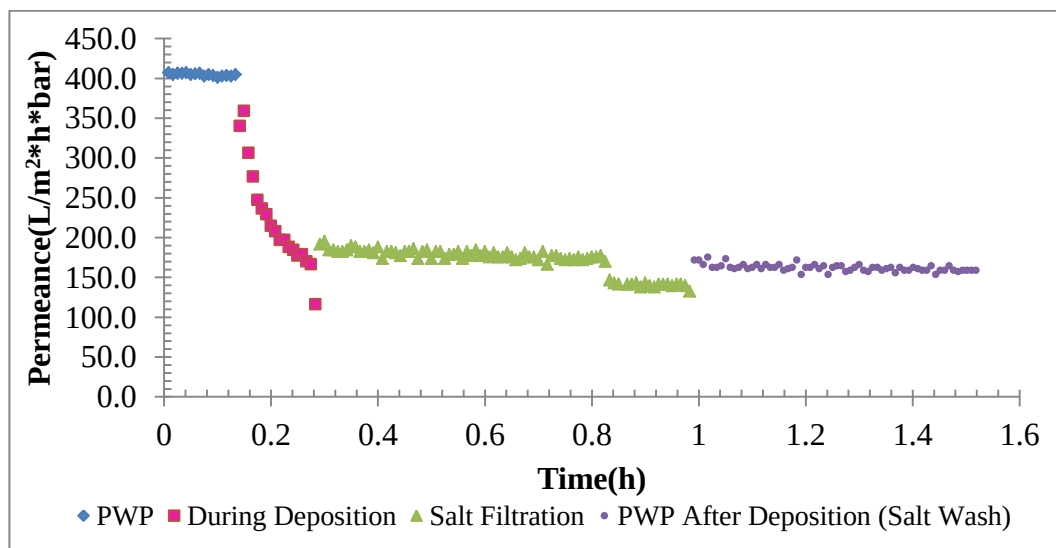


Figure E.17. The permeance results for the CA10D-P-THIN-S-Rep.Exp.1 during deposition procedure

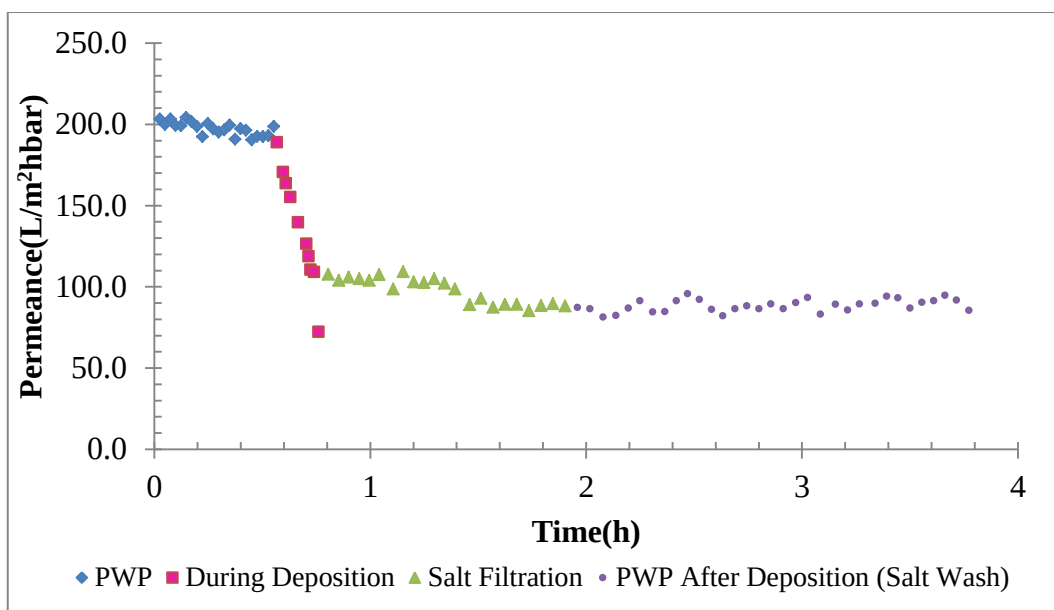


Figure E.18. The permeance results for the CA10D-P-THIN-S-Rep.Exp.2 during deposition procedure (Prepared for BD5 Filtration)

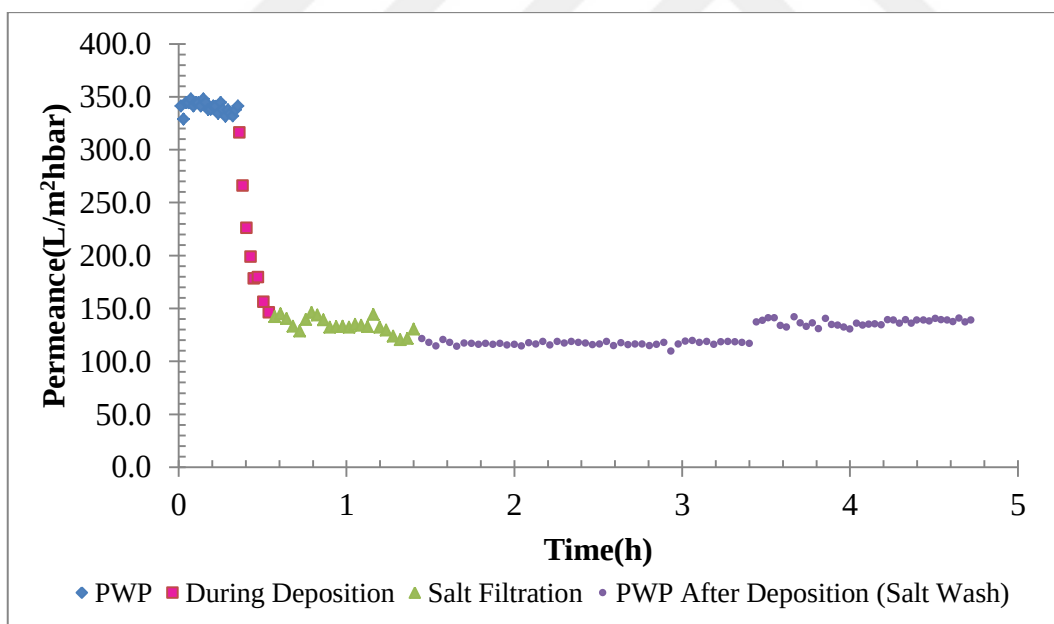


Figure E.19. The permeance results for the CA10D-P-THIN-S-Rep.Exp.3 during deposition procedure (Prepared for BD5 Filtration)

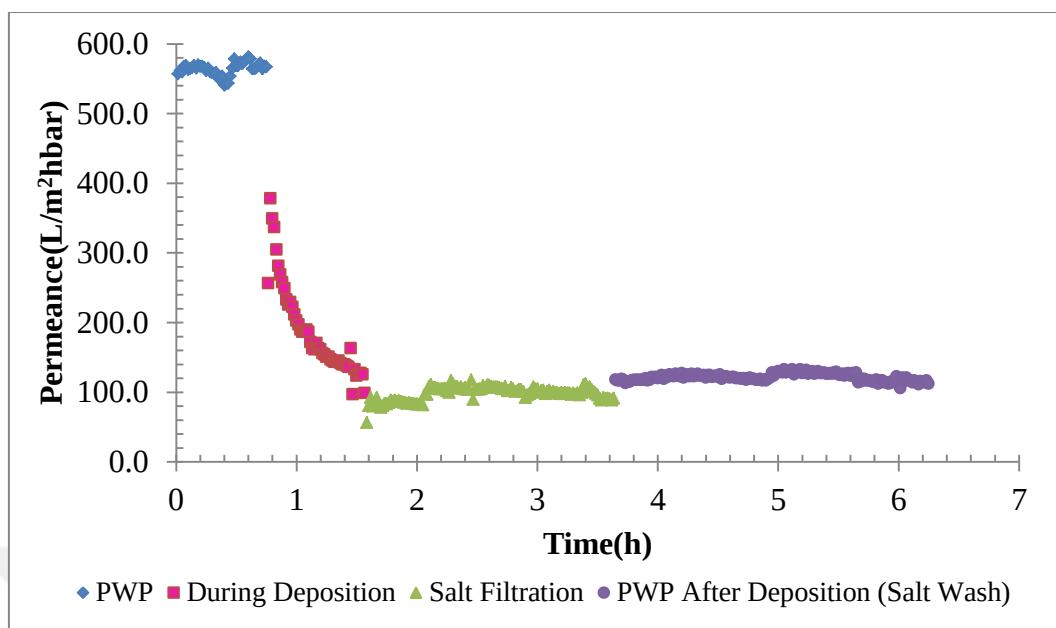


Figure E.20. The permeance results for the CA10D-P-NORMAL-S during deposition procedure

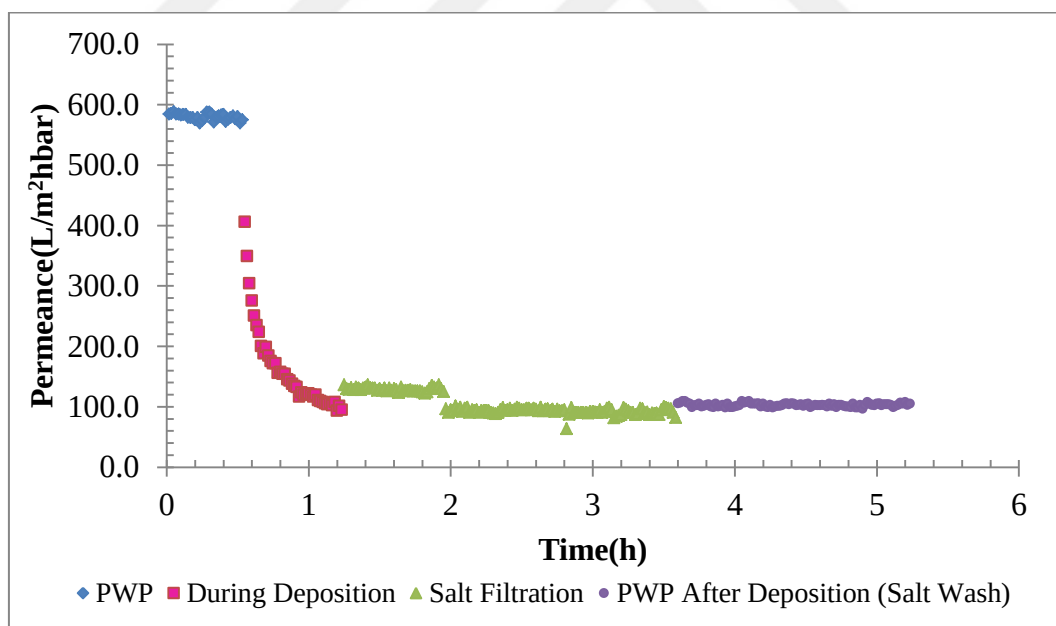


Figure E.21. The permeance results for the CA10D-P-NORMAL-S-Rep.Exp. during deposition procedure

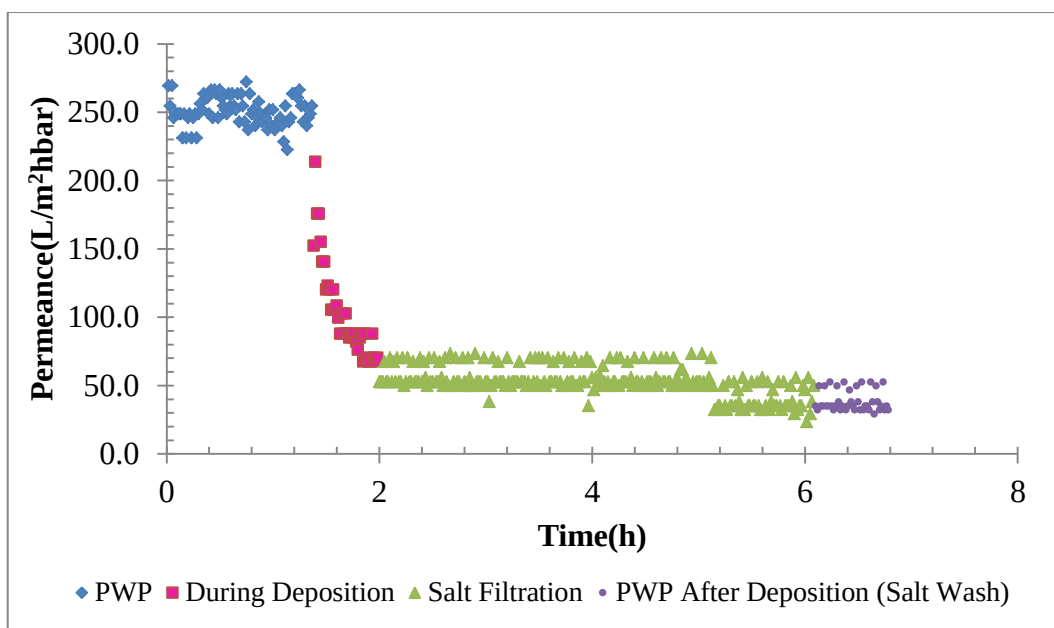


Figure E.22. The permeance results for the CA10D-P-NORMAL-S-Rep.Exp.2 during deposition procedure (For BD5 Filtration)

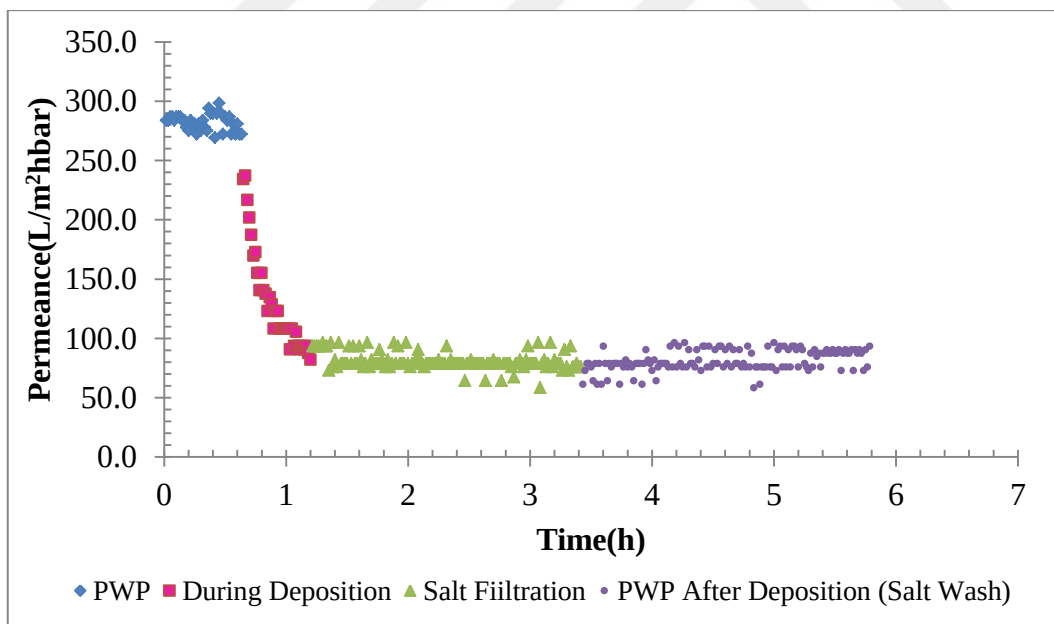


Figure E.23. The permeance results for the CA10D-P-NORMAL-S-Rep.Exp.3 during deposition procedure (For BD5 Filtration)

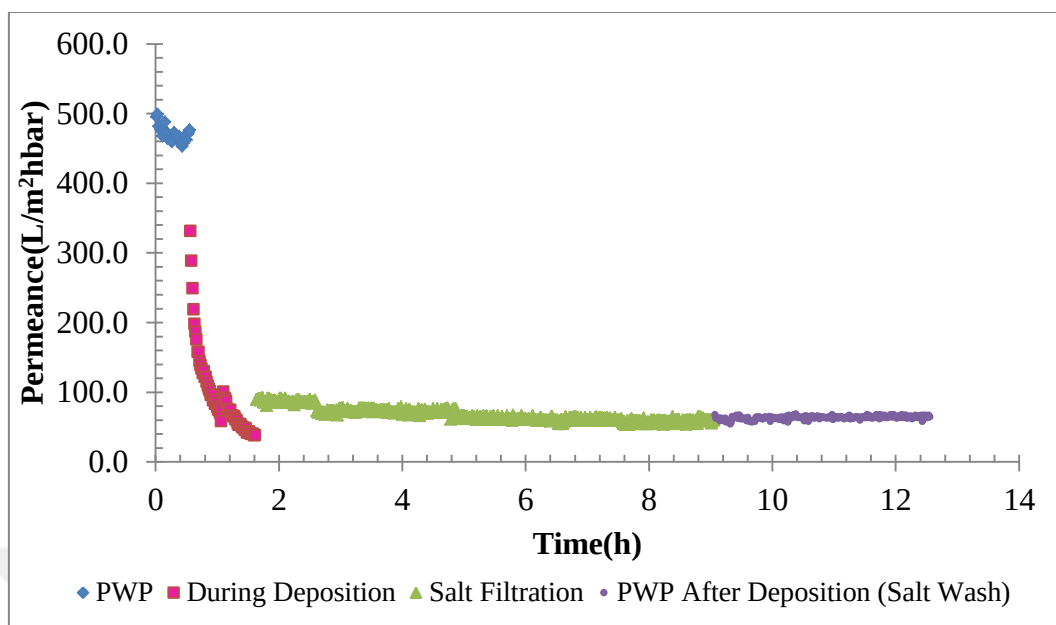


Figure E.24. The permeance results for the CA10D-P-THICK-S during deposition procedure

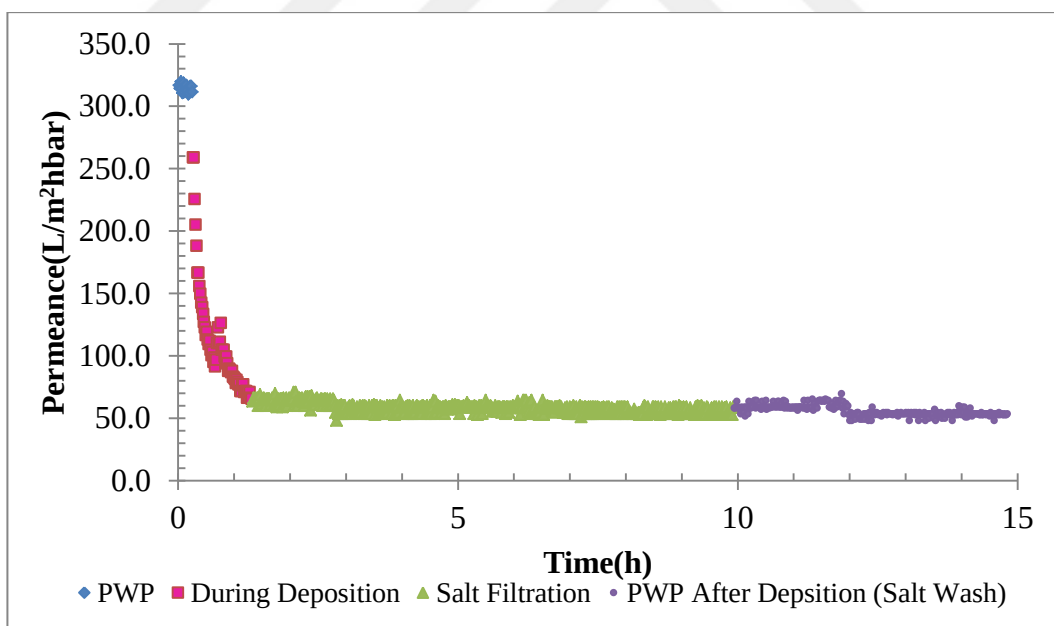


Figure E.25. The permeance results for the CA10D-P-THICK-S-Rep.Exp. during deposition procedure

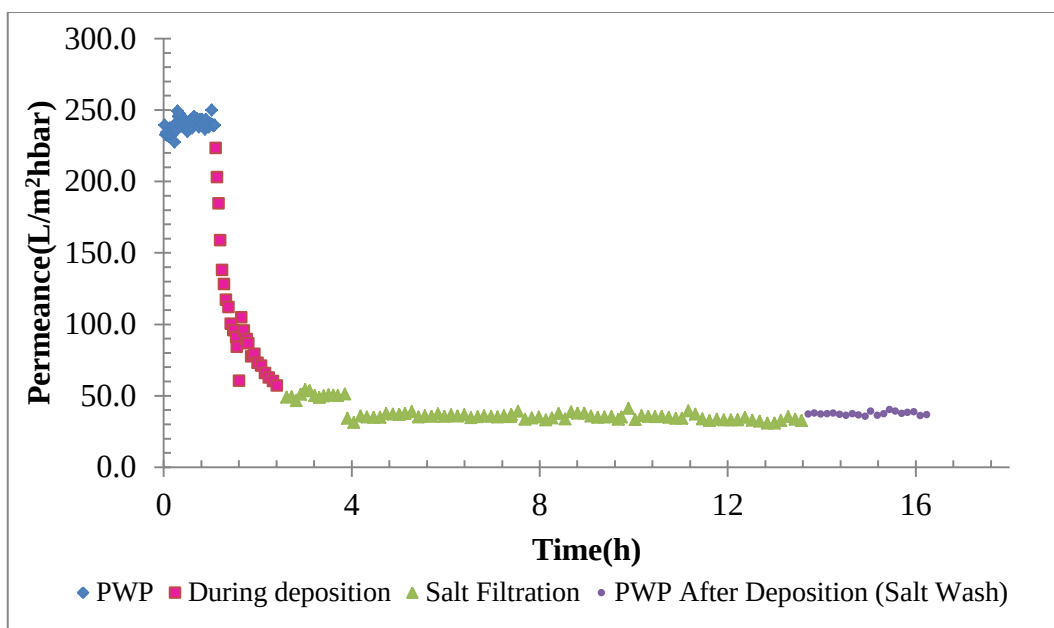


Figure E.26. The permeance results for the CA10D-P- THICK -S-Rep.Exp.2 during deposition procedure (For BD5 Filtration)

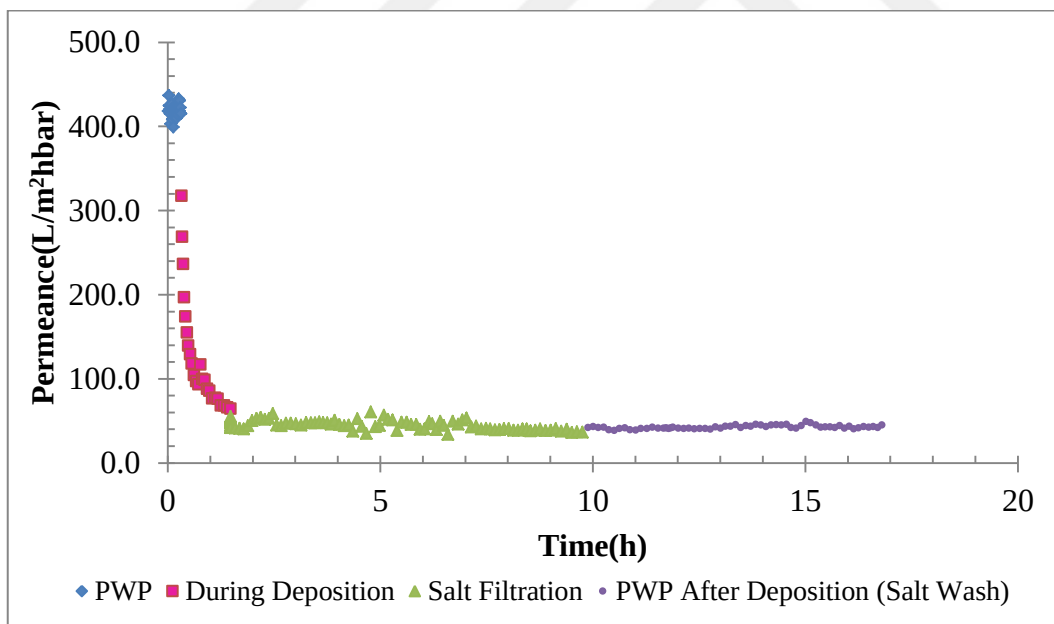


Figure E.27. The permeance results for the CA10D-P- THICK -S-Rep.Exp.3 during deposition procedure (For BD5 Filtration)

- The Average Resistance Results of the CA10D-P-S Membranes

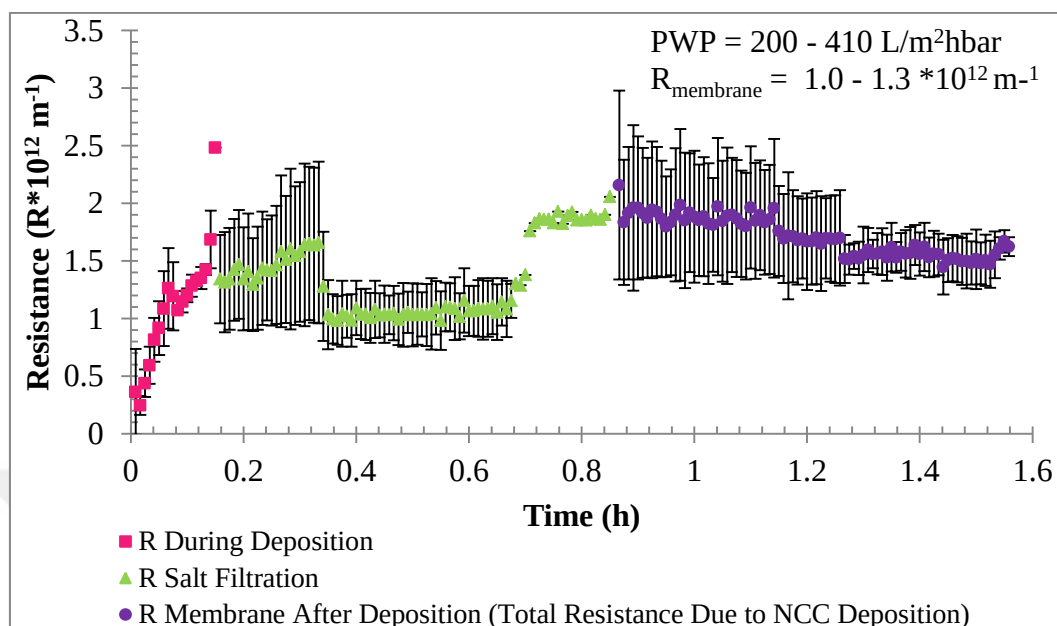


Figure E.28. The resistance values for all the CA10D-P-THIN-S membranes during deposition process

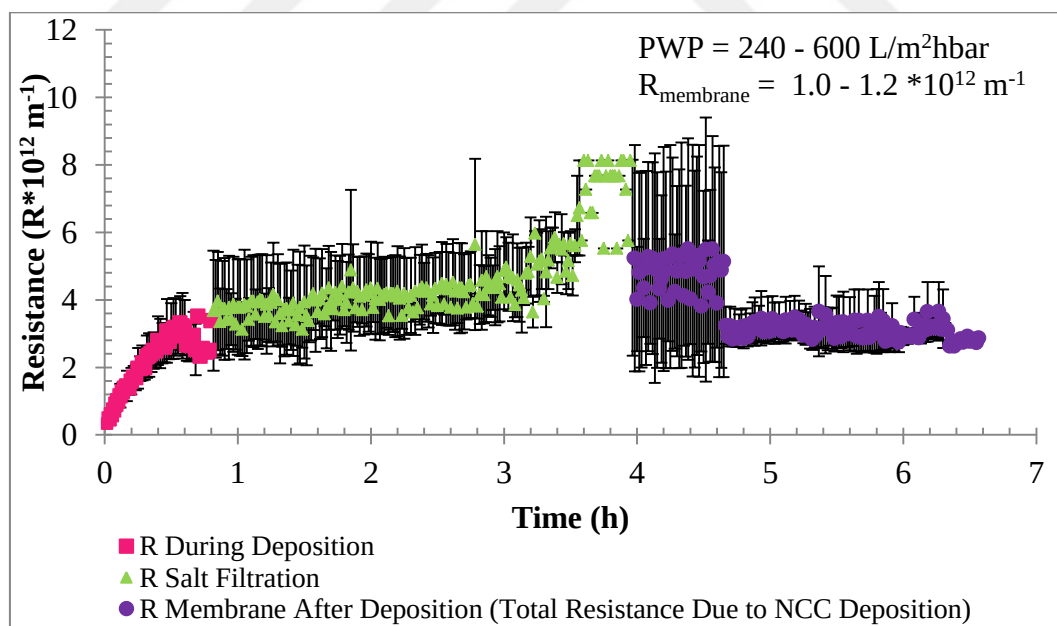


Figure E.29. The resistance values for all the CA10D-P-NORMAL-S membranes during deposition process

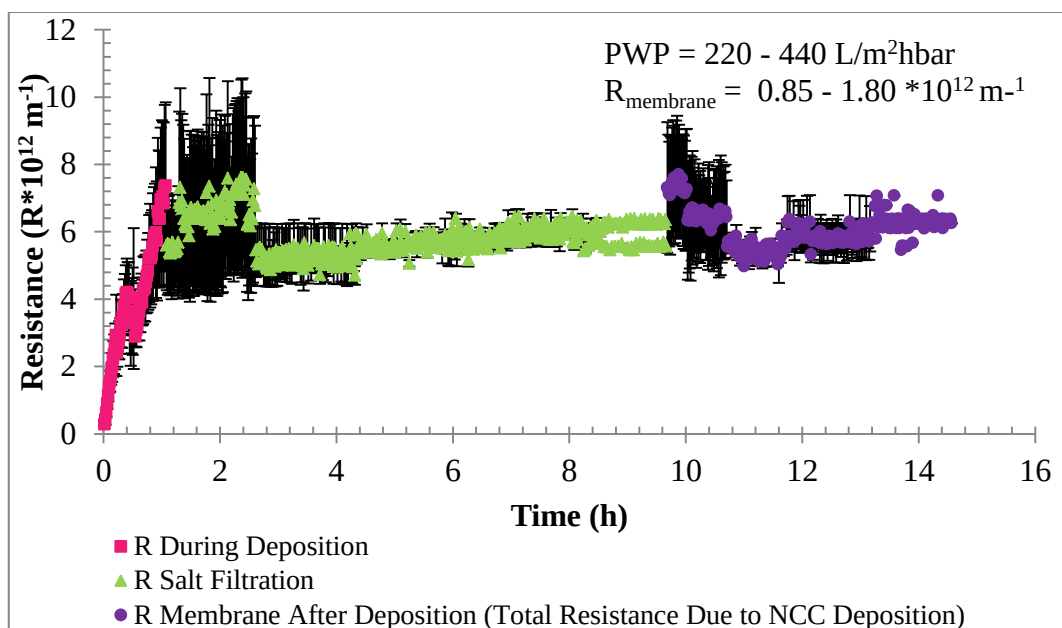


Figure E.30. The resistance values for all the CA10D-P-THICK-S membranes during deposition process

- **The Permeance Results of the CA20D-C-S Membranes**

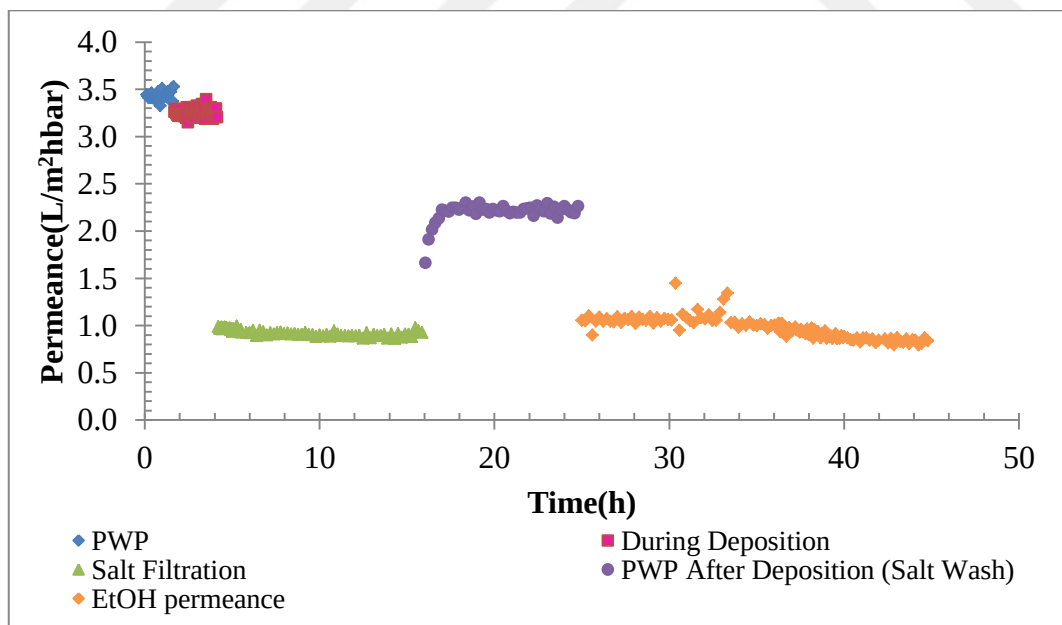


Figure E.31. The permeance results for the CA20C-P-NORMAL-S during deposition procedure (For BTB Filtration)

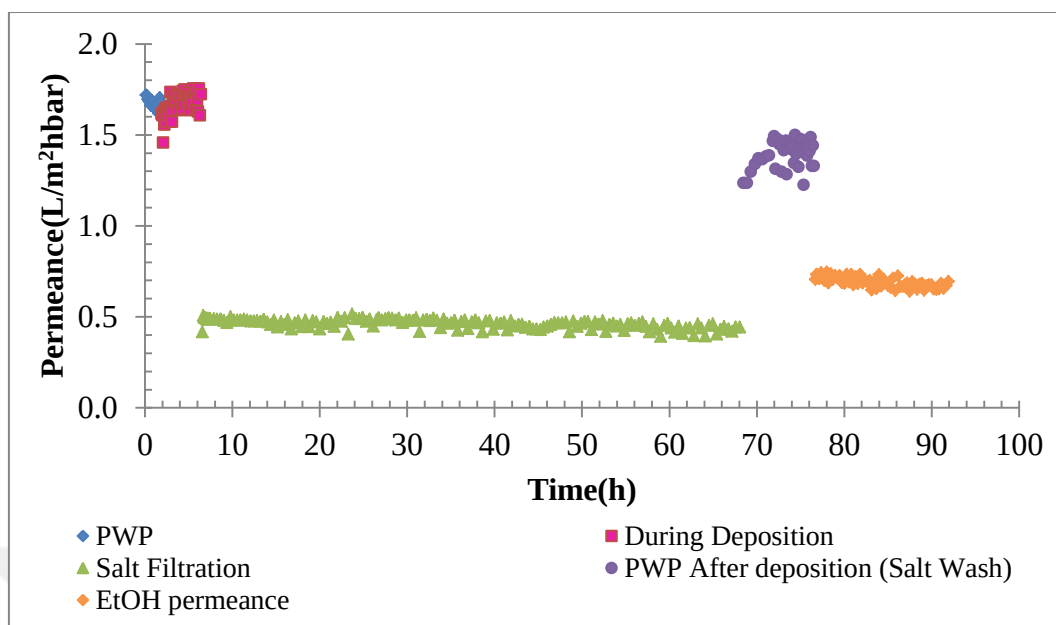


Figure E.32. The permeance results for the CA20C-P-NORMAL-S during deposition procedure (For CV Filtration)

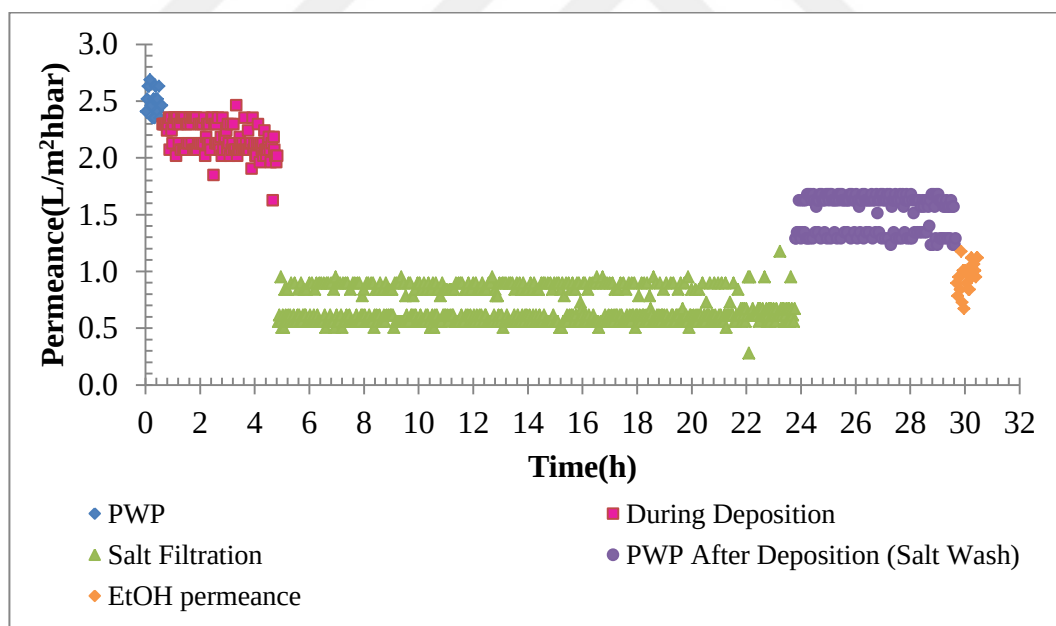


Figure E.33. The permeance results for the CA20C-P-NORMAL-S during deposition procedure (For RB Filtration)

- The Average Resistance Results of the CA20D-C-S Membranes

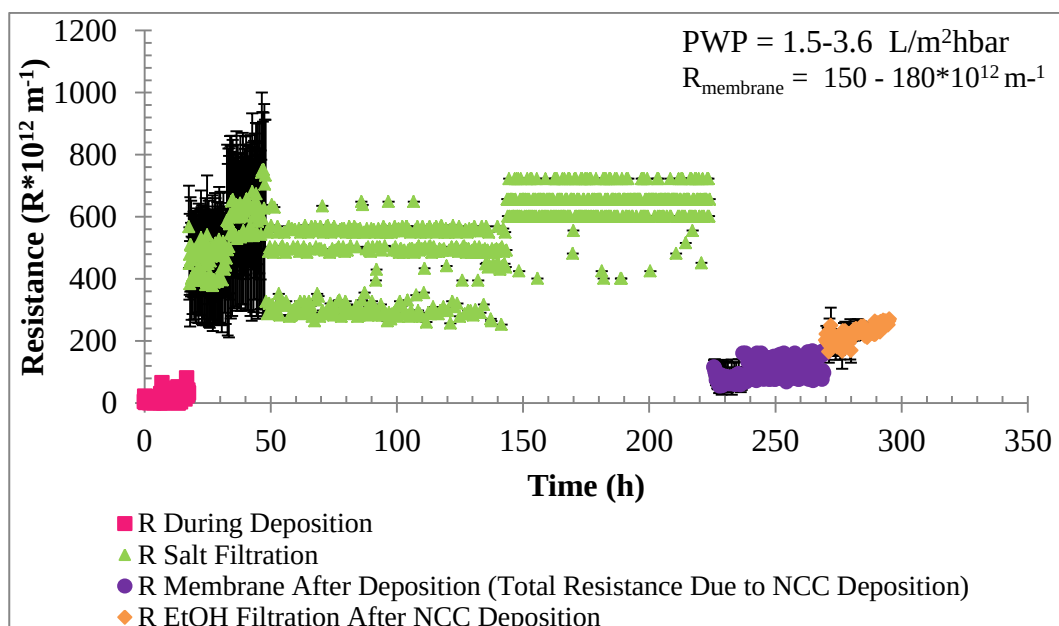


Figure E.34. The resistance values for all the CA20C-P-NORMAL-S membranes during deposition process

- The Permeance Result of the PES10PEG10-1MH-D-P-B

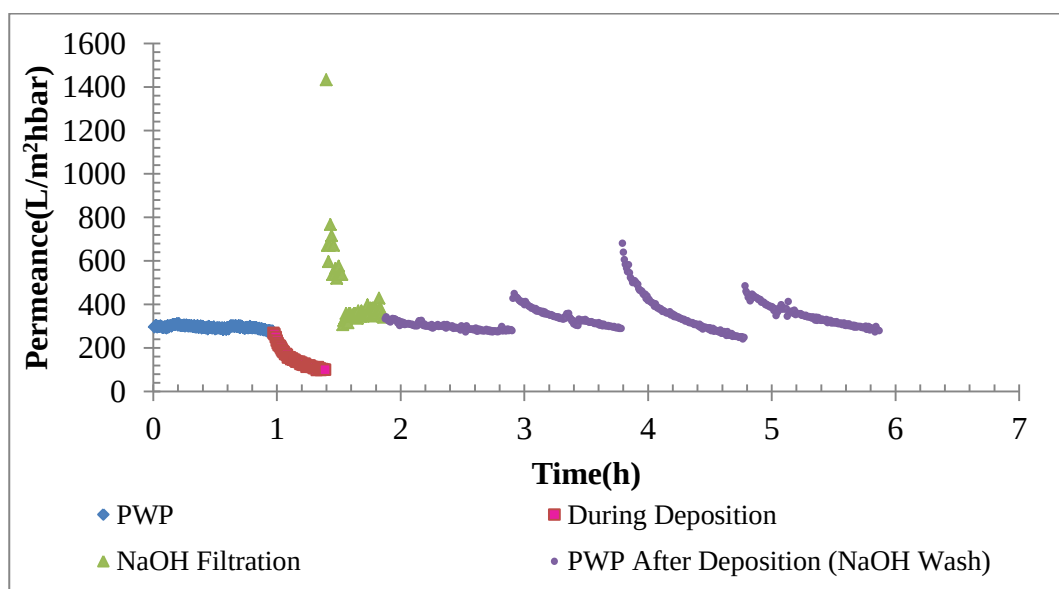


Figure E.35. The permeance results for the PES10PEG10-1MH-D-P-NORMAL-B during deposition procedure

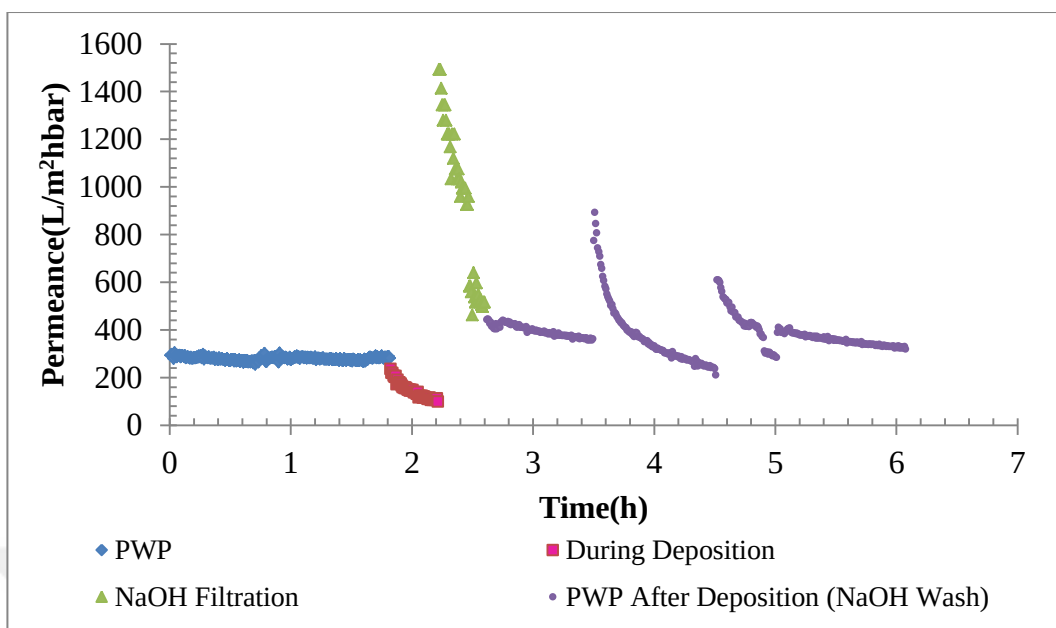


Figure E.36. The permeance results for the PES10PEG10-1MH-D-P-NORMAL-B during deposition procedure-Rep.Exp.

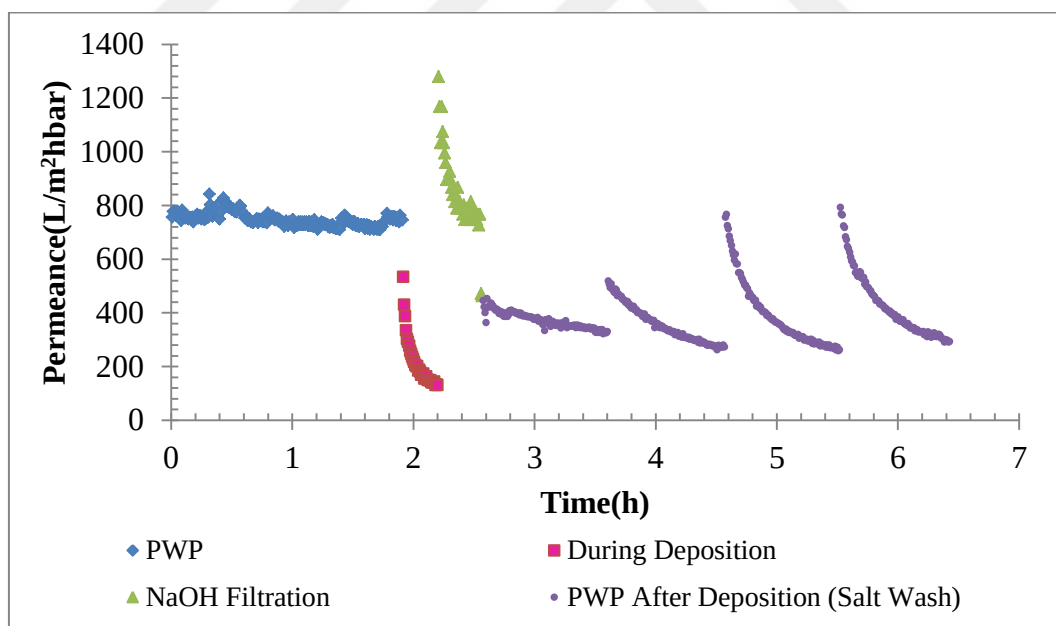


Figure E.37. The permeance results for the PES10PEG10-1MH-D-P-NORMAL-B during deposition procedure-Rep.Exp.2

- The Average Resistance Results of the PES10PEG10-1MH-D-P-NORMAL-B Membranes

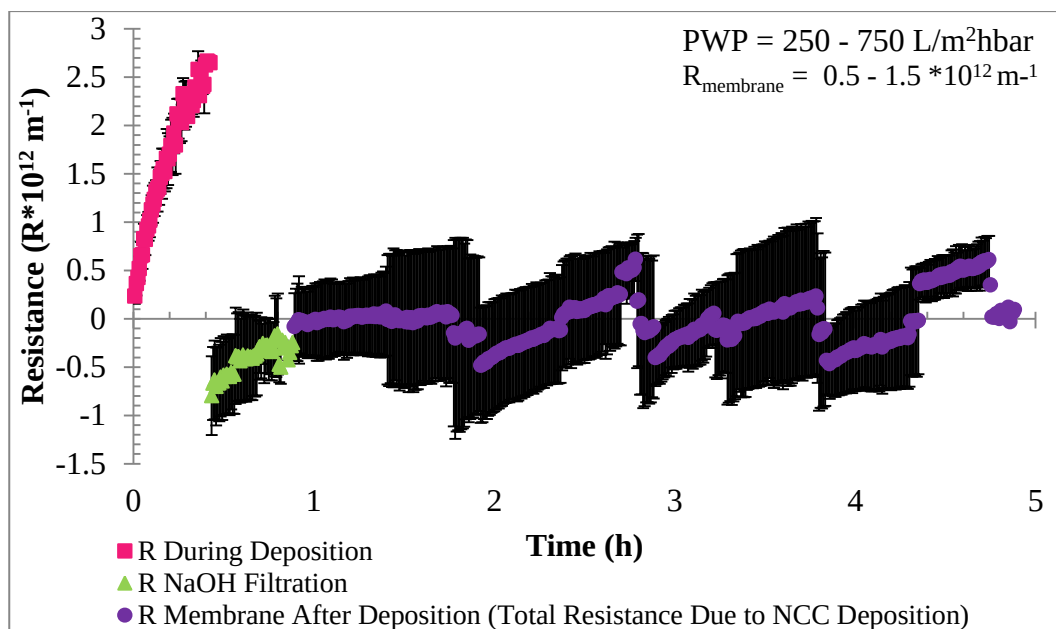


Figure E.38. The resistance values for all the PES10PEG10-1MH-D-P-NORMAL-B membranes during deposition process

F. The Porosity and The Deposited Layer Thickness Calculation Using the Kozeny-Carman Equation for the CA10D-P-S Membranes

To calculate deposited layer porosity theoretically, the Kozeny- Carman equation given in equation (13) was used for dead end filtration mode and 100 % rejection.

$$R_{\text{cake}} = \frac{m_{\text{cake}}}{\rho * (1 - \varepsilon) * A_{\text{membrane}}} * \frac{180 * (1 - \varepsilon)^2}{\varepsilon^3 * (\phi_s D_p)^2} \quad (13)$$

R_{cake} = Specific cake resistance

m_{cake} = Mass of cake

A_{membrane} = Area of membrane

ε = Cake porosity

ρ = Density of particle in cake

ϕ_s = Particle sphericity that represents how close the particle shape to sphere

D_p = Diameter of particle in cake (The diameter of the volume equivalent spherical paricle)⁸⁶

After calculating the porosities from the Kozeny-Carman equation, the equation (14) was used to calculate the deposited layer thickness.

$$\delta = \frac{m_{\text{cake}}}{\rho * (1 - \varepsilon) * A_{\text{membrane}}} \quad (14)$$

During calculations, $\frac{m_{\text{cake}}}{A_{\text{membrane}}}$ was taken as 0.12, 0.24 and 0.48 $\frac{\text{mg}}{\text{cm}^2}$ for thin, normal and thick thickness membrane depositions, respectively. Density of NCC was found as 1.6 $\frac{\text{g}}{\text{cm}^3}$ ¹²⁴. Also, sphericity (ϕ) was calculated using equation (15);

$$\phi = \frac{6}{\frac{D_p}{S} \frac{S}{V}} \quad (15)$$

S = Surface area of particle

V = Volume of particle

To calculate surface area and volume of the particle, due to rod like shape of the NCC, the NCC was assumed as cylinder, and the length and width of the particle was taken from the SEM images as 247 nm as length and 27 nm as width (diameter) of the particle.

The sample calculation for one of the CA10D-P-NORMAL-S membrane is given below. The other CA10D-P-S membranes calculations were made using similar way.

- **Sample Calculation For the CA10D-P-NORMAL-S-Rep. Exp. ;**

$$R_{\text{due to NCC Deposition}} = R_{\text{cake}} = 3.16 * 10^{12} \text{ m}^{-1}$$

$$\frac{m_{\text{cake}}}{A_{\text{membrane}}} = 0.24 \frac{\text{mg}}{\text{cm}^2} = 2.4 \frac{\text{g}}{\text{m}^2}$$

$$\rho = 1.6 \frac{\text{g}}{\text{cm}^3} = 1.6 * 10^6 \frac{\text{g}}{\text{m}^3}$$

$$V = \pi * r^2 * h = \pi * \frac{(27 \text{ nm})^2}{4} * 247 \text{ nm} = 141421.2 \text{ nm}^3 = 1.41 * 10^{-22} \text{ m}^3$$

$$\begin{aligned} S &= 2 * \pi * r^2 + 2 * \pi * r * h = 2 * \pi * \frac{(27 \text{ nm})^2}{4} + 2 * \pi * \frac{27 \text{ nm}}{2} * 247 \text{ nm} \\ &= 22069.39 \text{ nm}^2 = 2.21 * 10^{-14} \text{ m}^2 \end{aligned}$$

Then, the equation (15) was put into the equation (13) to eliminate D_p term.

$$R_{\text{cake}} = \frac{m_{\text{cake}}}{\rho * (1 - \varepsilon) * A_{\text{membrane}}} * \frac{180 * (1 - \varepsilon)^2}{\varepsilon^3 * \left(\frac{D_p}{\frac{S}{V}} * D_p \right)^2}$$

Finally, the equation (13) can be written like;

$$R_{\text{cake}} = \frac{m_{\text{cake}}}{\rho * (1 - \epsilon) * A_{\text{membrane}}} * \frac{180 * (1 - \epsilon)^2}{\epsilon^3 * \left(\frac{6V}{S}\right)^2}$$

After putting these values into the rewritten equation (13);

$$3.16 * 10^{12} \text{ m}^{-1} = \frac{2.4 \frac{\text{g}}{\text{m}^2}}{1.6 * 10^6 \frac{\text{g}}{\text{m}^3} * (1 - \epsilon)} * \frac{180 * (1 - \epsilon)^2}{\epsilon^3 * \left(\frac{6 * 1.41 * 10^{-22} \text{ m}^3}{2.21 * 10^{-14} \text{ m}^2}\right)^2}$$

From this equation, the porosity was found as;

$$\epsilon \cong 0.34$$

After that, using porosity value, the thickness of deposited layer was calculated by equation (14);

$$\delta = \frac{2.4 \frac{\text{g}}{\text{m}^2}}{1.6 * 10^6 \frac{\text{g}}{\text{m}^3} * (1 - 0.34)} = 2.27 * 10^{-6} \text{ m} = 2.27 \mu\text{m}$$

After calculating the porosity and the thickness of deposited NCC layer for all membranes, the average of these values was taken to compare results with SEM image results. These results were given in Table 4.6. After calculating the permeance values for deposition procedure and the resistance values due to the NCC deposition for the CA10D-P-S membranes, the porosity and the thickness of the NCC deposited layer were calculating using the Kozeny-Carman equation. The calculated thickness of the deposited NCC layer is belongs to wet NCC deposit layer.

G. The Precipitation of the Commercial NCC on the CA20 Support Membrane with HCl

- **Experimental Procedure to Prepare the NCC Membranes via Precipitation of the Commercial NCC on the CA20 Support Membrane with HCl**

To produce membranes using deposition method, firstly, the support membrane pure water permeance values were measured until reaching stable permeance value. Then, the nanocrystalline cellulose was dispersed completely into water using a magnetic stirrer and ultrasonic bath for commercial NCC. To prevent over heating during NCC dispersion in water by ultra-sonication procedure, the ice bath was used. The deposition NCC amount was determined as 3.4 mg for the membrane with a surface area of 13.4 cm² and 1 mg for the membrane with a surface area of 4.1 cm² for commercial NCC. After dispersing the NCC into water, the nanocrystalline cellulose was filtered through the membrane surface. To understand whether the NCC stays on the membrane surface or not, the turbidity of feed and the turbidity of permeate were controlled before and after the deposition procedure. After that, to decrease the NCC's stability and increase the NCC membrane stability i.e. to change the zeta potential of the commercial NCC on the support membrane surface, 1 M, 0.01 M or 0.005 M HCl (500 ml) was filtered through the commercial NCC deposited CA20 membrane. Filtration of HCl was done Buhner funnel via vacuum filtration as shown in Figure G.39 for 1 M and 0.01 M HCl filtration and Amicon stirrer cell for 0.005 M HCl filtration.. As a final step of deposition procedure, to wash NCC membrane from remaining acid, pure water was filtered through the NCC membrane. The permeance values of each step were recorded to see effects of these steps on support membrane and NCC membrane. These NCC membranes were called as of CA20D-C-NORMAL-1 M HCl, CA20D-C-NORMAL-0.01 M HCl and of CA20D-C-NORMAL-0.005 M depending on the filtrated HCl concentration.

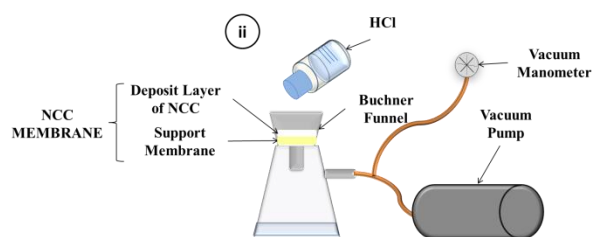


Figure G.39. Schematic representation of HCl filtration on the commercial NCC deposited CA20 support membrane

- **The ATR-FTIR Analysis Results of the NCC Membranes Prepared By Different HCl Concentrations**

The ATR-FTIR analysis results of the NCC membranes prepared using different HCl concentrations are given in Figure G.40, Figure G.41 and Figure G.42.

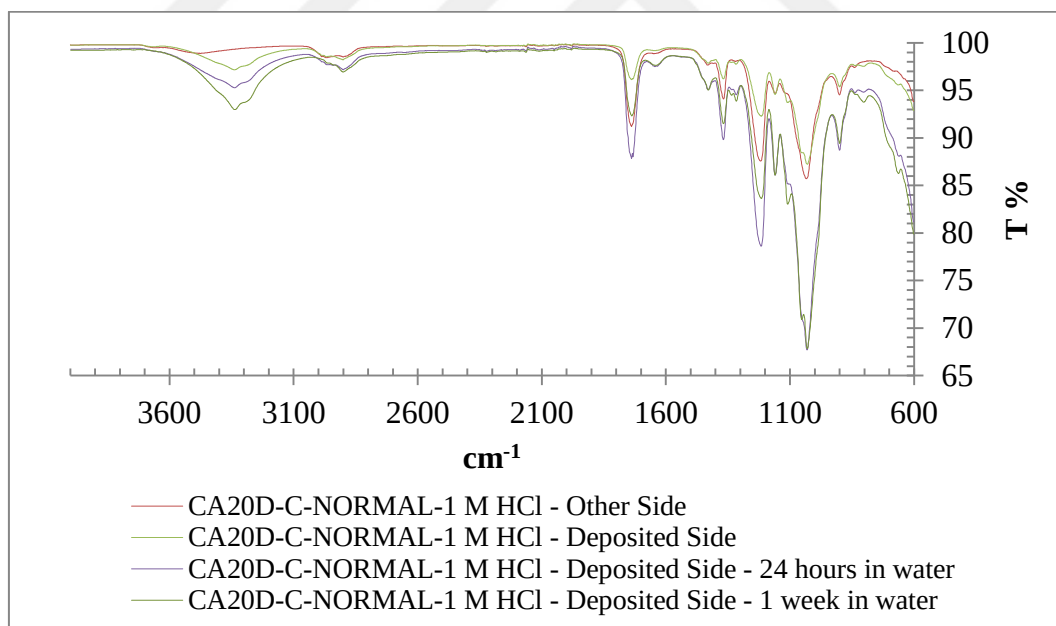


Figure G.40. The ATR-FTIR analysis result for the CA20D-C-NORMAL-1 M HCl

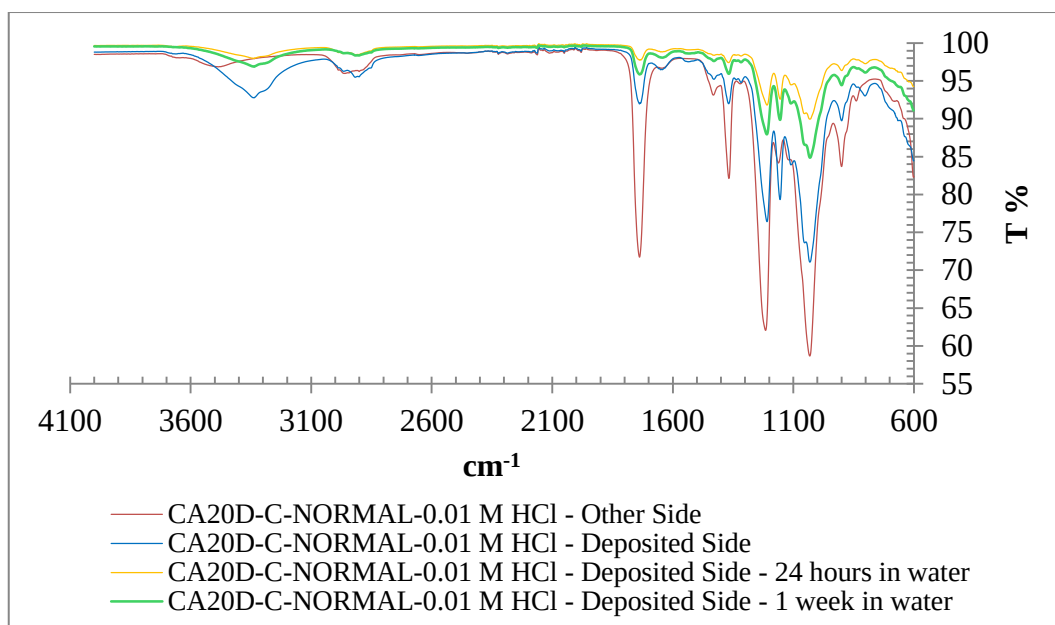


Figure G.41. The ATR-FTIR analysis result for the CA20D-C-NORMAL-0.01 M HCl

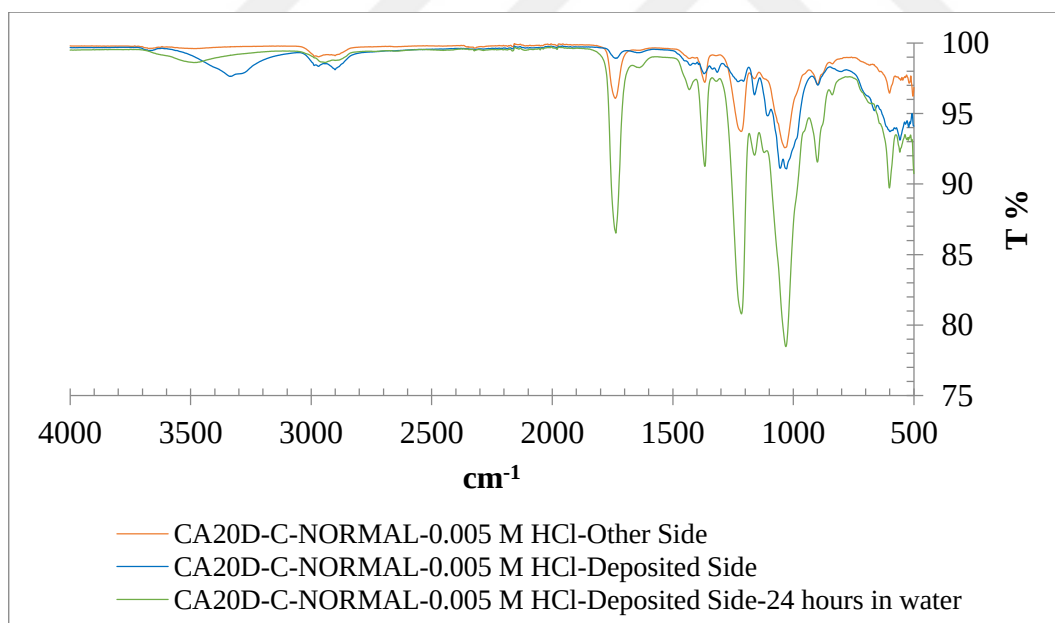


Figure G.42. The ATR-FTIR analysis result for the CA20D-C-NORMAL-0.005 M HCl

The cellulose peak/ cellulose acetate peak values are given in Table G.3 for all the NCC membranes prepared with HCl.

Table G.3 The Values of Area under the Cellulose Peak / the Area under the CA Peak for the NCC Membranes Prepared Using Different HCl Concentrations

Sample Name (NCC Membranes)	Deposited Side		
	Just After Deposition	24 Hours in Water	1 Weeks in Water
CA20D-C-NORMAL-1 M HCl	3.24	5.27	5.03
CA20D-C-NORMAL-0.01 M HCl	4.73	5.32	4.11
CA20D-C-NORMAL-0.005 M HCl	15.6	0.39	-

When the area under the peak ratio values were examined, it was observed that the stability of the NCC on the surface of the support membranes is high (As the time that the membrane waits in the water increases, the ratio of the area under the peaks is close to just after deposition ratio.). However, when the concentration value of the HCl decreases, the NCC on the surface lose their stability; however, the high HCl concentration values are damaged on cellulose acetate membranes. Besides, in the contrary of salt experiments, the CA peak (-CO stretching) always present in the NCC membrane deposited surface.

- **The Scanning Electron Microscope (SEM) Analysis Results of the Support and the NCC Membranes**

The SEM images of the CA20D-C-NORMAL-1 M HCl, the CA20D-C-NORMAL-0.01 M HCl and the CA20 support membranes were investigated to determine surface and cross section morphologies before and after deposition procedure. The surface SEM images of the CA20D-C-NORMAL-1 M HCl, the CA20D-C-NORMAL-0.01 M HCl and the CA20 membranes are given in Figure G.43.

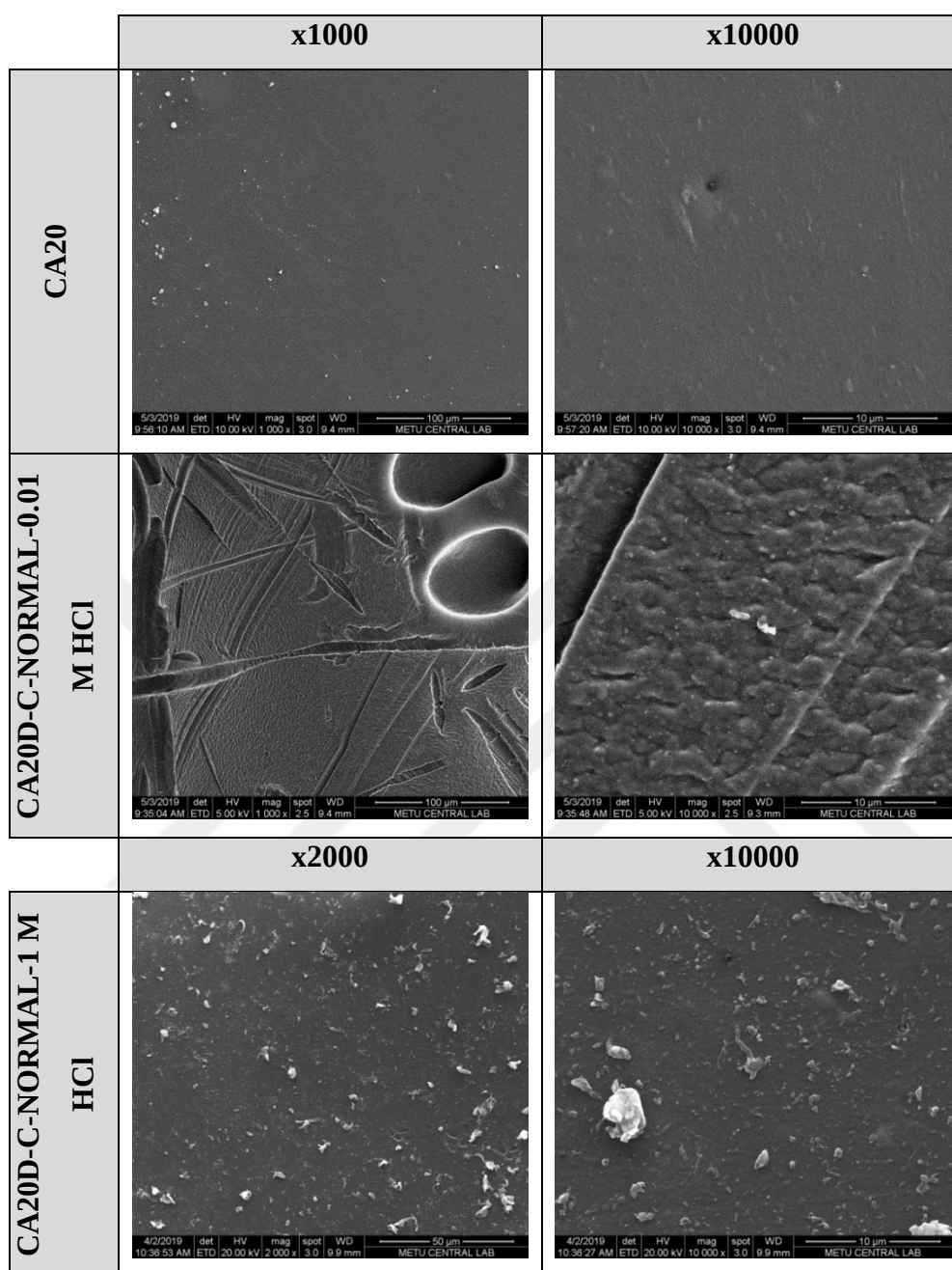


Figure G.43. The surface SEM images of the CA20D-C-NORMAL-1 M HCl, the CA20D-C-NORMAL-0.01 M HCl and the CA20 membranes at different magnifications that are 1000x and 10000x for the CA20 and the CA20D-C-NORMAL-0.01 M HCl, and 2000x and 10000x for the CA20D-C-NORMAL-1 M HCl

When the CA20D-C-NORMAL-1 M HCl and the CA20D-C-NORMAL-0.01 M HCl was examined, it can be said that there is no any NCC particles on the NCC membrane surface. In addition, the cross section SEM images of the CA20D-C-NORMAL-1 M HCl, the CA20D-C-NORMAL-0.01 M HCl and the CA20 membranes are given in Figure G.44.

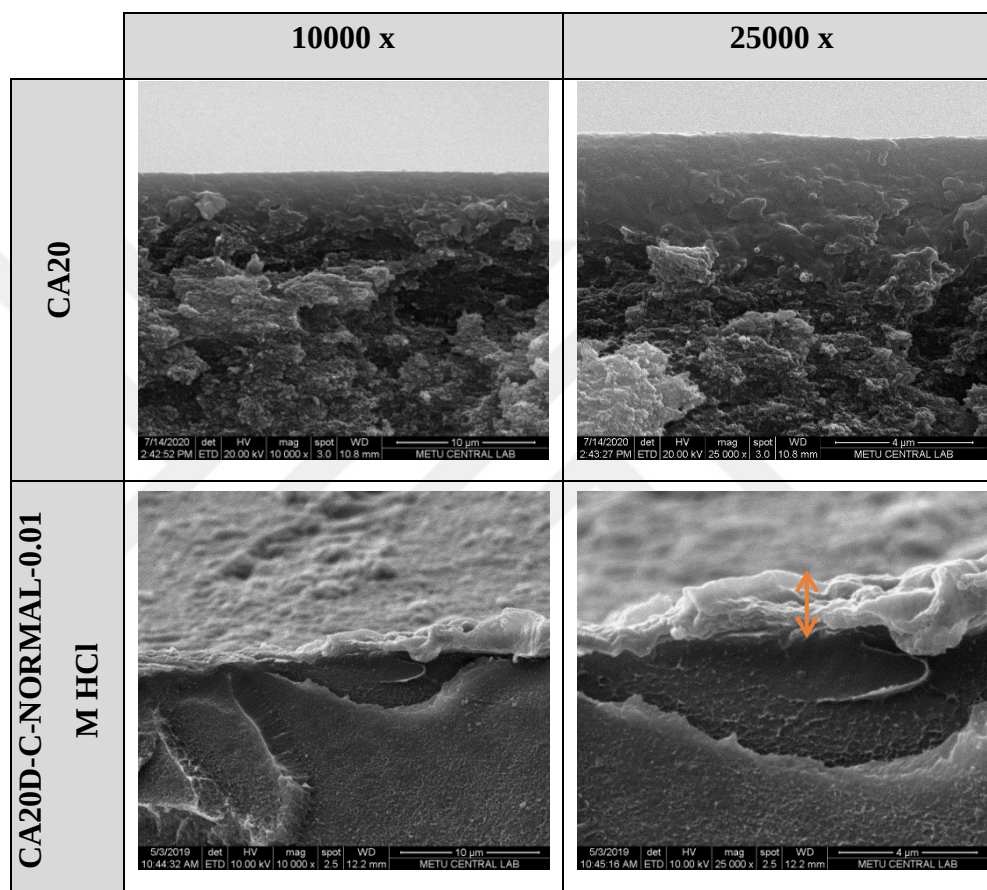


Figure G.44. The cross section SEM images of the CA20D-C-NORMAL-1 M HCl, the CA20D-C-NORMAL-0.01 M HCl and the CA20 Membranes at different magnifications that are 10000x and 25000x

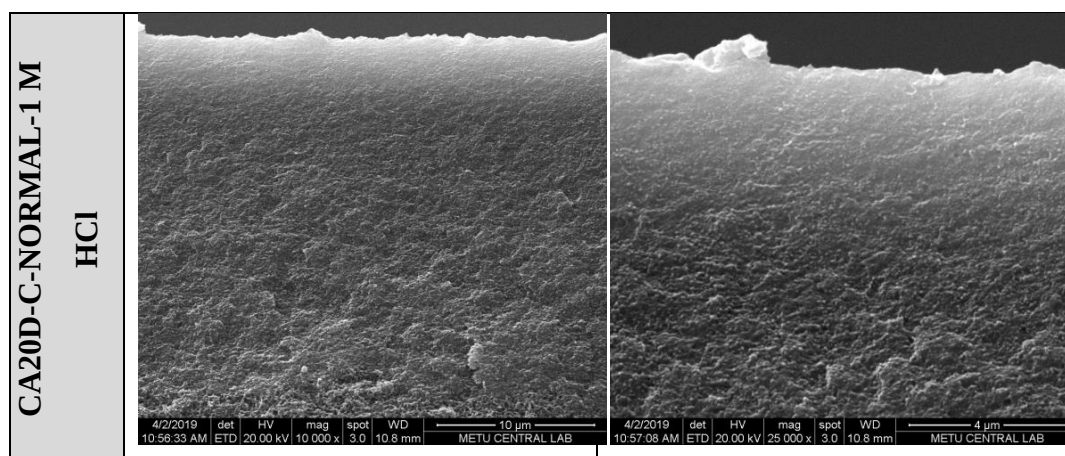


Figure G.44. (cont'd) The cross section SEM images of the CA20D-C-NORMAL-1 M HCl, the CA20D-C-NORMAL-0.01 M HCl and the CA20 Membranes at different magnifications that are 10000x and 25000x

When the cross section images of the CA20D-C-NORMAL-1 M HCl was examined, it can be said that there is no any NCC deposit layer on the cross section of the NCC membrane. However, although there are no any NCC particles on the surface of the CA20D-C-NORMAL-0.01 M HCl, there is a commercial NCC deposit layer on the membrane as seen from the cross section images, and the thickness of this layer was found as $1.65 \pm 0.36 \mu\text{m}$.

- **The Permeance Results For NCC Membranes During Deposition Procedure**

The flux results (PWF, deposition flux and HCl flux) of the CA20C-P-NORMAL-A are given in Figure G.45, Figure G.46 and Figure G.47. During these experiments, the flux values were taken into considerations since the pressure during HCl filtration could not be measured correctly under vacuum conditions.

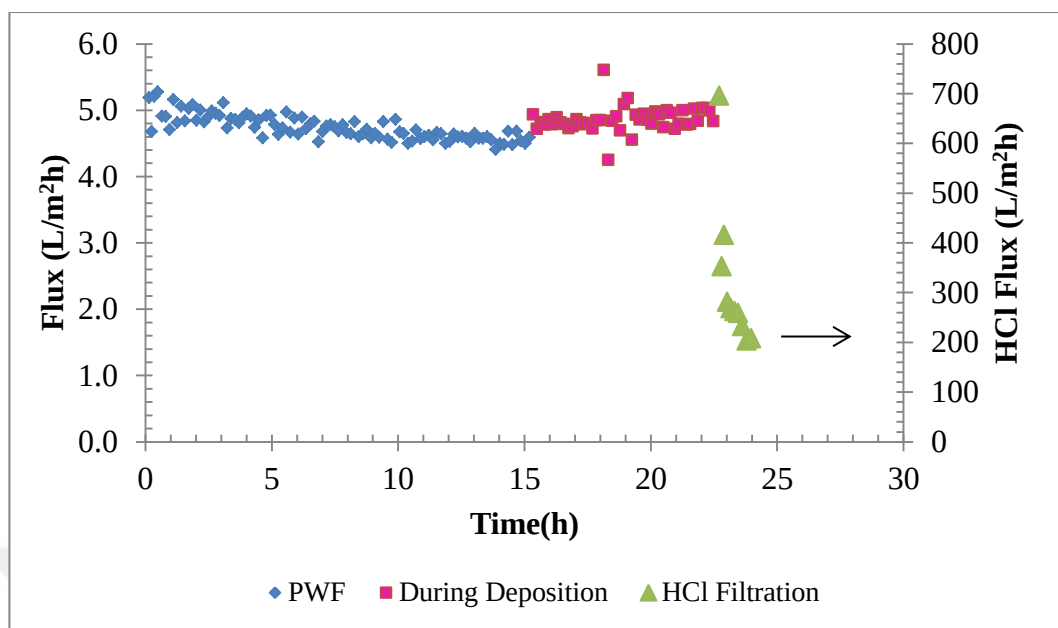


Figure G.45. The permeance results for the CA20C-P-NORMAL-1 M HCl during deposition procedure (TMP = 4 bar for PWP and during deposition)

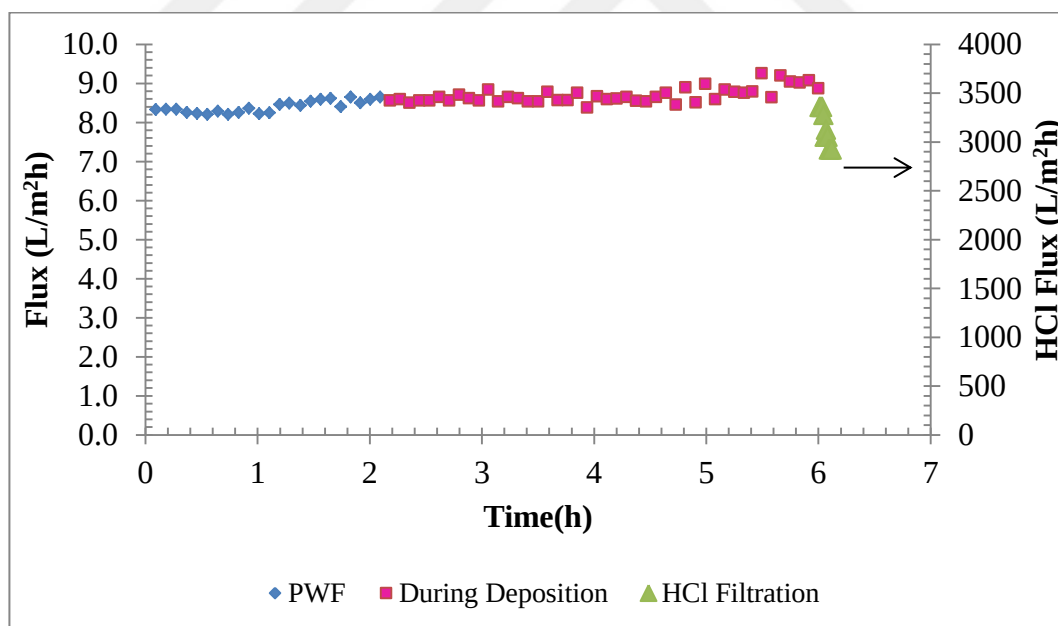


Figure G.46. The permeance results for the CA20C-P-NORMAL-0.01 M HCl during deposition procedure (TMP = 4 bar for PWP and during deposition)

When Figure G.45 and Figure G.46 were examined, it was seen that the HCl flux is much higher than the pure water flux and deposition flux that can be explained by the leaking of HCl from the NCC membrane during HCl filtration in Buchner funnel or the pressure values during HCl filtration could not be measurement correctly. Also, the permeance values during deposition stayed nearly same with PWF values in the CA20D-P-NORMAL-A membranes possibly due to having different type of NCC than the CA10D-C-S membranes. Therefore, these experiments were not suitable for further experiments.

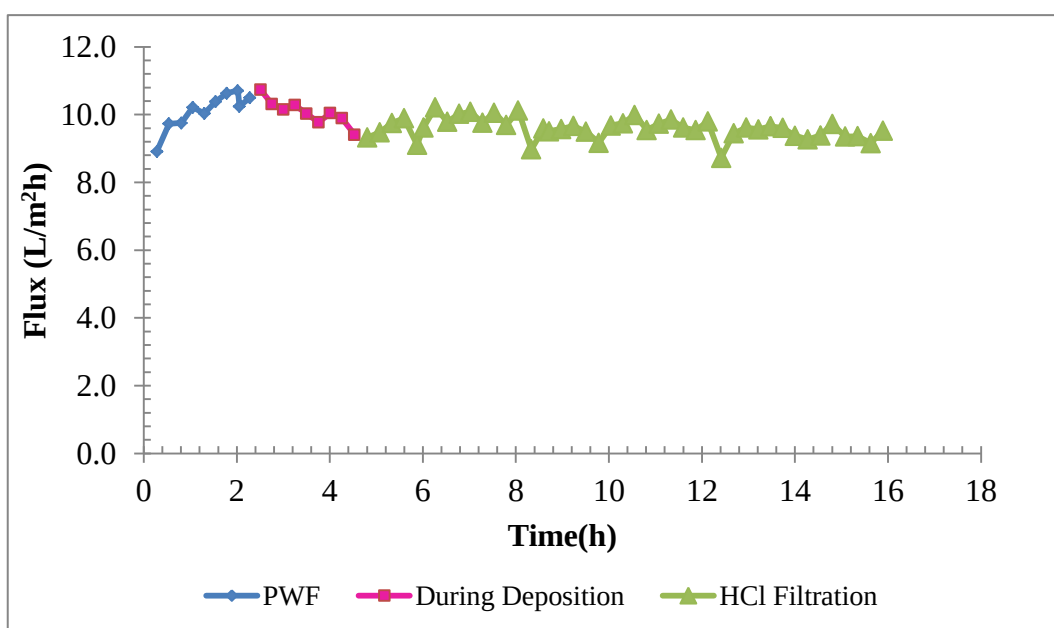


Figure G.47. The permeance results for the CA20C-P-NORMAL-0.005 M HCl during deposition procedure (TMP = 4 bar)

As a result of Figure G.47, there is no change in the flux values during deposition of the commercial NCC with 0.005 M HCl that can be attributed to there is no effect of HCl filtration on the deposited NCC layer. Also, this can be supported with the ATR-FTIR analysis results. Therefore, these experiments were not suitable for further experiments.

- **Solute Rejection Test of CA20C-P-NORMAL-0.005 M HCl Membrane**

The CA20D-C-NORMAL-0.005 M HCl was tested with CV/EtOH solution after deposition procedure, and its result was given in Figure G.48.

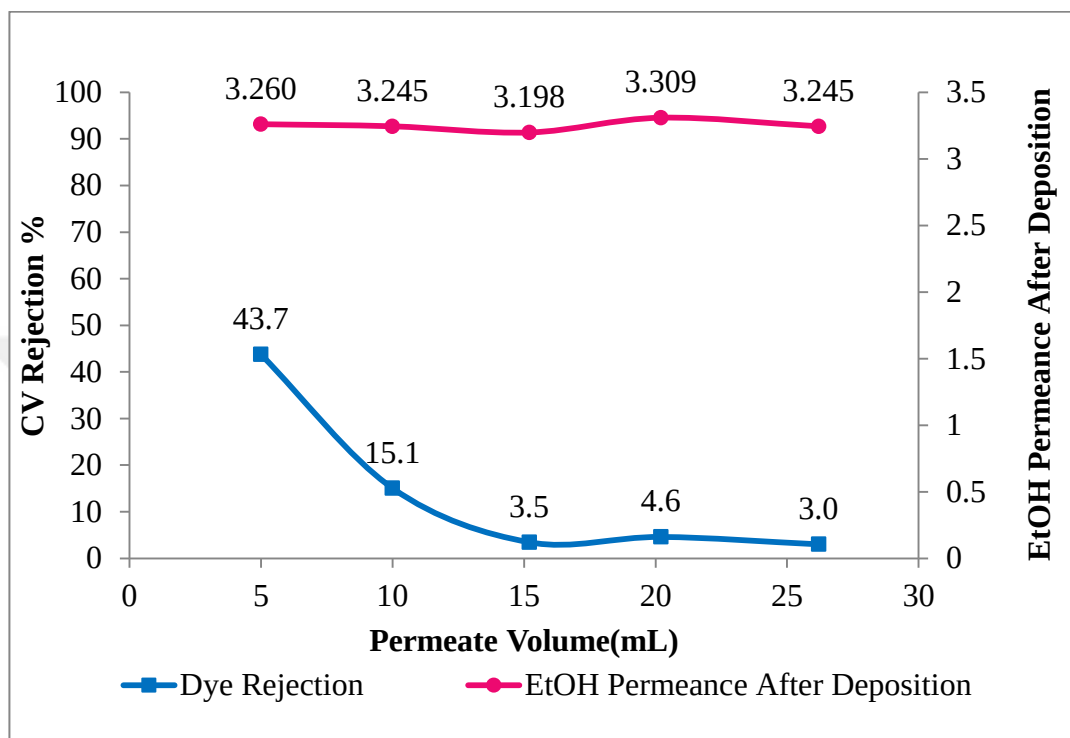


Figure G.48. The CV rejection and dye permeance/ EtOH permeance after deposition for the CA20D-C-NORMAL- 0.005 M HCl membrane

As a result of CV/EtOH test on the CA20D-C-NORMAL-0.005 M HCl, although the dye rejection value was high at the beginning of the experiment on the CA20D-C-NORMAL-0.005 M HCl membrane, the dye rejection value decreased drastically. In addition to this, CV Permeance/EtOH Permeance of this membrane was calculated as 1.34 ± 0.02 . Therefore, it can be said that there is no any effect on the NCC deposition on the membrane dye rejection.

H. The Precipitation of the NCC-HCl on the KK2D Membrane Using Water and EtOH

Firstly, the membrane casting solution which contains 12 % cellulose (cotton linter), 25 % acetone and 63 % [EMIM]OAC was prepared and named as KK2; however, to mix acetone and [EMIM]OAC completely, these were mixed through at least 40 minutes at 400 rpm, and then, cellulose was added to the top of this solution very slowly to prevent agglomeration of cellulose and fasten dissolving. After dissolving this solution completely, the membrane casting solution was cast on glass support via a casting bar whose thickness is 250 μm . After this step, the casted membrane was put into evaporation bath through 30 minutes under 0.6 L/min nitrogen flow to evaporate acetone from the casted membrane for increasing the polymer-solvent ratio. Then, after evaporation of acetone, the membrane was put into a coagulation bath and washed from its solvent by changing coagulation bath water. The detailed procedure was explained in section 3.3.1.2. After finishing the coagulation step, the KK2 membrane was dried under N_2 flow and room condition after waiting in EtOH at least 4 hours and named as KK2D. Then, for deposition, the dried NCC-HCl was dispersed in water or EtOH using $0.75 \frac{\text{mg}}{\text{cm}^2}$ concentration and magnetic stirrer and ultrasonic bath to obtain good dispersion of NCC. Then, after measuring support membrane's PWP or PEP value, the feed solution was put into stirrer cell to deposit NCC-HCl on the KK2D at 1.0 bar for EtOH/NCC-HCl and 0.6 bar for water/NCC-HCl. The deposition process was continued until collecting all fed. The schematic representation of deposition procedure for the KK2D membrane is given in Figure H.49.

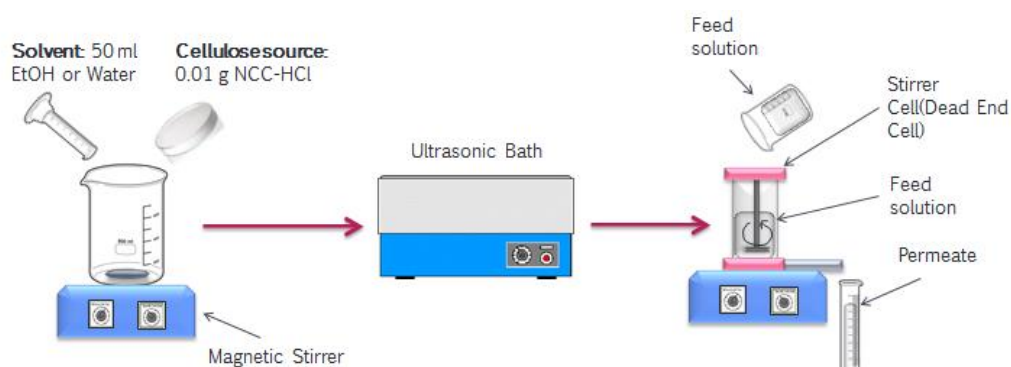


Figure H.49. The schematic representation of deposition of the NCC-HCl with water or EtOH on the KK2D membrane

- **The Performance Analysis During Deposition Procedure**

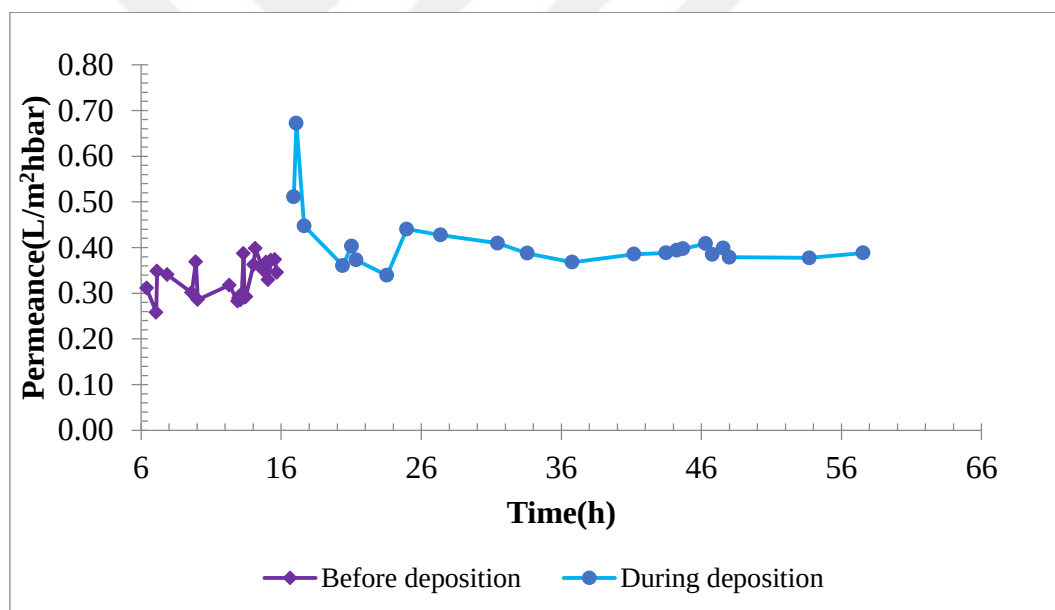


Figure H.50. The permeance results for the KK2D-Water membrane during deposition procedure

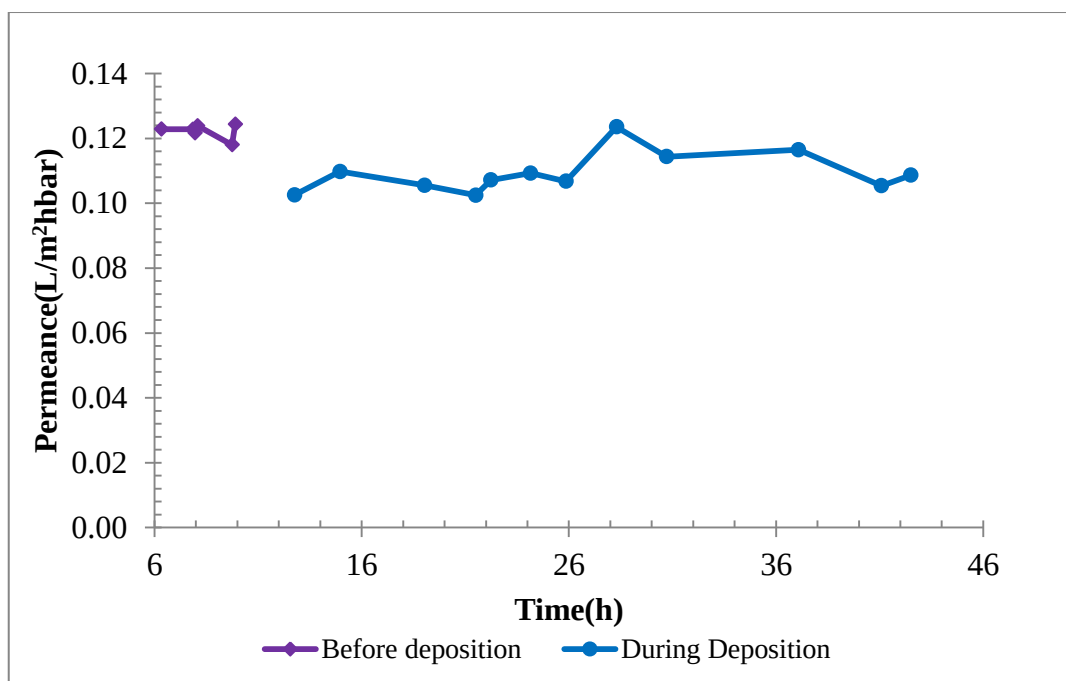


Figure H.51. The permeance results for the KK2D-EtOH membrane during deposition procedure

- **The XRD Analysis of These Membranes**

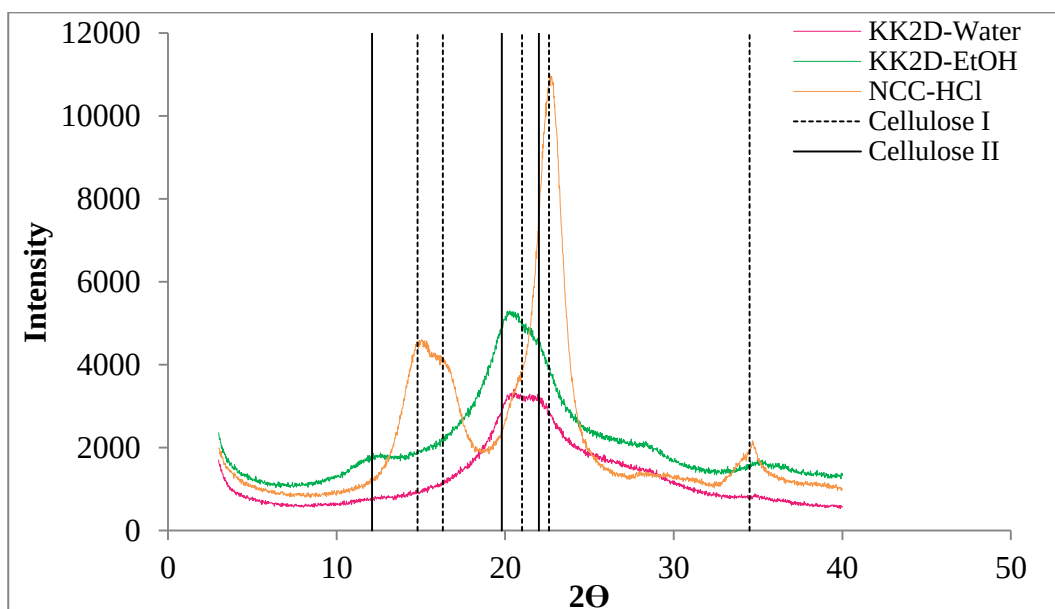


Figure H.52. The XRD analysis results for the KK2D-EtOH and the KK2D-Water with comparison NCC-HCl source

- **The Stability Analysis of These Membranes**

After deposition of the dried NCC-HCl to top of the KK2D membrane with water and EtOH, their stability was tested by waiting these membranes into EtOH and pure water depending on the deposition solvent. Their images are given in Figure H.53.

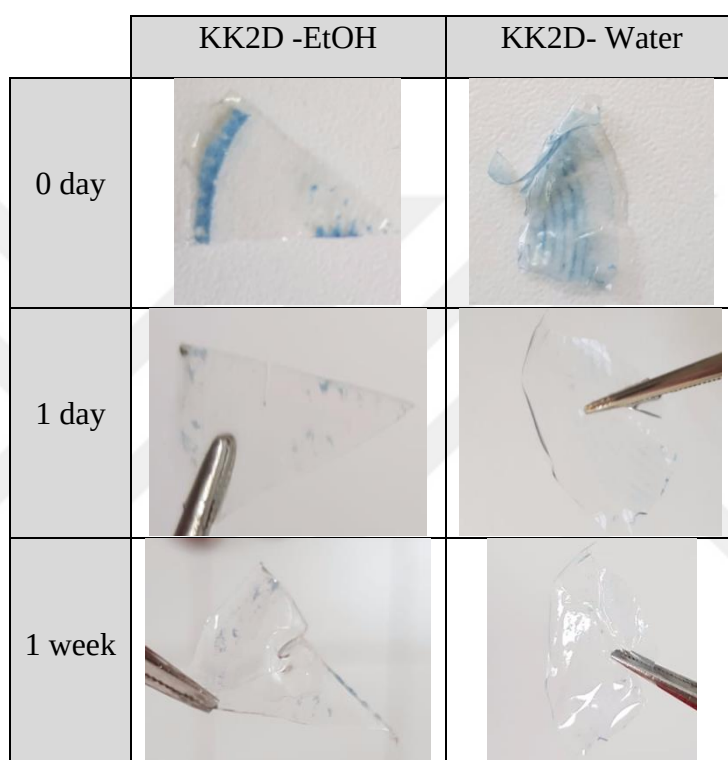


Figure H.53. The images of the KK2D deposited membranes to determine the NCC-HCl stability on the support membrane

- **The SEM Analysis of These Membranes**

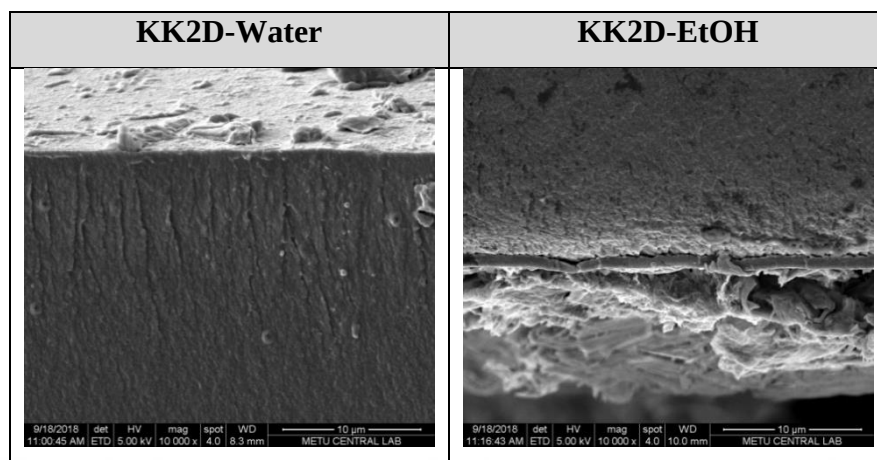


Figure H.54. The SEM images of the KK2D-Water and the KK2D-EtOH membranes

As a result of these analyses, the permeance values did not change during deposition procedure; however, for deposition from water, NCC-HCl can be deposit in the membrane, and it can be supported by looking the SEM image of the membrane. There is nothing accumulated top of the membrane. In contrast to the KK2D-Water membrane, for deposition from EtOH, the NCC-HCl can deposit on the membrane, and it can be supported by looking SEM image of the membrane. There is a layer top of the membrane. However, for both depositions, crystallinity due to NCC deposition is not observable in XRD. Besides, the deposited NCC layer stability is low for these membranes. When these results were compared with the CA10D-P-S membranes, these experiments were discontinued as these results were thought to be unreliable.

I. The Average Pore Size Calculation with Ferry-Renkin Equation

The Ferry-Renkin equation ¹⁹ which is given in equation (16) can be used to calculate pore size of ultrafiltration membranes from known rejection and solute size. The Stokes radius which can be defined as radius of a sphere that diffuse at the same rate with molecule of BD5 molecule is calculated as 1.68 nm using equation (15) ^{125,126}.

$$\log(r_s) = 0.470 \log(M_s) - 1.513 \quad (15)$$

r_s = Stokes radius of particle (nm)

M_s = Molecular weight of particle ($\frac{g}{mol}$)

For BD5 whose molecular size is 5000 Da or 5000 g/mol;

$$r_s \cong 1.68 \text{ nm}$$

$$R = [1 - 2(1 - \frac{r}{a})^2 + (1 - \frac{r}{a})^4] * 100 \quad (16)$$

R = Rejection value of solute

r = Solute radius

a = Pore size of membrane

The average pore size of CA10D-P-S membranes was calculated using BD5 rejection values.

- **Example calculation for CA10D-THIN-P-S;**

$$88.81 = [1 - 2(1 - \frac{1.68}{a})^2 + (1 - \frac{1.68}{a})^4] * 100 \rightarrow a \cong 2.21 \text{ nm}$$

J. The XRD Analysis Results of Some of Produced All-Cellulose Nanocomposite Membranes

The XRD analysis results of some of produced all-cellulose nanocomposite membranes which have amorphous structure due to complete cellulose dissolution are given in this chapter.

- The XRD Results of Membranes Produced with MCC, DMF and [EMIM]OAc;

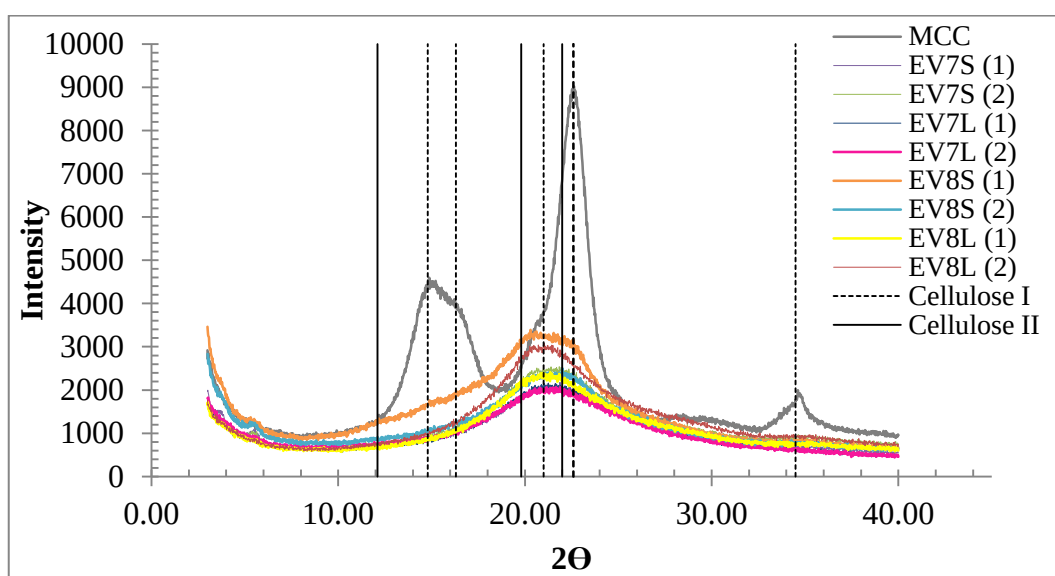


Figure J.55. The XRD results of the EV7S, the EV7L, the EV8S and the EV8L membranes comparative results MCC

- The XRD Results of Membranes Produced with Cotton Linter Cellulose, DMSO and [EMIM]OAc;

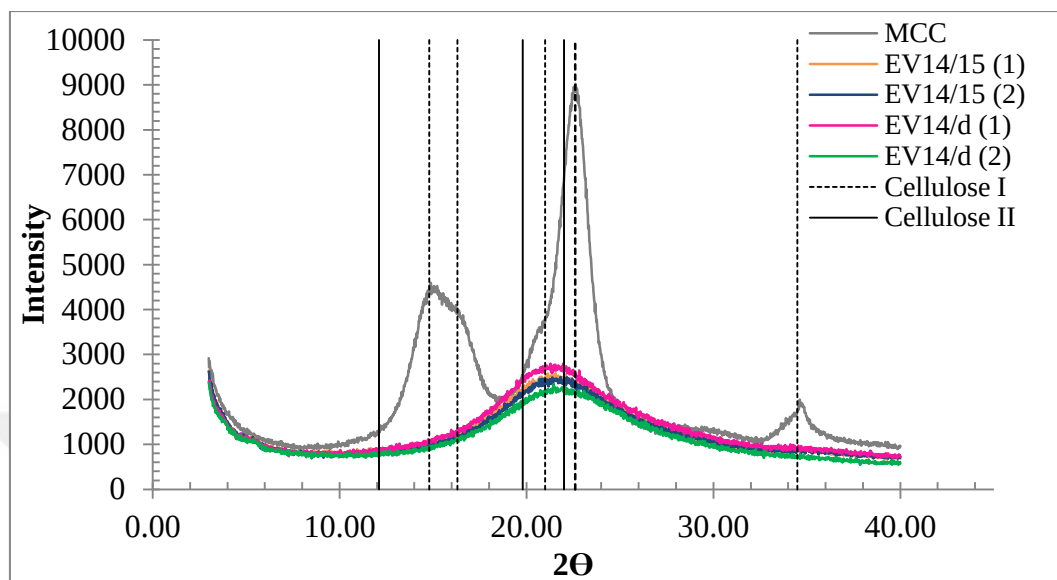


Figure J.56. The XRD results of the EV14 membranes comparative results MCC

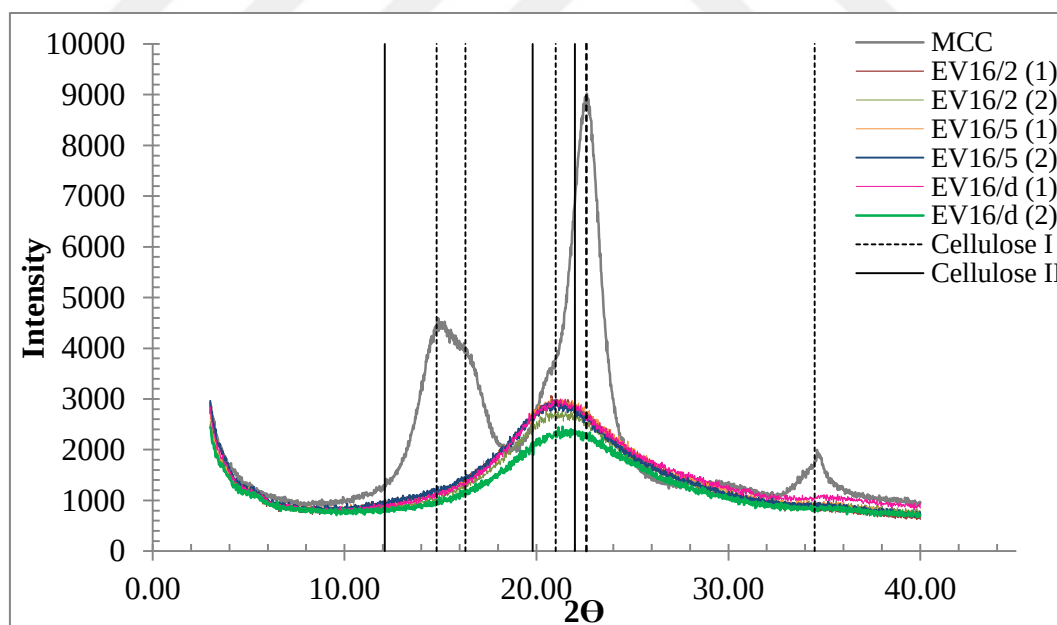


Figure J.57. The XRD results of the EV16 membranes comparative results MCC

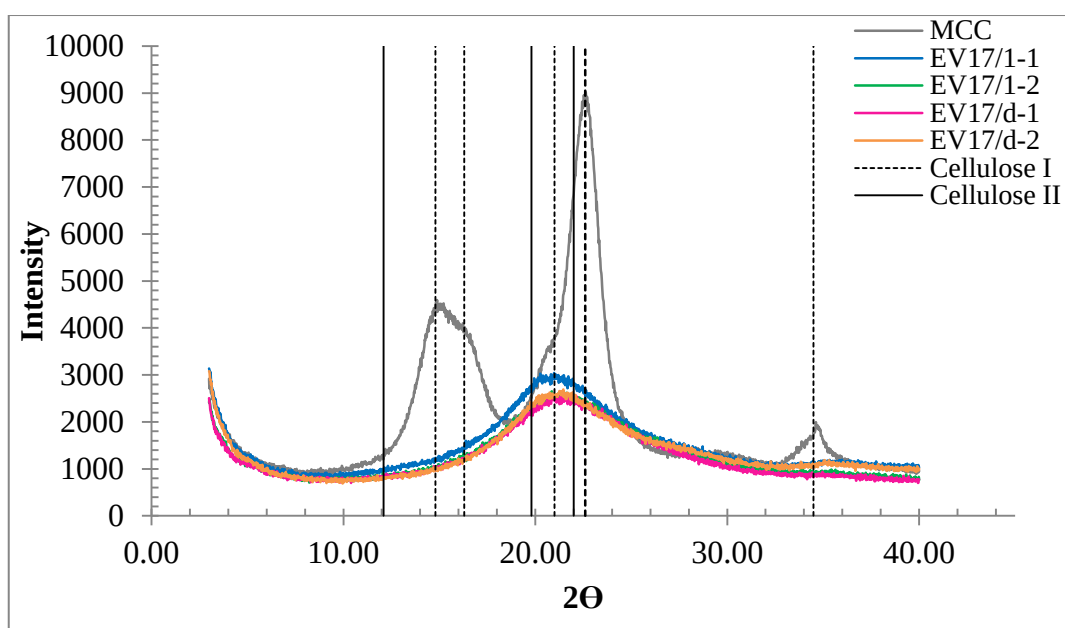


Figure J.58. The XRD results of the EV17 membranes comparative results MCC

As seen from figures, it can be said that the order of adding the membrane materials, using different types of cellulose or heating to the solvent has no effect on the crystalline of the membrane, and the structures of all the membranes produced are amorphous, and all celluloses are dissolved.

K. The SEM Images of Some of Produced All-Cellulose Nanocomposite Membranes

Some of the all-cellulose nanocomposite membranes were analyzed with the SEM to determine the cross-sectional morphology of the membranes.

- The SEM Images of Membranes Produced with MCC, DMF and [EMIM]OAc;

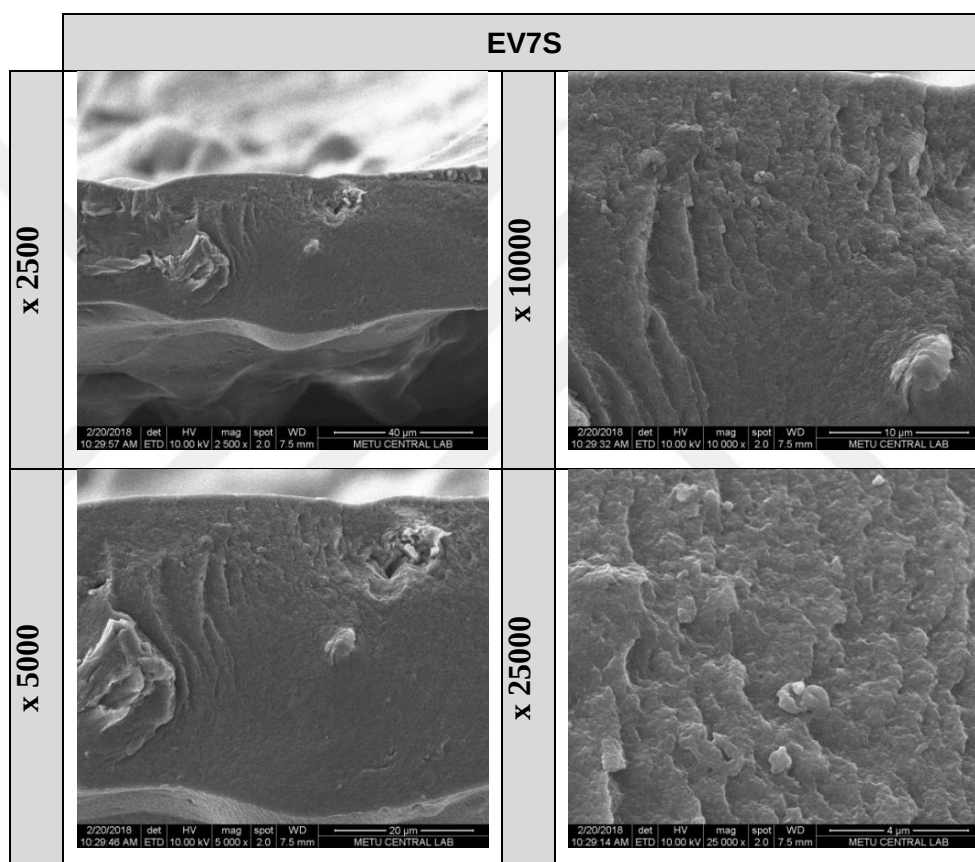


Figure K.59. The cross section SEM images of the EV7L and the EV7S

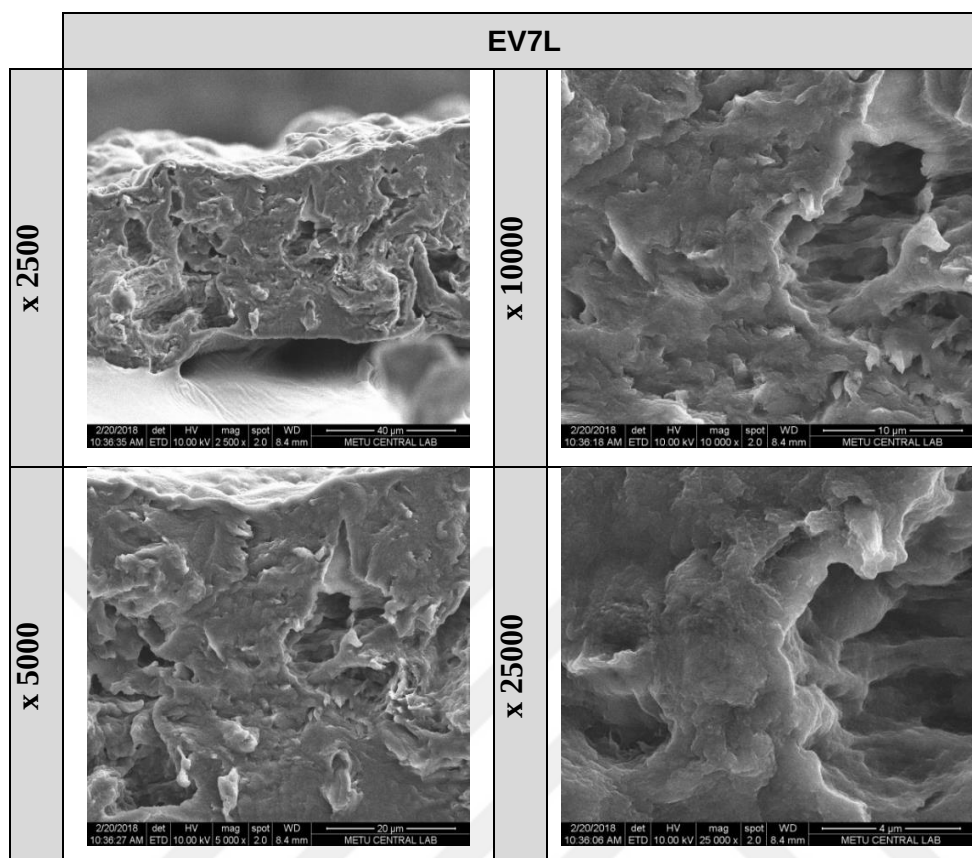


Figure K.59. (cont'd) The cross section SEM images of the EV7L and the EV7S

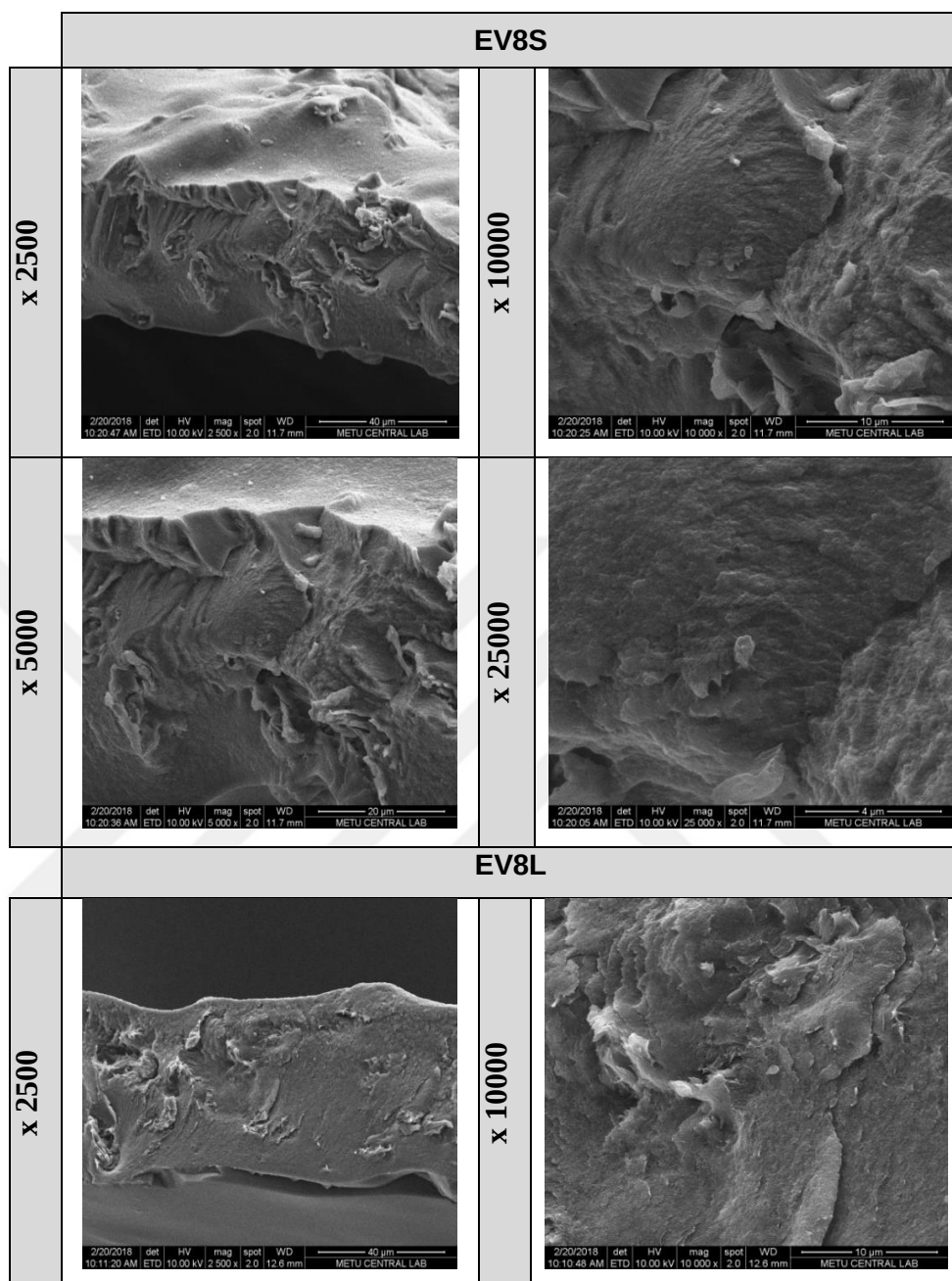


Figure K.60. The cross section SEM images of the EV8L and the EV8S

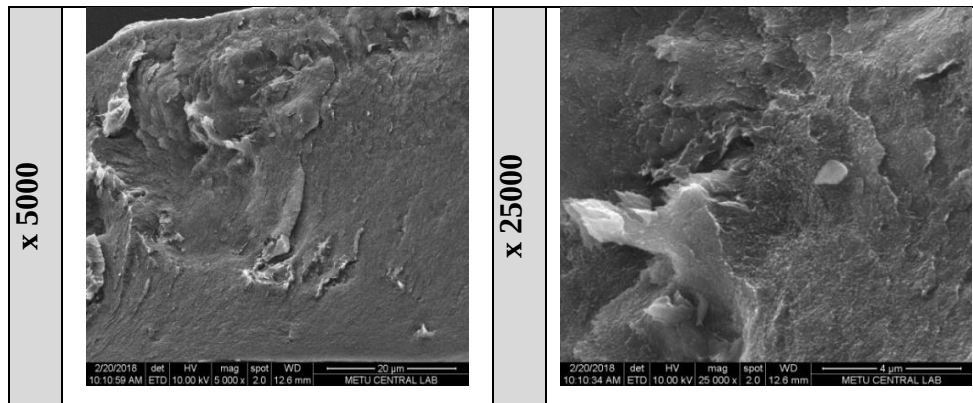


Figure K.60.(cont'd) The cross section SEM images of the EV8L and the EV8S

When these images were examined, there is no visual difference between the EV7 and the EV8, but the EV7L has a more porous structure than the EV7S.

L. The NCC Crystallinity Calculation from Calculated Yield Results

- **The Sample Calculation for NCC-HCl-avicel**

- The crystallinity of cellulose source: 77 %
- The yield of the NCC-HCl-avicel: 91 %

This means that 91 grams of NCC-HCl-avicel from 100 grams of cellulose source of which 77 grams of crystalline regions of cellulose source precipitated. If all crystallinity regions of cellulose source remain unaffected after the hydrolysis reaction, the NCC-HCl-avicel has 14 grams amorphous regions that obtained by subtracting 77 gram crystalline regions in NCC (The crystalline regions remain unaffected after the hydrolysis reaction) from 91 grams total NCC. So, the crystallinity of NCC can be calculated as;

$$\frac{14}{91} * 100 = \sim 15 \% \rightarrow \text{Percent amorphous regions in NCC - HCl - avicel}$$

$$100 - 15 = 85 \% \rightarrow \text{Percent crsyalline regions in NCC - HCl - avicel}$$

- **The Sample Calculation for NCC50H₂SO₄-cotton-30/10**

- The crystallinity of cellulose source: 74 %
- The yield of the NCC50H₂SO₄-cotton-30/10: 11.4 %

This means that 11.4 grams of NCC50H₂SO₄-cotton-30/10 from 100 grams of cellulose source of which 74 grams of crystalline regions of cellulose source precipitated. If the similar calculations with NCC-HCl-avicel were done, it is seen that the amount of NCC50H₂SO₄-cotton-30/10's amorphous regions is negative.