

CELLULOSE ULTRAFILTRATION MEMBRANES FOR SEPARATION OF
NANOPARTICLES FROM ORGANIC SOLVENTS

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NANOPARTICLES FROM ORGANIC SOLVENTS**

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ABSTRACT

CELLULOSE ULTRAFILTRATION MEMBRANES FOR SEPARATION OF NANOPARTICLES FROM ORGANIC SOLVENTS

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Membrane processes for concentration and solvent exchange in nanoparticle synthesis are attractive due to low energy consumption and easy integration into a continuous process. Fouling of membranes with nanoparticles can differ with the surrounding solvents medium due to changing interactions of particles in these media. Obtaining insight on fouling mechanism in organic solvent ultrafiltration is crucial for the use of this application. In this study, the cake layer formations of native and hydrophobized silica nanoparticles are examined in water, isopropyl alcohol, dimethylformamide and ethanol during ultrafiltration by cellulose membranes to observe the effect of solvents and hydrophobicity of particles on fouling. Concentration and diafiltration experiments are conducted to increase the nanoparticle concentration and to change the solvent. By particle size, permeance and turbidity analyses, cake layer properties such as thickness, porosity and resistance are calculated. With native particles the highest cake resistance is observed in water, the least in dimethylformamide. The highest cake resistance in water is consistent with the least porous cake structure calculated using the Kozeny-Carman equation. With hydrophobized particles, the highest cake resistance is observed in dimethylformamide, the least cake resistance is observed in water. The highest cake resistance in dimethylformamide is consistent with the thickest cake at 200 μ m. Hydrophobized particles formed substantially higher

cake resistance than native particles by the increased particle-particle interaction. In diafiltration experiments, hydrophobized and native particles both created insignificant cake resistance during transition from isopropyl alcohol to ethanol and dimethylformamide where tangential flow was effective in redispersing particles to the bulk. In water, the fouling resistance was more severe than other solvents which reveals the effect of medium in cake formation.

Consequently, organic solvent ultrafiltration is a promising method in concentration and solvent exchange of nanoparticles which display different fouling behaviors in different organic solvents.

Keywords: Organic solvent ultrafiltration, membrane fouling, silica nanoparticles, diafiltration, surface interactions

ÖZ

NANOPARÇACIKLARIN ORGANİK ÇÖZÜCÜLERDEN AYRIŞTIRILMASI İÇİN SELÜLOZ ULTRAFİLTRASYON MEMBRANLARI

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Nanoparçacık sentezinde konsantrasyon ve çözücü değişimine yönelik membran prosesleri, düşük enerji tüketimi ve sürekli bir prosese kolay entegrasyonu nedeniyle caziptir. Membranların nanoparçacıklarla kirlenmesi, bu ortamdaki parçacıkların değişen etkileşimleri sebebiyle etraftaki çözücü ortamına göre değişkenlik gösterebilir. Organik çözücü ultrafiltrasyonundaki birikim mekanizmasına dair anlayış elde etmek, bu uygulamanın kullanımı için çok önemlidir. Bu araştırmada, çözücülerin ve parçacıkların hidrofobikliğinin kirlenme üzerinde etkisini gözlemlemek için, DMOAP kaplamalı ve kaplamasız silika nanoparçacıkların selüloz membranla, suda, izopropil alkolde, etanolde, dimetil formamidde, ultrafiltrasyonu sırasındaki kek tabakası oluşumları incelenmiştir. Konsantrasyon ve diafiltrasyon deneyleri, silika nanoparçacık konsantrasyonunu arttırmak ve çözücüü değiştirmek için yapılmıştır. Parçacık boyutu, geçirgenlik ve bulanıklık analizleriyle, kalınlık, gözeneklilik ve direnç gibi kek tabakası özellikleri hesaplanmıştır. Kaplamasız parçacıklarla, en yüksek kek direnci suda, en düşük dimetil formamidde gözlemlendi. En yüksek kek direncinin suda olması, Kozeny-Carman denklemi kullanılarak hesaplanan en az gözenekli kek sonucuyla uyumludur. Hidrofobikleştirilen parçacıklarla, en yüksek kek direnci dimetil formamidde, en düşük suda gözlemlenmiştir. En yüksek kek direncinin dimetil formamidde olması, 200µm olarak hesaplanan en kalın kek sonucuyla

uyumludur. Artan paracık-paracık etkileşimiyle, hidrofobikleştirilen paracıklar kaplamasız paracıklardan önemli ölçüde daha yüksek kek direnci oluşturmuştur. Diafiltrasyon deneylerinde su hari, kaplamalı ve kaplamasız paracıkların ikisi de teğet akışın paracıkların ana kütleye yeniden dağılmasında etkili olduėu izopropil alkolden etanole ve dimetil formamide geişleri sırasında önemsiz derecede kek direnci oluşturdular. Sudaki kek direncinin diğerközücülerdekinden önemli ölçüde daha şiddetli olması kek oluşumda ortam etkisini ortaya çıkarıyor. Sonuç olarak, farklı organik közücülerde farklı birikim davranışı gösteren nanoparacıkların konsantrasyonunda ve ortam deėişiminde, organik közücü ultrafiltrasyonu gelecek vaat eden bir yöntemdir.

Anahtar Kelimeler: Organik közücü ultrafiltrasyonu, membran kirliliėi, silika nanoparacıklar, diafiltrasyon, yüzey interaksiyonları



To My Mom and Dad

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LIST OF ABBREVIATIONS

ABBREVIATIONS

AB: Acid-base

CA: Cellulose acetate

Da: Dalton

DLS: Dynamic light scattering

DLVO: Derjaguin-Landau-Verwey-Overbeek

DMF: Dimethylformamide

DMOAP: Dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride

DMSO: Dimethyl sulfoxide

DOTM: Direct Observation Through the Membrane

EtOH: Ethanol

EL: Electrostatic

GPC: Gel permeation chromatography

IPA: Isopropanol

LW: Lifshitz-van der Waals

MF: Microfiltration

NaOH: Sodium hydroxide

NF: Nanofiltration

NH₄OH: Ammonium hydroxide

OSU: Organic solvent ultrafiltration

PCTE: Polycarbonate track-etched

PEG: Polyethylene glycol

PES: Polyether sulfone

PGMEA: Propylene glycol monomethyl ether acetate

PPG: Polypropylene glycol

PS: Polysulfone

PSP: Pure solvent permeance

PVDF: polyvinylidene difluoride

PWP: Pure water permeance

R: Resistance

RC: Regenerated cellulose

RO: Reverse osmosis

SEM: Scanning electron microscopy

TEOS: Tetraethoxysilane

TMP: Transmembrane pressure

UF: Ultrafiltration

Up: Ultrapure

XDLVO: Extended Derjaguin-Landau-Verwey-Overbeek



CHAPTER 1

INTRODUCTION

A membrane is a semipermeable barrier permeating and rejecting some components selectively depending on various criteria such as particle size, particle charge, diffusivity, and solubility. Membrane processes operate under a driving force which could be pressure gradient, concentration gradient or electrical potential. Membranes have been investigated since 1900's, around 1930's the first commercial membranes were produced, and in 1940's membranes gained their first significant use for water testing.¹ Yet, until 1960's the severe problems of the membrane world continued as high cost, low selectivity, low flux, and unreliability. In 1960's Loeb and Sourirajan reported the fabrication of the first anisotropic cellulose acetate reverse osmosis membranes with defect free and thin skin layers supported by a macroporous support which brings high flux and high selectivity at the same time in a single-step membrane formation process.¹

Membranes today are used in many processes in large scale aqueous environments. However, their use in organic solvents is still limited, although increasing, due to the scarcity of solvent-resistant membranes and the difficulties in estimating membrane performance in different organic solvents.

Cellulose has emerged as a promising solvent-resistant membrane material and its performance in organic solvent nanofiltration, and ultrafiltration have recently been reported.²⁻⁶ In this study, the use of cellulose ultrafiltration membranes in downstream processing of nanoparticle synthesis is demonstrated.

1.1 Pressure Driven Membranes

A membrane process has three main streams, feed, permeate and retentate as it is seen in Figure 1.1. In Figure 1.1a, dead end filtration process is presented where the feed is pressured to flow through the membrane while the foulant accumulates on the membrane surface. Since the accumulation escalates, in order to keep the same flow, required pressure increases until a point that membrane replacement is necessary.¹ As an alternative, crossflow filtration where the feed flows tangential to membrane and is filtered through membrane by the driving force of transmembrane pressure, is designed as in Figure 1.1b.

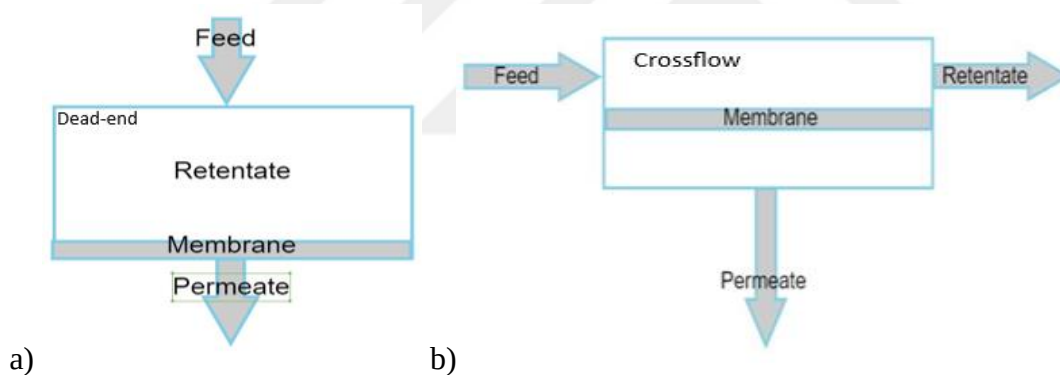


Figure 1.1. Basic demonstrations of a) dead-end b) crossflow membrane operations

Membrane processes, which utilize the pressure gradient between feed and permeate streams to operate, have four different types when they are categorized for their pore size: reverse osmosis, nanofiltration, ultrafiltration, microfiltration. These processes have two different transport mechanisms through membrane: pore-flow model and solution-diffusion model. Since ultrafiltration and microfiltration membranes are porous, pore-flow model is applied.¹ By the convective flow through pores developed by the pressure difference, the transport of the component smaller than membranes pores occurs. The

component that is bigger than the pores cannot pass through the membrane and is rejected. While ultrafiltration membranes have 1-100nm pore sizes, microfiltration membranes have 0.1-10 μ m. Solution-diffusion model is used to explain the transfer through non-porous membranes included in the reverse osmosis process.¹ According to this model, transport through membrane occurs by means of dissolution of components in the membrane and diffusion from the feed side to the permeate side.⁷

The nanofiltration process lies between ultrafiltration and reverse osmosis when the processes are lined by pore size as it is presented in Figure 1.2. For that reason, the transport mechanism for nanofiltration is considered to be both solution-diffusion and pore-flow.⁸

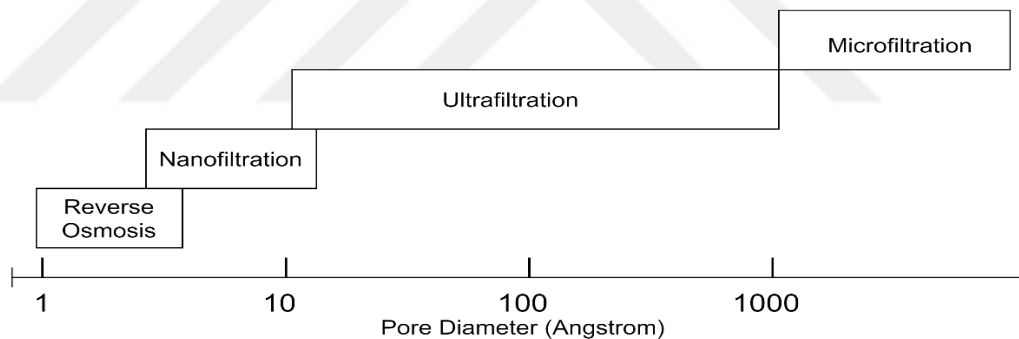


Figure 1.2. Pressure-driven membrane classification according to the average pore size

1.1.1 Ultrafiltration

Ultrafiltration is a process where colloids, proteins, macromolecules are rejected by the membrane having 1-100 nm-sized pores while the solvent and smaller components permeate through. Ultrafiltration membranes are generally made of polymers and have an anisotropic structure comprised of a thin, finely porous skin layer providing selectivity on

top of a highly porous support layer providing mechanical strength as in Figure 1.3. There are many factors affecting the performance of ultrafiltration membranes such as particle shape, pH of the medium, structure and charge of the membrane, particles and solvent, the interaction of the components. Ultrafiltration membranes can be formed out of many polymers and materials as cellulose acetate⁹⁻¹¹, polysulfone¹², polyvinylidene fluoride^{13,14}, aluminum oxide^{15,16}, ceramic^{7,8,17-19}, polyacrylonitrile²⁰. This process takes place in dairy processing for concentration of proteins^{21,22}, separation of lactose²², sterilization²³; in pharmaceuticals²⁴, for drug delivery²⁵, endotoxin removal²⁶; in automobile industry for recollection of electrocoat paint.²⁷ Even though ultrafiltration membranes are in common use in industry, their potential is way higher than their actual integration and application. However, the most significant obstacle in the way of the development of ultrafiltration applications is the fouling problem. Throughout the years, the fouling problem is thoroughly investigated for aqueous systems to understand the structure and to eliminate.

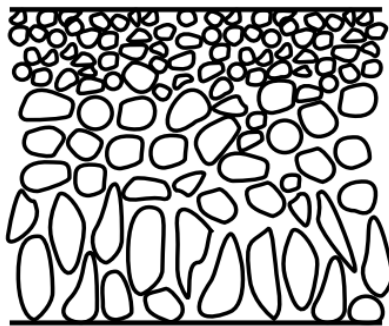


Figure 1.3 Anisotropic membrane structure with thin skin layer on top of the highly porous support layer¹

1.1.2 Organic Solvent Ultrafiltration

Organic solvent ultrafiltration process offers recovery of organic solvents, concentration of solution including organic solvents and diafiltration for exchange of the medium. Recovering organic solvents is significant for cost and energy saving in a process. Most typical solvent recovery method is distillation, which is a well-established, robust separation process. Replacing distillation units totally or partly with membranes has huge potential for energy saving and reducing carbon footprint since membrane separations use very little energy unlike distillation.

Similar to ultrafiltration in aqueous systems, ultrafiltration in organic solvents is prone to fouling due to the size of the rejected species and their relatively low back transport rates from the membranes surface resulting from their low diffusion coefficients.

In 2020, Yin et al. observed the fouling trends of spherical silica particles having 400 nm diameter, in methanol, ethanol, acetone, toluene and hexane, on polyacrylonitrile ultrafiltration membranes having average pore size as 54 nm, expected to detect only external fouling.²⁸ They obtained different fouling in every solvent even though the only changed parameter is the solvent medium. Repulsive interactions were attributed to the solvents with high polarity. The fouling parameters from three mechanism fouling model, confirmed flux trends in each with slight deviation sourced by polarity.²⁸ Yin et al. tried to explain the relationship between foulant-foulant and membrane-foulant interactions and fouling.²⁹ In this study, silicon dioxide, titanium dioxide and aluminum were used as particles; methanol, ethyl acetate and acetonitrile were used as solvents during ultrafiltration with polyacrylonitrile membranes. Zeta potentials and Gibbs free energies calculated by DLVO and XDLVO theories were utilized to compare and evaluate the flux trends. Interaction energies calculated for aluminum particles did not correlate with the least cake resistance result while zeta potential did not correlate at all for any particle. SiO₂ and TiO₂ particles showed fouling behavior which can be anticipated by particle interaction energies of DLVO.²⁹ Savaş-Alkan et al. conducted research for the recovery

of propylene glycol methyl ether acetate from photoresist solutions which is used in photolithography.² Water, methanol, DMSO, DMF and PGMEA permeances were compared to confirm that the pore-flow mechanism is applied. They reached 87% and 79% SU-8 rejection by the two-staged dead-end experiments respectively. Fouling by SU-8 was reversible by physical cleaning. Additionally, 80% recovered PGMEA was used to achieve for the recreation of a pattern on SU-8 film to show its reusability after the recovery process.² In 2022, Oxley et al. used polybenzimidazole membranes surface-modified by polyethylene glycol and polypropylene glycol to decrease fouling by steric hindering, in the filtrations with 20 nm silica particles in acetonitrile, methanol, toluene, and water.³⁰ Since the steric hindrance theory came from polymer modifications being a physical obstacle in front of the silica particles which try to foul on the membrane, physically large polymers would create a better anti-fouling feature. However, the physical properties of PEG and PPGP were related to the medium. Polar environments caused hydrophobic polymer to increase its hydrodynamic diameter leading to a greater prevention to fouling and vice versa. But the least anti-fouling property was observed in nonpolar solvents sourced by the decreased hydrodynamic diameter.³⁰ In 2023 by Tran et al., cellulose-cellulose composite ultrafiltration membranes were examined for the rejection of dextran, polyethylene glycol and polyethylene oxide in water and organic solvents such as acetone, acetonitrile, DMF, DMSO, ethanol. They reported that the rejection and permeance performance of the membrane depend on the viscosity of the solvent and its swelling effect on the membrane.³¹ Hamabe et al., explored the MFI-type zeolite coated tubular membrane in organic solvent ultrafiltration for the rejection of gold nanoparticles in DMF with pure DMF permeance as $1.56 \times 10^{-7} \text{ m}^3/\text{m}^2 \cdot \text{s} \cdot \text{MPa}$ in 2022. They estimated the real rejection as 100% and could be kept at that level for 80 days even though the permeate flux showed a gradual decrease.³² In 2022 by Oxley et al., the rejection and permeance performance and MWCO of grafted with long flexible polymer modifier and small molecule modifier polybenzimidazole membranes were investigated by using PEG as solute in methanol, acetonitrile, DMF and toluene. The membranes grafted with long modifier, the permeate flux and MWCO decreased by increasing modification extent in

polar solvents.³³ By de Melo et al., ceramic ultrafiltration membranes were tested to separate oil miscellas from organic solvents such as n-hexane, ethanol and isopropanol in 2015. They reported that permeation and rejection of oil-isopropanol had a decrease over experiment time caused by changing oil-membrane interaction which adsorbs isopropanol. The highest rejection was reached in oil-ethanol experiment close to 100%.³⁴ By Sánchez-Arévalo et al., a review for organic solvent ultrafiltration including application areas, structural membrane changes by organic solvent during ultrafiltration, permeate flux values of different solvents and conditioning process to increase flux was reported.³⁵

Since ultrafiltration and microfiltration are both pressure-driven processes and the only difference they have is pore size, the studies done for organic solvent microfiltration also can provide insight into organic solvent ultrafiltration. Lay et al. observed fouling trend of silica particles on Anopore microfiltration membranes using solvents as water, ethanol, formamide, and hexane by direct observation of critical flux.³⁶ The interaction energies calculated by DLVO theory correlated better with the critical flux data for water, ethanol and formamide at fixed Re , than XDLVO did. The interaction energies calculated by both DLVO and XDLVO suggested that silica particles' own interaction to each other and their interaction towards the membrane were attractive which was proved by the most severe fouling in hexane as in Figure 1.4. The least fouling in ethanol was not foreseen by DLVO or XDLVO but was explained by solvation film effect leading to the highest repulsive forces.³⁶

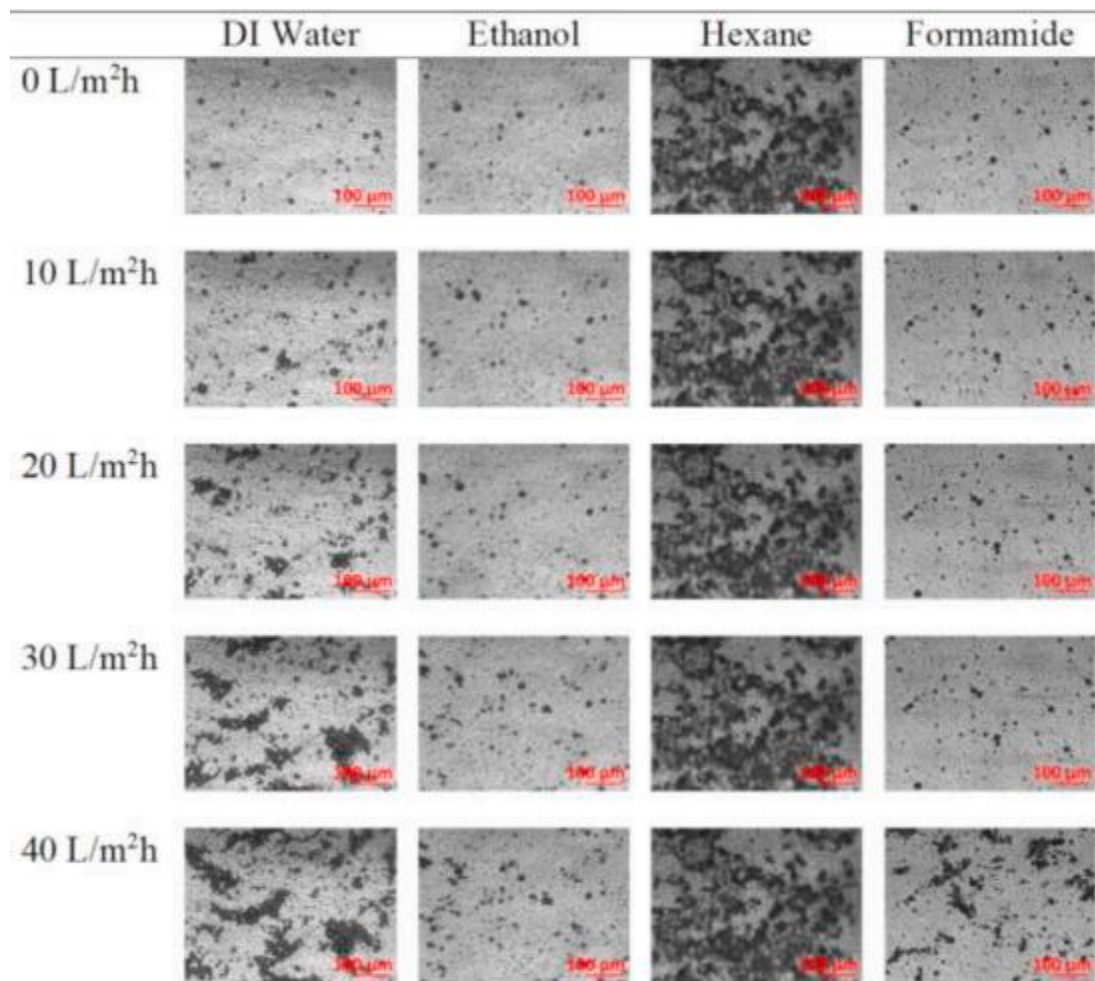


Figure 1.4. Membrane surface images by DOTM in water, ethanol, hexane, and formamide.³⁶ Reproduced with permission (Lay et al., 2020). Copyright 2020, Elsevier.

In 2022, Tanis-Kanbur et al. studied bovine serum albumin fouling on polytetrafluoroethylene membrane during microfiltration from water mixtures with IPA and DMSO which has 10 and 30 percent volume ratio.³⁷ Water mixtures with organic solvents resulted in more severe fouling than the case where only water was used. In the results, it was remarked that DMSO creates more fouling than IPA and provokes both external and internal fouling whereas IPA induces internal fouling more as it is seen in

Figure 1.5. DLVO and XDLVO theories did not correspond well with the flux trends meaning LW, AB and EL interactions should be investigated more thoroughly in organic solvents.³⁷

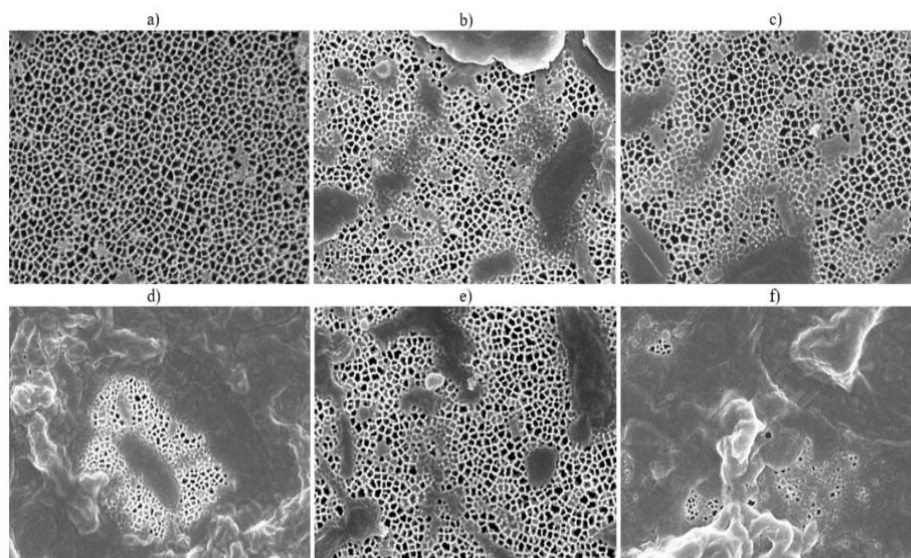


Figure 1.5. Membrane visuals by Field Emission Scanning Electron Microscope a) After pure water permeance, after the rejection tests with 0.5g/L BSA for fouling in b) Water c) 10v% IPA d) 10v% DMSO e) 30v% IPA f) 30v% DMSO.³⁷ Reproduced with permission (Tanis-Kanbur et al., 2022). Copyright 2022, Elsevier.

1.2 Cellulose Membranes for Organic Solvents

Increasing demand for sustainable processes requires consideration of material choice for many different products, including membranes. Cellulose is a low-cost, biopolymer which is abundant in nature, and has very high resistance towards organic solvents due to its inter and intramolecular hydrogen bonding.

In this study cellulose membranes were used for organic solvent ultrafiltration. Non-solvent induced phase separation was applied to obtain cellulose acetate membranes and

alkaline hydrolysis step was followed to obtain cellulose membranes. The reason for creating cellulose acetate membranes firstly was that cellulose does not dissolve in many solvents. By using cellulose acetate, membranes with desired morphology were obtained by phase inversion method using DMSO as solvent and PEG as pore-forming agent. Immersing the cast polymer solution into water creates two different phases as polymer-rich and polymer-poor phases during precipitation since the solvent transports to water. Membrane matrix is made of polymer-rich phase and the pores are comprised of polymer-poor phase. Later by alkaline hydrolysis, cellulose acetate was turned into cellulose which is resistant to solvents, biodegradable and has a hydrophilic nature.^{38,39}

There is no example of organic solvent microfiltration by cellulose membranes and only one study in literature using cellulose membranes for organic solvent ultrafiltration by Savaş-Alkan et al. In that study, regenerated cellulose membranes were used for SU-8 rejection in PGMEA which was found to be in the range of 87-89%. They investigated the effect of precursor solution composition on the membrane morphology to create tunable membranes for the separation of SU-8 from PGMEA. By permeance values of water, methanol, DMSO, DMF and PGMEA, they detected the dominant transport mechanism as pore-flow.² In 2023, Krupková et al. investigated the performance of commercial cellulose membranes on the edge of ultrafiltration and nanofiltration, on dendrimer purification and solute rejection in organic solvents which were the mixtures of methanol and dichloromethane with varying volume ratios. They declared that a single MWCO value for these membranes is not applicable since many parameters affect the membrane performance such as swelling in some solvents. They also remarked that no direct correlation between Hansen Solubility Parameter and solute rejection could be found.⁴⁰ In 2023, Abdellah et al., studied the effect of acetylation on the performance of cellulose acetate nanofiltration membranes in DMF, acetone, methanol, water and acetonitrile. They mentioned that as the acetylation degree increases, higher solvent resistance is reached, hydrophilicity of the membranes and permeance of polar aprotic solvents is increased while permeance of polar protic solvents decreased.⁴¹ In 2023, Song et al., investigated the effect of cellulose nanofiltration membrane thickness on solute

rejection and solvent permeance of ethanol, methanol, tetrahydrofuran, ethyl acetate and acetonitrile. They stated that increasing membrane thickness creates dense membranes providing higher solute rejection. Solvent permeance values complied with pore-flow mechanism and depended highly on the solvent viscosity. Another introduced result was that solute rejection was connected to molecular weight, stereochemical structure of the solute and membrane-solute interactions.⁴² In 2019, Falca et al., studied the performance of cellulose hollow fiber membranes with changing ionic liquid in polymer solution by dye rejection tests in water and ethanol. In water, 100% rejection was achieved for negatively charged particles by membranes prepared with [DMIM][DMP] and [EMIM][DEP]. They remarked that rejection is not only dependent on the solute size, but affinity to the membrane should also be strongly taken into consideration.⁵ In 2018, Sukma et al. investigated the effect of cellulose membrane morphology on the rejection of dyes such as Bromothymol Blue, Crystal Violet, Brilliant Blue R, Cresol Red, Rose Bengal, Methyl Orange and Janus Green and permeances of ethanol and water. The highest Bromothymol Blue rejection was reported to be 94% by a membrane cast from 12% cellulose - 63% [EMIM]OAc - 20% acetone solution. They reported that the dye rejection is mostly linked to the affinity between membrane and the dye.³ Konca et al. in 2019, investigated the crosslinking of cellulose membranes on the organic solvent nanofiltration performance by dye rejection tests in ethanol and DMSO. They linked the different rejection values before and after the crosslinking to the alteration of membrane charge leading to the change of electrostatic interaction between membrane and dye.⁴ In the research of Durmaz et al., cellulose membranes were cast by using [EMIM]OAc-DMSO mixtures as solvent and tested with dye rejection experiments. They achieved 80% Bromothymol Blue and 90% Blue Dextran rejection values in ethanol.⁴³

1.3 Concentration Polarization and Fouling

During ultrafiltration, the concentration of the rejected species increases on the membrane wall due to the slower back-diffusion of particles to the medium than the convective flux

towards the membrane. A boundary layer in front of the membrane is formed by the rejected component having an enriched concentration as in Figure 1.6. Since the concentration of rejected particle is higher on the membrane-feed interface than the feed solution, concentration gradient occurs which is called concentration polarization. This phenomenon causes the flux to decline since the boundary layer creates a resistance to flow in addition to membrane's own resistance.

When the concentration on the membrane wall reaches a maximum, which can be the solubility of the solute or the maximum packing density of particles, fouling develops which can be in the form of gel or cake and has an increasing thickness during ongoing filtration. The difference between concentration polarization and fouling is reversibility. Concentration polarization can be dissipated and reversed when the filtration stops. However, fouling may not always be reversed like concentration polarization, keeps building up and might damage the membrane for good by creating a permanent resistance layer leading to decreased permeability.

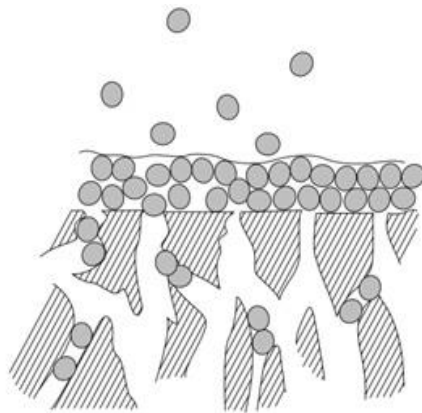


Figure 1.6. Fouling formation on the membrane surface and internal fouling in the pores of an ultrafiltration membrane¹

There are different types of fouling: pore blocking, adsorption fouling and cake formation. Particles blocking the pores completely or partly are called pore blockage. Adsorption fouling is observed when the particles are being adsorbed by the membrane material and its severity is proportional to the extent of adsorption. The third type, cake layer deposition happens with the particles fouling in front of the membrane. Cake layer structure may vary according to different parameters. Cake porosity and thickness are the main calculated components that give a prediction about its structure. Kozeny-Carman equation used in fluid dynamics for flow in packed bed, is utilized for this calculation.

$$\frac{\Delta P}{L} = -\frac{180\mu}{\varphi_s^2 D_p} \frac{(1-\varepsilon)^2}{\varepsilon^3} u_s \quad (1.1)$$

In the equation (1.1), Kozeny-Carman equation is written including ΔP as pressure drop, L as length of the bed, μ as dynamic viscosity of the fluid, ε as porosity of the bed, D_p as diameter of particles in bed, φ_s as the sphericity of the particles in bed, u_s as the superficial velocity of the fluid. In equation (1.2), Darcy's Law of flow in porous medium which is derived by the experiments of water flow in sand⁴⁴, is represented including Q as volumetric flowrate, A as cross-sectional area of flow, K as permeability, L is the length of porous medium and R is the resistance of the medium to flow.

$$u_s = \frac{Q}{A} = -\frac{K}{\mu} \frac{\Delta P}{L} \quad (1.2)$$

$$R = -\frac{L}{K} \quad (1.3)$$

The cake layer which forms on the surface of the membrane is considered as an additional resistance to membrane resistance which is presented in resistances-in-series model. By

this model, membrane resistance and resistance created by fouling adjacent to the surface are linked to each other as it is shown in equation 1.4. Resistance values of membranes against the flow are calculated by applying Darcy's Law and resistances-in-series model according to the equation 1.5 including μ_s as solvent viscosity and P as pure solvent permeance. R_{total} values show the total resistance shown by the membrane and the cake layer formed during the experiments. Since the total resistance is known by the experimental data and membrane resistance is known by pure solvent permeance values; cake resistances are calculated by the difference between them.

$$R_{total} = R_{cake} + R_{mem} \quad (1.4)$$

$$R_{mem} = \frac{\Delta P}{\mu_s J} = \frac{1}{\mu_s P} \text{ (m}^{-1}\text{)} \quad (1.5)$$

To understand how the particles behave when they are fouling on a membrane, there has been some studies investigating the effects of numerous possible impacts such as surface charge of particles, polydispersity, initial particle deposition rate, pH, and salinity. In 2021, Ozofo et al. tried to change pH, salinity, and concentration to see their impact on the cake structure comprehensively during ultrafiltration with polyether sulfone PES membrane in water.⁴⁵ The cake porosity, which is dependent on pH and salt concentration of the feed, was found to be increasing at the initial stage and later reached a steady point for all pH and salinity conditions. They explained that the severity of different fouling mechanisms differs with pH and ionic strength of feed.

Han et al. searched the effect of initial particle deposition rate on cake formation of 3 μ m latex particles, which is seen in Figure 1.7, in water during microfiltration with polycarbonate track-etched membrane and noticed that the relation is not linear.⁴⁶ To see the effect, they conducted experiments with four different initial deposition rates. At the highest and lowest values of the rates, particles were apt to assemble larger clusters and

more compact cake layer resulting in the highest cake resistances, while in the middle rates they tended to disperse more.⁴⁶

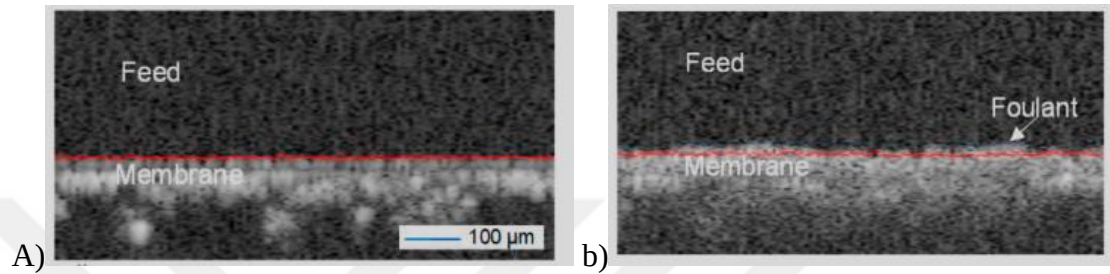


Figure 1.7. a) Clean PCTE membrane with the red line showing membrane surface b) fouled membrane after 50 minutes of filtration by 3 μ m latex particles at initial deposition rate 6L/h.⁴⁶ Reproduced with permission (Han et al., 2021). Copyright 2021, Elsevier.

In 2018, Han et al. inspected the effect of the particle surface charge on the cake structure by using 3 μ m latex particles with different surface charges during microfiltration with PCTE membranes.⁴⁷ Positively charged particles gave the least flux decline and the least severe fouling. Positive particles depositing on the pore areas and creating a more ordered cake layer resulted in giving the best performance. Because of the repulsive interaction between the negatively charged particles and the PCTE membrane, particles create a non-homogeneous cake by fouling on each other.⁴⁸ Zamani et al. analyzed the effect of particle interaction to each other and membrane by polystyrene and glass particles during microfiltration with Anopore membranes in water.⁴⁸ Glass particles which have repulsive interactions between membrane and each other by Gibbs free energies, resulted in providing a higher critical flux with less serious fouling. Since polystyrene particles have attractive interactions between themselves and membrane, relaxation method was less successful for the removal of fouling layer when it is compared to glass. Cluster formation was observed for polystyrene particles as it is seen in Figure 1.8, since their interaction is

attractive, they tended to foul on each other more than on the membrane, ended up creating a taller, tailed, and non-homogenous cake layer in contrast with glass particles who created a more ordered cake layer as a result of their choice to foul on the membrane rather than onto another particle.⁴⁸

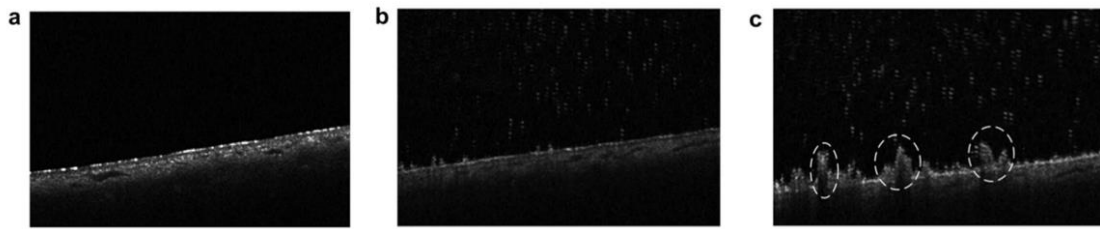


Figure 1.8. Optical coherence tomography images of clusters formed by polystyrene particles taken after a) 10 minutes b) 30 minutes c) 60 minutes of filtration while the crossflow velocity is fixed at 0.05 m/s.⁴⁸ Reproduced with permission (Zamani et al., 2016). Copyright 2016, Elsevier.

Wu et al. analyzed the effect of having particles with two different sizes on the structure of the internal fouling by using 200 nm and 40 nm fluorescent carboxylated microspheres during microfiltration with polyvinylidene difluoride (PVDF) membrane in IPA Triton X-100 mixture.⁴⁹ Fouling areas were formed by the immobilization of 200-nm particles first which was caused by the higher probability of bigger particles to contact with membrane and in most of the areas where 200 nm particles were settled there were 40 nm particles immobilized as well. The coexistence of both particles shows that 200 nm particles played a part as nucleation centers for fouling.⁵⁰

1.4 DLVO and XDLVO Theories of Surface Interactions

Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and Extended DLVO theory (XDLVO) are used to quantify the interaction energies between particles and the stability of colloids. DLVO theory utilizes Lifshitz-van der Waals forces (LW) and electrostatic

forces (EL) whereas XLDVO theory additionally includes Lewis Acid-Base interaction.^{51,52} Weak intermolecular forces which are called Van der Waals forces, include dipole-dipole forces, dipole-induced dipole forces and induced dipole-induced dipole forces (London) which is the weakest.⁵³ Dipole is called when a molecule has unbalanced charge dispersion and has polarity in the structure. Induced dipole is observed when a permanent dipole is close to a nonpolar component and creates polarity for momentarily.⁵² Electrostatic forces are dominant between charged components over Debye Length which is an indicator of how far the electrostatic force is effective.^{51,52,54} When two components are bounded with covalent bond, the one accepting the electrons is called Lewis acid and the one providing the electrons is Lewis base. The interaction energy between them, AB, is included in XDLVO theory. In this study, by DLVO and XDLVO theories, the interaction energy between particles in DMF, water, IPA and ethanol is calculated.

1.5 Aim

Nanoparticles are used in a wide variety of areas such as functional coatings, catalysis, textiles, paints, and drugs^{48,50,55,56} and are of great interest to researchers as well because of their unique nature due to their large surface area to volume ratios. There are many ways to produce nanoparticles like sol-gel method⁵⁷, hydrothermal synthesis⁵⁸ and microemulsion.⁵⁹ At the end of synthesis, they typically need to be concentrated without agglomeration. For post-processing or storage, their solvent medium may also need to change for reasons like surface functionalization. In lab scale, centrifugation is used for these, but on large scale especially for small particles this is costly. Membrane separation is a low cost, continuous alternative.

The objective of this study is to observe and understand the fouling behavior of two different types of nanoparticles in different organic solvent media which are dimethylformamide, water, isopropyl alcohol, and ethanol during ultrafiltration by cellulose membranes. Since these solvents have different features, the fouling behavior is expected to be different. Water, which is a highly swelling medium for cellulose, is polar protic like ethanol and isopropanol. However, these alcohol solvents do not cause swelling for cellulose membranes. Dimethylformamide is a polar aprotic solvent, and like ethanol and IPA it does not lead to swelling. The fouling behavior of native, hydrophilic and hydrophobized silica particles during concentration in these solvents and in diafiltration process where the medium is changed from IPA to ethanol, water and DMF was studied. Cake resistances and particle size before and after experiments are used for assessment of fouling. DLVO and XDLVO theories were used to calculate the interaction energies between particles in different solvents to explain the fouling behavior.

CHAPTER 2

EXPERIMENTAL METHOD

2.1 Materials

Cellulose acetate ($M_n \sim 50000$ Da by GPC), dimethyl sulfoxide (DMSO), polyethylene glycol (PEG400, 400 Da) sodium hydroxide (NaOH), N,N-dimethylformamide (DMF), ethanol and isopropanol (IPA), tetraethoxysilane (TEOS), ammonium hydroxide (NH_4OH), dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride (DMOAP) were purchased from Sigma-Aldrich.

2.2 Preparation of Polymer Solution and Fabrication of Membrane

To observe the fouling effect and to eliminate the effect of membrane morphology, a single composition of polymer solution was used to cast the membranes. 20wt.% cellulose acetate (CA) as the polymer, 10wt.% polyethylene glycol (PEG400) as the pore-forming agent and 70wt.% dimethyl sulfoxide (DMSO) as solvent, were added together and mixed until the solution is homogeneous. After the polymer solution was ready, the membranes were cast by using a 250 μm steel casting bar to obtain flat sheet membranes. Immediately, membranes were soaked into coagulation bath which was pure water, for phase inversion to take place. After coagulation bath step, membranes were taken into 1-L-beakers containing RO water. For 24 hours, their water was changed at least 5 times to dispose of remaining solvent. Following, membranes were placed in alkaline hydrolysis medium, which was 0.05 M NaOH in water to convert cellulose acetate membranes to cellulose. Prepared membranes were stored in 20v.% ethanol-water solution to avoid bacterial growth. The process is visualized in Figure 2.1.

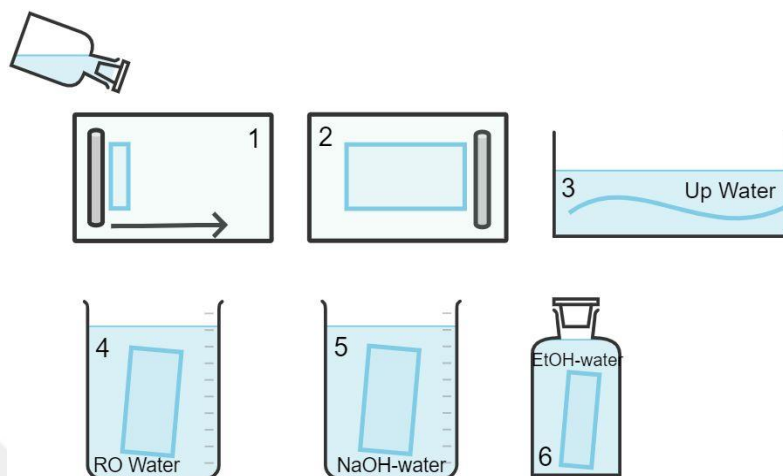


Figure 2.1 Flat sheet membrane fabrication process

2.2.1 Membrane Morphology Characterization

Scanning electron microscopy Quanta 400F Field Emission SEM in Metu Central Laboratory and Tescan Vega3 in Metu Chemical Engineering were used to visualize and analyze the morphology of membranes. Cross-section and surface analyses were performed. For cross-sectional analysis, samples from membranes are frozen and cracked in liquid nitrogen. For both types of analyses, samples were dried under vacuum and coated with gold-palladium prior to analysis.

2.3 Silica Synthesis & Coating

To synthesize silica nanoparticles, Stöber method was followed. 73.83 mL IPA, 1.98 mL ultrapure water, 0.27 mL NH_3OH mixture were stirred. After 10 minutes, 3.92 mL TEOS was added dropwise and stirred at 450 rpm for 24 hours. For coating the nanoparticles with DMOAP, freshly synthesized nanoparticles were moved from IPA to water by filtration in Sterlitech HP4750 dead-end cell through the same regenerated cellulose membranes used in the main experiments by following the procedure presented next.

- After synthesis, the concentration of the suspension was analyzed by Moisture Analyzer Shimadzu MOC63u by evaporating the solvent.
- According to the suspension concentration and required feed concentration of concentration and diafiltration experiments, the volume of the suspension that needs to be filtered was calculated.
- Filtration of SiO₂-IPA suspension was conducted at 1 bar while being stirred at 400 rpm until 5 mL of suspension was left inside the system.
- The cell was opened, and 10 mL of water was added over the left suspension inside the cell.
- Filtration of SiO₂-IPA-Water suspension was conducted at 1 bar while being stirred at 400 rpm until 5 mL of suspension was left inside the system.
- The cell was opened, and 10 mL of water was added over the left suspension inside the cell.
- Filtration of SiO₂-IPA-Water suspension was conducted at 1 bar while being stirred at 400 rpm until 5 mL of suspension was left inside the system.
- Following, a complementary amount of water was added according to the required particle concentration.
- Suspension (SiO₂-water) was stirred for 24 hours inside the cell.
- Obtained suspension was moved out of the cell and filtered through filter paper for two times to remove solid precipitation formed by coagulated nanoparticles. Precipitation stayed on the filter paper while the particle-solvent suspension permeated through the filter paper.
- 10 mL of suspension was used to analyze the suspension concentration by Moisture Analyzer.
- 1v.% DMOAP was added to the suspension for coating. The suspension was put into ultrasonic bath for 15 minutes for the completion of coating.

For concentration experiments in DMF and water, native particles are required to be in these solvents. For moving particles from IPA which is the synthesis medium, to DMF

and water; the same procedure was conducted except the last step. For the concentration of hydrophobized particles in DMF and IPA, particles are required to be in these solvents. For moving particles from water which is the coating medium, to DMF and IPA after the coating process, the same procedure was conducted except the last step. For diafiltration experiments of hydrophobized particles from IPA to ethanol, DMF and water, particles are required to be in IPA. For moving particles from water which is the coating medium, to IPA, the same procedure was conducted except the last step.

2.3.1 Particle Characterization

To determine the particle size, Multiangle Dynamic Light Scattering (Malvern Zetasizer Ultra) was used. Also, to determine particle surface charge before and after coating at 25°C, Malvern Zetasizer Ultra was used. Shimadzu MOC63u Moisture Analyzer was used to determine the concentration of nanoparticle suspensions which were used as feed suspensions in the experiments by evaporating the solvent. Since DMF is not suitable for moisture analyzer and DMOAP decomposes at low temperatures, manual gravimetric measurements were used for these samples where the samples before and after solvent evaporation were weighed by an analytical balance. The samples were heated by a heater in fume hood to evaporate the solvent as the first step. Secondly, they waited in vacuum furnace for a day before weighing.

2.3.2 Viscosity Measurement

Viscosity measurements were performed by Ubbelohde capillary viscometer at room temperature with IPA, DMF, water and their mixtures. By this method kinematic viscosities, were obtained which were used to calculate dynamic viscosities by division into densities.

2.3.3 Turbidity Analysis

To quantify the turbidity of nanoparticle suspensions, HI88703 HANNA Turbidimeter was used. Turbidity data were also used to correlate permeate concentrations by using known feed concentrations and to calculate rejection values.

2.4 Performance Tests

2.4.1 Concentration Experiments

In concentration experiments, firstly pure solvent permeance of the membrane was measured at 3, 2, 1 bar in Sterlitech HP4750 dead-end cell as the experimental setup is presented in Figure 2.2. Feed suspension concentrations were between 1.5-6.5wt.%. Before using the nanoparticles in experiments, the suspensions were put into ultrasonic bath (Branson-2510) for 15 minutes to prevent clustering and disperse the nanoparticles homogeneously. Experiments were conducted at 1 bar, 400 rpm. After experiments, the first cleaning step was applied which was putting 30 mL pure solvent into the system and stirring at 400 rpm for 15 minutes to remove the particles left on the membrane surface. The pure solvent permeance of membrane was measured at 1 bar after the cleaning step. The second step of cleaning was putting the membrane in ultrasonic bath for 15 minutes to remove particles left on the surface that were not recovered by the first cleaning step. Following, pure solvent permeance of membrane was measured at 1 bar again. Every concentration experiment code is represented in Table 2.1. The first letter of the code represents the particle type as N for native particles and H for hydrophobized particles. Second part of the code represents the solvent medium which is IPA for isopropanol, W for water and DMF for dimethylformamide. The third part of the code represents the experiment type as C for concentration and D for diafiltration. The number at the end of the code represents the experiment number in the set. Concentration of native particles in IPA and water was performed three times each, in DMF four repeats were performed.

Concentration of hydrophobized particles in DMF and water was performed three times each, in IPA four repeats were performed.

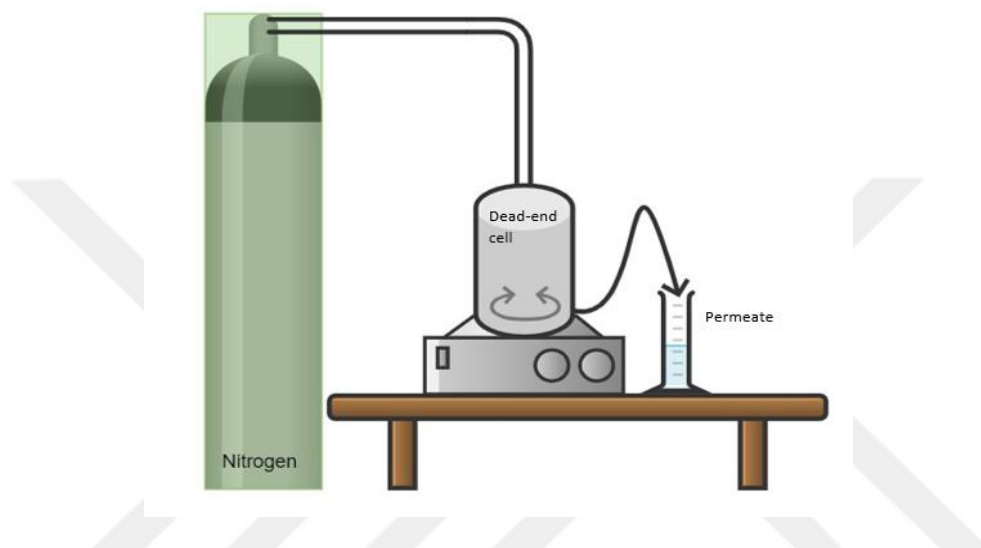


Figure 2.2 Schematic drawing of dead-end cell

Table 2.1 Experiment codes of concentration

Experiment Code	Particle Type	Solvent	Experiment Type
N-IPA-C-1	Native Particles	IPA	Concentration
N-W-C-1		Water	
N-DMF-C-1		DMF	
H-IPA-C-1	Hydrophobized Particles	IPA	
H-W-C-1		Water	
H-DMF-C-1		DMF	

The thickness and porosity of cake layer formed during concentration experiments are calculated by using following equations derived by Kozeny-Carman equation which is originally used to model the fluid flow in a packed bed and utilized to calculate porosity and thickness of the cake layer in membrane processes.

$$R_{cake} = \frac{m_{cake}}{(1-\varepsilon)\rho(A_{mem})} \frac{180(1-\varepsilon)^2}{\varepsilon^3(\varphi_s D_p)^2} \quad (2.1)$$

$$\delta = \frac{m_{cake}}{(1-\varepsilon)\rho(A_{mem})} \quad (2.2)$$

R_{cake} represents the cake layer resistance while ε stands for porosity in equation (2.1) and δ stands for thickness in equation (2.2). The cake layer weight m_{cake} is calculated by the particle concentration of the suspension and assuming all the permeate leaving the system left its particles in the cake. A_{mem} represents the membrane area while ρ represents the particle density. Particle size is represented by D_p whereas φ_s represents particle sphericity.

2.4.2 Diafiltration Experiments

In diafiltration experiments, the first step was to measure the pure solvent permeance of the membrane in Sterlitech CF042SS crossflow cell. The experimental setup includes a diaphragm pump, a back pressure valve in addition to the crossflow cell as it is seen in Figure 2.3. Feed suspension concentration was 1.1 l wt.%. The experiment was performed at 1 bar at a cross flow rate that gives Reynolds number between 20-50. After one hour of total recovery mode, the diafiltration part was started. For every 10 mL permeate taken, 10 mL of replaced new solvent was added to the system. When the experiment was finished, the suspension left in the system was circulated in the system without pressure for 15 minutes and taken out. Pure solvent permeance was measured at 1 bar. As the

second step of cleaning procedure, pure solvent permeance was measured again at 1 bar after the membrane was put into ultrasonic bath for 15 minutes.

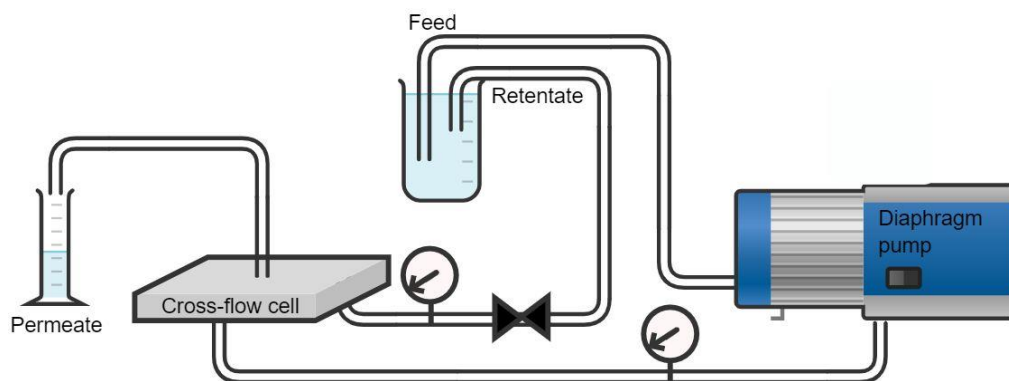


Figure 2.3 Schematic drawing of crossflow cell

Every diafiltration experiment code is represented in Table 2.2. Coding structure is the same as concentration experiments. Diafiltration of native particles to DMF and ethanol was performed three times each, in water six repeats were performed. Diafiltration of hydrophobized particles in DMF and ethanol was performed three times each, in water four repeats were performed.

Table 2.2 Experiment codes of diafiltration

Experiment Code	Particle Type	Exchanged Solvent	Experiment Type
N-ETOH-D-1	Native Particles	ETOH	Diafiltration
N-W-D-1		Water	
N-DMF-D-1		DMF	
H-ETOH-D-1	Hydrophobized Particles	ETOH	
H-W-D-1		Water	
H-DMF-D-1		DMF	

2.4.3 Membrane Performance Parameters

Pure solvent permeance values were calculated by dividing flux J (L/hm²) into transmembrane pressure (bar) ΔP in equation (2.3) as follows:

$$P = \frac{J}{\Delta P} \text{ (L/hm}^2\text{bar)} \quad (2.3)$$

To evaluate the ability of the membrane to separate nanoparticles from solvents, rejection was calculated as follows:

$$R_i = \left(1 - \frac{C_i^{per}}{C_i^{feed}}\right) 100 \quad (2.4)$$

In the equation (2.4), R_i stands for rejection while permeate concentration and feed concentration are shown as C_i^{per} , C_i^{feed} respectively.

2.5 DLVO & XDLVO Theory Calculations

DLVO and XDLVO theories are used to quantify the interaction energy between nanoparticles in different solvents. For DLVO theory, the van der Waals and electrostatic interactions are considered. For XDLVO theory, acid-base interaction is added to the energy calculated by DLVO theory. For identical two spheres:

$$W_{LW} = -\frac{(A_{sls}R)}{(12d)} \quad (2.5)$$

$$A_{sls} = (\sqrt{A_s} - \sqrt{A_l})^2 \quad (2.6)$$

The LW interaction energy equation in equation (2.5) has A_{sls} Hamaker constant for silica-solvent media, R is the radius of nanoparticles and d is the distance between particles. To calculate the Hamaker constant of silica-solvent, equation (2.6) is utilized including A_s as Hamaker constant of silica, A_l as Hamaker constant of liquid medium.

$$W_{EL} = R(4.61 \times 10^{-11})e^{-KD} [\tanh\left(\frac{\psi_0}{103}\right)] \quad (2.7)$$

The EL interaction energy equation (2.7) has K , the inverse Debye Length, ψ_0 , and the surface potential, which was estimated as the zeta potential of particles. The Debye Length is calculated as follows in all solvents⁵²:

$$K^{-1} = \sqrt{\frac{D_{eff}\epsilon_0\epsilon_r}{\sigma}} \quad (2.8)$$

D_{eff} is the effective diffusion coefficient taken as $10^{-9} \text{ m}^2/\text{s}$ ⁵². ϵ_r is solvent's dielectric constant and ϵ_0 is vacuum permittivity. σ is solvent's electrical conductivity. Since the ion concentrations in organic solvents is hard to predict, the Debye Length equation for water is not used. In equation 2.8, the challenging part is obtaining effective diffusion coefficient. However, since this value is in a definite range and Debye Length is affected by the square root of it, the error is minor sourced by this unknown parameter.

$$W_{AB} = \pi R \lambda \Delta G_{sls}^{AB} \exp\left(\frac{d_0 - d}{\lambda}\right) \quad (2.9)$$

$$\Delta G_{sls}^{AB} = -4(\sqrt{\gamma_s^+ \gamma_s^-} + \sqrt{\gamma_l^+ \gamma_l^-} - \sqrt{\gamma_s^+ \gamma_l^-} - \sqrt{\gamma_s^- \gamma_l^+}) \quad (2.10)$$

The AB interaction energy equation (2.9) has λ the characteristic decay length that is taken as 0.6 nm ²⁸; ΔG_{sls}^{AB} the Gibbs free energy between particles; d_0 is the minimum separation distance taken as 0.157 nm .²⁸ To calculate Gibbs free energy between particles, equation (2.10) is utilized, including surface tension components; γ^+ electron acceptor parameter and γ^- electron donor parameter.



CHAPTER 3

RESULTS AND DISCUSSION

3.1 Characterization of Nanoparticles

3.1.1 Native Silica Nanoparticles

In this study, silica nanoparticles were produced by Stöber method and used as foulant in experiments.⁶⁰ In literature, there are various recipes to produce different sized silica nanoparticles by this method by changing the solvent medium or the concentration of reactants.^{60–64} Both SEM images of native silica nanoparticles on membrane surface in Figure 3.1a and DLS analysis of freshly synthesized particles as in Figure 3.1b show nanoparticles around 50nm.

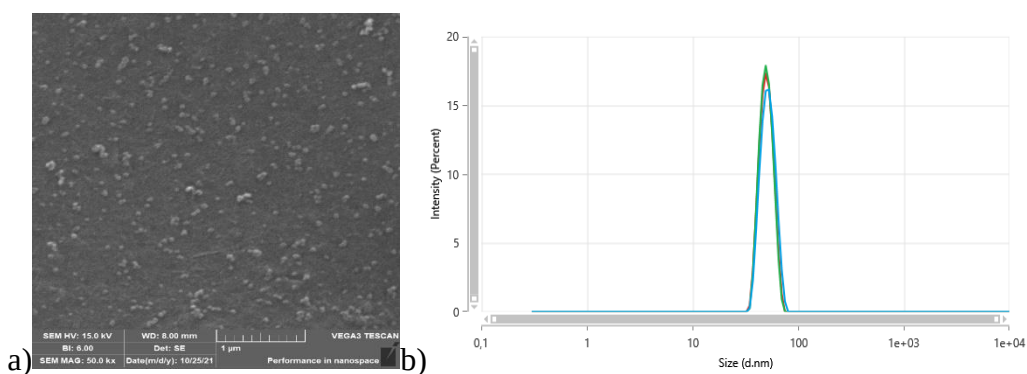


Figure 3.1 a) SEM image of a membrane showing of silica nanoparticles on the surface b) Particle size analysis by DLS after synthesis (red line represents the first analysis, green line represents the second analysis, blue line represents the third analysis)

For evaluating performance of membranes in concentrating the nanoparticles, the solvent medium was changed via batch diafiltration as described in chapter 2.4.2. This leads to the need for the particle size analysis in different solvents to see if particle size is changing. Particles are transported to ethanol, DMF and water by filtration processes the same as the feed suspensions are prepared for concentration experiments. Also, particle size analysis is performed daily in IPA in two different versions. The purple data set (IPA UNF) in Figure 3.2 shows the particles in IPA which were not filtered or underwent additional steps after synthesis. The orange data set (IPA F) shows the particles in IPA which went through a filtration process as the particles in other solvents to see the effect of feed preparation filtration on particle size. Particle size data was taken daily until day 11 without stirring. After day 11, the samples were stirred at 400 rpm to see if there is any aggregation upon stirring. Figure 3.2 shows that nanoparticle size does not vary significantly within the experimental measurement uncertainties.

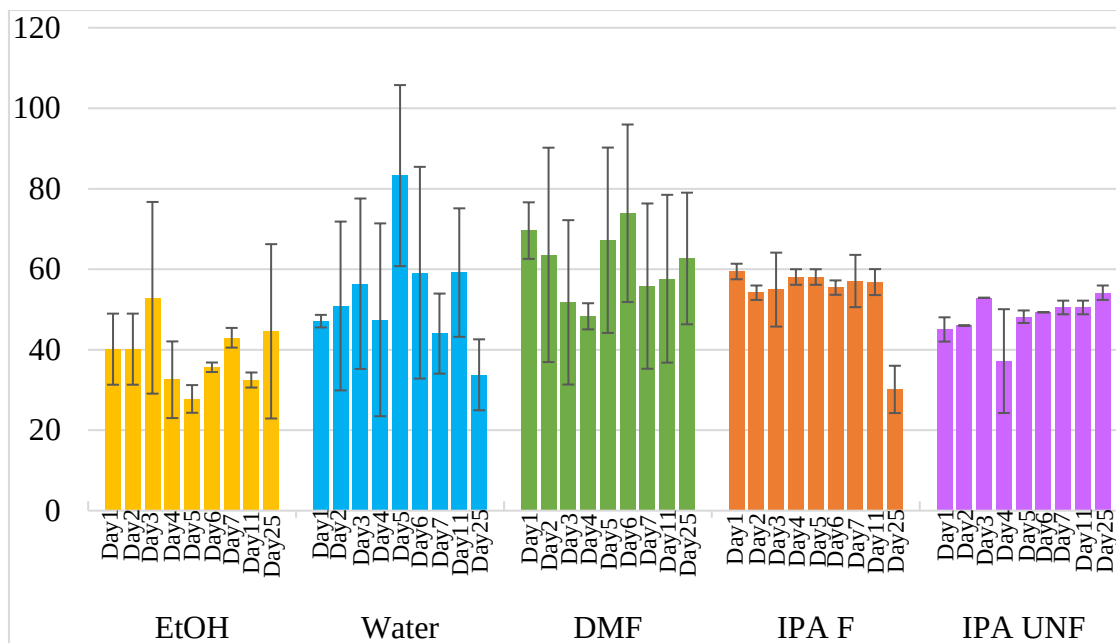


Figure 3.2 Silica nanoparticle size in different solvents at days 1, 2, 3, 4, 5, 6, 7, 11 and 25

3.1.2 Hydrophobized Nanoparticles

To see the effect of hydrophobicity on fouling, silica particles underwent a coating process with DMOAP. The structures of native and hydrophobized particles are presented in Figure 3.3. Particle size and zeta potential are analyzed to determine the success of coating process as in Figure 3.4.

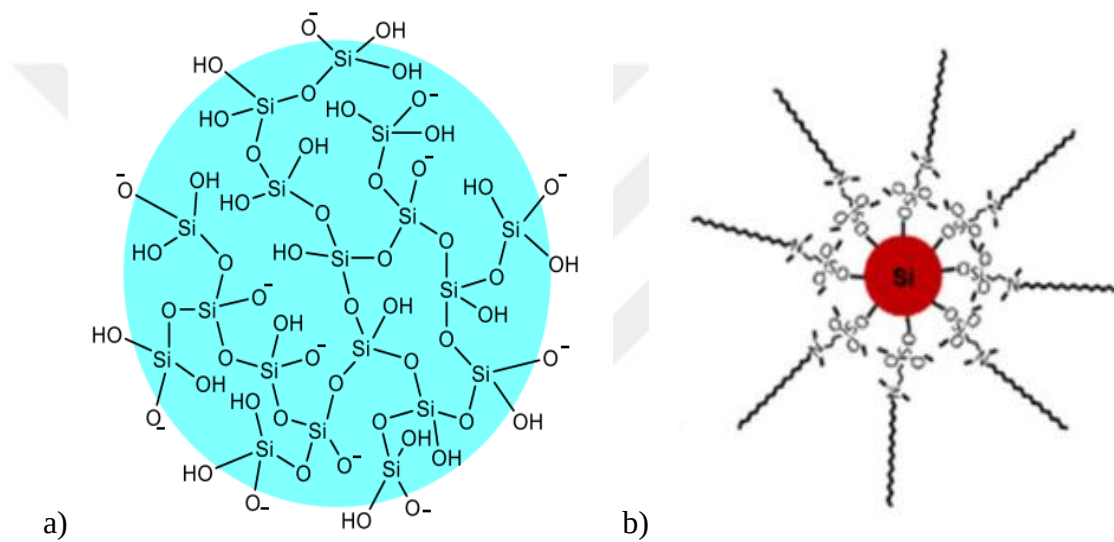


Figure 3.3 a) Native silica nanoparticles⁶⁰ b) Hydrophobized silica nanoparticles.⁶⁵

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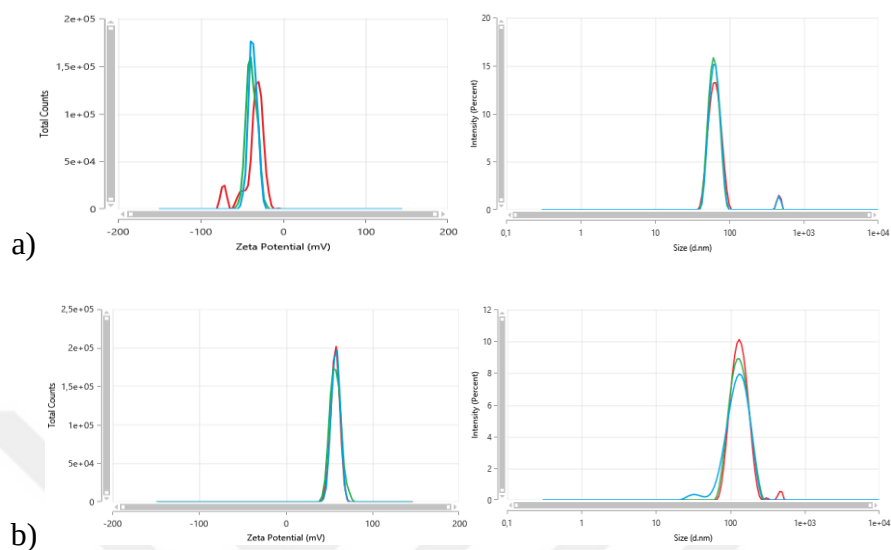


Figure 3.4 Zeta potential and particle size of silica nanoparticles in water a) before coating and b) after coating (red line represents the first analysis, green line represents the second analysis, blue line represents the third analysis)

The values are also listed in Table 3.1 which shows the growth of particle size after coating from 62 nm to 131 nm. This indicates some agglomeration of hydrophobized nanoparticles in water, which is expected. Zeta potential change is also observed from -36 mV to 57.3 mV which also proves the coating, where the positive charge is due to the quaternary ammonium groups in DMOAP.^{65–67}

Table 3.1 Nanoparticle DLS and zeta potential analyses in water before and after coating

Sample	Zeta Potential (mV)	Z-average Particle Diameter (nm)
Before Coating	-36.6	62.3
After Coating	57.3	131

3.2 Membrane Fouling with Nanoparticles

In this study, fouling of cellulose membranes with silica nanoparticles during concentration and diafiltration experiments is observed. In concentration experiments, the concentration of the feed suspension is increased throughout the filtration and in diafiltration experiments the solvent medium is changed in a continuous process without change in nanoparticle concentration in the feed side. Same membranes which are cast from same polymer solution were used for each experiment. To observe the surface and cross section membrane structure, SEM analysis is used. By the conducted experiments, changes in cake layer resistance were observed.

3.2.1 Membrane Morphology

Cellulose membranes were formed by first fabricating cellulose acetate membranes by phase inversion followed by conversion into cellulose via alkaline hydrolysis. The membranes' molecular weight cut-off (MWCO) was determined² as 10 kDa by Savaş-Alkan et al., which is suitable for complete nanoparticle rejection.

In Figure 3.5 and 3.6, SEM images of fresh membrane surfaces are shown. Freeze drying method is conducted before SEM analysis as the results are presented in Figure 3.6. Cross-sectional SEM analysis results are represented in Figure 3.7a displaying the support layer at the bottom. More porous support layer structure is clearly visible in Figure 3.7 with a tighter skin layer. Cross-sectional SEM images show the anisotropic structure of the regenerated cellulose membrane as it was anticipated.^{2,68} Even though the exact pore size of the membranes is not distinguishable from surface and cross section SEM images, the permeance values and MWCO indicate porous structure of the membranes.²⁷

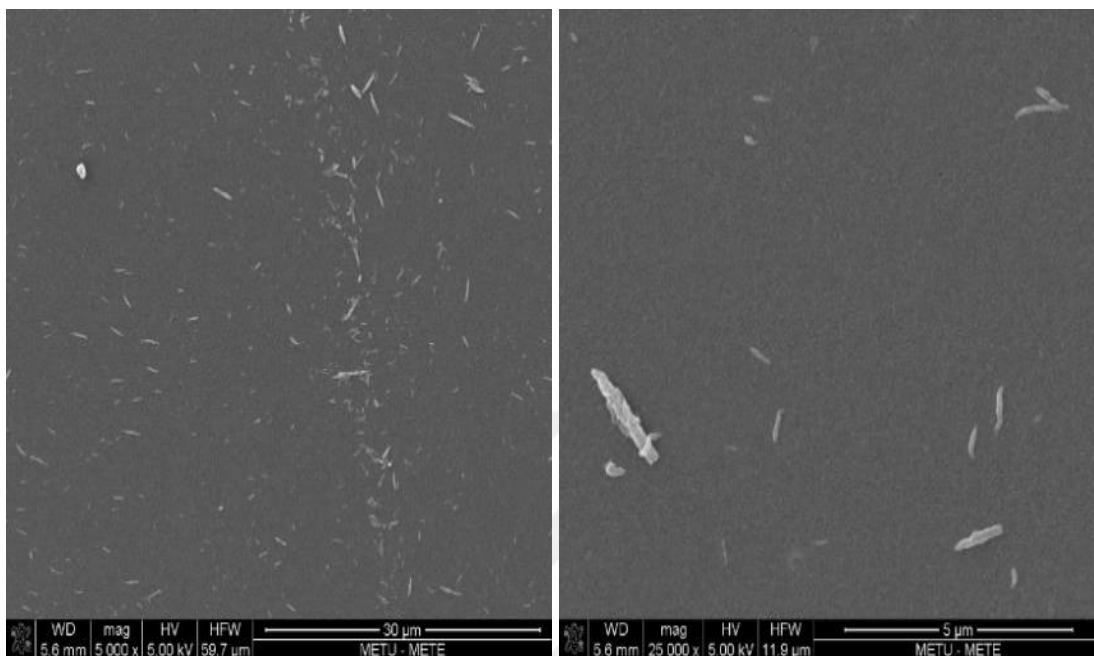


Figure 3.5 Unused regenerated cellulose membrane surface

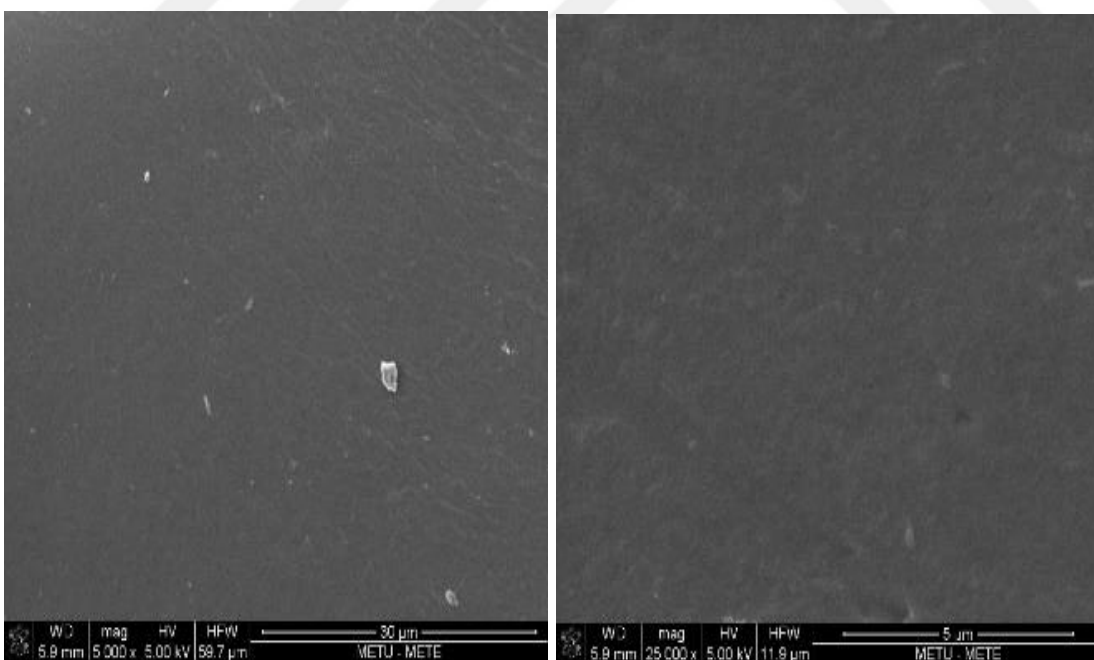


Figure 3.6 Freeze-dried membrane surface analysis

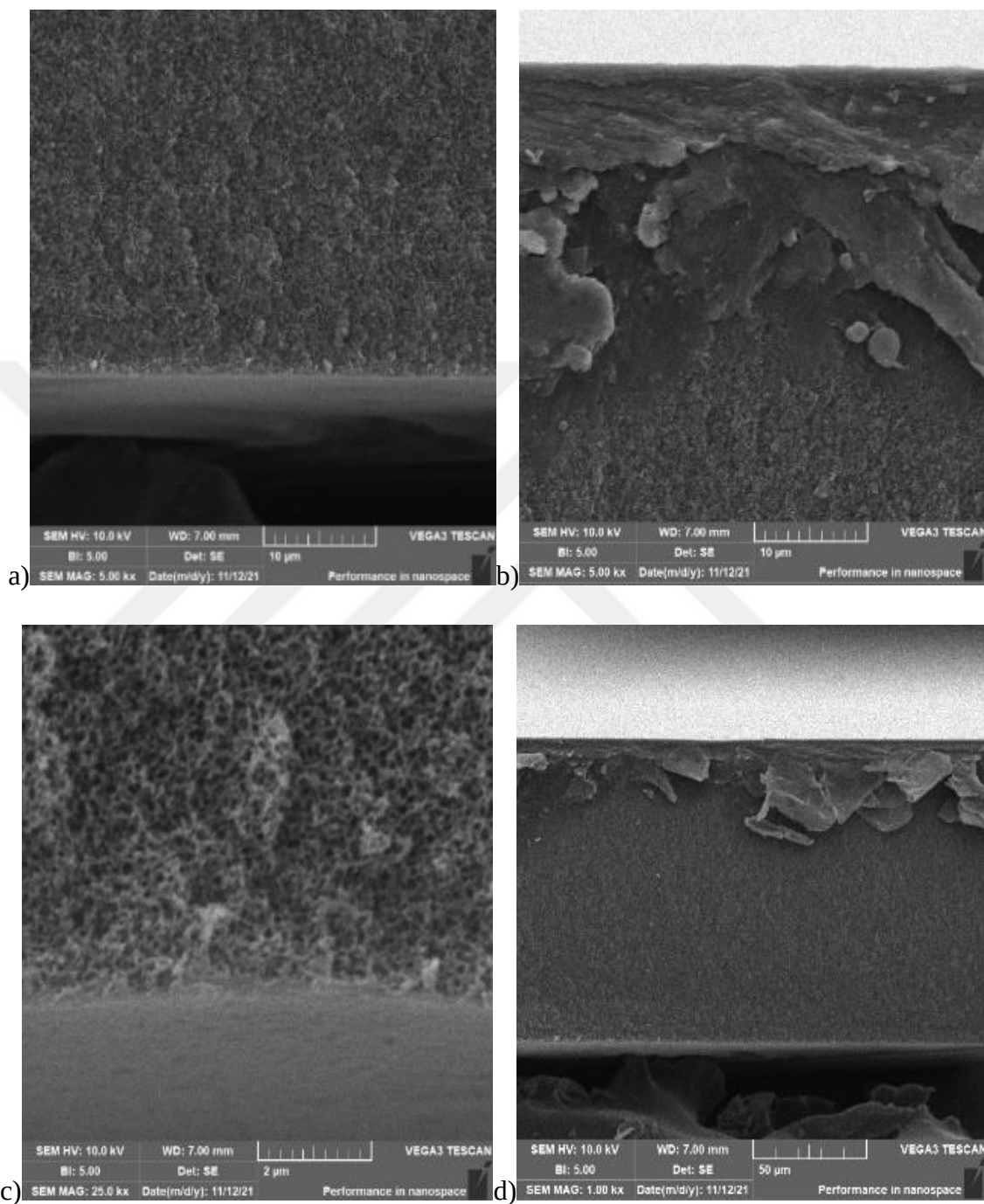


Figure 3.7 Cross-sectional SEM images of membranes a) displaying support layer at the bottom b) displaying skin layer c) displaying support layer at the bottom d) displaying support layer at the bottom and skin layer at the upper part

3.2.2 Concentration of Nanoparticles via Dead-end Filtration

Silica nanoparticles in IPA, water and DMF, are concentrated in dead-end cells to observe the cake layer formation. DLS analysis and turbidity analysis for particle size and concentration determination, are performed. By fouling, a cake layer on the membrane surface formed. To understand and compare the cake layer formation, membrane resistance and total resistance during the experiments are calculated by permeance values. To understand the structure of the cake, porosity and thickness of the cake layer are calculated using the Kozeny-Carman equation. To assess the success of membrane on separating solvent and nanoparticles, rejection is calculated and listed as experimental average in Table 3.2 for native and hydrophobized particles. In the first concentration experiment of native particles in IPA, N-IPA-C-1, the rejection throughout the experiment is presented in Figure 3.8 showing that minimum rejection over 99.9% while the suspension is concentrated from 3.18‰ to 6.18‰ around 1.5 times. Even though the recovery ratio is 80%, silica nanoparticle concentration has not increased close to 5 times as would be expected from material balance since most nanoparticles reside in the cake layer on the membrane surface. By looking at Figure 3.8 and Table 3.2 the minimum rejection is seen as 99% which means particles are separated from solvent perfectly as it was expected because the particles are significantly larger than pores. The solvent medium and particle coating does not affect the rejection since it is higher than 99% in every solvent with native and hydrophobized particles.

Table 3.2 Average rejection values of each concentration experiment for native and hydrophobized particles

Native Particles	Rejection%	Hydrophobized Particles	Rejection%
N-IPA-C-1	99.95	H-IPA-C-1	99.87
N-IPA-C-2	99.90	H-IPA-C-2	99.77
N-IPA-C-3	99.94	H-IPA-C-3	99.71
N-W-C-1	99.79	H-IPA-C-4	99.84
N-W-C-2	99.86	H-W-C-1	99.98
N-W-C-3	99.91	H-W-C-2	99.97
N-DMF-C-1	99.27	H-W-C-3	99.92
N-DMF-C-2	99.59	H-DMF-C-1	99.73
N-DMF-C-3	99.62	H-DMF-C-2	99.97
N-DMF-C-4	99.03	H-DMF-C-3	99.85

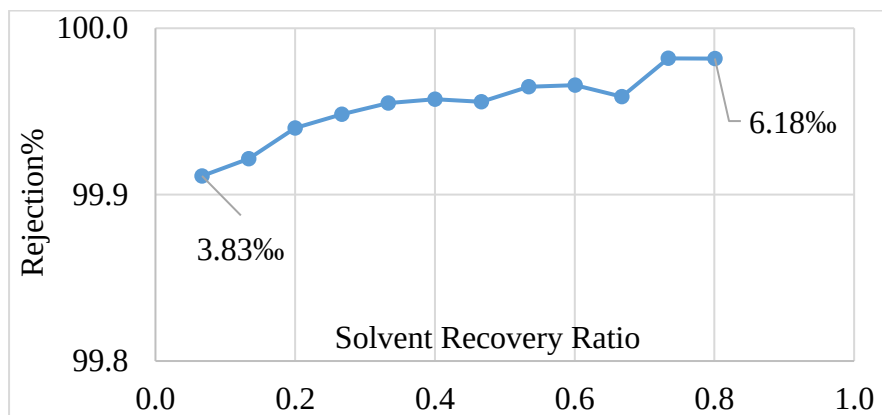


Figure 3.8 Native silica particles concentration experiment in IPA, N-IPA-C-1, and rejection during experiment vs. Solvent Recovery Ratio as Permeate Volume/Feed Volume with particle concentration at the beginning: 3.83‰ at the end: 6.18‰

In concentration experiments, native silica nanoparticles demonstrate different fouling behavior in different solvents as it was anticipated by previous studies.^{28,29,36,37} In Figure 3.9a the ratio of permeance during nanoparticle filtration to pure solvent permeance of the clean membrane (P/PSP) is shown to decrease for all solvents. The different fouling behavior can be compared better using cake resistances presented in Figure 3.9b. Cake layer resistance in every solvent follows a different path but their common point is that it is increasing constantly from beginning until 80% solvent recovery ratio. The fouling in the polar aprotic solvent DMF is less than the fouling in polar protic solvents water and IPA which both show similar resistance trend. There might be several reasons for closer cake resistance in IPA and water such as solvent type, particle size and cake structure. Firstly, in IPA and water, particle size is close to each other and around 60-70 nm as it is seen Figure 3.10. However, in DMF, particles which are agglomerated during the feed preparation process comprised of filtration, are around 100 nm which differentiates the structure of cake layer. While the same amount of particles are being filtered, larger particles create less resistant cake layers according to the Kozeny-Carman equation.

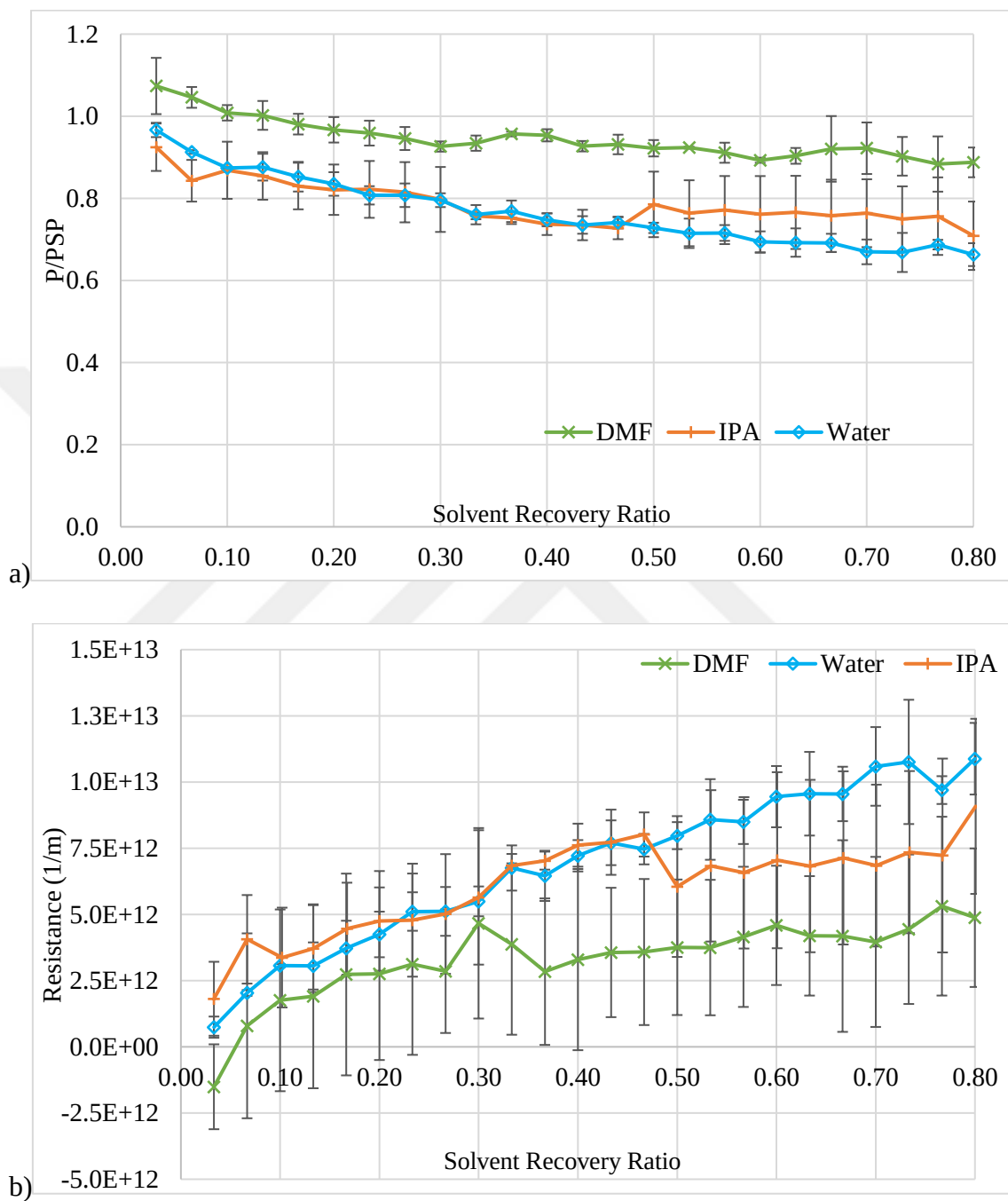


Figure 3.9 a) P/PSP values of concentration experiments with native nanoparticles, b) Cake layer resistance; both versus Solvent Recovery Ratio as Permeate Volume/Feed Volume

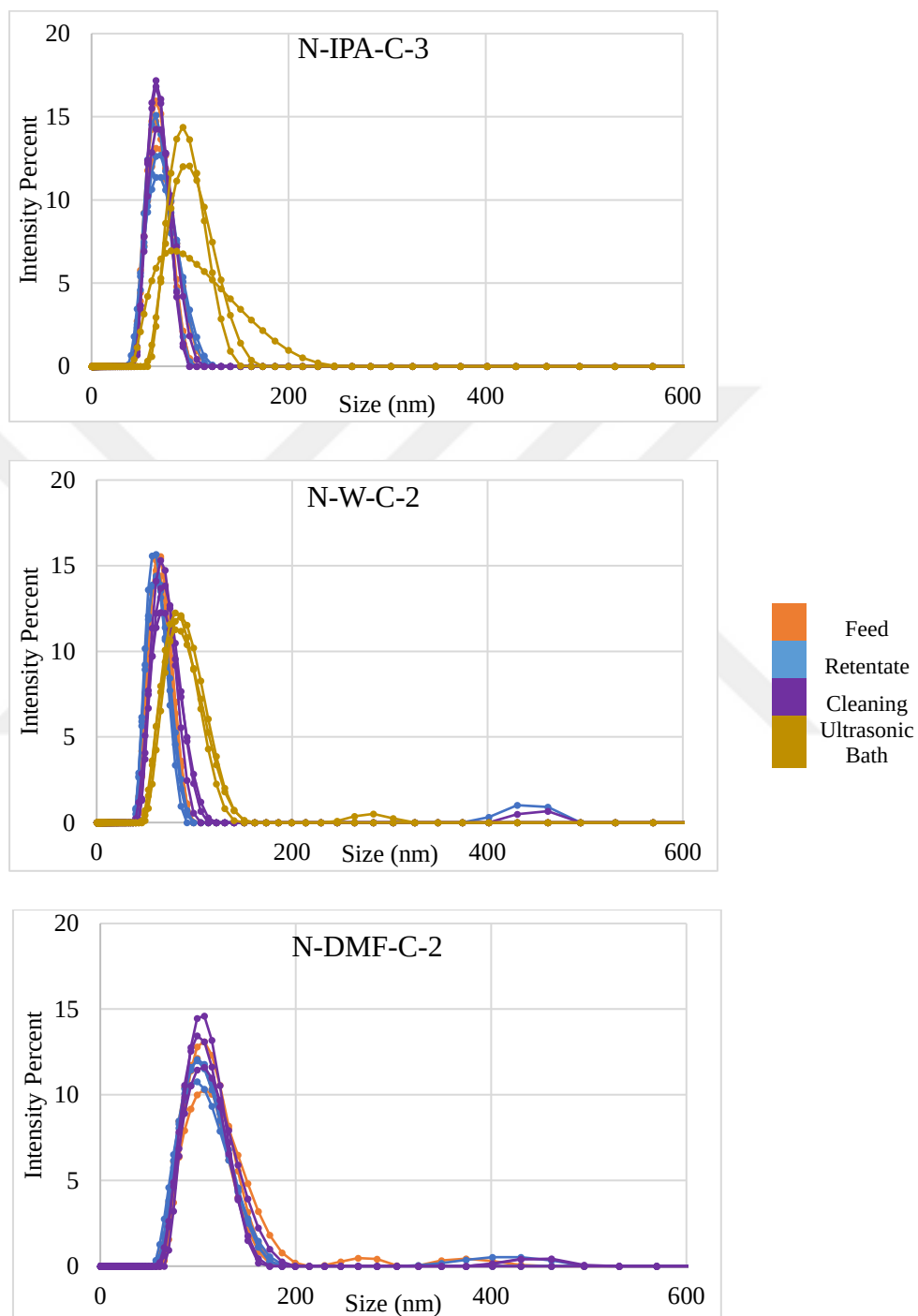


Figure 3.10 The experiments of silica concentration in IPA, water, and DMF, N-IPA-C-3, N-W-C-2, N-DMF-C-2 respectively, particle size results by DLS

The porosity and thickness of the cake are calculated by Kozeny-Carman equation, using the fact that in dead end filtration and close to full rejection, the total mass of the cake layer is formed by all the nanoparticles which accompany the amount of solvent taken in the permeate. The sphericity of the particles is taken as 1 and particle diameter values are taken from DLS analysis. The final cake resistances at 80% recovery are utilized to calculate the porosity which later is used for thickness calculation. When the porosity and thickness of cake layer are compared as it is presented in Figure 3.11, the cake thickness is 260 μm in IPA, 210 μm in DMF and 200 μm in water. The highest porosity of cake layers formed by native silica nanoparticles, is created in IPA as 0.65. In DMF and water, it is calculated as 0.60 and 0.50 respectively as in Figure 3.11. The porosity and thickness values are considered to be quite close to each other. The thickest cake layer in IPA could be balanced by the most porous structure which leads to creating cake resistance closer to water. Even though the porosity and thickness values in DMF are in between water and IPA, comprising of bigger particles creates less resistance.

The particle size analyses which are presented in Figure 3.10, show that particle sizes do not change during ultrafiltration since the feed and retentate are the same in all solvents. The analysis of the suspension used in the first step of cleaning shows that particles recovered at this step are not agglomerated in all solvents. However, when the suspension recovered from ultrasonic cleaning is analyzed, recovered particles at this step are agglomerated.

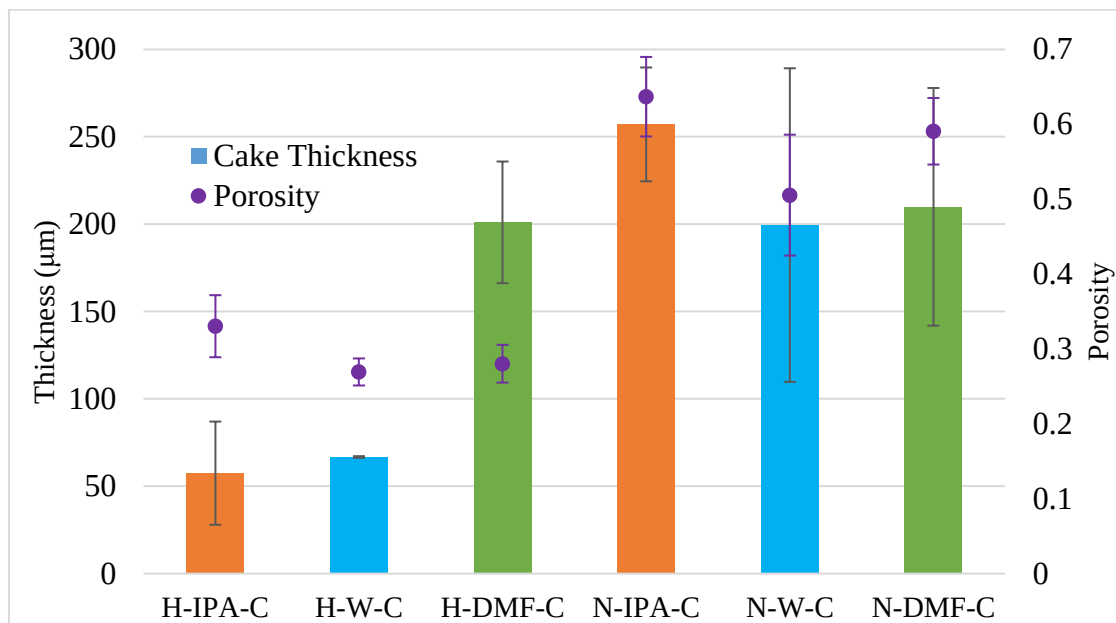


Figure 3.11 Cake layer properties as porosity and thickness for concentration experiments with native and hydrophobized particles

Particles were coated with DMOAP which creates hydrophobic natured silica particles.⁶⁵ As it is seen in Figure 3.12a permeance throughout all concentration of hydrophobized particles is decreasing by P/PSP data which exposes cake formation. The most severe fouling of hydrophobized particles is observed in DMF as it is seen in Figure 3.12a and Figure 3.12b. Cake resistance values, calculated by permeance data, in IPA and water are close to each other, while the resistance trend in DMF is distinctly different. At the beginning, a higher increase in cake resistance is observed in DMF as $8.7 \times 10^{12} \text{ m}^{-1}$ while water and IPA starts from similar cake resistances as $1.6 \times 10^{12} \text{ m}^{-1}$. A more rapid cake formation is observed in DMF initially, which may indicate higher nanoparticle-membrane interactions compared to those in water and IPA. Even though the increase rate in DMF is similar to water, initial deposition created the difference. After 80% solvent recovery ratio is reached, the least cake resistance is observed in water. Calculated cake porosity and thickness display the difference as well in Figure 3.11. Thickness is

calculated around 70 μm in water, 60 μm in IPA and 200 μm in DMF. The least thickness in IPA could be caused by low solvent recovery ratios used in this calculation. Since IPA has the highest viscosity, it has the lowest permeance which leads to longer experiments over 24 hours for 80% solvent recovery ratio. For that reason, 80% solvent recovery ratio is only reached in one experiment for the concentration of hydrophobized particles in IPA. If the experiments could be conducted until 80% solvent recovery ratio, thicker cake layers could be observed in IPA. The porosity is about 0.35 in DMF and water, while it is 0.4 in IPA which means hydrophobized particles form a thicker cake layer in DMF, having approximately the same porosity, explaining the higher resistance in DMF. Even though the particle size is ~ 100 nm in IPA and water, ~ 200 nm in DMF as it is presented in Figure 3.13, the bigger particles in DMF build a thicker layer. Since again DMF gives an obvious consistently different trend, the highest cake resistance is most probably motivated by polar aprotic structure of the solvent.

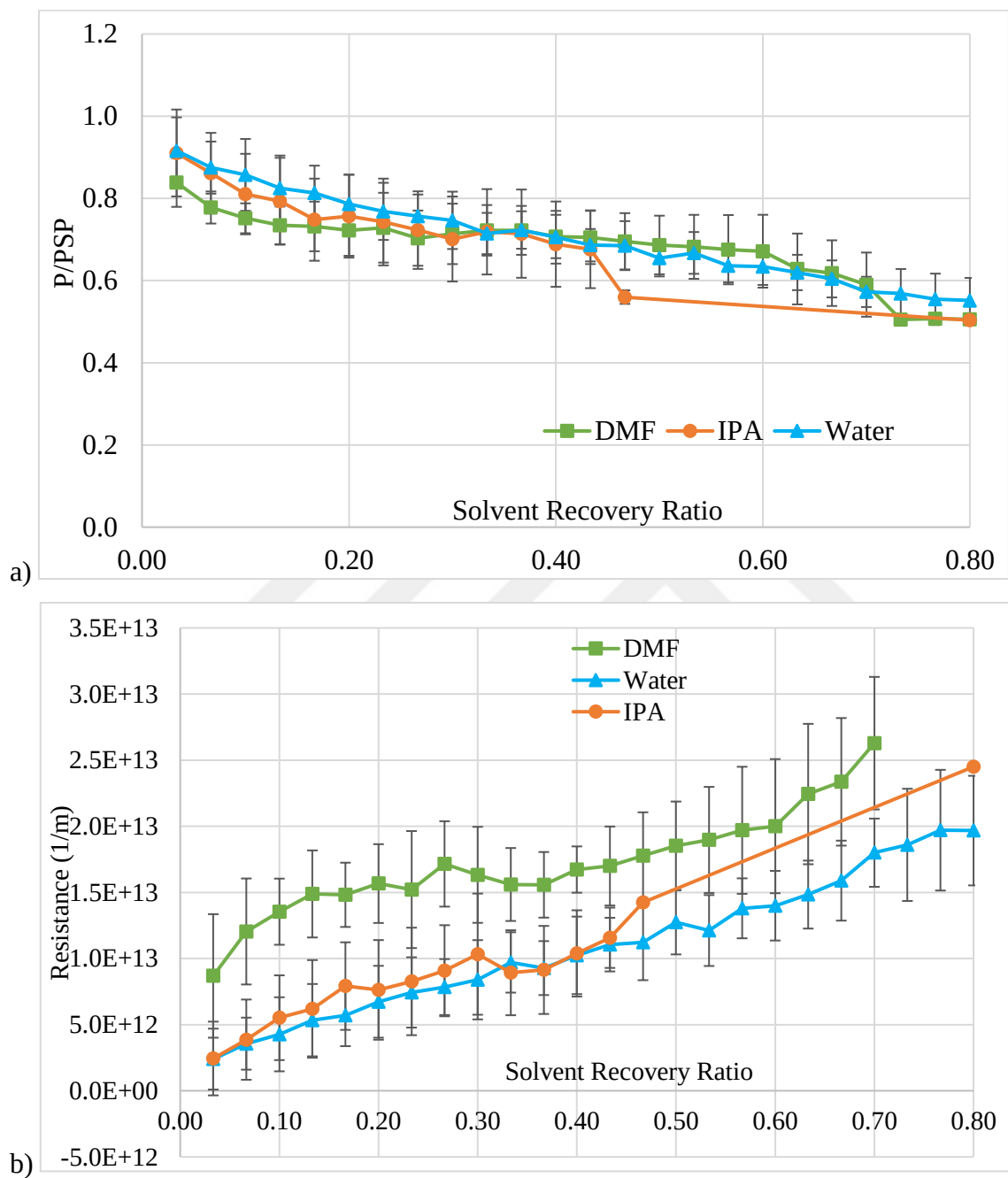


Figure 3.12 a) P/PSP values of concentration experiments with hydrophobized nanoparticles b) Cake layer resistance; both versus Solvent Recovery Ratio as Permeate Volume/Feed Volume

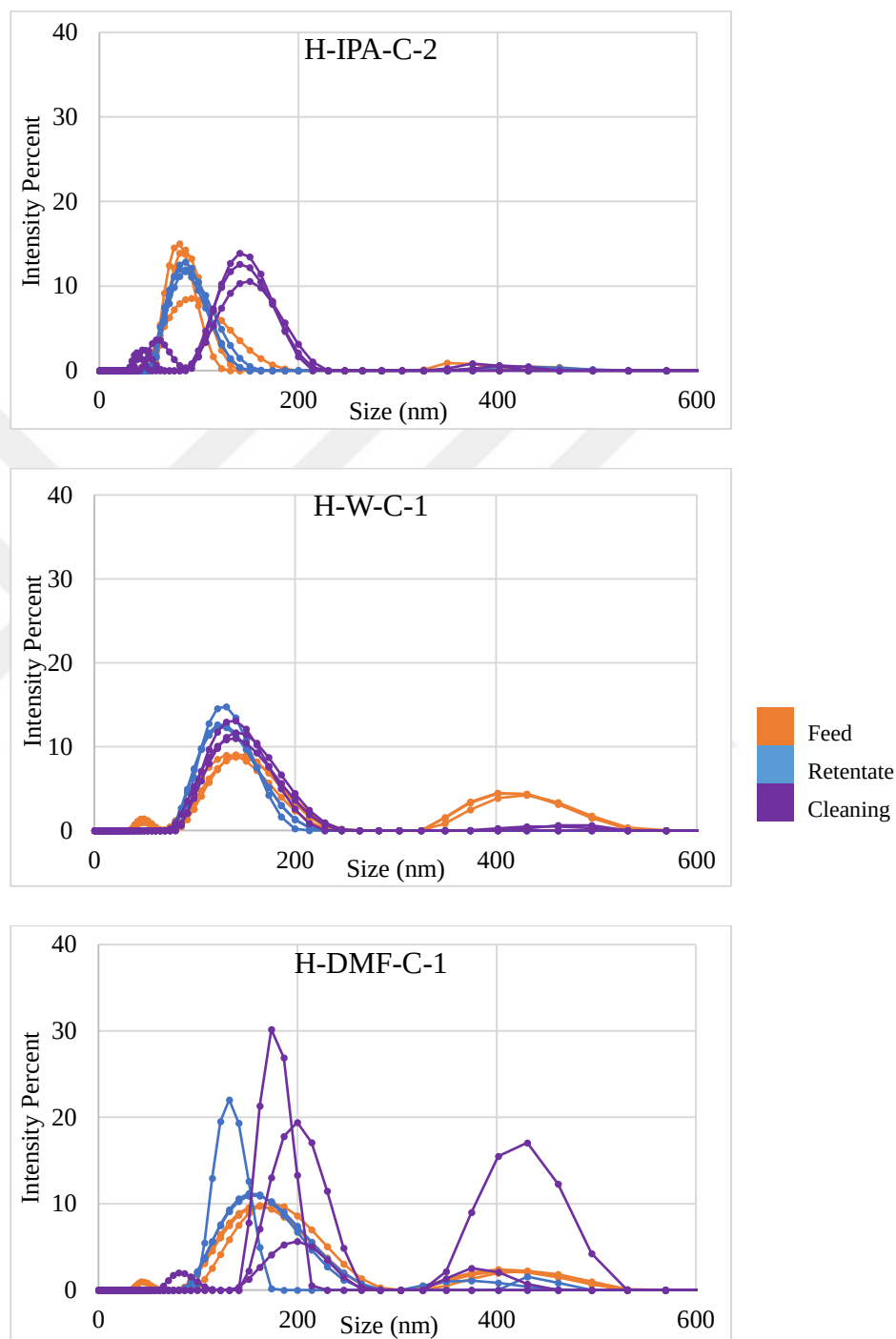


Figure 3.13 The experiments of hydrophobized silica concentration in IPA, water, and DMF, H-IPA-C-2, H-W-C-1, H-DMF-C-1, respectively, particle size results by DLS

When the particle size analyses of hydrophobized particles are examined, it is seen in Figure 3.13 that feed and retentate particle sizes are the same in all solvents. However, cleaning suspension which is used in the first step, has particles agglomerated in DMF and IPA but not in water.

When the cake resistances of hydrophobized and native particles are compared, hydrophobized particles generate more resistance in all solvents by forming tighter cake layers due to higher attraction between them as it is presented in Figure 3.11. The attraction between particles created by coating surpasses the increased repulsiveness between membrane and particles since majority of the resistance to fouling is due to the cake layer. It was observed that the biggest resistance difference by coating exists in DMF. It could be caused by the various particle sizes of feed suspension in DMF after coating as it is seen in Figure 3.10 and 3.13. The drastic resistance difference between hydrophobized and native particles comes from the cake layer structure which is seen to be more compact of hydrophobized particles by the porosity in Figure 3.11. The porosity is around 0.6 for native nanoparticles whereas it is 0.3 for hydrophobized particles. More repulsive interaction between native, hydrophilic silica particles results in looser cakes and lower resistance due to the cake.

It is observed that the remaining resistance due to particles left on the membrane was present after the experiments. However, by a two-step cleaning process the resistance values returned to their original value as in Figure 3.14 which is also supported by the recovered silica ratio in Figure 3.15. For the native particles, in DMF 100% recovery of resistance is observed by the first step of cleaning. 70% of silica is recovered at the end of the experiment which is the highest recovery ratio for native particles. By the resistance values, it was already proven that native particles tend to form fouling in IPA and water more than in DMF which supports the highest silica recovery ratio of experiment in DMF. By the first step of cleaning, 10% further silica recovery is achieved and leads to negligible resistance difference in DMF. The second step of cleaning removed the remaining 20% silica since the resistance is completely the same as before. In water and IPA, 100%

resistance recovery is achieved after the second step. However, according to SEM images in Figure 3.16 there were still silica particles left on the membrane surfaces in IPA.³⁸ Since the membrane resistances fully recovered, the left particles did not affect the membrane performance by adsorbing onto the membrane surface individually and not on the pores. In water, after the concentration experiment 50% silica, after the first step of cleaning 15% more silica is recovered. 35% of silica particles left in the system keep creating resistance around $5 \times 10^{12} \text{ m}^{-1}$, which can be considered marginal, until it is removed by the second step of cleaning. In IPA, 50% silica recovery by the experiment, 5% recovery by the first step of cleaning, the least silica recovery ratios are observed. The left silica in the system 45%, created resistance around $1.5 \times 10^{13} \text{ m}^{-1}$ until it is removed by the second step of cleaning. The particle-membrane interaction seems to be the highest in IPA since the cleaning process recovered the least 5% silica in IPA.

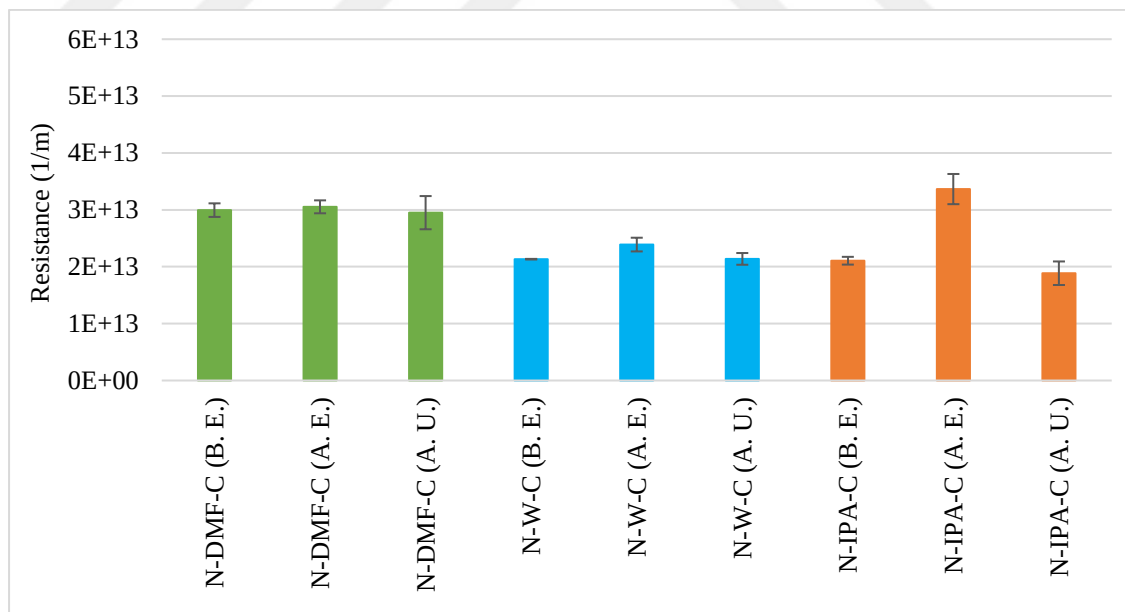


Figure 3.14 Resistance values of membranes before concentration experiments with native particles, after 1st step cleaning and after 2nd step cleaning

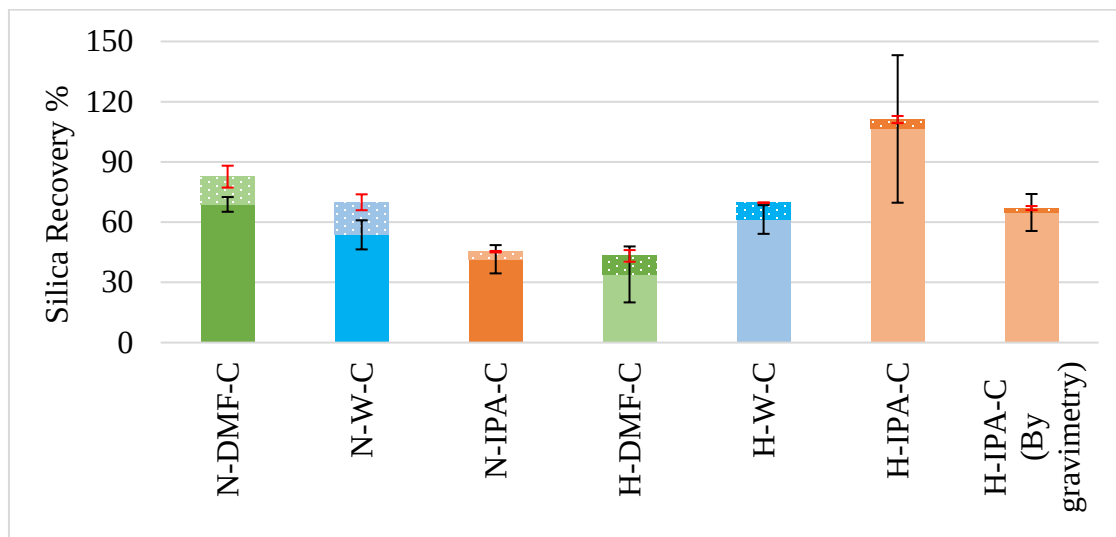


Figure 3.15 Silica recovery ratio in concentration experiments after experiments and by first-step cleaning

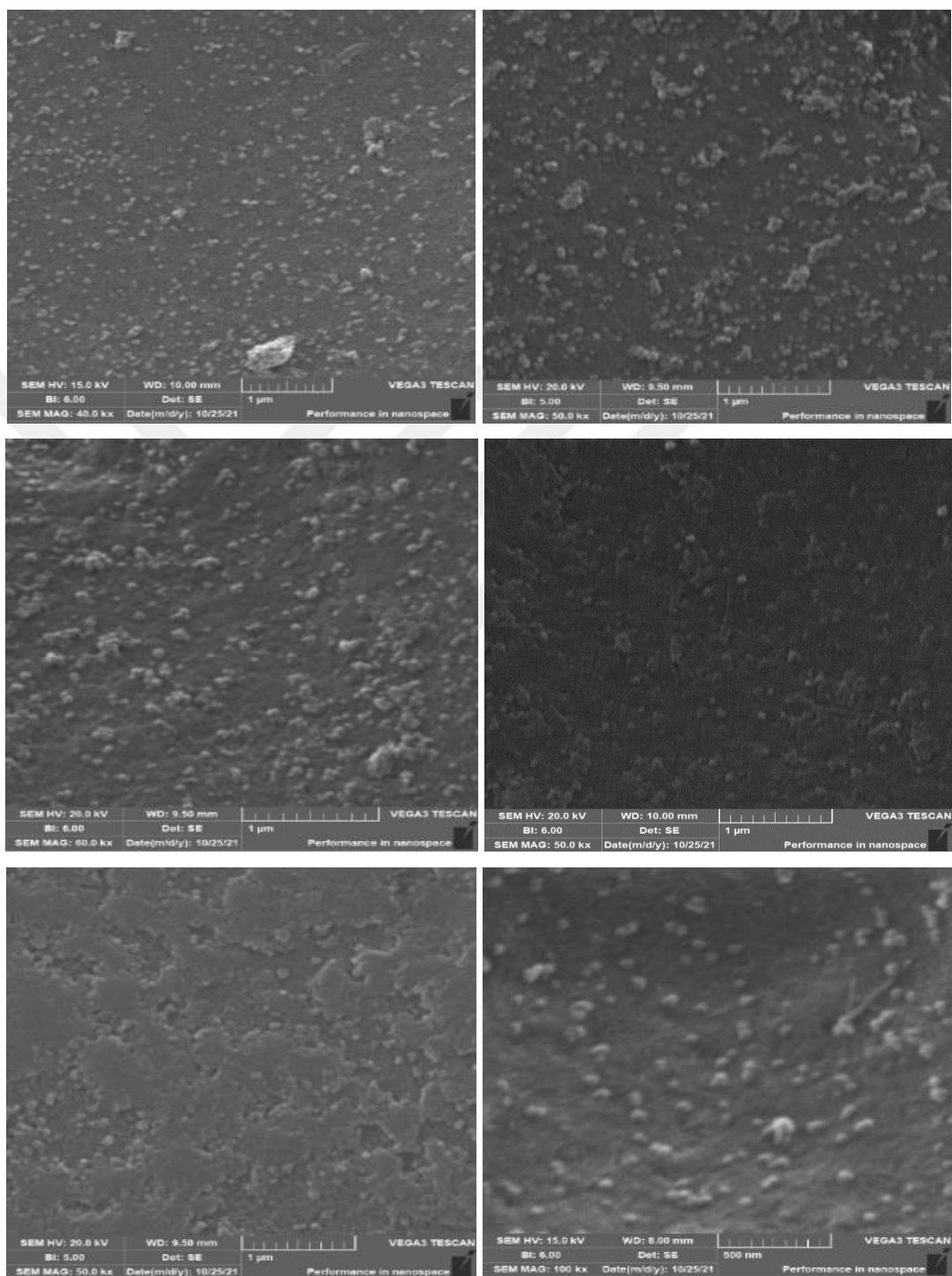


Figure 3.16 SEM images of membrane surfaces after concentration experiments in IPA

For hydrophobized particles, in Figure 3.17, the resistance values before and after the experiments are presented which shows the highest resistance in DMF after first step of cleaning. In hydrophobized particles, the least particle recovery after the experiment is observed in DMF at 30% which is consistent with the most resistant cake layer formation. After the first step of cleaning, 10% of particles are removed which means 60% of particles stayed on the membrane causing resistance at $4.5 \times 10^{13} \text{ m}^{-1}$ as it is seen in Figure 3.17. After the second step, membrane resistance is completely recovered meaning all hydrophobized silica particles are recovered. In water, hydrophobized silica particles are recovered 60% after the experiment and 10% by the first step of cleaning. Left 30% of particles generated a marginal resistance which is presented in Figure 3.17 in blue. After the second step, membrane resistance is completely recovered in water and in DMF meaning all hydrophobized silica particles are recovered. For hydrophobized particles in IPA the results by turbidity did not give reasonable data since the recovery of silica nanoparticles is above 100%. It could be caused by the agglomeration of particles leading to increased turbidity data by increased particle size. For that reason, the gravimetric results of hydrophobized particle concentration in IPA is also presented in Figure 3.17 which gives more reasonable insight. The highest hydrophobized silica recovery is observed in IPA around 62% after experiment. However, unlike other solvents, the first step of cleaning was the least efficient recovering 1-2% particles. Left particles in the system created a minimal resistance in the system as it can be seen in Figure 3.17 in orange. However, after the second step of cleaning, the membrane resistance is recovered fully, meaning hydrophobized silica particles must be recovered completely as well.

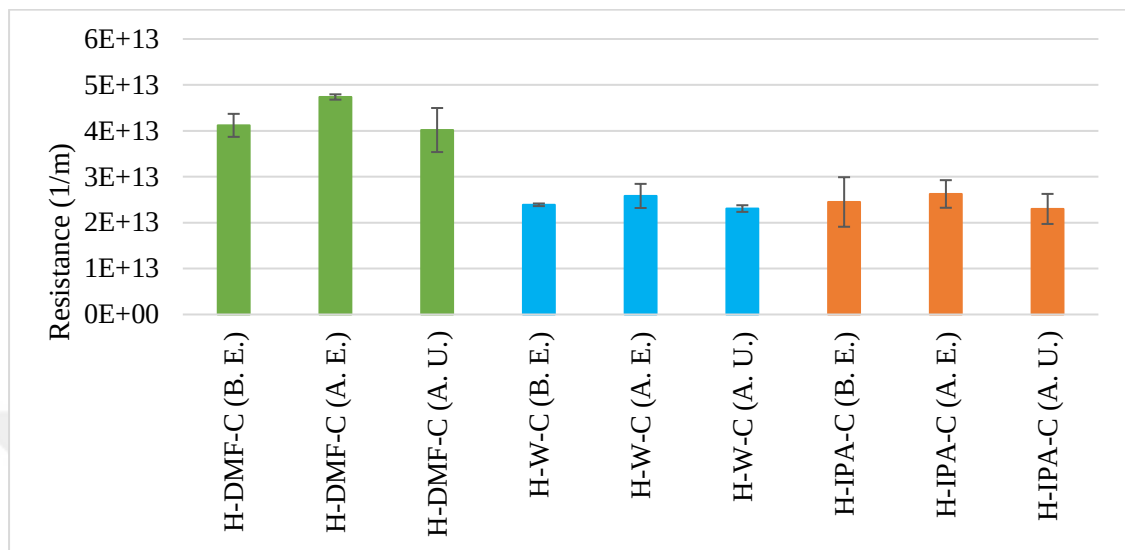


Figure 3.17 Resistance values of membranes before concentration experiments with hydrophobized particles, after 1st step cleaning and after 2nd step cleaning

By the particle size data, it is interpreted that concentration process did not cause native particles to aggregate or form clusters inside the suspension by checking Figure 3.10. The same interpretation can be made for concentration process in water performed with hydrophobized particles as in Figure 3.13. However, the concentration experiments in IPA and DMF performed with hydrophobized particles, lead to cluster formation in the cake layer since the particle size in the retentate is the same with feed suspension but cleaning suspension have higher particle sizes which means the particles removed from the surface are clustered. First cake resistance data of DMF is higher than IPA and water. The cake might be formed loose in IPA since the cake resistance value starts with the same level as water; but after some time of cluster formation, a more rigid form emerges by the cake layer formed at 40% recovery ratio which acts as another layer of membrane generating a faster cake layer formation by means of attractive hydrophobized particle interaction. Even if the cake layers are considered to be rigid, their interaction with the membrane is less attractive than their interaction with solvents since the cleaning process is able to remove cake layer from membrane surfaces.

3.2.3 Solvent Exchange via Diafiltration

Diafiltration experiments were performed to exchange the environment of particles from the synthesis solvent IPA to different solvents such as ethanol, water and DMF to observe the fouling behavior during medium change. In diafiltration experiments, in the first hour, total recovery mode is followed as it is presented in Figure 3.18 and 3.19.

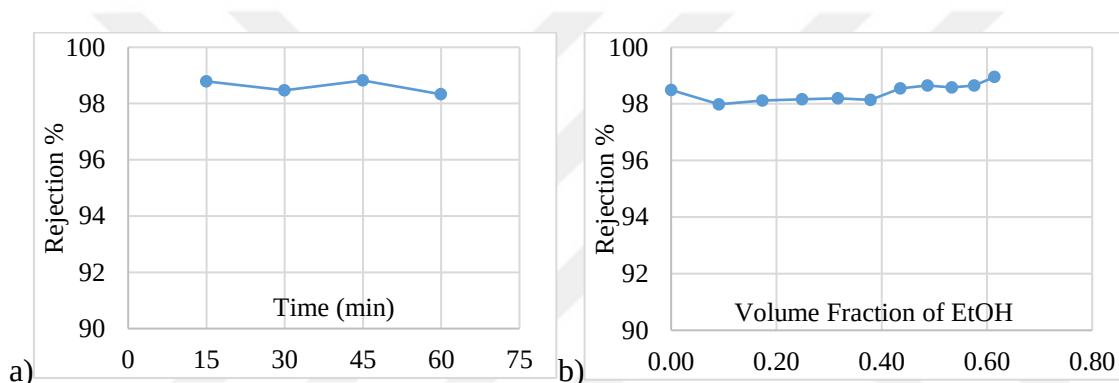


Figure 3.18 Rejection values during diafiltration to ethanol experiment, N-ETOH-D-1,
a) At total recovery mode b) At diafiltration mode

As it was observed in concentration experiments, rejection is 98% minimum in diafiltration experiments as it is presented in Table 3.3, which is anticipated since the particles are larger than pores. In crossflow mode, membranes are again successful in separating solvents from nanoparticles.

Table 3.3 Average rejection values of each diafiltration experiment for native and hydrophobized particles

Native Particles	Rejection%	Hydrophobized Particles	Rejection%
N-ETOH-D-1	98.46	H-ETOH-D-1	99.24
N-ETOH-D-2	99.85	H-ETOH-D-2	99.51
N-ETOH-D-3	99.03	H-ETOH-D-3	99.18
N-W-D-1	99.12	H-W-D-1	99.43
N-W-D-2	99.81	H-W-D-2	99.31
N-W-D-3	99.51	H-W-D-3	99.44
N-W-D-4	99.74	H-W-D-4	99.22
N-W-D-5	99.13	H-DMF-D-1	98.08
N-W-D-6	99.36	H-DMF-D-2	98.50
N-DMF-D-1	99.36	H-DMF-D-3	98.60
N-DMF-D-2	99.60		
N-DMF-D-3	99.64		

In the total recovery mode, P/PSP values are presented in Figure 3.19 showing that there is no decrease of permeance. Considering this, it can be said that no cake layer formation occurs during total recovery mode of experiments with hydrophobized and native particles.

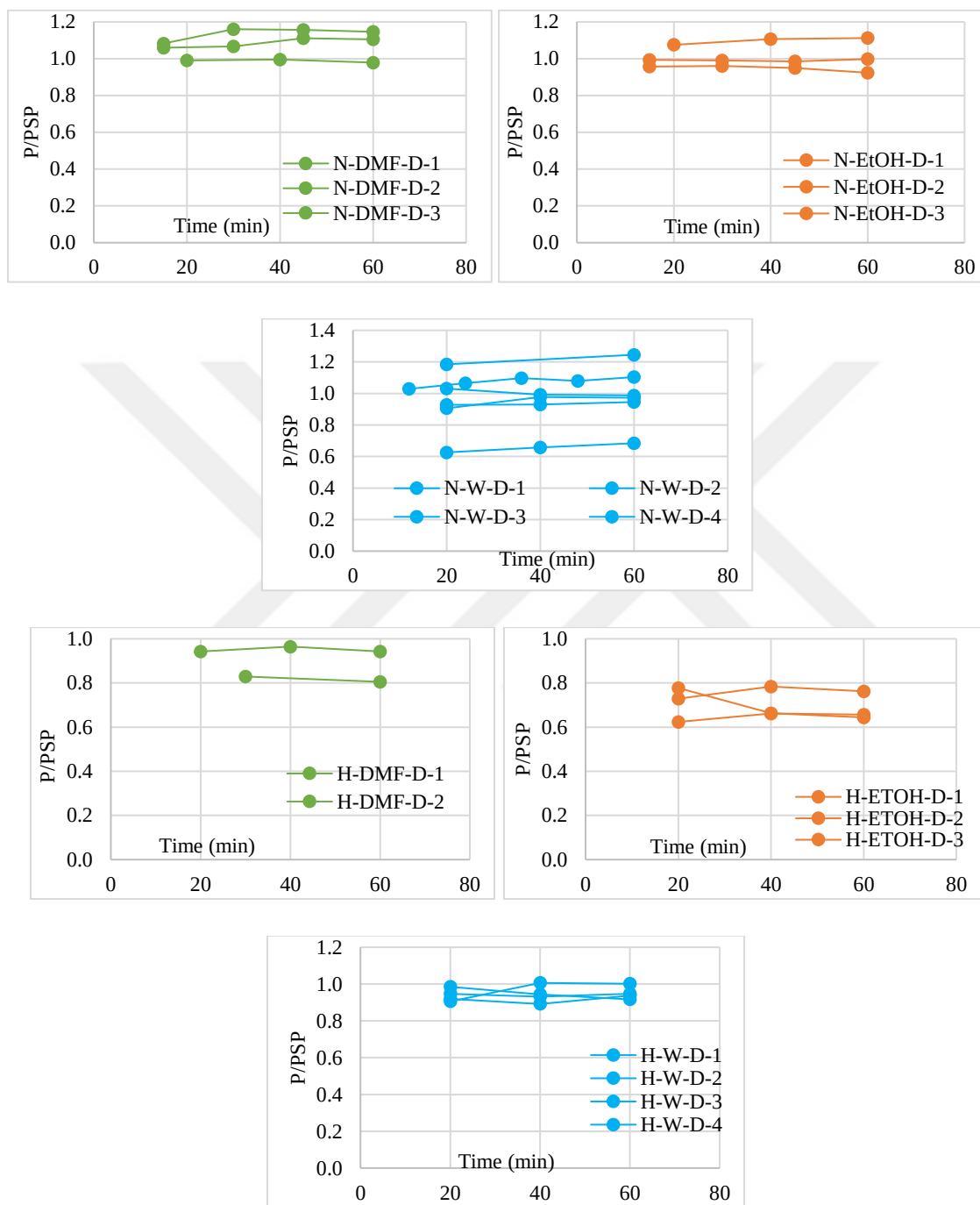


Figure 3.19 P/PSP values during total recovery mode

3.2.3.1 Viscosity of Solvent Mixtures

Viscosity of the solvents are used in the calculation of resistances. Since in diafiltration experiments, as medium we have solvent mixtures whose volume ratio is constantly changing during the experiment, the viscosity of the mixtures is required. IPA-water and DMF-IPA do not form ideal mixtures while IPA-ethanol mixtures can be considered ideal. The viscosity of water-IPA and IPA-DMF are measured by using Ubbelohde viscometer and also found from experimental data reported in literature. The dynamic viscosity values for IPA-water and IPA-DMF mixtures by literature^{69,70} and by measurement are compared in Figure 3.20. For both, experimental measurements and data in literature are very close to each other. In calculations, data from literature are used.

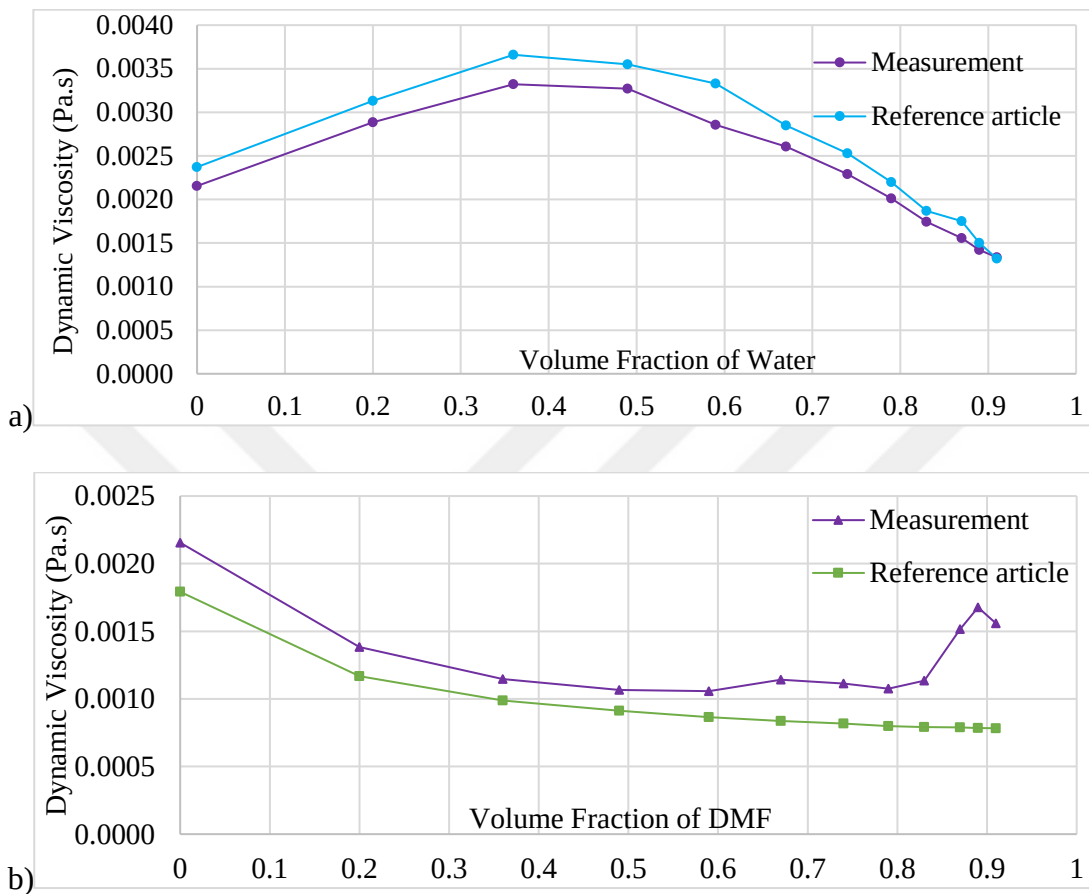


Figure 3.20 Dynamic viscosity (Pa.s) values of a) IPA-water mixture b) IPA-DMF mixture

3.2.3.2 Permeance of Solvent Mixtures through the Membranes

Water-IPA mixture permeances vary inversely with viscosity as in Figure 3.21. This means that the membrane structure, and hence resistance, remains the same regardless of permeate composition. However, as it is seen in Figure 3.22, permeances of DMF-IPA mixtures do not follow viscosity inversely possibly caused by the swelling of the membrane with increasing DMF or leaching of small molecular weight polymers from the membrane during permeation of DMF-IPA mixtures. Hence, the permeance values measured as a function of DMF-IPA composition (Figure 3.22 and Table D.4) are used in membrane resistance calculations, and the following cake layer resistance calculations.

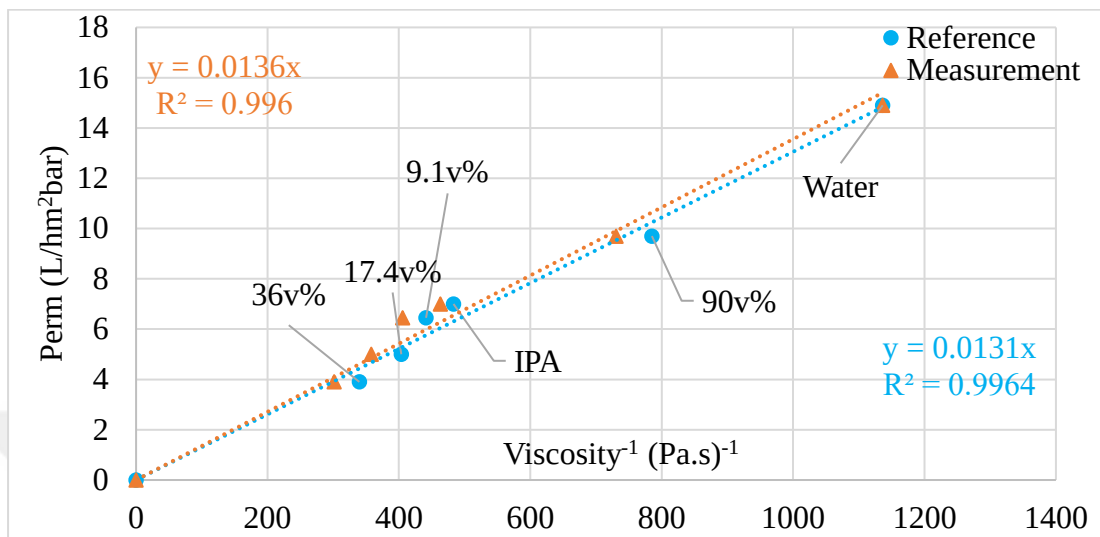


Figure 3.21 Permeance vs. viscosity⁻¹ graph for water-IPA mixture with viscosity by analysis and by reference

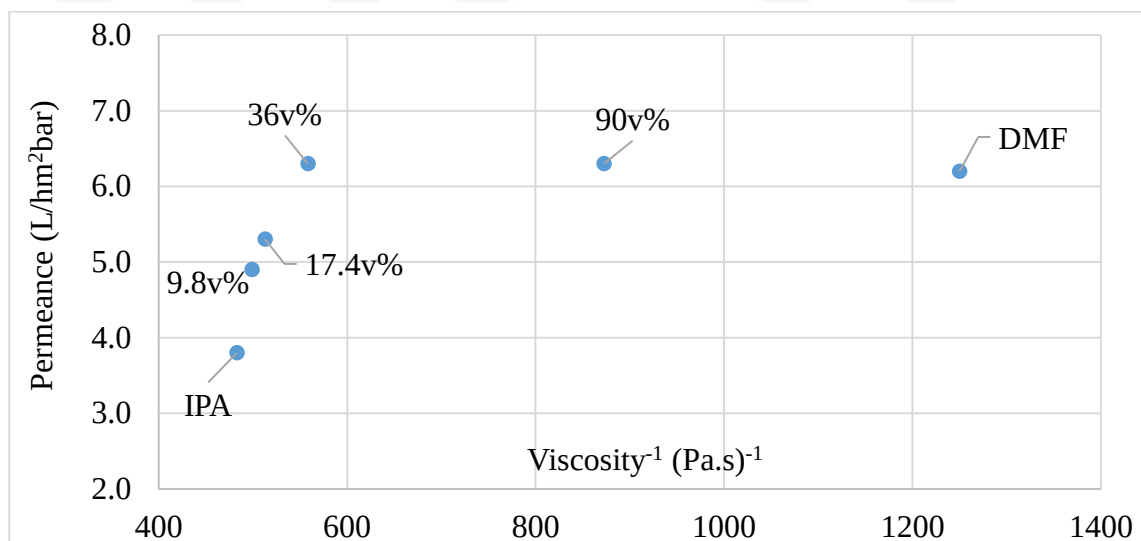


Figure 3.22 Permeance vs. viscosity⁻¹ graph for DMF-IPA mixture with viscosity by reference

In diafiltration experiments, for native particles, transitions to ethanol and DMF show no cake resistance which means the flow in the system can sweep the membrane surface enough so there is no fouling forming on the membrane. Sweeping effect can also be seen in the total recovery mode in Figure 3.19 since there is no fouling as well. P/PSP values are presented in Figure 3.23a and 3.23b showing an increasing trend for DMF and ethanol for both hydrophobized and native particles whereas decreasing trend is observed for water with both particles. During transitions to DMF and ethanol, the viscosity in the system decreases since ethanol and DMF have lower viscosities than IPA. Hence, for P/PSP value to increase is meaningful with no cake layer formation and decreasing viscosities and the cake resistance gives a clearer comparison of fouling. The viscosity also decreases transitioning to water whose viscosity is less than IPA while P/PSP graph shows decrease unlike DMF and ethanol, indicating the formation of cake layer. In transition to DMF, until 20% volume fraction, a minimal increase in resistance is seen in Figure 3.24a, however after that point the fouling is dispersed by the flow. In diafiltration to water, the cake resistance is significantly higher than other solvents. Interaction between particles appears to be the highest since it is seen that the particles agglomerate in water significantly more than in the other solvents by the particle size data comparing feed and retentate values as in Figure 3.25. On the other hand, this kind of agglomeration is not observed in diafiltration to ethanol and DMF as it can be seen in Figure 3.25. For hydrophobized particles, again, diafiltrations to ethanol and DMF do not show cake resistance which means sweeping effect also works in these systems. The tangential flow can outweigh the interaction between particles. In diafiltration to ethanol, there is no significant cluster formation. However, transitions to DMF show serious cluster formation as it is also proved by the highest cake resistance in concentration experiments in DMF of hydrophobized particles. It can be interpreted as the clusters keep moving in the system by the flow and do not accumulate on membrane surface since there is no cake resistance observed. In diafiltration of hydrophobized particles to water, there is again severe cake resistance following the trend of diafiltration of native particles to water. By the particle

size data, agglomeration formation is again proved, although it is not as serious as cluster formation of hydrophobized particles in DMF as it is seen in Figure 3.26.

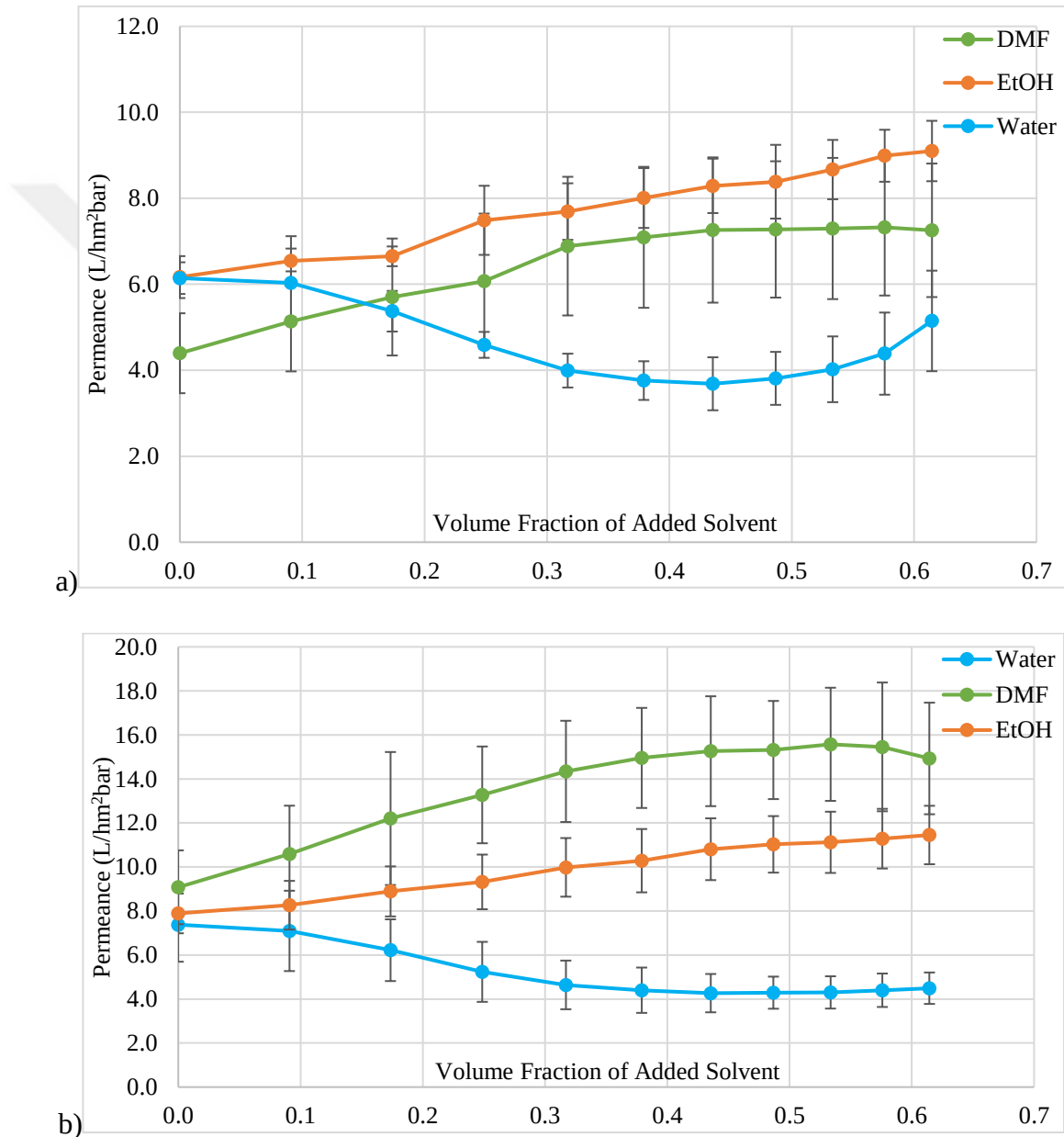


Figure 3.23 Permeance values during diafiltration experiments with a) hydrophobized particles
b) native particles; both versus Volume Fraction as Added Solvent/Total Solvent

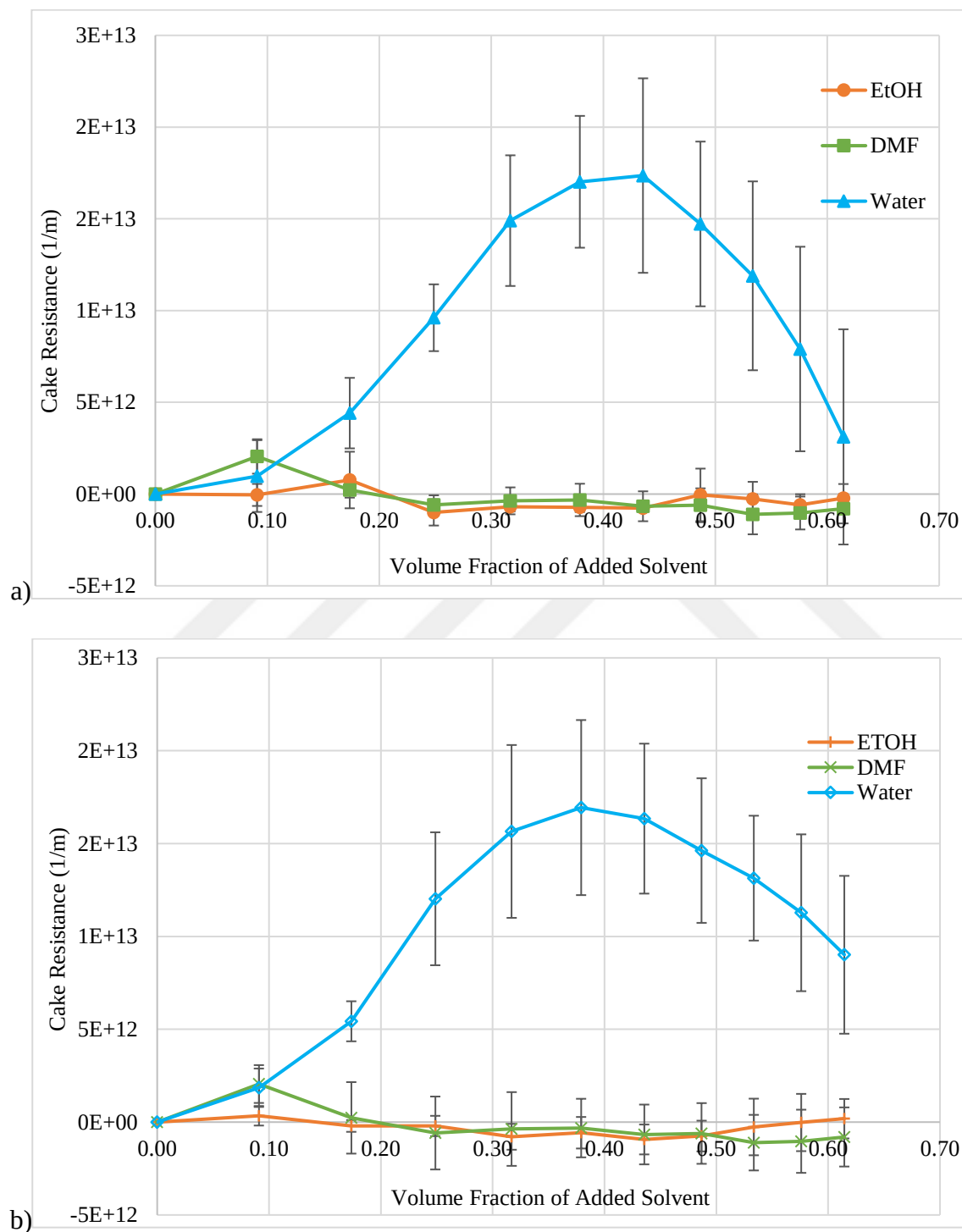


Figure 3.24 Cake resistance values during diafiltration experiments with a) hydrophobized particles b) native particles; both versus Volume Fraction as Added Solvent/Total Solvent

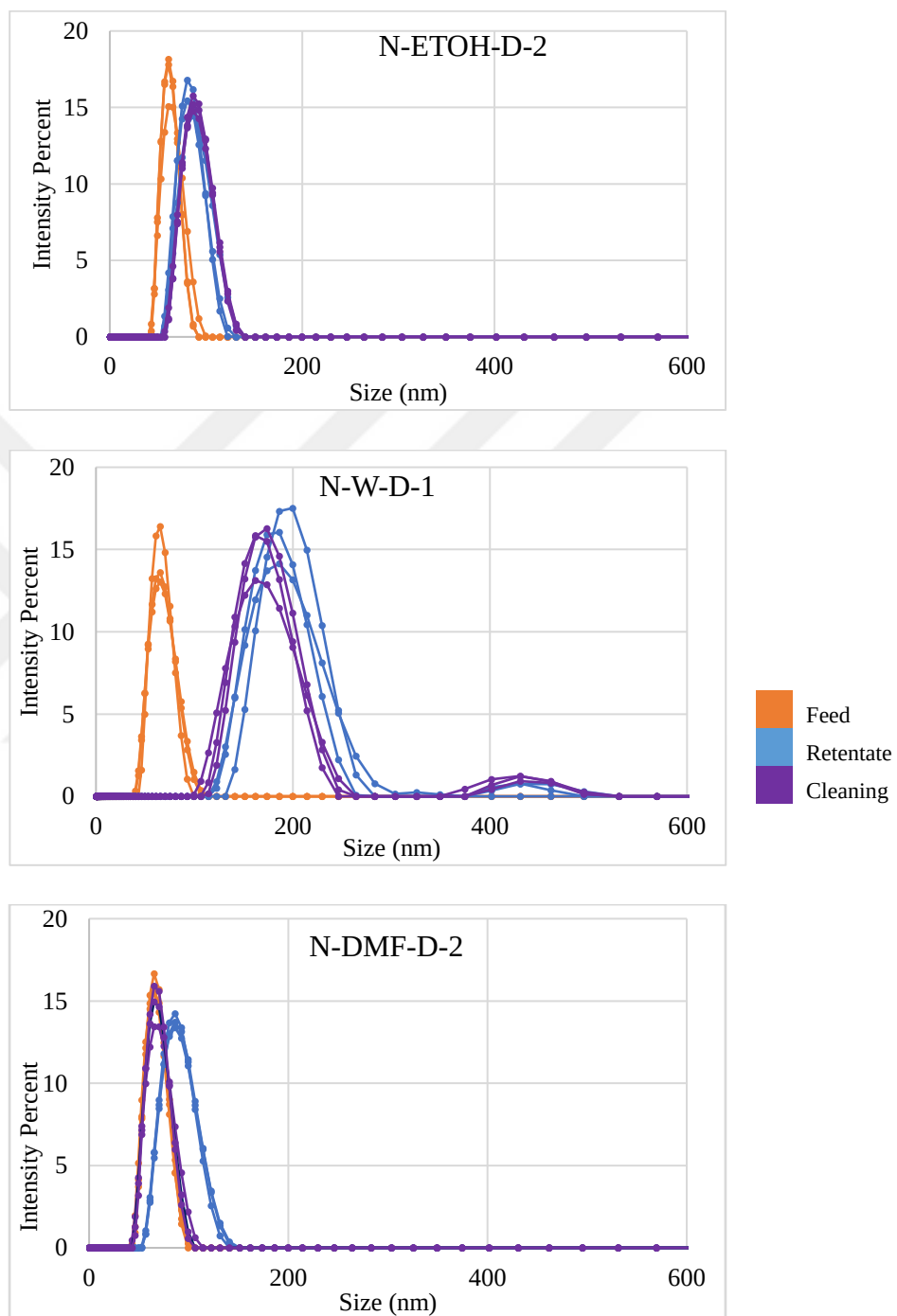


Figure 3.25 The experiments of silica diafiltration in EtOH, water, and DMF, N-ETOH-D-2, N-W-D-1, N-DMF-D-2 respectively, particle size results by DLS

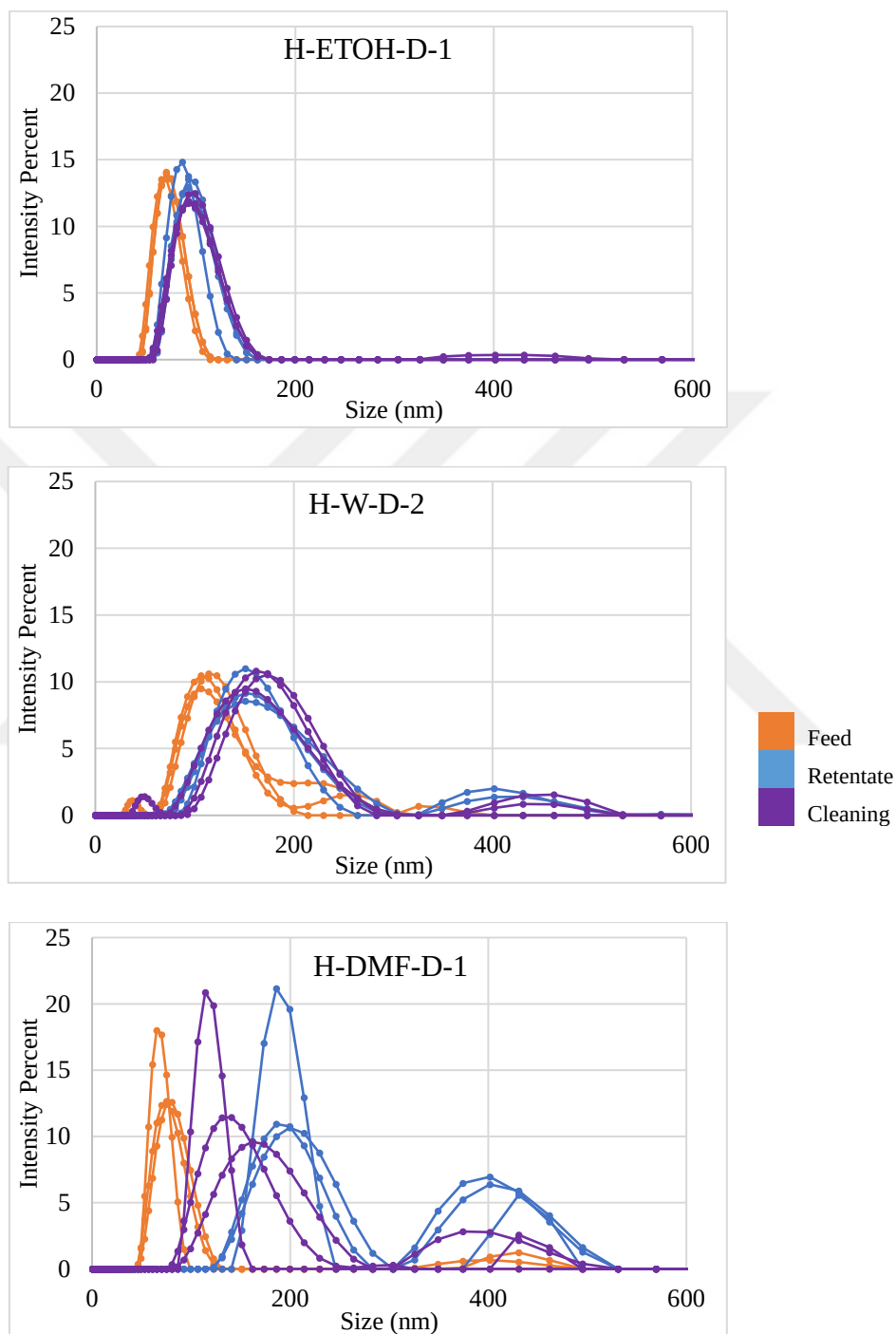


Figure 3.26 The experiments of hydrophobized silica diafiltration in EtOH, water, and DMF, H-ETOH-D-1, H-W-D-2, H-DMF-D-1 respectively, particle size results by DLS

In the experiments performed with native particles, cleaning process included one step, and ultrasonic bath step was not conducted. Without the second step of cleaning process membrane resistances did not go back to their original value except ethanol since there was already insignificant resistance increase as it is seen in Figure 3.27. Resistance values increased to 1.5 times higher than original values in water and DMF. In the experiments performed with hydrophobized particles, cleaning process recovers the resistance values of membranes in water and IPA after the second step. However, for DMF, the cleaning process helps to decrease the resistance noticeably, yet it does not return the membrane resistance to its original point. Even though the highest resistance is reached in diafiltration to water, the resistance increase was reversible. On the other hand, the resistance increase in DMF was not as extreme as water, but it is irreversible possibly caused by the cluster formation.

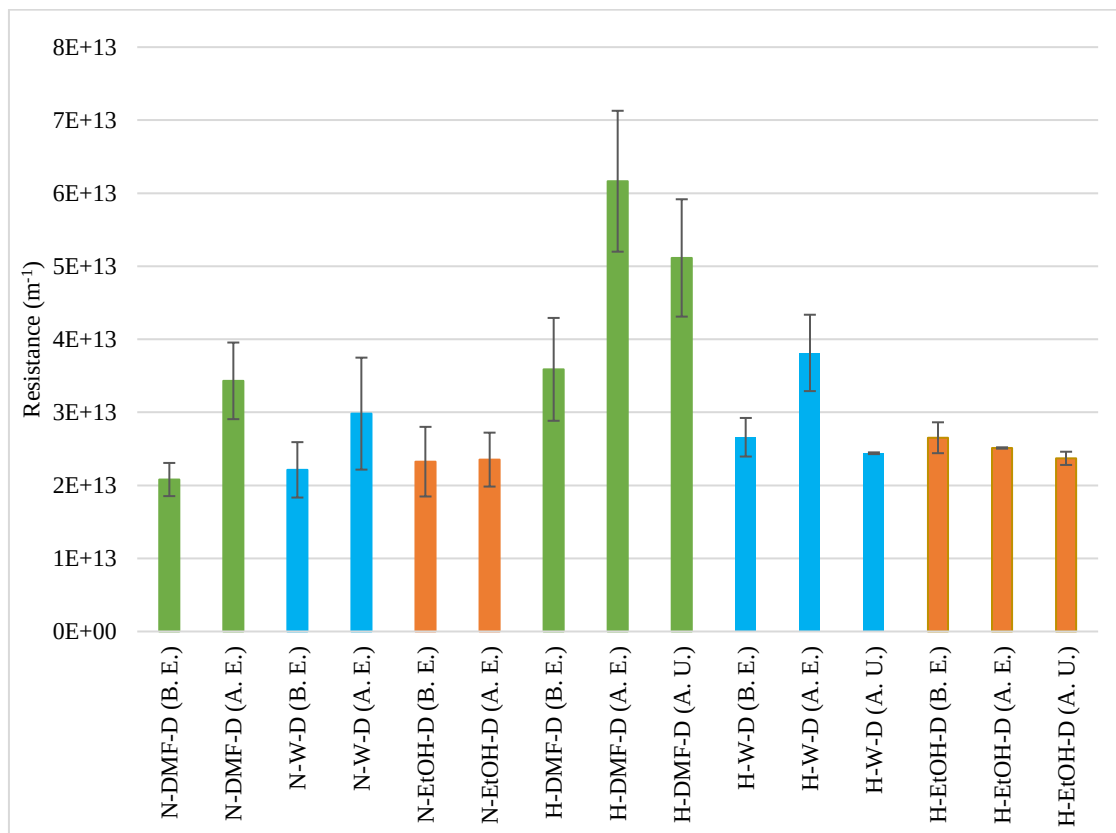


Figure 3.27 Comparison of resistance values before and after diafiltration experiments

3.2.4 DLVO and X-DLVO Calculations on Nanoparticle Interactions

DLVO and XDLVO theories are used to calculate the interaction energies between particles in different solvents showing colloidal stability, which includes different type of intermolecular forces as Lifshitz-Van der Waals forces, electrostatic forces, and acid-base interactions. Firstly, interaction energies are calculated by DLVO. For Lifshitz-Van der Waals forces, the parameters in equation (2.5) are found such as Hamaker constant of silica, A_S , and solvents, A_L , which are needed to calculate the Hamaker constant of silica in the specific solvents, A_{SLs} by equation (2.6). Hamaker constant is a measure of the strength of LW forces between materials which takes into consideration the polarizability

of materials and their separation distance. Hamaker constants of IPA, ethanol and water are found in the literature.⁷¹ However, Hamaker constant of DMF could not be found in the literature and Hamaker constant of formamide is used instead.⁷² For electrostatic forces, the parameters in equation (2.7) are required such as Debye Length and surface potential which is taken as the zeta potential. Zeta potential of native particles in water is measured, in ethanol is taken from literature²⁸ and also used for IPA since it could not be measured or found from literature. For DMF, analysis was not tried since there was not solvent-resistant vial for Zetasizer. However, zeta potential of native particles in formamide is found in literature and used instead.³⁶ For Debye Length, which shows the measure of how far electric fields and charges can affect each other in the medium of an electrolyte solution, dielectric constant, electrical conductivity, and effective diffusion coefficient are required. Effective diffusion coefficient is taken as 10^{-9} m²/s as suggested by Lay et al.^{36,71} Dielectric constants^{71,73} and electrical conductivities^{28,74,75} of each solvent are found in the literature.

For acid-base interaction which included in XDLO Theory, decay length (λ) which indicates the length where the repulsive and attractive forces decay between particles, minimum distance between particles (z_0) which refers to the distance that neighboring particles' outer electron shells can get the closest to each other, particle diameter are required. Acid-base interaction is due to the ability of a component to donate or accept electrons. Decay length and minimum distance between particles (z_0) are taken from literature.³⁶ For acid-base interaction energy calculations, surface tension components of both solute and solvents should be known. Surface tension components which are electron donor and acceptor parameters are found in the literature as well for water and ethanol.³⁶ However, the surface tension components for DMF and IPA could not be found in the literature. For that reason, by analysis and calculations, parameters are tried to be reached. Particle diameters are required for both EL, AB and LW forces which are analyzed by DLS.

3.2.4.1 Surface Tension Components for the Solvents

To calculate surface tension components by Young-Dupre equation, contact angle of solvents with surfaces whose electron acceptor and donor surface tension components are known, are found in literature and calculations are done accordingly as it is presented in Table 3.4. Young-Dupre equation is used to show the relation of interfacial energies between solid-gas, gas-liquid and solid-liquid interfaces when a liquid drop is on the solid surface. The meniscus by the liquid is formed on the surface by means of the equilibrium between adhesion and cohesion. Contact angles and surface tension components of surfaces are found in the literature.⁷⁶ Surface tension components of liquids γ_L^+ γ_L^- are calculated, and the results are in a wide range, extremely different than each other (Table 3.4). Additionally, contact angle of DMF and IPA with PDMS and silicon wafer surfaces are measured as in Figure 3.28 to estimate the γ^+ and γ^- values for these surfaces and use them as well to calculate γ^+ and γ^- values for the solvents. For calculating the surface tension components of PDMS and silicon wafer surfaces, three more solvents are used for contact angle measurements which are glycerol, water and diiodomethane⁷⁷⁻⁸¹ as it is presented in Figure 3.29. Water and glycerol are used since they are polar, and their energy and surface tension component values are high whereas diiodomethane is chosen for its nonpolar structure and high energy.⁸² Silicon wafer surface tension components and IPA components by PDMS could not be calculated since the roots of the equation could not be found. Only DMF surface tension components are calculated by contact angle measurements on PDMS by firstly finding surface tension components of PDMS.

$$\gamma_L = \gamma_L^{LW} + \gamma_L^{AB} \quad (3.1)$$

$$\gamma_L^{AB} = 2\sqrt{\gamma_L^+ \gamma_L^-} \quad (3.2)$$

$$\gamma_L(1 - \cos\theta) = 2(\sqrt{\gamma_L^{LW} \gamma_S^{LW}} + \sqrt{\gamma_L^- \gamma_S^+} + \sqrt{\gamma_L^+ \gamma_S^-}) \quad (3.3)$$

Table 3.4 Calculated surface tension components of the DMF and IPA by contact angles with various surfaces found in the literature (l for liquid, s for solid surface)

Solvent	Surface	γ_L	γ_L^{LW}	γ_L^{AB}	θ	$\cos\theta$	γ_s^+ mJ/m ²	γ_s^- mJ/m ²	γ_s^{LW} mJ/m ²	γ_L^+	γ_L^-
DMF	PTFE	36.5	25.2	11.3	79 ⁷⁶	0.19	0.0	0.1	15.7	0.2	132.2
	FEP	36.5	25.2	11.3	80 ⁷⁶	0.17	0.1	0.1	15.2	0.6	53.1
	PFA	36.5	25.2	11.3	78 ⁷⁶	0.21	0.2	0.3	15.5	0.6	51.0
	ETFE	36.5	25.2	11.3	66 ⁷⁶	0.41	0.1	1.0	16.5	0.1	248.7
	ECTFE	36.5	25.2	11.3	43 ⁷⁶	0.73	0.2	0.4	28.9	0.3	126.7
	PVDF	36.5	25.2	11.3	19 ⁷⁶	0.95	0.3	11.7	24.4	0.1	497.0
IPA	PMMA	23 ⁸³	19.5 ⁸³	3.5 ⁸³	0 ⁸⁴	1.0	0	12	40.6	2.20	1.39
	PTFE	23	19.5	3.5	42 ⁸⁴	0.7	0.03	0.13	15.37	0.1	55.7

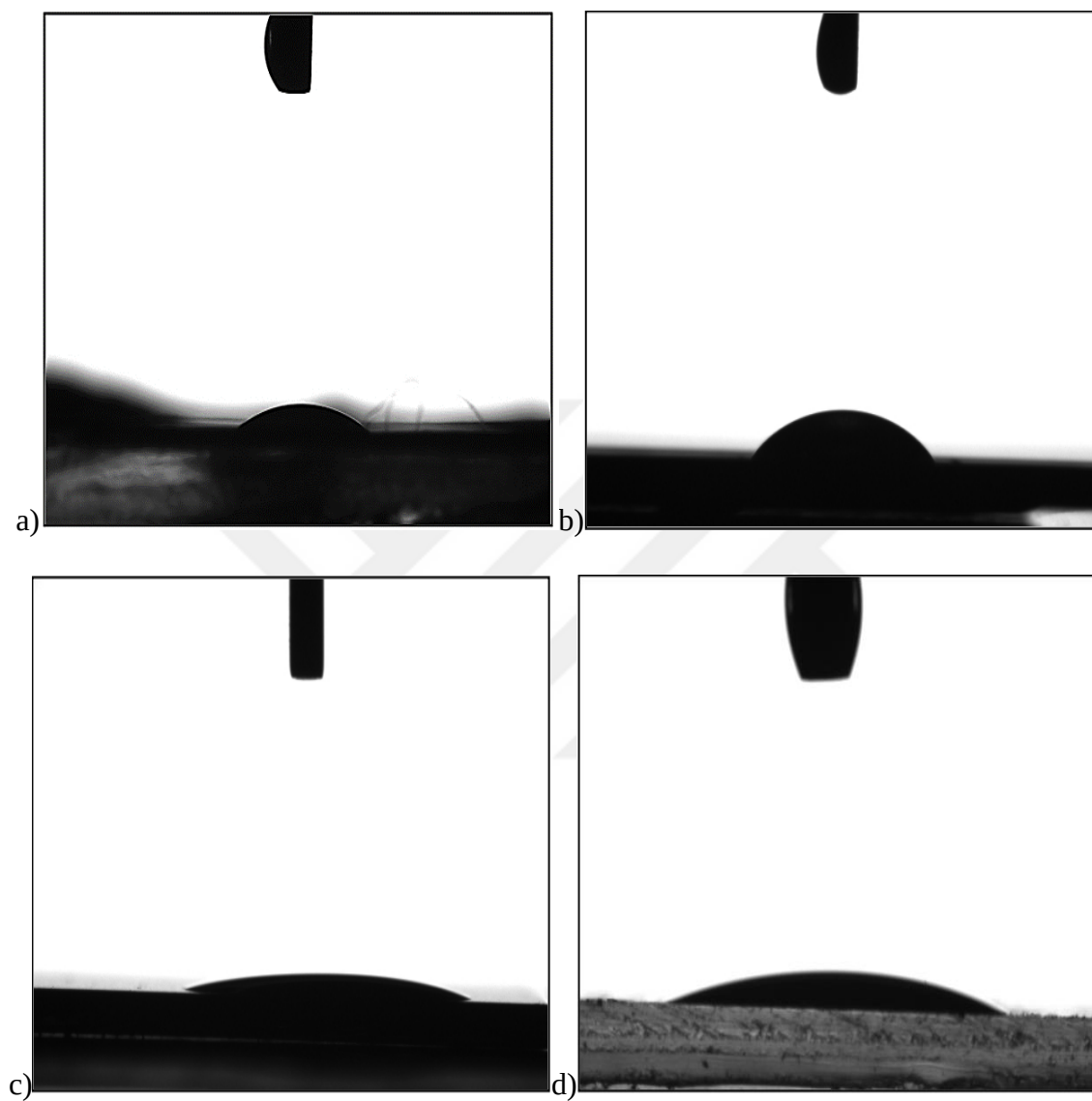


Figure 3.28 Contact angle images of a) PDMS-DMF b) SW-DMF c) SW-IPA d) PDMS-IPA

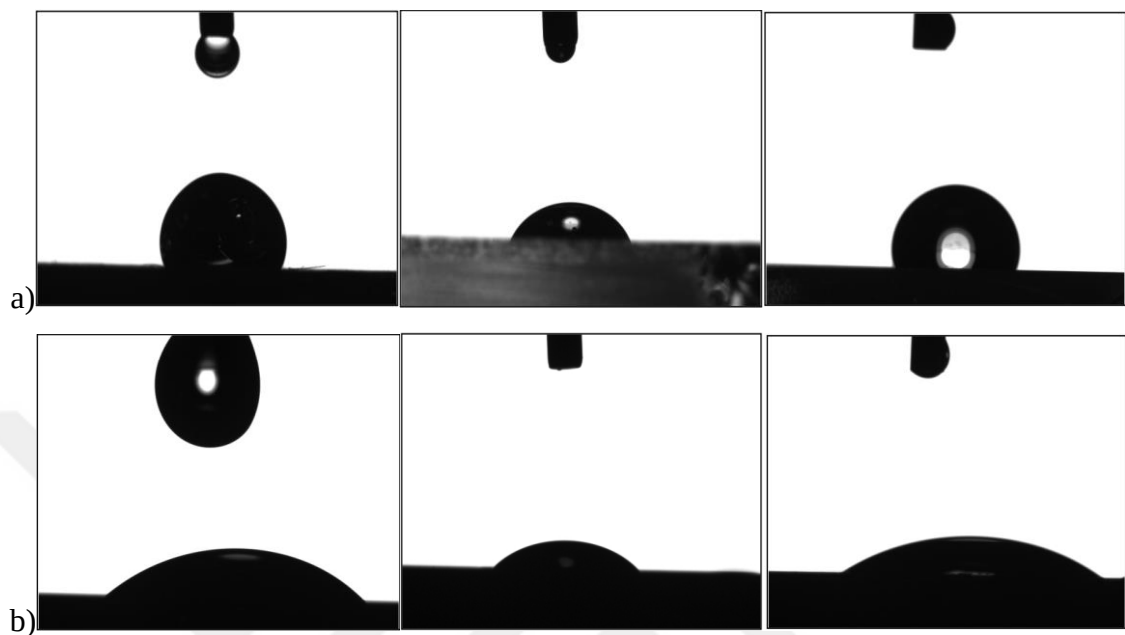


Figure 3.29 Contact angle images of a) PDMS-Glycerol; PDMS-DIM; PDMS-Water b) SW-Glycerol; SW-DIM; SW-Water

By placing the contact angle data and the properties of surface into the Young-Dupre equation, surface tension components of solvent are calculated by known dispersive and polar surface tension values of solvents. At the end of solving all 3 equations (3.1) to (3.3) simultaneously, the roots of the equation give surface tension components of the solvent.

Table 3.5 Calculated surface tension components of DMF and PDMS

Solvent	Surface	γ_L mJ/m ²	γ_L^{LW} mJ/m ²	γ_L^{AB} mJ/m ²	θ	$\cos\theta$	γ_s^+ mJ/m ²	γ_s^- mJ/m ²	γ_s^{LW} mJ/m ²	γ_L^+ mJ/m ²	γ_L^- mJ/m ²
DMF	PDMS	36.5	25.2	11.3	28.9	0.9	0.9	0.3	21.7	0.3	125.5

Table 3.6 Parameters of solvents used in DLVO and XDLVO calculation

Solvent	Symbols	Water	Ethanol	DMF	IPA
Electron acceptor parameter solvent	γ^+	25.5	0.019	-	-
Electron donor parameter solvent	γ^*	25.5	68	-	-
Zeta potential (mV)	ζ	-40.1	-17.3	47.4	-17.3
Hamaker Constant (J)	A	4×10^{-20}	4×10^{-20}	6×10^{-20}	4×10^{-20}
Debye length (m)	K^{-1}	5×10^{-8}	4×10^{-8}	1×10^{-7}	2×10^{-7}
Inverse Debye Length (m^{-1})	K	2×10^7	3×10^7	1×10^7	6×10^6
Dielectric Constant	ϵ_r	80.4	25.2	38.3	18.3
Electric conductivity (S/m)	σ	3×10^{-4}	2×10^{-4}	3×10^{-5}	7×10^{-6}

Table 3.7 Parameters of nanoparticle, used in DLVO and XDLVO calculation

Hamaker Silica (J)	Minimum separation distance(m)	Dielectric permittivity of vacuum (F/m)	Electron donor parameter	Electron acceptor parameter	Effective Diffusion Coefficient (m^2/s)	Decay Length (m)
A	z_0	ϵ_0	γ^*	γ^+	D	σ
7×10^{-20}	2×10^{-10}	9×10^{-12}	31.7	1.0	1×10^{-9}	6×10^{-10}

In water and ethanol, DLVO and XDLO theories are used to calculate the interaction energy between nanoparticles as it is presented in Figure 3.30 in blue and orange respectively. By DLVO a repulsive barrier is not seen for both solvents. However, particles did not form clusters in the stability experiments in different solvents as it is presented in Figure B.3. For water and ethanol, XDLVO gives a repulsive barrier which is expected to be more accurate than DLVO. For DMF and IPA, DLVO also does not give

a repulsive barrier. In Figure 3.31, XDLVO for IPA is calculated with two different surface tension components; one of them is ethanol's surface tension components, the other is calculated with contact angle found in the literature. By both values, XDLVO does not give a repulsive barrier for IPA. In Figure 3.32, the interaction energy between particles by XDLVO in DMF with different surface tension components is calculated. Surface tension components which are 50.97-0.63 (mJ/m²), were calculated by contact angle found in the literature. Surface tension components which are 125.47-0.25 (mJ/m²) were calculated by contact angle analyzed with PDMS. Surface tension components of formamide which are 39.6-2.28 (mJ/m²), and of dimethyl sulfoxide which are 24-3.1 (mJ/m²) are also used to calculate interaction energy between particles. With four different surface tension components XDLVO theory did not give any repulsive barrier for DMF. However, this is also not consistent with the experimental observations in this study.

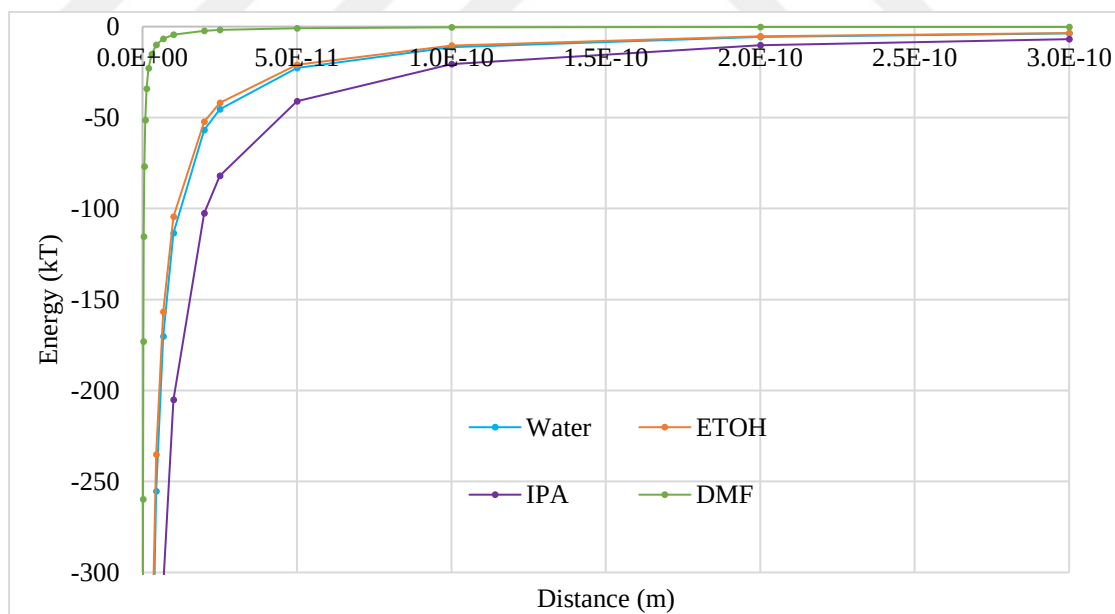


Figure 3.30 Interaction energy between particles calculated by DLVO in water, ethanol, IPA, DMF

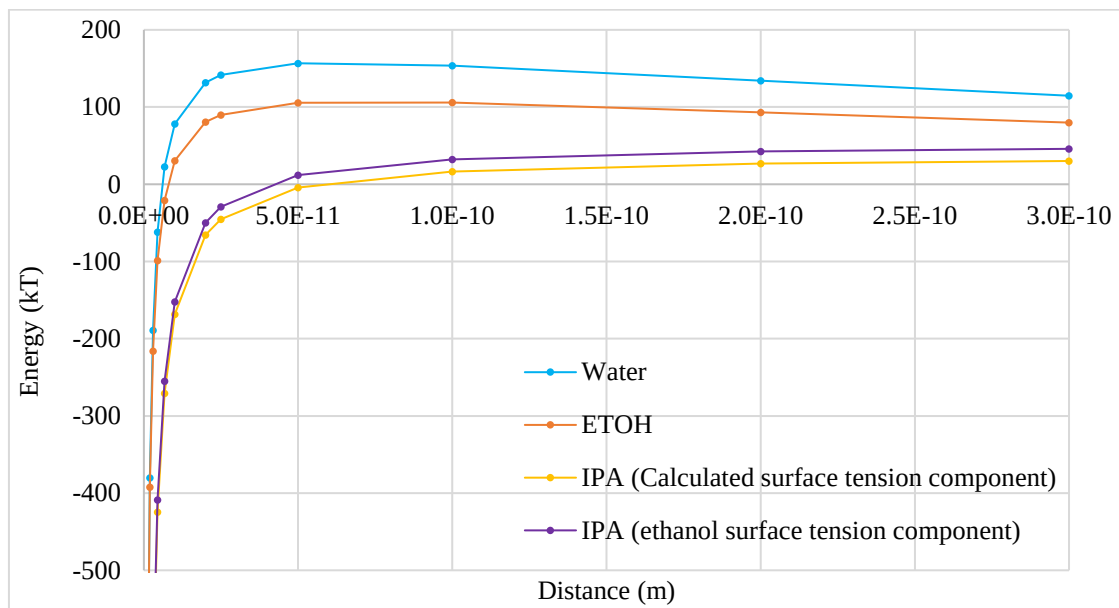


Figure 3.31 Interaction energy between particles calculated by XDLVO in water, ethanol, IPA

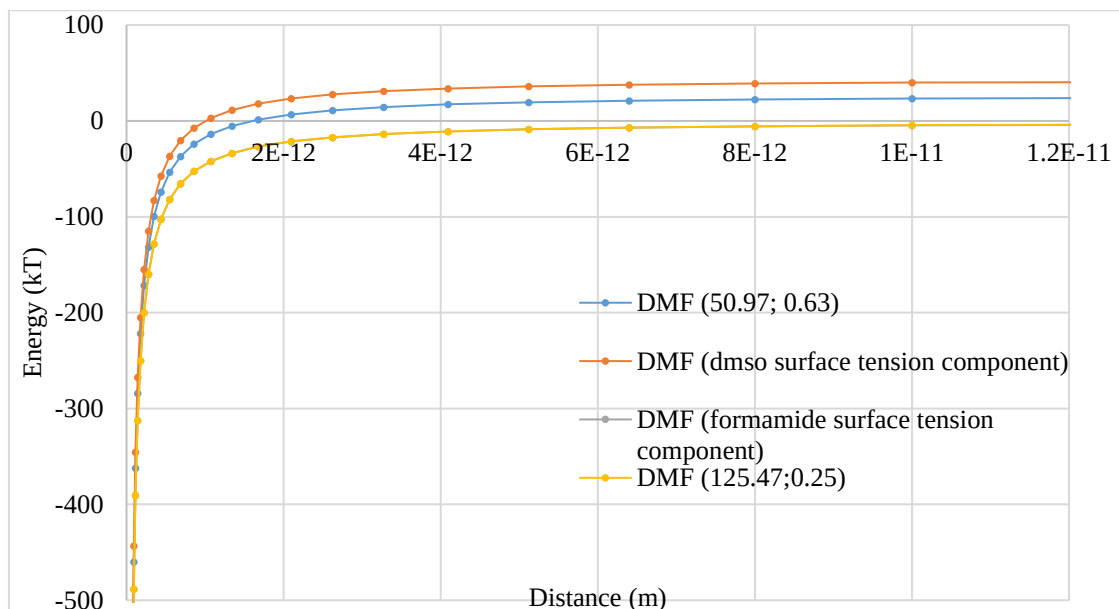


Figure 3.32 Interaction energy between particles calculated by XDLVO in DMF with different surface tension components

In summary, silica nanoparticles form different structured cake layers in different organic solvents according to our results. Interaction energies calculated by DLVO and XDLVO did not completely follow our findings by experiments. Yin et al. also comes to the conclusion that further investigation for organic solvent ultrafiltration is needed since XDLVO and DLVO theories may not explain experimental observations in all cases although XDLVO usually gives a better prediction than DLVO.^{28,29}





CHAPTER 4

CONCLUSION

In this study, the fouling trends of silica nanoparticles in different organic solvents by cellulose ultrafiltration membranes, are reported. Two modes of experiments are conducted to see the effect of medium, polar protic water, ethanol, isopropanol and polar aprotic DMF, on fouling behavior of native and hydrophobized particles. In all experiments, rejection is observed to be higher than 98% as it was anticipated. In concentration mode with native particles, the highest and the least cake resistance is observed in water and in DMF respectively. On the other hand, with hydrophobized particles, the highest and the least cake resistance is observed in DMF and in water. The thickest cake in DMF by hydrophobized particles creates the highest resistance while the least porous cake determines the highest resistance in water by native particles. Hydrophobized particles create more cake layer resistance due to increased particle-particle interaction than native silica nanoparticles create. Consequently, it is observed that particles create different structured cake layers and show different fouling behavior in different solvents.

In diafiltration, hydrophobized and native particles did not form a significant cake layer in exchange from IPA to DMF and ethanol under the effect of sweeping by tangential flow. However, in water changing cake resistance with changing water content is observed. Having almost the same cake layer resistances by hydrophobized and native particles during diafiltrations underlines the effect of medium on fouling. XDLVO and DLXO theories are used to calculate the interaction energy between particles in currently used solvents. While DLVO does not give an accurate result for any of the solvents, XDLVO provides a better prediction for water and ethanol by showing the repulsive barrier between particles. DLVO and XDLVO theories did not provide interaction

energies that entirely comply with the results of this study. Native and hydrophobized silica nanoparticles are observed to follow particular fouling paths in each solvent which should be investigated more to gain a deeper understanding of organic solvent ultrafiltration. Extensive research should be performed about organic solvent ultrafiltration due to the lack of explanations of all experimental findings by DLVO and XDLVO. In conclusion, for concentration and solvent exchange processes of nanoparticles, membrane application is a promising practice.



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APPENDICES

A. Calibration Curve

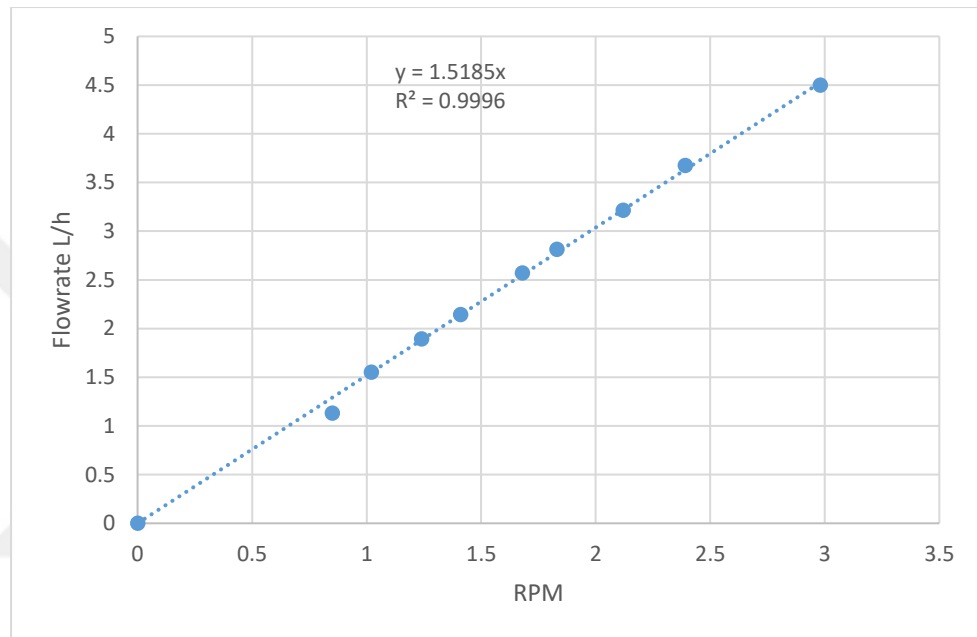


Figure A.1 Calibration curve of flowrate in crossflow system with RPM

B. DLS Analysis of Silica Synthesis during First 24 Hours

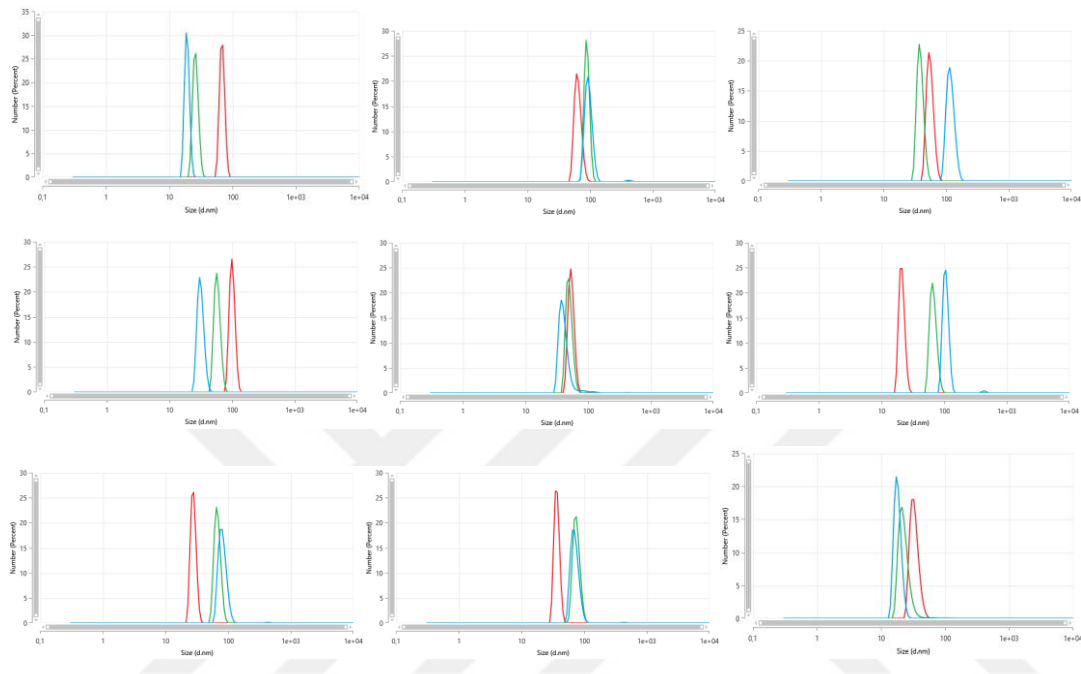


Figure B.1 Particle size analysis of silica nanoparticles during synthesis at 1st, 2nd hour, 3rd hour, 4th hour, 5th hour, 6th hour, 7th hour and 8th hour, 24th hour (red line represents the first analysis, green line represents the second analysis, blue line represents the third analysis)

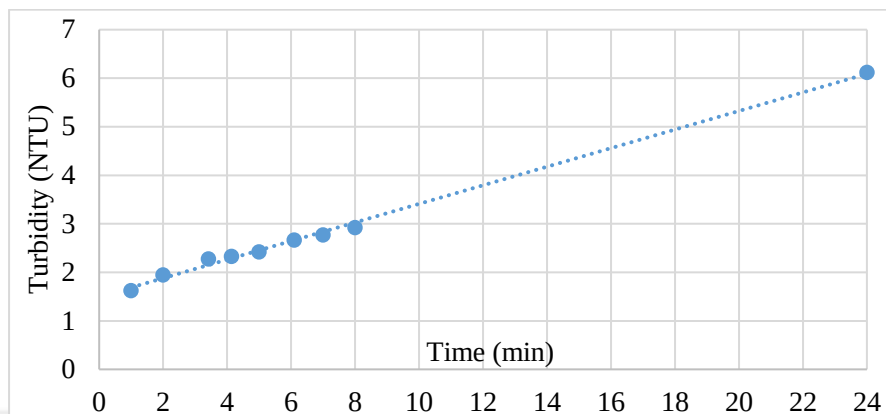


Figure B.2. Turbidity analysis of silica nanoparticle synthesis for the first 24 hours

To understand the synthesis process of nanoparticles, during the first 24 hours of the procedure and later day by day the turbidity and DLS analyses are conducted to see the growth. As it is presented in Figure B.1, the particle formation in 24 hours is proved by the increasing turbidity values from 1.5 NTU to 6 NTU which is also affected by the growing particles size.

The particle size by DLS at every hour is listed in Table B.1 which shows the growth of the nanoparticles and the polydispersity. As it is also presented in Figure B.1, DLS analysis shows the growth of particles as well as bigger particles at 90 nm scale which is not expected to form since 30 nm particle size is aimed. They might be formed because of agglomeration caused by stirring creating turbulence.

Table B.1 DLS analysis of silica nanoparticles during the first 24 hours of synthesis

Time (hr)	Smallest (nm)	Medium (nm)	Highest (nm)
1	18.5	26.3	70
2	60.8	86.3	92.5
3	37.3	52.9	114
4	30.2	56.7	99.2
5	37.3	49.3	52.9
6	21.3	65.2	65.2
7	28.2	65.2	80.5
8	34.8	70	75
24	17.3	21.3	32.4

When the sythesis is controlled daily after 24 hours, as it is presented in Figure B.1, the particle sizes are more stabilized but still increasing daily from 30 nm to 50 nm after 10 days. Between day10 and day26 it is seen in Figure B.3 that the particle size is stabilized around 45-50nm. The weight concentration is seen to be increasing until day 26 from 2‰ to 15‰. After 15‰ is reached, the concentration is observed to be stabilized. However, turbidity analysis does not stabilize which might be caused by the coagulation of particles after the saturation is reached at 15‰ concentration. Physically it is observed that particles are coagulated at the bottom of the flask which supports the turbidity increase.

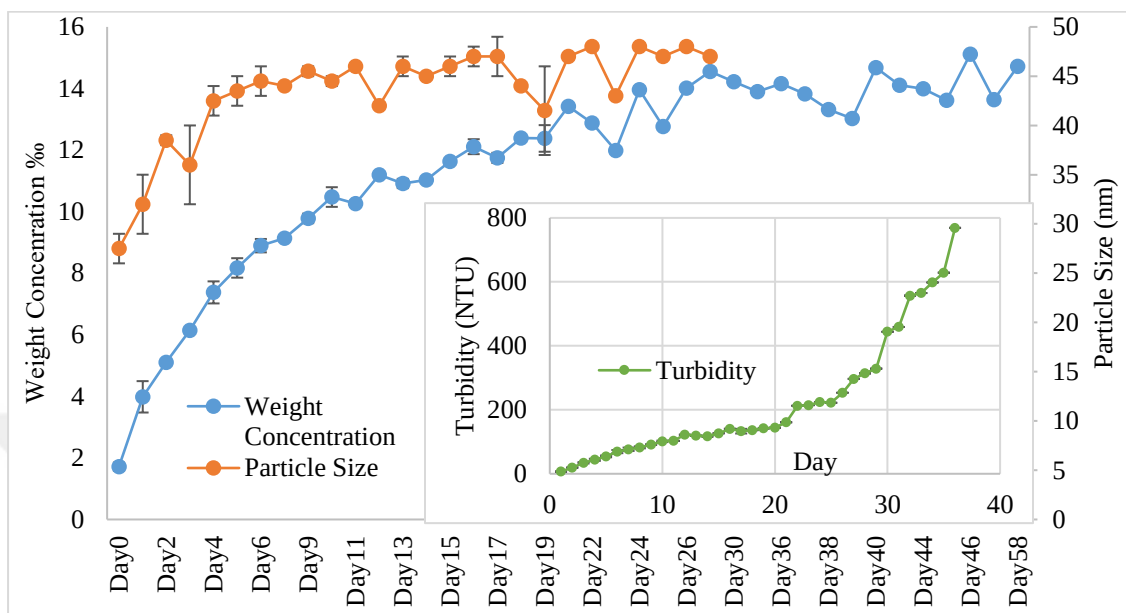


Figure B.3. Turbidity, DLS and weight concentration analyses of silica nanoparticle synthesis in IPA

Particle size is also checked in IPA-water mixture at different ratios to see if it changes with increasing amount of water. In different mixtures of IPA-water, DLS results are listed in Table B.2 which proves that particle size does not change by changing water amount and it is stable around 50 nm.

Table B.2 Particle size in IPA-water mixture at different weight concentrations

IPA w. %	Refractive Index	Particle Size by Intensity (nm)
100	1.33	50.5
75.9	1.37	49.3
58.3	1.37	49.4
45.2	1.36	46

C. DLS Analysis of Concentration and Diafiltration Experiments

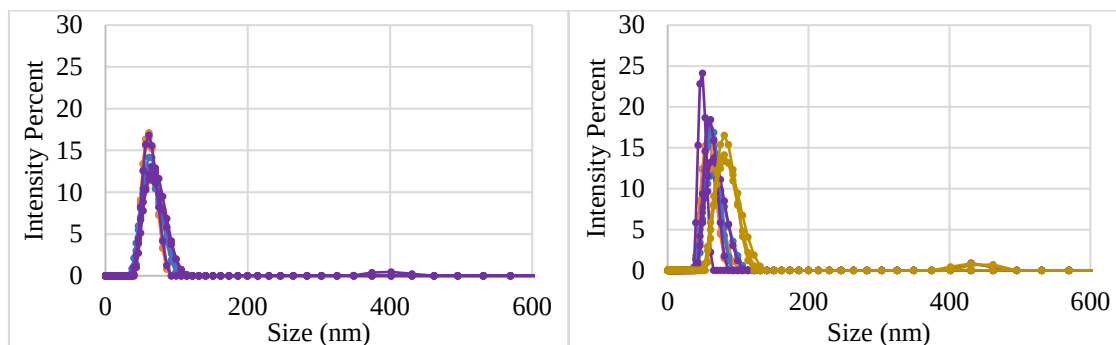


Figure C.1 N-IPA-C-1 and N-IPA-C-2 DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate, gold represents ultrasonic bath solution)

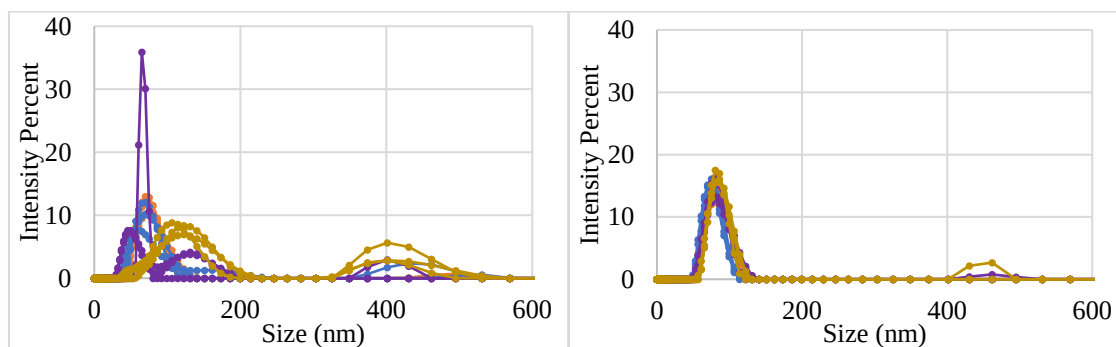


Figure C.2 N-W-C-1 and N-W-C-3 DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate, gold represents ultrasonic bath solution)

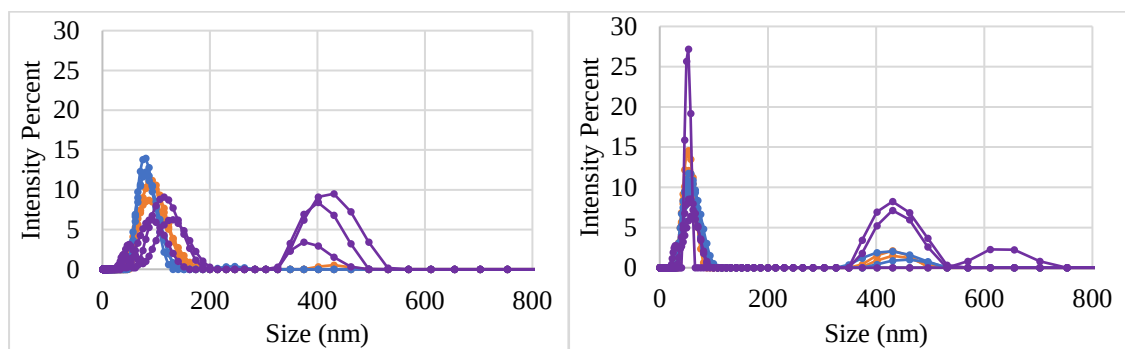


Figure C.3 N-DMF-C-1 and N-DMF-C-4 DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate)

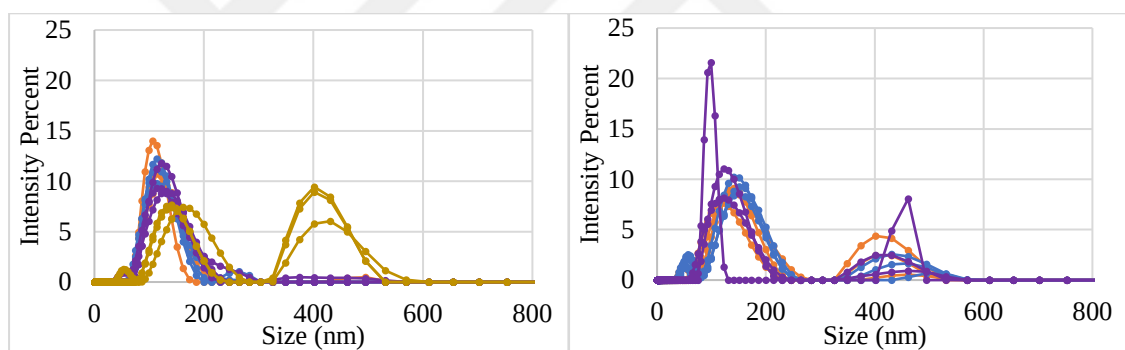


Figure C.4 H-W-C-2 and H-W-C-3 DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate, gold represents ultrasonic bath solution)

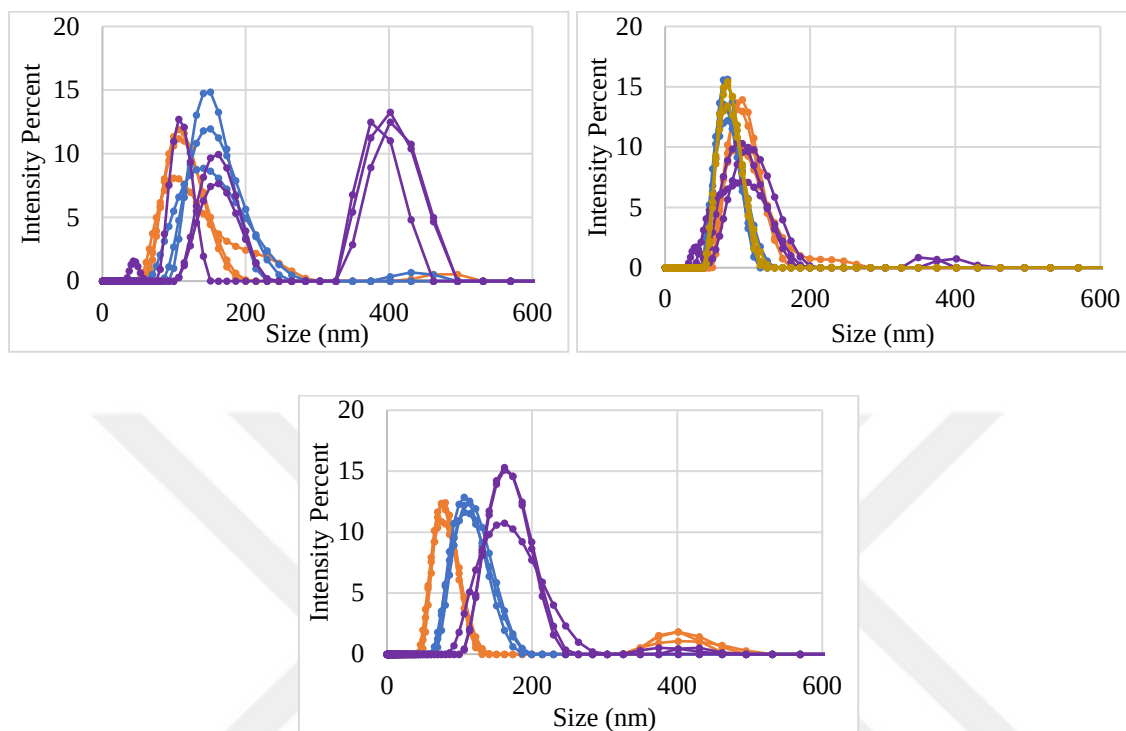


Figure C.5 H-IPA-C-1, H-IPA-C-3, H-IPA-C-4, DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate, gold represents ultrasonic bath solution)

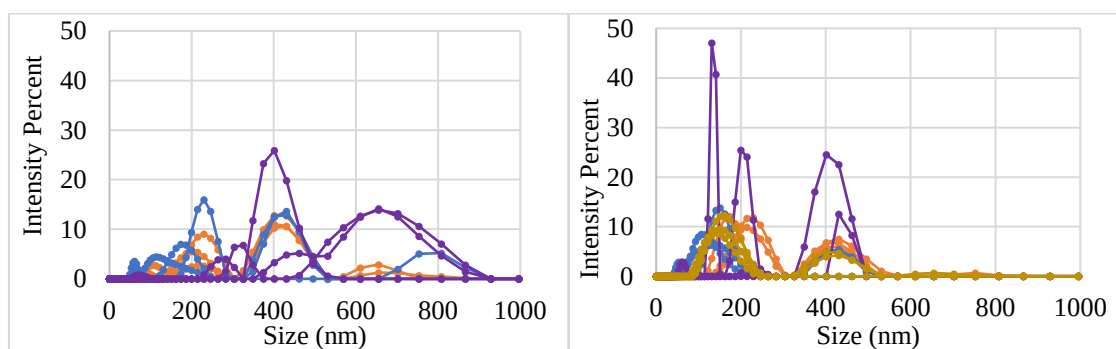


Figure C.6 H-DMF-C-2, H-DMF-C-3 DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate, gold represents ultrasonic bath solution)

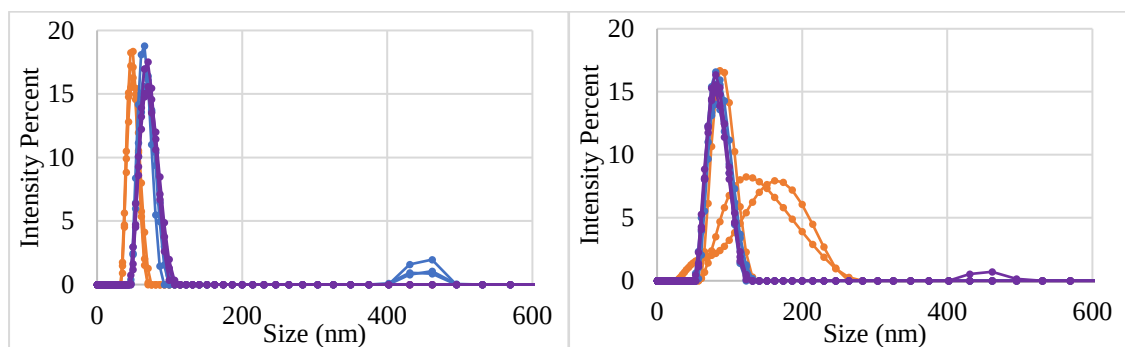


Figure C.7 N-ETOH-D-1, N-ETOH-D-3 DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate)

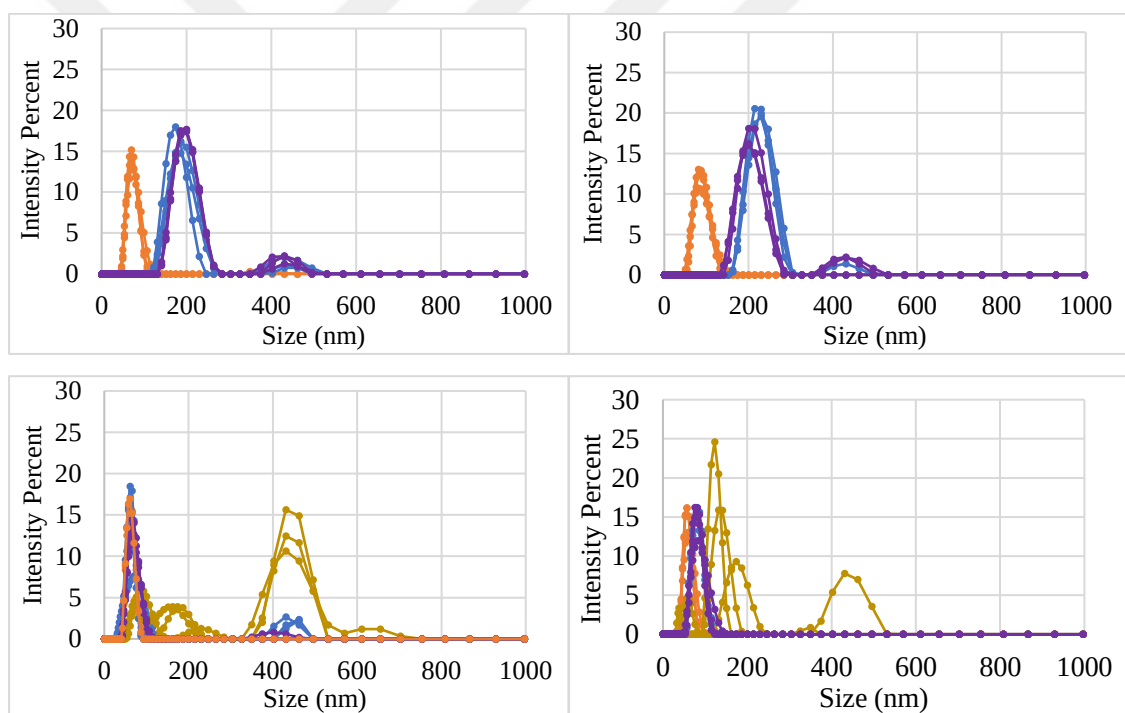


Figure C.8 N-W-D-2, N-W-D-3, N-W-D-4, N-W-D-5 DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate, gold represents ultrasonic bath solution)

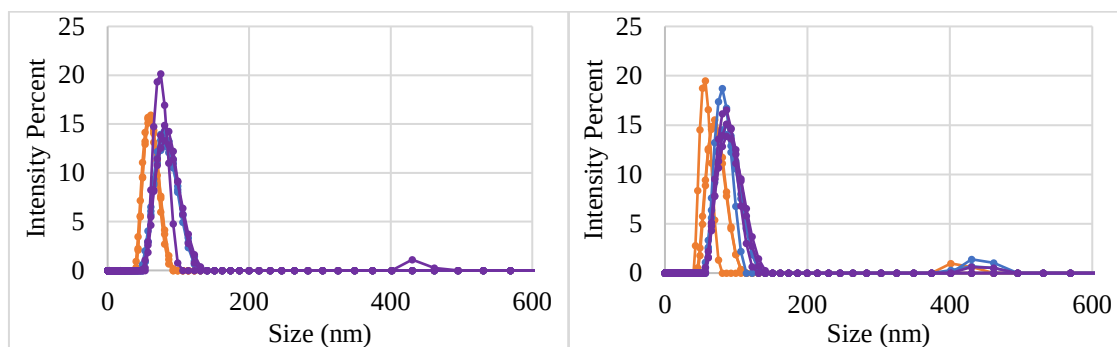


Figure C.9 N-DMF-D-1, N-DMF-D-3 DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate)

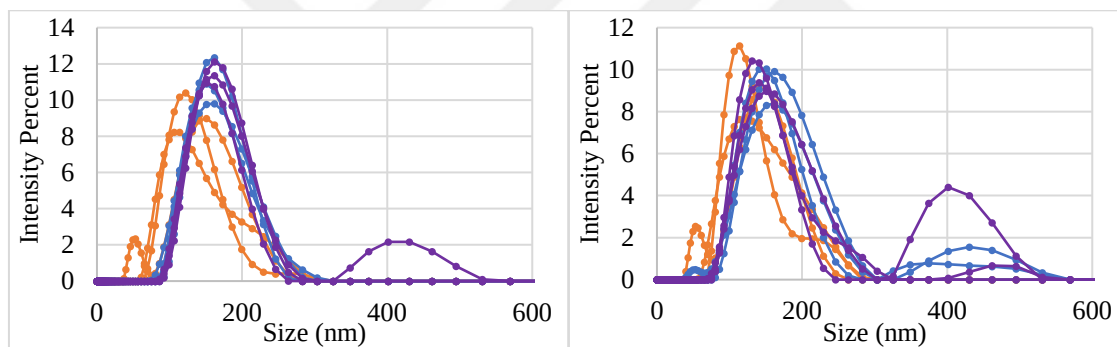


Figure C.10 H-ETOH-D-2, N-ETOH-D-3 DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate)

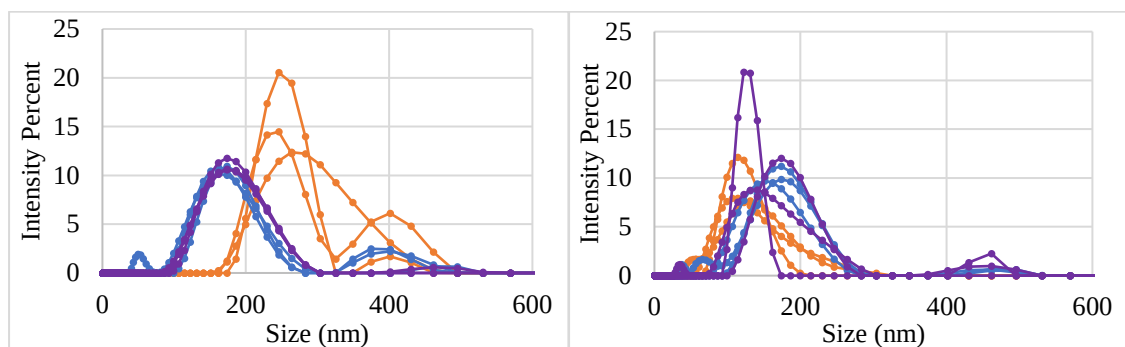


Figure C.11 H-W-D-1, H-W-D-3 DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate)

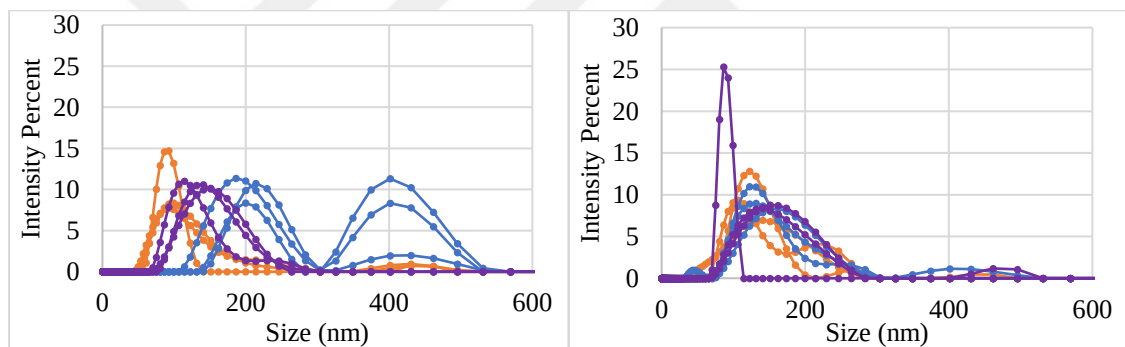


Figure C.12 H-DMF-D-2, H-DMF-D-3, DLS analysis (Orange represent feed solution, purple represents cleaning solution, blue represents retentate)

D. Sample Calculations

1. Rejection Sample Calculation in the First Concentration in IPA Experiment

Rejection calculation was done by feed solution concentration and by retentate solution concentration to see the amount of silica left on the surface. Sample calculation is done for N-W-C-1.

Table D.1 N-W-C-1 concentrations and calculated rejection by feed concentration which is analyzed by turbidimeter

Feed Vol (mL)	Feed conc ‰	Volume of Retentate (mL)	Volume of Permeate (mL)	Conc of Retentate ‰	Conc of Permeate ‰	R%
150	3.830	140	10	4.103	0.0093	99.76
140	4.103	130	10	4.418	0.0104	99.76
130	4.418	120	10	4.785	0.0131	99.72
120	4.785	110	10	5.219	0.0103	99.79
110	5.219	100	10	5.739	0.0176	99.68
100	5.739	90	10	6.375	0.0124	99.79
90	6.375	80	10	7.170	0.0154	99.77
80	7.170	70	10	8.193	0.0121	99.84
70	8.193	60	10	9.556	0.0126	99.86
60	9.556	50	10	11.465	0.0132	99.87
50	11.465	40	10	14.327	0.0145	99.89

$$R_i = \left(1 - \frac{C_i^{per}}{C_i^{feed}} \right) 100$$

$$R_1 = \left(1 - \frac{0.0093}{\frac{4.103 + 3.830}{2}} \right) 100 = 99.76\%$$

Table D.2 Concentrations and calculated rejection by retentate concentration which is analyzed by turbidimeter, of W-C-1 experiment

Feed Vol (mL)	Feed conc ‰	Volume of Retentate (mL)	Volume of Permeate (mL)	Conc of Retentate ‰	Conc of Permeate ‰	R%
150	2.416	140	10	2.587	0.0093	99.63
140	2.587	130	10	2.786	0.0104	99.61
130	2.786	120	10	3.017	0.0131	99.55
120	3.017	110	10	3.290	0.0103	99.67
110	3.290	100	10	3.617	0.0176	99.49
100	3.617	90	10	4.018	0.0124	99.67
90	4.018	80	10	4.518	0.0154	99.64
80	4.518	70	10	5.162	0.0121	99.75
70	5.162	60	10	6.020	0.0126	99.77
60	6.020	50	10	7.221	0.0132	99.80
50	7.221	40	10	9.023	0.0145	99.82

$$R_{11} = \left(1 - \frac{0.0145}{\frac{9.023 + 7.221}{2}} \right) 100 = 99.82\%$$

The difference between the retentate concentration by turbidity and calculated value;

$$14.327 - 9.023 = 5.304$$

shows that silica particles stay on the membrane surface after the experiment.

2. Reynolds number sample calculation in the first diafiltration experiment to ethanol from IPA

Table D.3 Velocity, density, hydrodynamic diameter and viscosity values of N-ETOH-D-1 experiment for Reynolds number calculation

Volume % of ETOH	Density (kg/m ³)	Hydraulic diameter (m)	Dynamic viscosity (Pa.s)	Mean velocity (L/h)	Mean velocity (m ³ /s)	Velocity (m/s)	Re
Total Recovery	786	0.0044	0.0024	3.10	8.62E-07	0.008	11.76
Total Recovery	786	0.0044	0.0024	3.13	8.68E-07	0.008	11.84
Total Recovery	786	0.0044	0.0024	3.29	9.14E-07	0.009	12.47
Total Recovery	786	0.0044	0.0024	3.03	8.42E-07	0.008	11.49
0	787	0.0044	0.0021	3.22	8.93E-07	0.008	13.93
0.09	787	0.0044	0.0019	3.13	8.69E-07	0.008	15.13
0.17	787	0.0044	0.0017	3.30	9.16E-07	0.009	17.42
0.25	788	0.0044	0.0016	3.16	8.79E-07	0.008	17.97
0.32	788	0.0044	0.0015	3.34	9.27E-07	0.009	20.09
0.38	788	0.0044	0.0014	3.44	9.55E-07	0.009	21.71
0.44	788	0.0044	0.0014	3.30	9.17E-07	0.009	21.68
0.49	788	0.0044	0.0013	3.36	9.33E-07	0.009	22.76
0.53	789	0.0044	0.0013	2.07	5.75E-07	0.005	14.40
0.58	789	0.0044	0.0013	1.95	5.42E-07	0.005	13.84
0.61	789	0.0044	0.0013	2.12	5.88E-07	0.006	15.26

$$Re = \frac{\rho.V.D}{\mu}$$

For total recovery;

$$Re_1 = \frac{786 \times 0.008 \times 0.0044}{0.0024} = 11.76$$

Table D.4 Permeance values of membranes used in diafiltration to DMF experiments by different volume fraction

Permeance (L/hm²bar)						
Volume Fraction of DMF %	H-DMF- D-3	H-DMF- D-2	H-DMF- D-1	N-DMF- D-1	N-DMF- D-2	N-DMF- D-3
0	3.8	5.2	6.3	9.8	8.1	7.5
9.8	4.9	6.7	8.1	12.6	10.4	9.7
17.4	5.3	7.3	8.8	13.7	11.3	10.5
36	6.3	8.6	10.4	16.2	13.4	12.4
90	6.3	8.6	10.4	16.2	13.4	12.4
100	6.2	8.5	10.3	16.0	13.2	12.2