Solmaz Şebnem FABRICATION OF NEW GENERATION MEMBRANES AND AGU
SEVERCAN THEIR APPLICATIONS IN FRUIT JUICE INDUSTRY 2018

FABRICATION OF NEW GENERATION MEMBRANES AND THEIR APPLICATIONS IN FRUIT JUICE INDUSTRY

A THESIS
SUBMITTED TO THE DEPARTMENT OF
ADVANCED MATERIALS AND NANOTECHNOLOGY
AND THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE
OF ABDULLAH GUL UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER

By
Solmaz Şebnem SEVERCAN
August, 2018

FABRICATION OF NEW GENERATION MEMBRANES AND THEIR APPLICATIONS IN FRUIT JUICE INDUSTRY

A THESIS
SUBMITTED TO THE DEPARTMENT OF
ADVANCED MATERIALS AND NANOTECHNOLOGY
AND THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE OF
ABDULLAH GUL UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER

By
Solmaz Şebnem SEVERCAN
August, 2018

SCIENTIFIC ETHICS COMPLIANCE

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

Solmaz Şebmem SEVERCAN

REGULATORY COMPLIANCE

M.Sc. thesis titled **"Fabrication of new generation membranes and their applications in fruit juice industry"** has been prepared in accordance with the Thesis Writing Guidelines of the Abdullah Gül University, Graduate School of Engineering & Science.

Prepared By ;
Solmaz Şebnem Severcan

Advisor — Co- Advisor

Asst. Prof. Dr. Kevser KAHRAMAN — Assoc. Prof. Dr. Niğmet UZAL

Head of the Advanced Materials and Nanotechnology Program
Prof. Dr. Murat DURANDURDU

ACCEPTANCE AND APPROVAL

M.Sc. thesis titled "Fabrication of new generation membranes and their applications in fruit juice industry"and prepared by Solmaz Şebnem SEVERCAN has been accepted by jury in the Advanced Materials and Nanotechnology Graduate Program at Abdullah Gül University, Graduate School of Engineering & Science.

17/08/2018

JURY:

Advisor :Asst. Prof. Dr. Kevser KAHRAMAN

Co-Advisor :Assoc. Prof. Dr. Niğmet UZAL

Member :Asst. Prof. Dr. Ayşe ÖZBEY

Member :Asst. Prof. Dr. Yusuf Çağatay ERŞAN

APPROVAL:

The acceptance of this M.Sc thesis has been approved by the decision of the Abdullah Gül University, Graduate School of Engineering & Science, Executive Board dated ….. /….. / ……….. and numbered .……

……….. /……….. / ………..

Prof. Dr. İrfan ALAN

ABSTRACT

FABRICATION OF NEW GENERATION MEMBRANES AND THEIR APPLICATIONS IN FRUIT JUICE INDUSTRY

Solmaz Şebnem Severcan

MSc. in Advanced Materials and Nanotechnology

Advisor: Asst. Prof. Dr. Kevser KAHRAMAN

Co-Advisor: Assoc. Prof. Dr. Niğmet UZAL

August, 2018

When membrane processes are compared to conventional processes, they have significant advantages for instance, providing decrease in operation time and cost with saving nutritious components and sensory parameters in food production plants. Especially, in fruit juice industry, UF membranes are utilized for clarification by eliminating big molecules like suspend proteins, fat and polysaccharides, which leads turbidity. Although, UF membranes have many advantages like its affordable cost, higher film forming ability, excellent mechanical properties, and superior chemical and thermal resistance, it has a major drawback leading the fouling of the membrane. To get rid of this problem, many researchers focused on the modification of membrane surface to both increase hydrophilicity and enhance antifouling characteristics. In this study, PSF/PEI (20wt%, 2wt%) UF membranes and PSF/PEI (17wt%, 2wt%) MF membranes were prepared with the addition of different concentrations of TiO_2 and Al_2O_3 nanoparticles (0.01, 0.03, 0.05 wt %) using phase inversion method to alter the structural and morphological properties of membranes. Turbid apple and pomegranate juice samples supplied from Döhler Inc. (Karaman, Turkey) were clarified by using cross flow membrane filtration system and dead-end filtration system at 5.4 bar trans-membrane pressure, respectively. Prepared nanocomposite membranes were characterized by using scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FT-IR), water-contact angle porosity and pure water flux. To investigate fouling resistance of nanocomposite membranes flux recovery ratio (FRR), flux decay ratio (DR), relative flux reduction (RFR) values were also calculated. In addition, clarified apple and pomegranate juice samples were characterized in terms of color, turbidity, total soluble solid, total antioxidant capacity (ABTS radical scavenging method and DPPH radical scavenging method) and total phenolic content. Total monomeric anthocyanin pigment content of pomegranate juice was also determined. The clarified juices obtained using new generation nanocomposite membranes were compared with the clarified product juice samples supplied from Döhler Inc. Membrane characterization and fruit juice characterization results demonstrated that fabricated new generation nanocomposite membranes were effective in apple and pomegranate juice clarification. Among these fabricated new generation nanocomposite membranes, the ones prepared with the addition of 0.01% of TiO_2 UF membrane and prepared with the addition of 0.05% Al_2O_3 MF membrane exhibits superior performance in terms of clarification of apple juice and pomegranate juice, respectively.

Keywords: nanocomposite membrane, TiO_2 nanoparticle, Al_2O_3 nanoparticle, clarification, apple juice, pomegranate juice.

ÖZET

YENİ NESİL MEMBRANLARIN ÜRETİMİ VE MEYVE SUYU ENDÜSTRİSİNDE UYGULAMALARI

Solmaz Şebnem SEVERCAN
İleri Malzeme ve Nanoteknoloji Yüksek Lisans Programı
Tez Yöneticisi: Dr. Öğr. Üyesi. Kevser Kahraman
Yardımcı Tez Yöneticisi: Doç. Dr. Niğmet Uzal
Ağustos-2018

Gıda endüstrisinde kullanılan membran ayırma süreçleri, geleneksel yöntemlerle kıyaslandığında; işletim süresini ve maaliyeti azaltma ve aynı zaman da ürünün besinsel bileşenlerini ve duyusal karakterini koruma gibi önemli avantajlara sahiptir. UF membranlar, bulanıklığa neden olan, askıdaki proteinler, yağ ve polisakkaritler gibi büyük molekülleri gidererek berraklaştıma sağlamak için kullanılırlar. UF membranlar, uygun maaliyet, yüksek film oluşturma özelliği, üstün kimyasal ve termal direnç gibi birçok avantaja sahip olmasına rağmen, tıkanma problemi en büyük dezavantajıdır. Bu sorunun üstesinden gelmek için, bir çok araştırmacı membran hidrofilikliğni ve tıkanma direncini artırmak için membran modifikasyonu üzerine çalışmışlardır. Bu çalışmada, membranın yapısal ve morfolojik özelliklerini değiştirmek için, PSF/PEI (20%/2%) UF ve PSF/PEI (17%/2%) MF membranlara farklı konsantrasyonlarda (0.01, 0.03, 0.05 %) TiO_2 and Al_2O_3 nanoparçacıları eklenerek, faz dönüşümü yöntemi ile nanokompozit membranlar hazırlanmıştır. Döhler Gıda San. ve Tic. Ltd. Şti.(Karaman, Türkiye) firmasından temin edilen elma ve nar suyu pulp örnekleri, sırasıyla çapraz akış filtrasyon sistemi ve sonlu filtrasyon sitemi 5.4 bar da işletilerek, berraklaştırılmıştır. Üretilen yeni nesil nanokompozit membranlar, taramalı elektron mikroskobu (SEM), Fourier dönüşümlü kızılötesi spekrometre (FT-IR), temas açısı, gözeneklilik ve saf su akısı ölçümleri ile karakterize edilmiştir. Ayrıca, üretilen nanokompozit membranların tıkanma direç performansının tayini için, akı geri kazanım oranı (FRR), saf su akı azalma oranı (DR) ve bağıl akı azalma oranı (RFR) hesaplanmıştır. Bunlara ek olarak, elde edilen berrak elma ve nar suyu renk, bulanıklık, toplam çözünmüş madde, toplam antioksidan aktivitesi (ABTS radikal yakalama metodu ve DPPH radikal yakalama

metodu) ve toplam fenolik madde analizleri ile karakterize edilmiştir. Ayrıca, berrak nar suyu için toplam monomerik antosiyanin tayini yapılmıştır. Üretilen nanokompozit membranlar kullanılarak elde edilen berrak meyve suyu analiz sonuçları, firmadan temin edilen berrak meyve suları ile karşılaştırılmıştır. Membran ve meyve suyu karakterizasyon sonuçları, üretilen yeni nesil nanokompozit membranların, elma ve nar suyu berraklaştırmasında etkili bir şekilde kullanılabileceğini göstermiştir. Üretilen nanokompozit membranlar arasında %0.01 TiO_2 eklenen PSF/PEI UF membran ve %0.05 Al_2O_3 eklenen PSF/PEI MF membranlar, sırasıyla elma ve nar suyu berraklaştırması açısından üstün performans göstermiştir.

Anahtar kelimeler: nanokompozit membran, TiO_2 ve Al_2O_3 nanomalzemeler, berraklaştırma, elma suyu, nar suyu

Acknowledgements

First of all, I would like to feel of thankfulness and appreciation to my supervisor, Asst. Prof. Kevser KAHRAMAN and co-advisor, Assoc. Prof. Dr. Niğmet UZAL for bringing me to this interesting and promising topic and their many valuable discussions and wonderful suggestions, and their permanent support, encouragements, positive attitude and numerous hours spent helping me to complete this thesis.

I'd also like to express my special thanks to respected committee members, Asst. Prof. Dr. Ayşe ÖZBEY and Asst. Prof. Dr. Yusuf Çağatay ERŞAN for showing kindness to accept to read and review this thesis and the efforts to provide valuable comments during my proposal presentation.

I sincerely thank my colleague Seda SAKİ for her kindness support, encouragement and valuable comments and suggestions during the experimental studies.

Next, I would like to thank Döhler Inc. for providing resources and Scientific Research Foundation of Abdullah Gül University (Project No: FCD-2017-92) for funding this study.

My deepest thanks are for my family; my dearest mother and father for all of their concerns and supports.

Finally, I'd also like to express my special thanks to my husband, Mehmet SEVERCAN, for his love, infinite patience, understanding and encouragements. Without his support and tolerance, this work would never end up successfully.

Table of Contents

List of Figures

List of Tables

Chapter 1

1. Introduction

In the past two decades, using membrane technology in food industry has been increased rapidly. Nowadays, the second largest membrane market following water and wastewater treatment is food industry with € 800-850 million market volume [1]. Although these processes are comparatively late technology, food industry has already used remarkably MF, UF, NF and RO pressure-driven membrane processes. In these processes, UF has the biggest market share at a rate of 35% [2]. Dairy industry has the major share of membrane process, then beverage industries such as beer, fruit juices and wine follows it. Since, high selectivity and low energy consumption are more desirable for processes in food industry membrane processes are much more attractive than conventional processes [3]. In addition, when membrane processes are compared to conventional processes, they have significant advantages in terms of saving nutritious components like anthocyanins, carotenoids, vitamins and bioactive proteins [4], [5] and sensory parameters like color, aroma, flavor [6] which are affected negatively from some kinds of treatments like chemical, biological and heat.

In fruit juice production industry, MF membranes are utilized by clarification for eliminating big molecules like suspended solids, high molecular weight proteins, which lead turbidity [7], [8]. UF membrane are also used in fruit juice clarification to remove yeast, molds, microscopic organisms and colloids besides proteins, tannins and polysaccharides and to concentrate the juice as well [9]. Before, applying filtration process, enzymatic treatment may be conducted to increase permeate flux and extend membrane duration [10]. UF and MF membranes made up of polysulfone (PSF) have been mostly used in many industries like food industry due to their affordable cost, higher film forming ability, excellent mechanical properties, and superior chemical and thermal resistance [11], [12].

However, hydrophobic nature of PSF membrane is the major drawback causing the fouling of the membrane resulting from accumulation of feed on the surface of the membrane and in the pore channel [13]–[15]. Fouling cause a decrease in flux and rejection of the product while operating pressure and time and energy consumption increases [16]–[18]. There are many studies on enhancement of anti-fouling properties of the membrane. Modification of membrane surface is the way to improve the anti-fouling characteristics by increasing the hydrophilicity. These researches may be divided into three main groups, adding some materials with hydrophilic nature like polyvinylpyrrolidone (PVP) [11], polyethylenimine (PEI) [19], polyvinyl alcohol (PVA) [20] polyetyleneglycol [21], adding some minerals like silica and zirconium dioxide (ZrO_2) [22] or inorganic nanoparticles such as TiO_2, Al_2O_3, SiO_2 and $CaCO_3$ [19], [23]–[26], and grafting or coating with hydrophilic polymers such as polyvinylalcohol (PVA), polyethylenimine (PEI), polyvinylpyrorlidone (PVP) and polyethelene glycol (PEG) [27], [28]. Among these hydrophilic polymers, PEI is the most preferred modifying agent since it has the ability to make pores [29] . However, pore former ability of PEI can cause decrease in mechanical strength and selectivity of the membranes [30]. To get rid of this drawback, researchers were dealed with addition of nanoparticles in PSF membrane matrix [31], [32]. Modification with nanoparticles enables PSF membranes to enhance selectivity, permeability, tensile strength and thermal and chemical resistance [33], [34] .

In this study, new generation nanocomposite membranes are fabricated and applied for clarification of apple and pomegranate juices. To the best of our knowledge, there are no reported data on applying TiO_2 and Al_2O_3 incorporated nanocomposite membranes for clarifying apple and pomegranate juices. This study was carried out in two main parts. In the first part of the study, PSF/PEI UF membranes were modified by using TiO_2, Al_2O_3 and SiO_2 nanoparticles and the performance of these membranes were evaluated by using dead-end and cross flow membrane filtration system in terms of both water fluxes and apple juice quality to determine the most efficient nanoparticle type and optimum conditions for UF membranes in terms of nanoparticle concentration and apple juice clarification. All fabricated membranes were characterized by using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), contact angle, porosity, water and apple juice fluxes and flux recovery experiments.

Also, clarified apple juices were characterized, in terms of color (Pt-Co), total soluble solid content (ºBrix), turbidity (NTU), total phenolic content (mg GAE/L), total antioxidant activity (mmol TEAC/L). In the second part of the thesis, for the clarification of pomegranate juices, at initial PSF/PEI/TiO_2 and PSF/PEI/Al_2O_3 nanocomposite UF membranes were fabricated and they were used to clarify pomegranate juices by applying dead-end filtration system. Then, TiO_2 and Al_2O_3 incorporated nanocomposite MF membranes were fabricated and tested for pomegranate juice clarification using dead-end filtration system. Also, MF membranes were characterized by using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), contact angle, porosity and pure water fluxes. In addition, clarified pomegranate juices were characterized in terms of color, total soluble solid content, turbidity, total phenolic content, total antioxidant activity and total monomeric anthocyanin content. The findings of this study demonstrated that fabricated nanocomposite membranes exhibits superior performance than commercial membranes for the clarification of apple and pomegranate juices.

Chapter 2

2. Literature Review

2.1. Membrane Technology

Membrane technology is one of the most developing areas in separation technology. The recent innovations in membrane technology like production of novel membrane processes are mostly developing fields of process technology. Although membrane processes are comparatively late kind of separation technology, many membrane processes, especially, pressure-driven membrane processes are already performed in several industries. Membrane separation technology has been widely conducted for various areas, like water treatment [35], [36], gas purification [37], food processing [38], pharmaceutical industry [39] and environmental protection [40]. Diffusivity differences of components in the membrane matrix enable the membrane technology to be applied in separation process. Figure 2.1 represents schematic diagram of membrane processes [41], [42].

Membrane filtration is applied to separate particles with different size in liquid or gas mixtures. The semi-permeable membrane allows tiny molecules to cross into membrane to gain permeate, whereas membrane acts as a barrier to prevent passing larger particles in retentate, simultaneously [43].

When membrane processes are compared to conventional processes, they have significant advantages such as high removal capacity, flexibility of operation and cost effectiveness also less energy requirement and easy availability of membrane materials [44]. In addition membrane process is more desirable than conventional process in food industry. Since, chemical, biological or heat processes are not required in membrane processes, it is much more applicable than conventional processes. Although these conventional processes are comparatively late technology, food industry has already used membrane processes especially pressure-driven membrane processes [45].

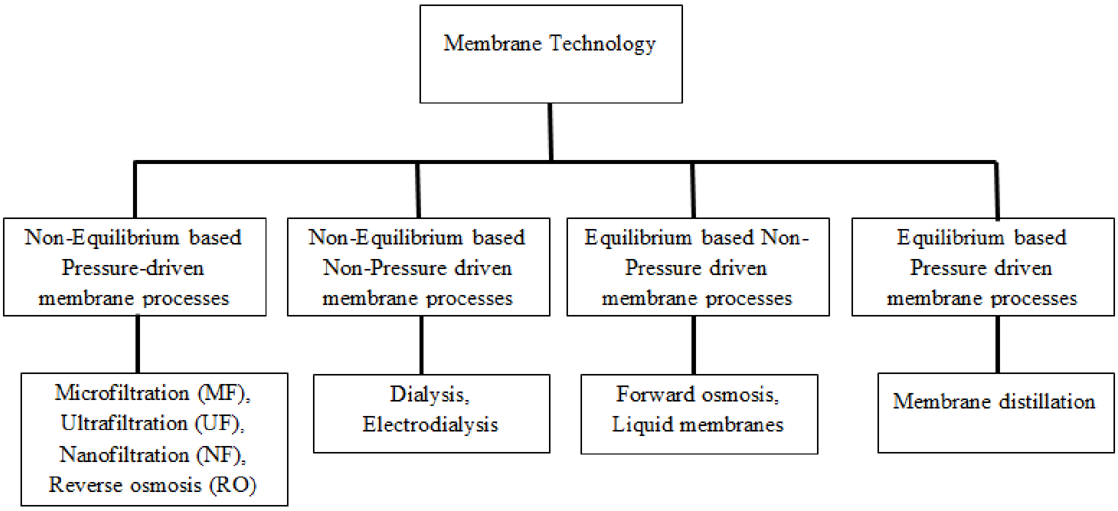

Figure 2.1. Schematic diagram of membrane processes

Under natural conditions, water molecules flow from areas with lower concentration to higher. However, by applying external pressure, molecules may be moved from low concentration side to high concentration side. Driving-force for the mass transport in these membranes is pressure gradient. Pressure difference occurring between two sides of the membrane enables the viscous flow of liquids or gases to pass through membrane pores at a steady state [46].

Pressure-driven membrane may be categorized in four main groups, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) according to pore sizes and required transmembrane pressure [47], [48]. Table 2.1 represents a classification of pressure-driven membrane processes in terms of pressure, pore size, separation mechanism and application areas.

Table 2.1. Overview of Pressure-Driven Membrane Processes and Their Characteristics

	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (OS)
Membrane structure	Symmetrical-asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical-composite
Pressure (bar)	1-10	1-10	10-30	310-100
Pore size (nm)	100-10,000	1-100	0.5-10	<0.5
Separation Mechanism	Sieving	Sieving	Sieving Charge effects	Solution-Diffusion
Applications	Clarification; pretreatment; removal of bacteria	Removal of macromolecules, bacteria, viruses; concentration	Removal of (multivalent) ions and relatively small organics	Ultrapure water; desalination

MF membranes have the pores with the largest diameter on surface range from 0.1μm to 10 μm [43], [49]. Due to its relatively high permeability, low pressure can be applied to get adequate water flux rate. MF is applied to eliminate microorganism in feed stream and obtain more clarified product. Also, this membrane is used generally in food and beverage industry to treat wastewater [50].

There are smaller pores ranging from 1 nm to 100 nm in UF membranes, so it has lower permeability than MF. UF membranes are generally applied to get rid of the large dissolved molecules [51].

Pore size of NF membranes is smaller than that of UF. This enables NF to remove relatively small molecules. Moreover, surface of these membranes has negative charge, so these ions attract positive charge ions and repel negative charge ions due to Donnan effect. The Donnan effect provides the elimination of ions with smaller size than pore size of the membrane [43].

Reverse osmosis (RO) membranes do not have predefined pores, so permeation is much slower. Also, separation process of this membrane is based on the "solution-diffusion" mechanism. This membrane requires high pressures (310-1000 bar) and consumes high energy because of low permeation rate [52]. RO process is applied for desalination and production of pure water [48].

There are two different operation types for the application of pressure-driven membrane processes (Figure 2.2). The first is dead-end operation in which feed is pumped or pressurized through membrane vertically and only one stream comes out from membrane. In dead-end filtration, retentate is not rejected consistently. The second is cross-flow mode of filtration where feed flows parallel to the surface of membrane and two streams, permeate and retentate stream, leave unlike dead-end mechanism. Dead-end mode is generally used in MF because of large pore size to clarify and sterilize. In this mode, rejected particles accumulate on membrane surface causing reduction in permeate flux by increasing height of cake layer on the surface. On the other hand, in cross-flow mechanism, due to tangential feed flow, accumulation on the surface of membrane is hindered, so flux of permeate is much higher than flux in the dead-end mechanism [53].

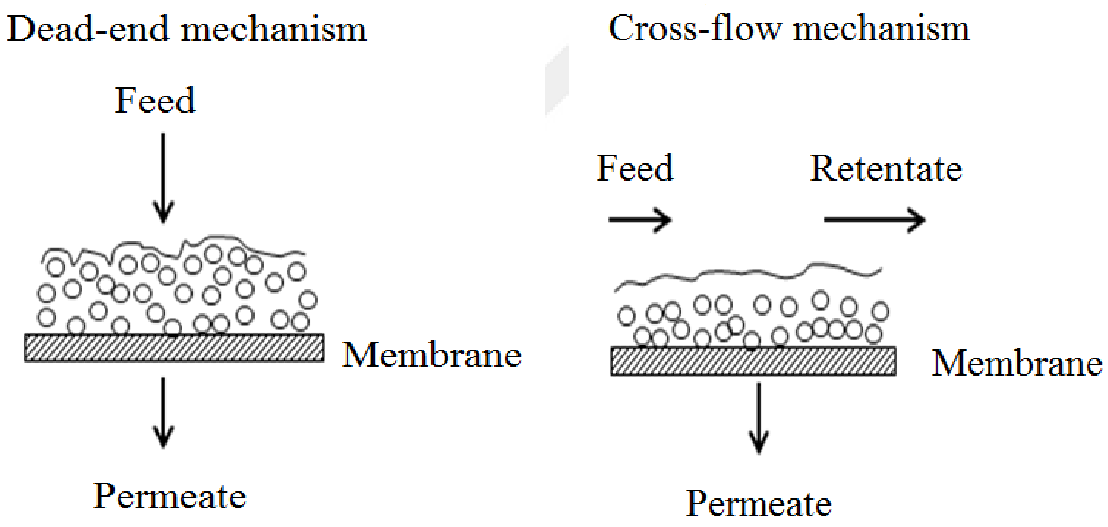

Figure 2.2. The schematic representation of the dead-end and cross-flow mechanism

2.1.1. Membrane Materials and Membrane Structures

High permeability and selectivity, at the same time mechanical stability are crucial features for membranes. According to the structure, membranes can be categorized into four groups; 1) porous membranes, 2) homogeneous dense membranes, 3) dense membranes carrying electrical charges and 4) supported or unsupported liquid membranes. Also, membrane structure can be classified as isotropic or symmetric and anisotropic or asymmetric. Entire cross-section of symmetric membrane has an identical structural and transport property, whereas entire cross-section of asymmetric membrane has a distinct structural and transport property. Symmetric membranes have more resistance and low flux, because of narrow pore size distribution. Anisotropic membranes have thin, finely porous skin layer and porous sub-layer [54]. Asymmetric membranes are used in pressure-driven membrane process. In addition membranes can be categorized into three groups depending on materials used in preparation of membrane; 1) polymeric or organic membranes, 2) ceramic or inorganic membranes and 3) metallic membranes. Both the intrinsic chemical and physical properties like hydrophobic or hydrophilic nature and the glass transition temperature or pore size and pore size distribution of membrane are affected membrane materials. Also, materials directly affects membrane selectivity and permeability [55].

Due to its affordable price, offering wide pore size range and large usage area, polymeric materials are used traditionally in pressure-driven membrane processes [56], [57]. Microfiltration membranes are generated by sintering, track-etching, streching, or phase inversion techniques by using polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polypropylene (PP), polyethylene (PE), and the hydrophilic materials cellulose esters, polycarbonate (PC), polysulfone/polyethersulfone (PSF/PES), polyimide/polyetherimide (PVPEI), aliphatic polyamide (PA), and polyetheretherketone (PEEK). In addition, ultrafiltration membranes are manufactured via phase inversion. Polysulfone/poly(ether sulfone)/sulfonated polysulfone, polyvinylidenefluoride, polyacrylonitrile and related block-copolymers, cellulosic such as cellulose acetate (CA), polyimide/poly(ether imide), aliphatic polyamide, and polyetheretherketone are used as material. Moreover, nanofiltration membranes are made of aromatic polyamide, polysulfone/polyethersulfone/sulfonated polysulfone, cellulose acetate, or polypiperazine amide. In membrane materials, PSF is the most widely applied because of its perfect chemical stability and thermal stability [42]. Furthermore, RO membranes may be produced using cellulose triacetate, aromatic polyamide or interfacial polymerization of polyamide and polyether urea. However, most of the organic membranes have some disadvantages in terms of one or more conditions during operation. For instance, the skinned membrane can be prepared usually using cellulose acetate as the classic material. Nevertheless, it is affected negatively, when exposed to high temperature, high chlorine concentration and high pH. In addition the performance of polymeric membranes reduces with time because of fouling, chemical deterioration, less thermal stability and reduction of fluxes [58]. In other words, polymeric membranes have some drawbacks such as high hydrophobicity, exposure the fouling, low fluxes and mechanical strength [56].

On the other hand, to get rid of these limitations in polymeric membranes, inorganic membranes have been used since the early 1980s. Ceramic membranes have obvious advantages such as higher mechanical, chemical and thermal stability than commercial polymeric membranes [59]. Thus, ceramic membrane can be durable even under extreme operating conditions. Alumina ($A1_2O_3$), titania (TiO_2), silica (SiO_2), and zirconia (ZrO_2) are the main materials for ceramic membranes. However, inorganic membranes also have some limitations. For example, inorganic membranes, used in microfiltration and ultrafiltration, are not available for nanofiltration and reverse osmosis. Also, its biggest disadvantage is that ceramic membranes are much more expensive than organic membranes and fragile structure of ceramic membrane prevent production of large inorganic membranes [60]. The last membrane type is metallic membrane which is used in MF. They are produced via sintering metal powders or stain-less filaments. These membranes are more stable during operation at high temperature. Also, they can be used in extreme environmental conditions due to their noncorrosive properties. In spite of their extraordinary permeation and selectivity properties, metal membranes have very limited industrial applications [43]. Therefore, many researchers focused on improvement of disadvantages of polymeric membranes. Recently, modification of polymeric membrane with incorporation of inorganic nanoparticles have become popular in the field of membrane technology [56].

2.1.2. Membrane Fabrication and Modification

Several methods such as phase inversion, electrospinning, sheet-streching and track-etching can be applied to generate membrane. Asymmetric (anisotropic) membranes are fabricated by using phase separation method, whereas symmetric (isotropic) membrane can be generated by the other methods [44]. Phase separation method can be conducted by different ways; non-solvent induced phase separation (NIPS), thermally induced phase separation (TIPS) and evaporation induced phase separation (EIPS) [61]–[63]. In non-solvent phase separation method, the casting polymer solution is immersed in a non-solvent bath. Removal of solvent by absorption of the water leads to precipitate the membrane film immediately [43]. In the thermally induced phase separation method, after polymer membrane materials are dissolved in solvent with high boiling point temperature and low molecular at raised temperature until creating the solution with desired shape, solvent is cooled to conduct phase separation. Finally, solvent is removed by exposing another solvent to fabricate membrane structure [64]–[68]. In evaporation induced phase separation method, polymer casting solutions is composed of a mixture of solvents. One of these solvents is evaporated to occur precipitation due to changing composition of casting solution [43]. Electrospinning has attracted most interest because of offering controlled structural properties like porosity, hydrophilicity and morphology [69]. Also, it can be applied in several applications like protective clothing, advanced composites, sensors, tissue engineering, pharmaceutical industries and air filters [69]–[71]. Sheet-streching method has been applied to produce generally microporous membranes. In this method, membrane solution is heated above the melting temperature and then extruded into thin sheet forms followed by stretching to obtain porous membrane structure [72], [73]. Membranes fabricated by track-etch have controlled structure, so they are more preferred in industrial applications. Pore size, shape and density of track-etch membranes may be defined according to properties of transport and retention [74].

Different techniques such as blending [75], grafting [76], surface chemical reaction [77] and nanoparticle incorporation [78] can be applied to modify membranes. Using several nanoparticles to fabricate new modified polymeric membrane is the recent trend. Among the modification methods, nanoparticle incorporation has been gained more interest in recent years.

2.1.2.1. Polymeric Nanocomposite Membranes

Nanocomposite membranes are divided into two groups depending on the preparation method. Firstly, nanoparticles are added into membrane matrix and phase inversion method is conducted [79]. Secondly, nanocomposite membranes are prepared by immersion into an aqueous suspension of nanoparticles [80]. Recently, membrane modification with incorporation of nanoparticles in membrane matrix is getting more and more attractive in order to enhance membrane performance in terms of permeability, selectivity, strength and hydrophilicity [81], [82]. Specific functional groups of nanoparticles, ionic form or lone pair electron, are bonded to polymer chain to alter the chemical and physical characterization of polymer [83]. Including nanoparticles which are TiO_2, Al_2O_3, SiO_2, $CaCO_3$, nanoclay alter the structural and morphological properties of the membrane [84]. Also, antibacterial property and photocatalytic capability are gained by incorporation of nano-Ag and bi-metallic nanoparticles [85]. Many researchers focused on the effect of metal oxide nano particles to enhance performance of polymeric membranes. Usage of inorganic nanoparticles as modifying agents leads to occur synergistic effect to improve membrane performance [86], [87]. Titania (TiO_2) nanoparticles are one of the most widely used nanoparticles as inorganic additives to modify polymer membrane [88]–[90]. Titania was used generally with UV irradiation due to phytocatalyst ability to increase anti-fouling property and the flux of permeation [91]. However, using polymer as membrane material causes oxidation reaction when exposing UV irradiation [92]. Recently, to provide hydrophilicity for hydrophobic polymeric membranes like polysulfone, polyethersulfone, titania nanoparticle has been used as modifier without UV irradiation [90], [91], [93], [94].

Damodar et al. [95] fabricated mixed-matrix nanocomposite membranes entrapping different amounts of TiO_2 nanoparticles in PVDF membranes. They prepared membranes by phase inversion method and reported that addition of TiO_2 nanoparticles significantly enhances flux, permeability and hydrophilicity. In addition, Pourjafar [96] prepared thin-film nanocomposite membranes with mixing polyvinyl alcohol (PVA) and TiO_2 nanoparticles in polyethersulfone and they reported that incorporating with TiO_2 nanoparticles affects membrane morphology and filtration performance. Also, Madaeni and Ghaemi [97] coated the composite membranes with TiO_2 nanoparticles and indicated that TiO_2 addition leads to increase in hydrophilicity and permeate flux. Moreover, dispersion of nanoparticles in membrane matrix have been applied in many fields of membrane technology like gas separation [98] and UF [99]–[102].

Vatanpour et al. [103] prepared mixed matrix nanocomposite membrane with entrapping TiO_2 nanoparticles in polyethersulfone (PES) membrane by using phase inversion method. Also, Razmjou et al. [104] modified hollow fiber PES membrane by using TiO_2 nanoparticles. They reported that TiO_2 embedded membranes had better hydrophilic properties and pure water flux.

Razmjou et al. [105] investigated effect of nanoparticles on polymeric membrane. They used TiO_2 as nanoparticle additives and PES as polymeric material. Phase inversion method was applied with blending nanoparticles in the solution. They conducted AFM, SEM, FT-IR analysis and also contact angle goniometry, molecular weight cut-off, surface free energy measurement to demonstrate effects of nanoparticle modification. According to their results, nanoparticle incorporation concluded significant effect in terms of surface free energy, roughness, pore size and hydrophilicity.

Yang et al. [106] also examined polysulfone UF membrane treated with TiO_2 nanoparticle. PSF (18 wt%) and TiO_2 (2 wt%) were dispersed for casting solution. Membranes were prepared with phase-inversion method. Methods of SEM, XRD, contact angle meter, UF experiments and mechanical strength test were applied to evaluate effect of TiO_2 nanoparticle on polysulfone membrane. Nanocomposite membranes exhibited perfect water permeability, hydrophilicty, mechanical strength and good anti-fouling ability. However higher TiO_2 content (more than 2 wt %) caused a serious nanoparticle aggregation to result in the performances of PSF/TiO_2 membranes decline.

Sotto et al. [32] demonstrated that the structure of membrane converted from a sponge-like structure into a finger-like structure after modification of membrnane with addition of TiO_2 nanoparticle. Also, they showed that TiO_2 nanoparticles in the casting solution directly related with the rates of permeation, pore size and porosity of membrane. In addition, TiO_2 concentration is directly proportional with membrane porosity, only if it is in the low concentration interval.

Especially, Al_2O_3 nanoparticles greatly improve the membrane hydrophilicity and mechanical strength [107]. Yan et al. [108] modified a polyvinylidene fluoride (PVDF) UF membrane. In the experiment Al_2O_3 particles at nano-scale were used as a modifier. Nanoparticles provided increase in efficient filtration area of membrane and the surface hydrophilicity leading to improve anti-fouling property and mechanical strength.

Uzal et al. [109] embedded 2 wt % PEI and 0.05 wt % Al_2O_3 nanoparticles in PSF solution to prepare nanofiber membranes (NFM) by using electrospinning method. The characteristics of the nanocomposite membrane were determined by using scanning electron microscopy (SEM), Fourier transform infrared FT-IR spectroscopy, and also porosity, water contact angle and tensile strength were measured. Adding PEI and Al_2O_3 nanoparticle caused increase in both porosity and mechanical strength. Also decrease in contact angle exhibited obtaining more hydrophilic membrane.

In Garcia-Ivers' research [110], UF polymeric membranes were modified using Polyethyleneglycol (PEG) and alumina (Al_2O_3) as additives. Membranes obtained from phase inversion method, exhibited superior antifouling properties and desirable ultrafiltration performance. According to results of permeation and morphological analyzes results, a dense top layer and a porous sponge-like sublayer were formed with high hydrophilicity with addition of Al_2O_3.

In addition, Maximous et al. [111] examined the effect of Al_2O_3 nanoparticles on the performance of PES UF membranes in terms of fouling. Phase inversion method was used to fabricate the flat sheet membranes and according to their results, these modified membranes had higher anti-fouling performance, porosity and pseudo steady-state permeability than composite membranes.

2.1. Fruit Juice Process

Separation and purification are the main processes of food industry. Moreover, as, biotechnology and nanotechnology industries grow, these processes are becoming more important.

Membrane technology has covered major part in food processing for more than 25 years [112]. Beverages industry is the second largest application area of membrane technology after the dairy industry among food industry [112]. Applying membrane technology in beverage industry is a good alternative in terms of economical, working conditions, environmental and product quality [113]. In food industry, production of fruit juice and concentration are increased day by day, because of increasing tendency of fruit juice consumption. Since fruit juices contain high concentration of vitamins, minerals, antioxidants and dietary fibers, responsible for facilitating digestion, they have become popular. Recently, consumption of fruits is decreased while consumption of fruit juices and processed fruit is increased by 60%, because in terms of nutrient content fruit juices are closest to fruits [114]. Also, consumption of fruit and vegetable juices is increased to reach at 46.8 billion liters per year[114].

In concentration of fruit juice process, there are 3 main steps. First step is raw fruit juice production which covers washing, crushing, adding pectinase enzyme and pressing respectively. Second step is clear fruit juice production. In this step, after clarification enzyme addition, active carbon treatment is conducted and finally membrane process is applied to obtain clear juice. In addition, to concentrate clear juice, vacuum evaporation or reverse osmosis process is carried out as the last step [115], [116]. Enzyme treatment is required before applying membrane process to enhance filtration performance.

According to Alvarez et al. [117] pectinase enzymes digest pectin into poly-d-galacturonic acidity fragments, so viscosity of the pulp decrease which leads increase in penetrate flux. MF and UF membranes can be applied for clarification of fruit juice [1].

Membrane technology has greater interest than conventional techniques for separation process in fruit juice industry. Therefore, using membrane processes in food industry have three main advantages [112], [118]. Firstly, products obtained using membrane technology has higher quality than products obtained using conventional process. Secondly, membrane process is much cheaper than conventional process due to providing to eliminate some process steps. Lastly, it is more environment-friendly as there is no polluting material.

2.1.3. Clarification

Clarification of fruit juice is a simple membrane process. Although, both ceramic and polymeric membranes are applied for fruit juice clarification, polymeric membranes are most popular. After fruit juice extraction, the product is usually turbid because of some water insoluble molecules such as fibers, cellulose, hemicellulose, protopectin, starch and lipids, and also, colloid macromolecules, like pectin, proteins and certain polyphenols [119]. The concentration of polysaccharides, such as pectin, cellulose, lignin and starch, proteins, tannins and metals affects the turbidity [120]. Clarification method used in fruit juice industry has been improved day by day, because clarity of the product is a decisive factor for consumers. Clarification is applied as a pretreatment process of concentration. Clarification is required to attain low viscous product with less turbidity and brighter color. Decreasing viscosity is important to provide less fouling and greater concentration. Clarification can be operated with both conventional methods and membranes.

Conventional clarification methods including clarification methods applied in fruit juice industry is composed of many steps which are enzymatic treatment (depectinization), cooling, flocculation (gelatin, silica sol, bentonite and diatomaceous earth), decantation, centrifugation and filtration. This conventional methods lead to extend of processing time, since flocculation step occupies 6-18 hours to accomplish adequate sedimentation [120]. In addition, there are some other drawbacks of using clarifying agents, bentonite and gelatin. Bentonite is used as a clarifying agent because, it has negative charge and react immediately molecules with positive charge to occur sedimentation and obtain clear juice [10]. Using bentonite as clarifying agent prevent fruit juice from occurring dark color during the enzymatic treatment. Although bentonite has advantage to stabilize protein, it leads to decrease fruit juice quality via removing of polyphenol [121], [122]. Moreover, gelatin with positive charges, causes to react easily with phenolics having negative charge [121]. Also, disposal of these agents leads to environmental pollution [123]. Membrane separation process is more efficient than conventional process because of saving organoleptic and nutritional properties of the juice [124].

On the other hand, recently, membrane processes, MF and UF have been preferred over the conventional process as a clarification method [10]. Pressure-driven membrane processes enables fruit juice industry to decrease in operating time by eliminating cooling, flocculation, decantation and centrifugation steps applied in the conventional process. Also, membrane process will lead to eliminate negative effects of fining agents in terms of nutritional value of product, process yield and environmental. Many research have demonstrated that using cross-flow MF and UF leads to reduce in operation time and save energy input [10]. In addition, traditional process contains thermal pasteurization which leads juice quality deterioration [124]. Exceeding temperature over 50°C degrades the sensory parameter and nutritional values which cause the loss of fresh juice flavor [125]. However, products obtained from membrane process are aseptic without all undesirable microorganisms [50].

Actually, UF process is the most powerful method to get rid of cloudy juice from fruit and vegetable [126]. Cassano [126] performed two-step membrane process at room temperature for clarification and concentration by using hollow fiber UF method and osmotic distillation respectively. In clarification unit suspend solids like microorganisms, lipids, proteins and colloids are totally removed, whereas organic acids and soluble solids such as vitamins and sugars are recovered. The analytical measurement performed both clarified and concentrated juices to demonstrate preservation of sugars, organic acids, polyphenols and anthocyanins. According to Cassano’s [126] research about clarification of citrus juices and he applied membrane technology for clarification instead of clarifying agents. They have indicated that clarification times is decreased, clarification process is made much simple, clarification can be operated at room temperature so the fruit juice freshness and development of the final product quality are provided with preserving aroma and nutritional value. In addition, clarification of fruit juice with UF process was also performed by Tallarico et al. [127] ultrafiltration provide to minimized microbial contamination in fruit juice due to eliminating microorganism without applying thermal treatment causes loss of volatile compounds.

Water soluble molecules such as vitamins, salts, and sugars flow together with water can flow through the UF membrane, whereas water insoluble molecules like microorganisms can retain on the membrane surface [128].

According to Fukumoto et al. [116] UF has many advantages over traditional fruit juice operating. They reported that, it enables to operate in a single step without using finning agents, eliminate pasteurization process by removing microorganisms, reduce filtration time while increase juice yield, and obtain better juice clarity**.** Therefore, when membrane technology is compared with traditional method, it enables fruit juice industry not only to enhance the product quality but also to save energy by decreasing processing time.

For apple juice clarification, the UF membranes normally used at 100-200 kDa nominal molecular weight cut off [51]. The usual plant arrangement for apple juice clarification is indicated in Figure 2.3 Borneman et al.[129] and Lukanin et al. [130], reported that polyphenols in apple juice is removed using single ultrafiltration membrane and also they investigated the performance of ultrafiltration method in membrane distillation to eliminate turbidity in apple juice. Before clarification process with ultrafiltration, pectinase and amylase were used as enzymes for enzymatic treatment. As results of ultrafiltration process, biopolymers concentration was minimized, juice viscosity was reduced and also trans membrane flux has increased.

On the other hand, MF membranes with a 0.1 μm cut-off are sometimes applied for colored juice clarification to retain color adequately [51]. Product from UF membranes has lighter color. The usual plant arrangement for pomegranate juice clarification is indicated in Figure 2.4 [115]. Red fruits have a rich polyphenol content like anthocyanins, flavonols, flavan-3-ols, benzoic and hydroxicinnamic acid derivatives [131]. Many experiments showed that red fruits inhibit oxidation of liposome due to its antiradical activity. In addition, it can prevent formation of cancer cells and tumor by influencing immune systems and scavenging free radicals [132]. Pomegranate (Punica granatum) juice production obtains huge interest among the red fruits juice because of its high anthocyanins concentration which leads formation of bright red color and increase in antioxidant capacity [133]. Since, polyphenols in pomegranate juice leads to haze formation; they are the most undesirable components in view of marketing. In traditional clarification method, to enhance appearance of pomegranate juice by removing polyphenols, agglomeration of this compound was performed by enzyme addition which is high-priced and requires much time and distracted with filtration [134].

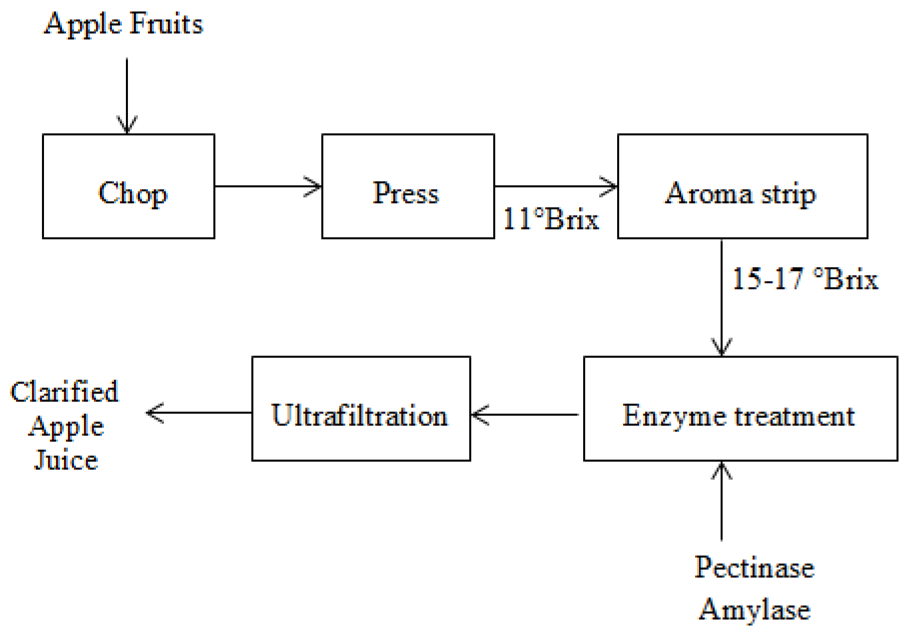

Figure 2.3. Apple juice clarification process [129]**.**

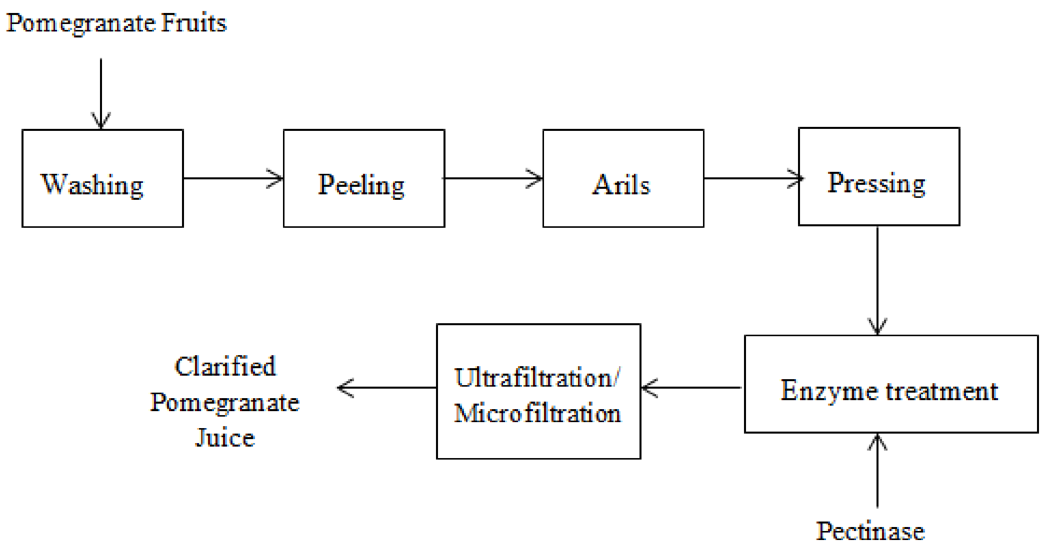

Figure 2.4. Pomegranate juice clarification process [115]**.**

Chapter 3

3. Materials and Methods

3.1. Chemicals

All the chemicals and standards used in the experiments were: polysulfone (PSF, Acros Organics); polyethylenimine (PEI, Sigma-Aldrich, USA); hydrophilic nanoparticles (titanium dioxide, aliminum oxide, silisium dioxide, Nanografi, Turkey); N,N-dimethylformamite (DMF, Merck, Germany); 1-methyl-2-pirolidon (NMP, Merck, Germany); Folin-Ciocalteu phenol reagent (2N) sodium carbonate anhydrate; gallic acid monohydrate (Merck, Germany); 2,2-Diphenyl-1-picrylhydrazyl (DPPH, Sigma-Aldrich, USA), methanol (merck, Germany); 3-ethylbenzothiazoline-6-sulfonic acid (ABTS, Sigma-Aldirich, USA); potassium persulphate (Merck, Germany); 6-Hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox, Sigma-Aldrich, USA); ethanol (Merck, Germany); potassium chloride (Merck, Germany).

3.2. Fruit Juice Samples

Apple and pomegranate juice samples were supplied from Döhler Inc. (Karaman, Turkey) in December, 2017 and November, 2017, respectively, according to the production seasons. Samples were stored at -18°C until use. The flow chart of juice clarification process used by Döhler Inc. is given in Figure 3.1 briefly. In this thesis, the turbid fruit juice samples (S1) supplied from Döhler Inc. were subjected to clarification process using new generation nanocomposite UF/MF membranes to obtain clarified fruit juice. Samples clarified with commercial UF membrane (S2) were also provided from the company for comparison.

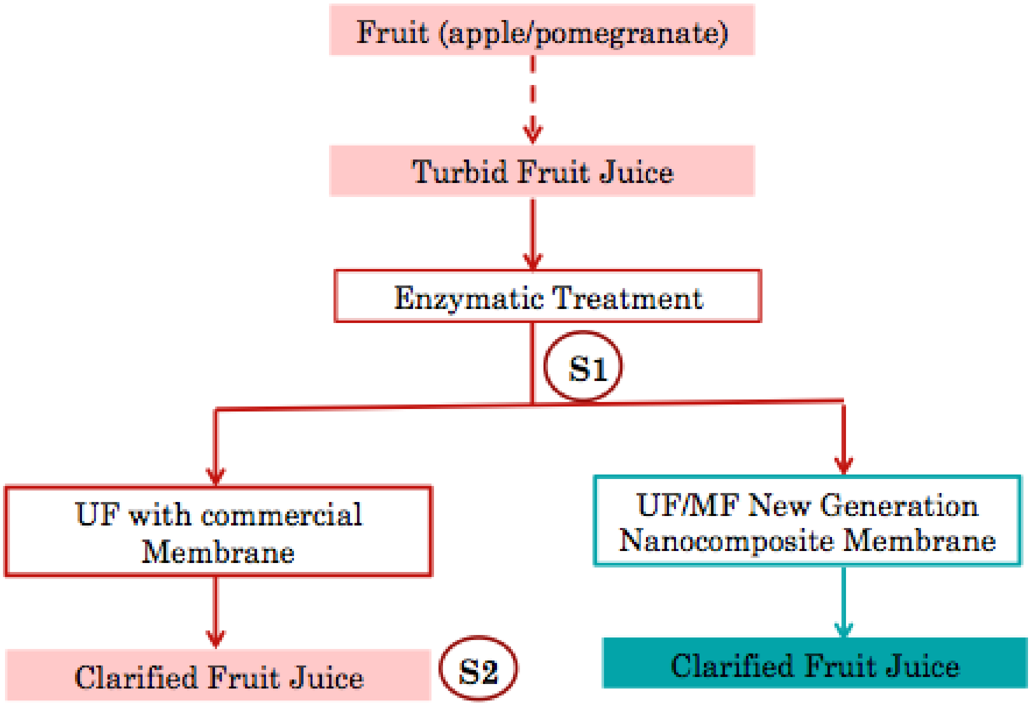

Figure 3.1. Flow chart of fruit juice clarification process used by Döhler Inc.

3.3. Membrane Fabrication

Pressure-driven ultrafiltration (UF) membrane and microfiltration (MF) membrane were fabricated by applying phase inversion method (Figure 3.2). For the fabrication of the membranes, polysulfone (PSF, MW 60.000, Acros Organics, USA) was used with 20 wt % and 17 wt % concentration as base polymer for UF and MF membranes, respectively. Polyethylenimine (PEI, MW 25,000, Sigma-Aldrich, USA) was added as a pore forming agent with 2 wt % concentration. N,N-dimethylformamite (DMF, anhydrous, 99.8 %, Merck, Germany) and 1-methyl-2-pirolidon (NMP, Merck, Germany) solutions were used as solvents. PSF and PEI concentration in the membrane solution were adjusted from Saki's research [135]. To increase mechanical resistance and hydrophobicity, TiO_2 (10-25 nm, Nanografi, Turkey), Al_2O_3 (20 nm, Nanografi, Turkey) and SiO_2 (15-25 nm, Nanografi, Turkey) nanomaterials was added to the solution in different concentrations. The composition of the membrane solutions prepared for apple juice and pomegranate juice clarification are shown in Table 3.1 and Table 3.2, respectively. Solutions were mixed at 400 rpm using a magnetic stirrer for 12 h to obtain homogenous mixtures. Then, the solutions were treated in an ultrasonic bath for at least 2 h to remove the bubbles.

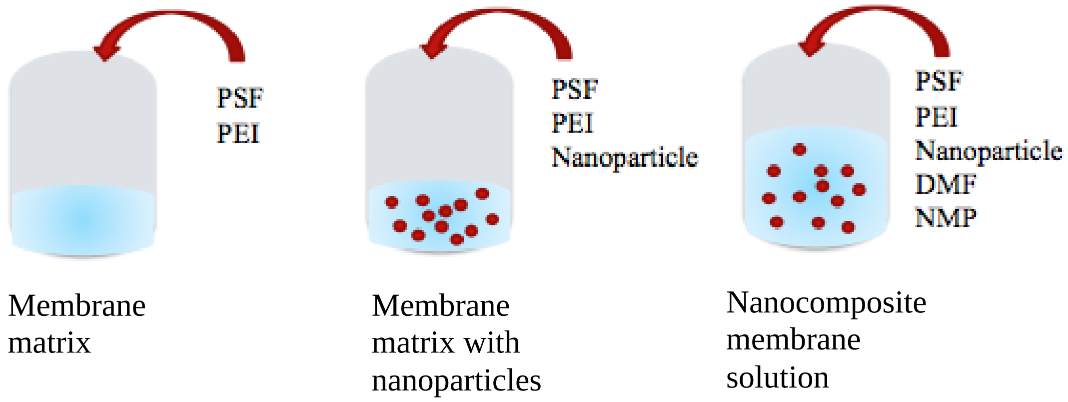

Figure 3.2. Schematic diagram for the preparation of nanocomposite membrane solution.

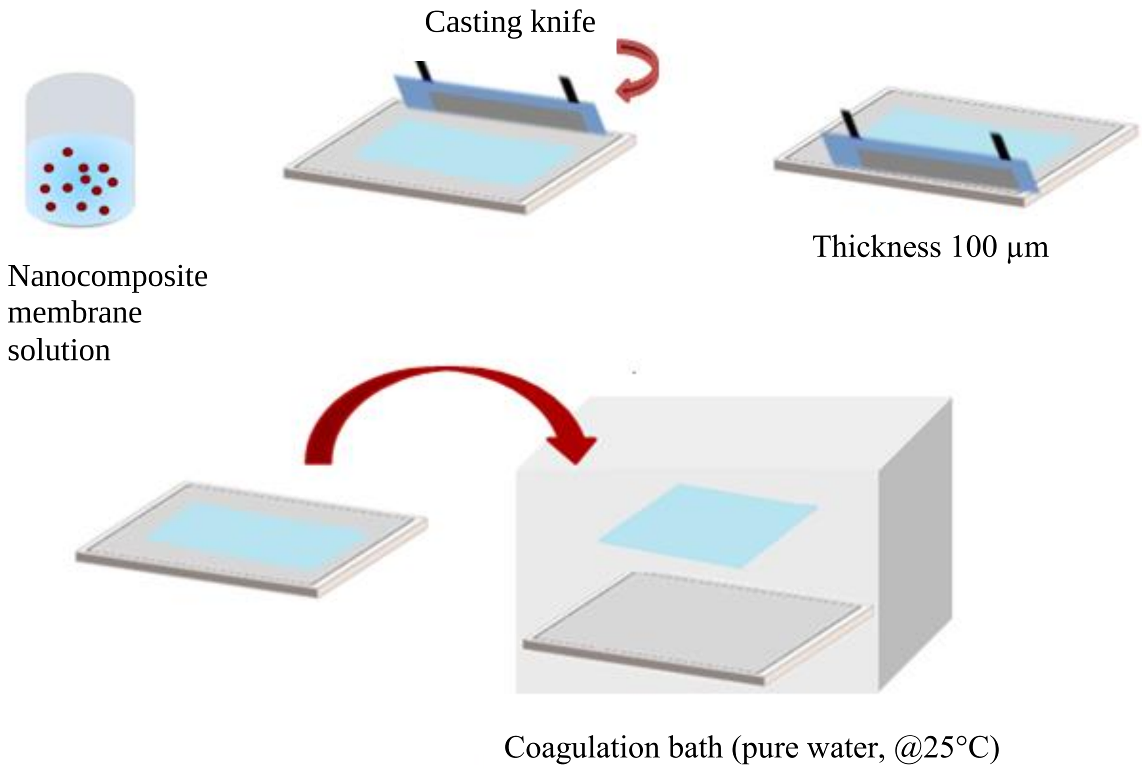

Figure 3.3. Schematic diagram for fabrication of nanocomposite membrane by using phase inversion method.

Table 3.1. Composition of the nanocomposite UF membranes used for apple juice clarification

Membrane	PSF (wt%)	PEI (wt%)	TiO_2 (wt%)	Al_2O_3 (wt%)	SiO_2 (wt%)
UF1	20	-	-	-	-
UF2	20	2	-	-	-
UFT1	20	2	0.01	-	-
UFT3	20	2	0.03	-	-
UFT5	20	2	0.05	-	-
UFA1	20	2	-	0.01	-
UFA3	20	2	-	0.03	-
UFA5	20	2	-	0.05	-
UFS1	20	2	-	-	0.01
UFS3	20	2	-	-	0.03
UFS5	20	2	-	-	0.05

Table 3.2. Composition of the nanocomposite MF membranes used for pomegranate juice clarification

Substrate	PSF (wt%)	PEI (wt%)	TiO_2 (wt%)	Al_2O_3 (wt%)
MF1	17	-	-	-
MF2	17	2	-	-
MFT1	17	2	0.01	-
MFT3	17	2	0.03	-
MFT5	17	2	0.05	-
MFA1	17	2	-	0.01
MFA3	17	2	-	0.03
MFA5	17	2	-	0.05

The solutions were poured onto a clean glass plate (20x30 cm) and immediately spreaded using a steel casting knife to obtain membrane film with 100±10 μm thickness. The films were immediately immersed into a coagulation bath in order to remove any residual solvent. All membranes were stored in distilled water at 4˚C until use.

3.4. Membrane Characterization

3.4.1. SEM Analysis

Scanning electronmicroscope (Zeis Evo LS10, Germany) at 10kV was used to analyze the top surface and cross-section morphologies of the membranes were also analyzed. The size of membrane pieces were adjusted at approximately 1 cm^2. Prior to the analysis, the samples were coated with platinum applying a JEOL JFC 1600 Autofine coater. Measurements were carried out for 50 different positions and results were given as average. Magnification in a SEM was adjusted at 300,000 and 25,000 for surface and cross-section analyzes respectively.

3.4.2. Fourier-Transform Infrared Spectroscopy (FT-IR) Analysis

FT-IR measurement was conducted to determine the functional groups on the surface of the membrane after addition of modifying agents. New chemical bonds may occur when modifying agents connect to the membrane polymer. For this purpose, an FT-IR with ATR crystal was used (Thermo Nicolet Avatar 370, USA). Before FT-IR analysis, membranes were dried at 50°C for one night. Measurement was carried out at the interval 400-4.000 cm^{-1} wavelength (between the visible and microwave wavelength range). Each spectrum was received after 32 scans. FT-IR graphs of transmittance vs wavelength (nm) were plotted.

3.4.3. Water Contact Angle

Hydrophilicity of the membrane samples was determined by the sessile drop method at room temperature using Attension-Theta-Lite tensiometer (Biolin Scientific, Finland). For this purpose contact angle between membrane surface and distilled water droplets (5 μL) was determined. Measurement was replicated on three different points of membrane and contact angle value was given as average.

3.4.4. Porosity

For the porosity measurements, the membranes, that have surface area of 4 cm^2, were immersed in ethanol for 2 hours. The membranes were removed from ethanol and dried in the oven at 50˚C overnight to remove alcohol. The porosity (ε) of the membranes were calculated using Eq. (3.1);

$$\varepsilon = \frac{(W_i - W_f)/de}{\left(\frac{W_i - W_f}{dw} + W_f\right)/dp} \qquad (3.1)$$

where, W_i is the weight of membrane (g) before ethanol immersion, W_f is weight of membrane (g) after drying, de and dp represents density of ethanol (0.788 g/cm^3) and density of polymer (1.24 g/cm^3), respectively.

3.4.5. Filtration Process

3.4.5.1. Dead-End Filtration

Dead-end filtration was conducted before cross-flow filtration to obtain preliminary information about the membrane performance in terms of pure water flux and fruit juice clarification. A dead-end filtration system (Sterlich, HP4750, Washington, USA) with 14.6 cm^2 effective membrane area and 300 mL reservoir was used. The membrane samples were placed to the bottom of the reservoir which was filled with 250 ml sample (distilled water/turbid fruit juice). The filtration pressure was maintained by a compressed N_2. The filtration experiments were carried out at a stirring speed of 250 rpm, 25±3˚C. System pressure was set as 5.4 bar, coherent with the pressure used by Döhler Inc. in their clarification process. Pure water permeate was collected in a graduated cylinder (25 mL) at certain interval and flux was calculated by using from Eq (3.2).

$$J_w = \frac{V}{A \times t} \qquad (3.2)$$

where, J is the water flux (L/m^{2}h), V (L) is the permeate volume (L), A (m^2) is the effective membrane area, and t (h) is the permeation time.

3.4.5.2. Cross-Flow Filtration

Cross-flow filtration system (Sterlitech, Sepa CF, USA) that has a filtration area of 150 cm^2 was used to perform cross-flow filtration process. Feed tank of cross-flow filtration system was filled with 2 L of raw fruit juice. Similar to Dead-End Filtration process, the pressure of cross-flow filtration system was adjusted to 5.4 bar, which is also used by Döhler Inc. Cross-flow filtration system was carried out for 120 minutes until reaching steady-state conditions. Cross-flow filtration system was operated at total recycle mode in which the permeate was returned to feed tank, and reflects the real system conditions. Samples were collected in 15 mL graduated cylinder at intervals of 15 minutes and flux was calculated by using from Eq (3.2) and the analyses were performed to see the membrane performance.

3.4.6. Flux Recovery

In cross-flow filtration, before and after fruit juice filtration, distilled water was passed through all membranes until reaching steady-state conditions for determining the water fluxes of membranes. Anti-fouling property of the membranes in terms of flux decay ratio (DR), flux recovery ratio (FRR), relative flux reduction (RFR) was determined by using the water flux values according to the Eqn. (3.3), (3.4) and (3.5) respectively.

$$DR = \frac{J1-J}{J1} \times 100 \qquad (3.3)$$

$$FRR = \frac{J2}{J1} \times 100 \qquad (3.4)$$

$$RFR = (1 - \frac{J2}{J1}) \times 100 \qquad (3.5)$$

where, J is flux of fruit juices at steady-state (L/m^{2}h); J_1 is the pure water flux before fruit juice filtration at steady-state (L/m^{2}h); J_2 is the pure water flux value after fruit juice filtration at steady-state (L/m^{2}h).

3.5. Characterization of the juice samples

3.5.1. Color

The color of the samples was determined using spectrophotometer with RFID technology (DR 6000, Hach, UK). The absorbance value of the samples was measured at 465 nm. The measurements were made in 3 triplicates and given as an average and standard deviation.

3.5.2. Turbidity

Turbidity of the samples were determined using a turbidity meter (Thermo Scientific, Eutech TN-100, Singapore) and the results were expressed as NTU. Calibration was conducted before each measurement. Glass cuvettes containing 10 ml of sample were placed into the instrument and the measurements were made in 3 replicates and given as an average and standard-deviation.

3.5.3. Total Soluble Solid (TSS)

Total soluble solid content of the samples were measured using a refractometer (DR-A1, Abbe ATAGO, Japan) and expressed in ˚Brix. For this purpose, 100 µL samples were dropped on the refractometer surface at room temperature and TSS content was recorded.

3.5.4. Total Antioxidant Capacity

Total antioxidant capacity of the samples was determined by conducting two different methods; $ABTS^{\cdot}$ radical scavenging and DPPH radical scavenging.

3.5.4.1. $ABTS^{\cdot}$ Radical Scavenging Method

ABTS radical activity was determined according to the method of Re et al. [136]. To obtain radical solution, 7 mM ABTS solution containing 2.45 mM potassium persulphate was prepared daily. For this purpose 19.2 mg ABTS (Sigma-Aldrich, USA) was dissolved in 2.5 mL of distilled water, and 3.31 mg potassium persulphate (Merck, Germany) was dissolved in 2.5 mL of distilled water. These two solutions were mixed and incubated in dark at room temperature for 12-16 hours to provide the formation of $ABTS^{\cdot +}$ radical cation. Absorbance of $ABTS^{\cdot +}$ solution was adjusted to 0.70-0.80 at 732 nm by diluting with 50% ethanol solution (v/v). The apple and pomegranate juice samples were diluted at 1:2 and 1:70 ratio with 50% EtOH before analysis to adjust the absorbance value between 0.300-0.600, respectively. Diluted samples (50 µL) were mixed with 3 mL $ABTS^{\cdot +}$ solution and the absorbance at 732 nm was read against 50% EtOH after 6 minutes (UV-1800, Shimadzu 1601, Japan). Inhibition percentage was calculated according to the Eq. (3.6)

$$\%\ \text{Inhibition} = \left[1 - \left(A_{sample} - A_{radical\ solution}\right)\right] \times 100 \qquad (3.6)$$

where A_{sample} is the absorbance of the sample 6 minutes after $ABTS^{\cdot +}$ solution addition, $A_{radical\ solution}$ is the absorbance of $ABTS^{\cdot +}$ solution.

Trolox was used as calibration reference standard, and calibration solutions containing 0.5, 1.0, 1.5 and 2.0 mM trolox standard were prepared by diluting trolox stock solution (2.5 mM) with 50% Ethanol. The calibration curve is shown in Figure 3.4. The results were expressed as milimol trolox equivalent per liter of sample (mmol TEAC/L). All the analyses were repeated two times and the results were given as the average.

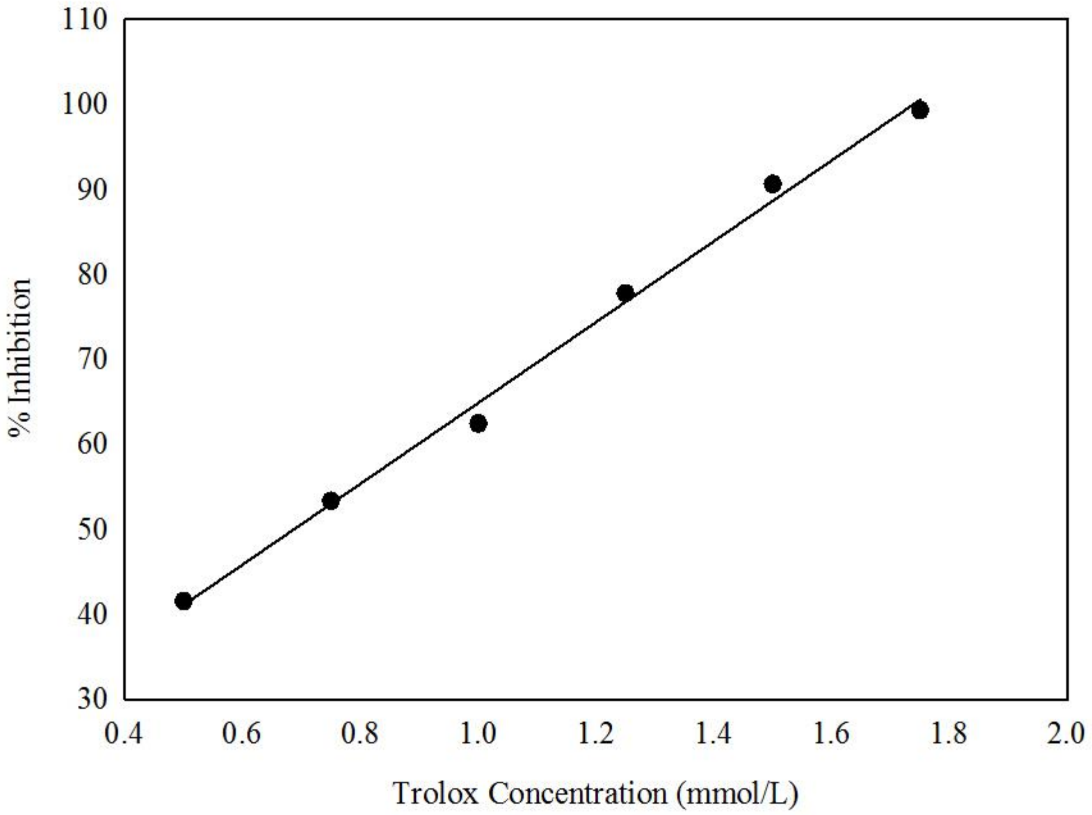

Figure 3.4. Trolox calibration curve for ABTS˙ Radical Scavenging Method. Y= 68.889x-5.4167 and R^2 =0.992.

3.5.4.2. DPPH Radical Scavenging Method

DPPH Radical Scavenging was determined according to the method of Anton et al. [137]. Prior to the analysis, 0.1 mM DPPH solution was prepared by dissolving 7.8 mg of DPPH (Sigma-Aldrich, USA) in 200 mL methanol. The apple juice samples were used directly without dilution, whereas pomegranate juice samples were diluted at 1:75 ratios with 60% methanol before analysis. The samples (200 μL) were mixed with 4 mL of DPPH solution and the tubes were capped immediately and incubated in dark at room temperature for 30 minutes. The absorbance value of the samples was measured at 517 nm (UV-1800, Shimadzu, Japan) at the end of the incubation. DPPH Radical Scavenging inhibition was calculated using Eq. (3.7)

$$\text{Inhibition}\ (\%) = \frac{\text{Ac}-\text{As}}{\text{Ac}} \text{x}100 \qquad (3.7)$$

where A_s is absorbance value of fruit juice samples and A_c is absorbance value of 60% methanol.

Trolox was used as calibration reference standard, and calibration solutions containing 0.1, 0.25, 0.35, and 0.50 mM trolox standard were prepared by diluting trolox stock solution (2 mM) with 60% Methanol. The calibration curve is shown in Figure 3.5. The results were expressed as milimol trolox equivalent per liter of sample (mmol TEAC/L). All the analyses were repeated two times and the results were given as the average.

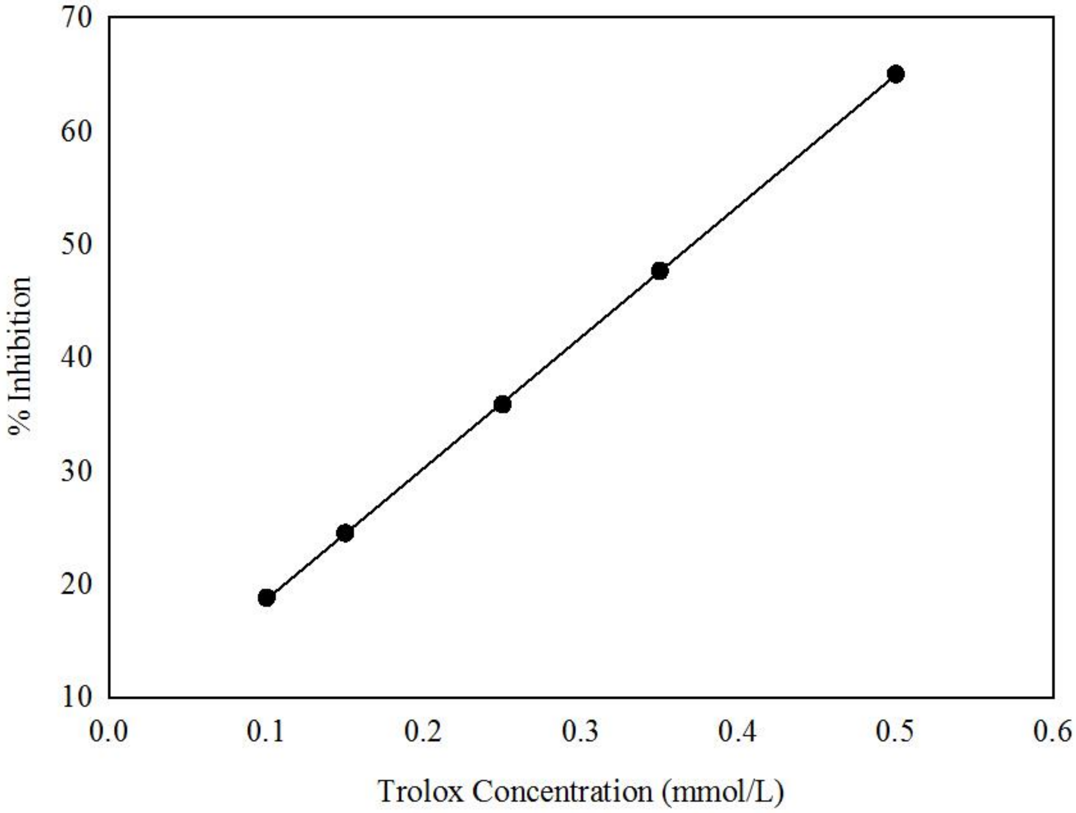

Figure 3.5. Trolox calibration curve for DPPH Radical Scavenging Method. Y= 115.69x+7.079 and R^2 =1.

3.5.5. Determination of Total Phenolic Content

Total phenolics content of the samples were measured using the method described by Spanos and Wrolsdat [138]. Tenfold diluted Folin-Ciocalteu reagent solution (0.2 N) was prepared by diluting 10 mL Folin-Ciocalteu's Phenol Reagent (Merck, Germany) reagent with distilled water to 100 mL. Sodium carbonate solution (75 g/L) was prepared by dissolving 7.5 g of sodium carbonate (ISOLAB, Germany) in 100 mL of distilled water and stirred and heated at 70-80°C for 8-10 minutes until completely dissolved. The apple juice samples were used directly without dilution, whereas pomegranate juice samples were diluted at 1:10 ratio with distilled water before analysis. The samples (100 μL) were mixed with 900 μL distilled water in glass tubes and 5 mL of Folin-Ciocalteu reagent solution (0.2 N) was to the tubes. The tubes were capped immediately and incubated in dark at room temperature for 8 minutes. At the end of the incubation, 4 mL of sodium carbonate solution (75 g/L) was added to the tubes and the capped tubes were incubated in dark at room temperature for 2 hours. After incubation, the absorbance value of the solutions was measured at 765 nm (UV-1800, Shimadzu, Japan). Gallic acid (Merck, Germany) was used as calibration reference standard, and calibration solutions containing 100-500 mg gallic acid/L methanol. Calibration curve is shown in Figure 3.6.

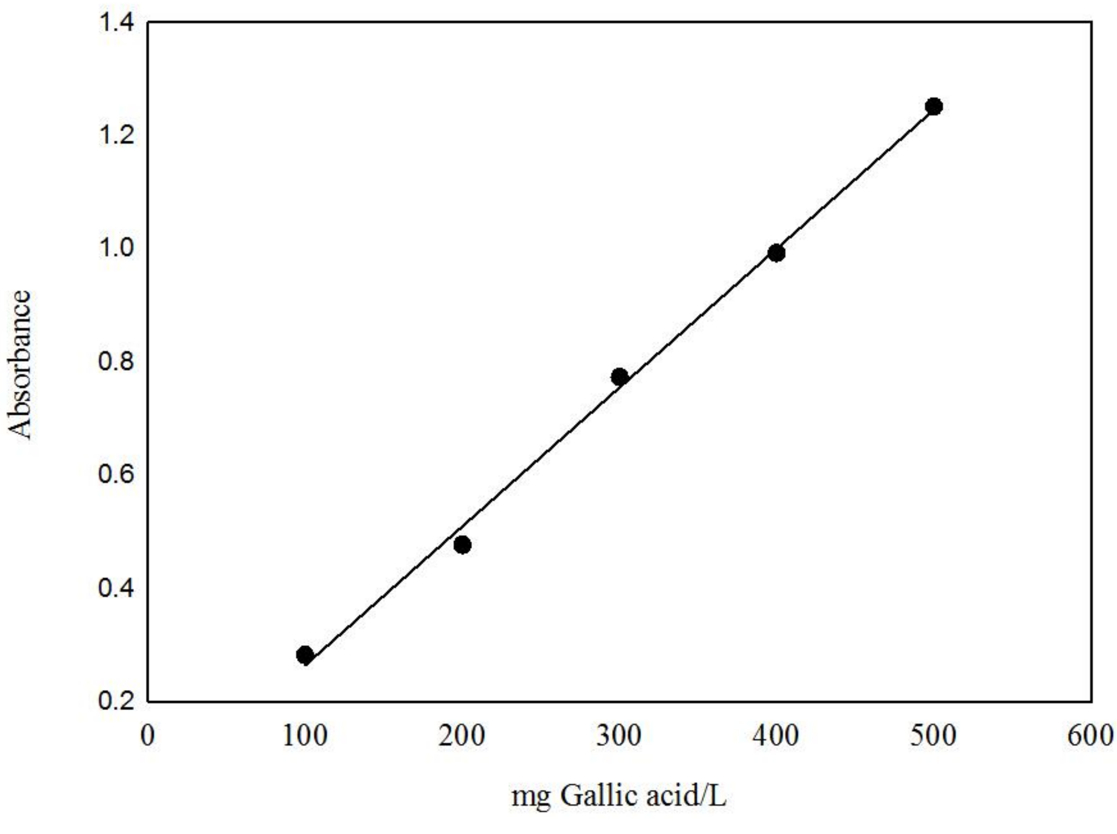

Figure 3.6. Gallic Acid calibration curve for the determination of total phenolic content. Y=0.0025x +0.0178 and R^2= 0.997.

3.5.6. Total Monomeric Anthocyanin Pigment Content

Anthocyanins are phenolic compounds and responsible for red, blue or purple color of fruits. Therefore, total monomeric anthocyanin pigment content determination was carried out for only pomegranate juice. The total monomeric anthocyanin content of the samples was determined using the pH-differential method [139]. Samples (0.32 μL) were mixed with 3.6 mL of two different potassium chloride buffer solutions (0.4 M, pH 4.5 and 0.025 M, pH 1.0). The samples were incubated for 30 minutes. At the end of the incubation the absorbance values of the samples were recorded at both 510 nm and 700 nm (UV-1800, Shimadzu 1601, Japan). Total monomeric anthocyanin content was expressed in cyanidin-3-glucoside was calculated according to Eq. (3.8);

$$Total\ monomeric\ anthocyanin\ (\frac{mg}{L}) = \frac{\mathrm{A} \times \mathrm{MW} \times \mathrm{DF} \times 1000}{\mathcal{E} \times l} \quad (3.8)$$

where, MW is the molecular weight of cyanidin-3-glucoside (449.2 g/mol), DF is the dilution factor, l is the length of light path (cm), Ɛ is the molar extinction coefficient for cyanidin-3-glucoside (26,900 $Lmol^{-1}cm^{-1}$). A value was calculated from Eq. (3.10).

$$DF = \frac{V_{sample} + V_{KCL\ buffer}}{V_{sample}} \quad (3.9)$$

$$\mathrm{A} = (\mathrm{A}_{1,150} - A_{1,700}) - (A_{2,510} - A_{2,700}) \quad (3.10)$$

where $A_{1,510}$ and $A_{1,700}$ is the absorbance value for first buffer solution (pH 1.0) at 510 nm and 700 nm, respectively. Similarly A_{2510} and A_{2700} absorbance value for second buffer solution (pH 4.5) at 510 nm and 700 nm respectively.

Chapter 4

4. RESULTS AND DISCUSSION

4.1. Apple Juice Clarification

4.1.1. Dead-End Filtration Experiments for Apple Juice Clarification Using UF Membranes

4.1.1.1. Pure Water Flux

The effect of nanomaterial addition on the performance of PSF/PEI membrane was analyzed in terms of pure water flux using dead-end filtration system. The pure water flux results of nanocomposite UF membranes prepared with the addition of TiO_2, Al_2O_3 and SiO_2 nanoparticles (0.01, 0.03, 0.05%wt) are shown in Figure 4.1, 4.2 and 4.3, respectively. Pure water flux of the membranes prepared with only 20% of PSF (UF1) was 24 L/m^{2}h (not shown in Figure 4.1), whereas pure water flux of the PSF/PEI membrane (UF2) was recorded as 192 L/m^{2}h. In the study of Chiang et al. [140], the effect of three different amines; ethylenediamine (EDA), diethylenetriamine (DETA) and hyperbranched polyethyleneimine (PEI) on membrane performance was determined. Similar to our results, they have also found that the membrane with PEI had the highest pore size and also highest permeation flux [140].

As can be seen from Figure 4.1, 4.2 and 4.3, the addition of nanoparticles generally caused increase in pure water fluxes of the PSF membranes. The highest pure water flux (2241±64 L/m^{2}h) was achieved with the membrane prepared with the addition of 0.01% of TiO_2 (UFT1). Among the UF membranes prepared with SiO_2 nanoparticles, the one prepared with the addition of 0.01% of SiO_2 (UFS1) had the highest performance in terms of pure water flux (514±15 L/m^2h). The pure water flux values of the membranes prepared with Al_2O_3 nanoparticles increased as the nanoparticle concentration increased, and the highest pure water flux was achieved when using the membrane prepared with the addition of 0.05% of Al_2O_3 (UFA5). In general, among the UF membranes prepared with nanoparticles, the ones containing TiO_2 and Al_2O_3 nanoparticles showed higher performance in terms of pure water flux than UF membrane containing SiO_2 nanoparticle. There are some studies investigating the effect of nanoparticles on the performance of membranes and their results were comparable with the findings in this study Livari et al. [141] examined pure water flux of PES (polyethersulfone) and TiO_2 incorporated PES membranes (TiO_2/PES). According to their results, the pure water flux of the membrane prepared with TiO_2 nanoparticle was slightly higher (236 kg/m^2h) than that of the control one (PES; 217 kg/m^2h). Similarly, Luo et al. [142] showed that incorporation of TiO_2 nanoparticles in PES matrix lead an increase of 59% in pure water flux.

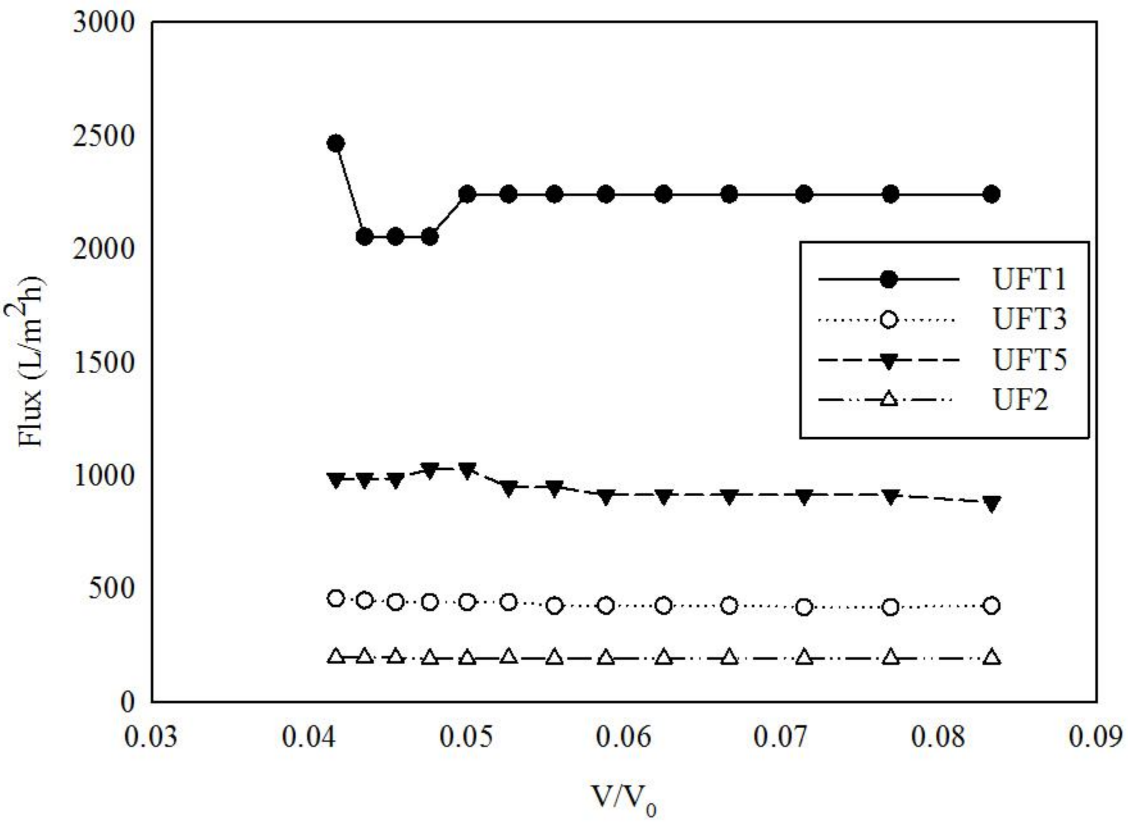

Figure 4.1. Pure water flux values of PSF/PEI and TiO_2 added nanocomposite UF membranes. TMP=5.4 bar, T= 25±5°C. UF2: 20%PSF/2%PEI; UFT1: 20%PSF/2%PEI/0.01%TiO_2; UFT3: 20%PSF/2%PEI/0.03%TiO_2; UFT5: 20%PSF/2%PEI/0.05% TiO_2. V_0: apple juice volume (L) in the system before sampling; V: apple juice volume (L) in the system after sampling.

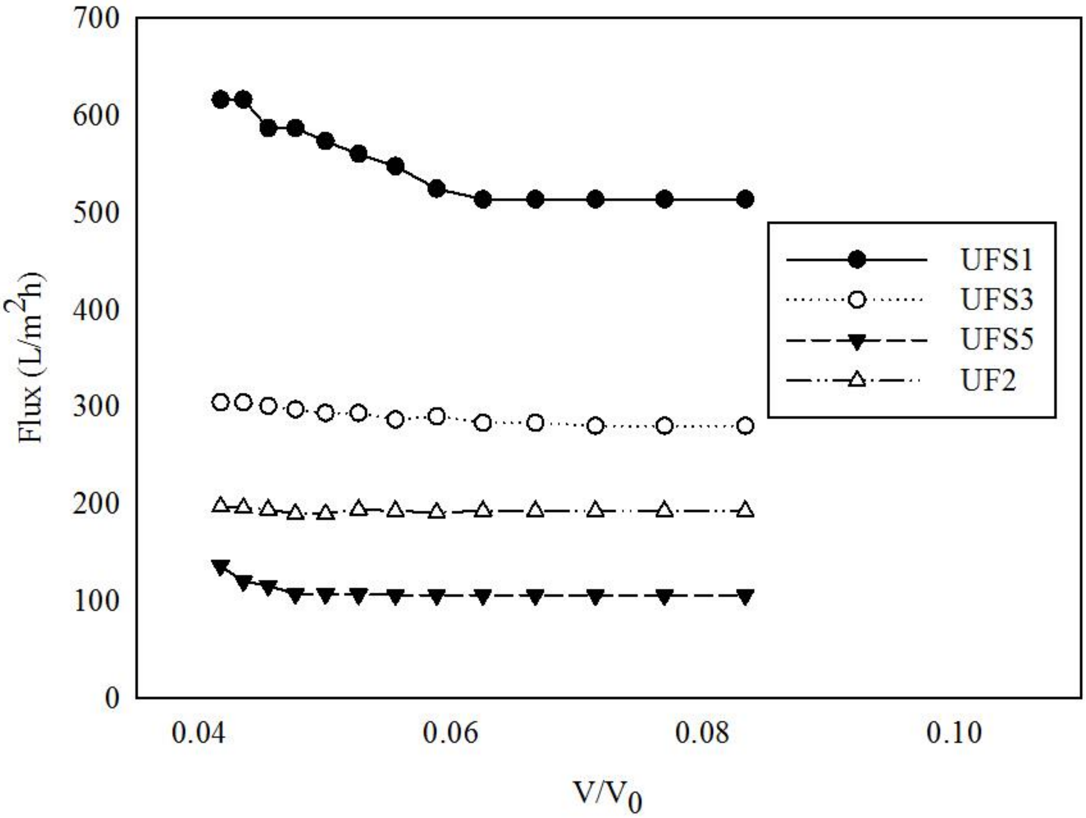

Figure 4.2. Pure water flux values of PSF/PEI and SiO_2 added nanocomposite UF membranes. TMP=5.4 bar, T= 25±5°C. UF2: 20%PSF/2%PEI; UFS1: 20%PSF/2%PEI/0.01%SiO_2; UFS3: 20%PSF/2%PEI/0.03%SiO_2; UFS5: 20%PSF/2%PEI/0.05%SiO_2. V_0: apple juice volume (L) in the system before sampling; V: apple juice volume (L) in the system after sampling.

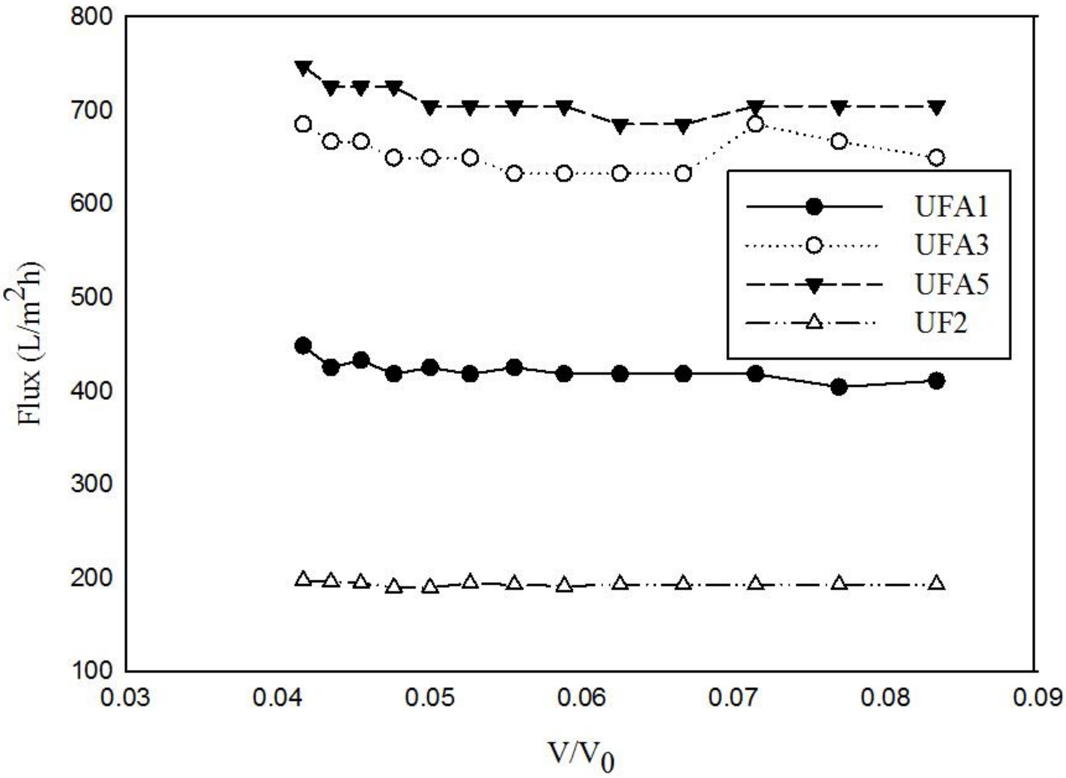

Figure 4.3. Pure water flux values of PSF/PEI and Al_2O_3 added nanocomposite UF membranes. TMP=5.4 bar, T=25±5°C. UF2: 20%PSF/2%PEI; UFA1: 20%PSF/2%PEI/0.01% Al_2O_3; UFA3: 20%PSF/2%PEI/0.03% Al_2O_3; UFA5: 20%PSF/2%PEI/0.05% Al_2O_3. V_0: apple juice volume (L) in the system before sampling; V: apple juice volume (L) in the system after sampling.

4.1.1.2. Clarified Apple Juice Characterization

The effect of nanomaterial addition on the performance of PSF/PEI membrane in terms of fruit juice clarification was also analyzed using dead-end filtration system. The color, turbidity and total soluble content of the samples are shown in Table 4.1. According to the results, clarified apple juices obtained using UF membranes modified with TiO_2 and Al_2O_3 nanoparticles (UFT and UFAs) had lower turbidity, higher color and total soluble solid content than the one obtained using UF membrane prepared with SiO_2 nanoparticle (UFS). In addition, color, turbidity and total soluble solid content values of the clarified apple juice obtained using UF membranes prepared with TiO_2 and Al_2O_3 nanoparticles were closer to the clarified apple juice supplied from Döhler Inc. than the ones obtained using SiO_2 incorporated membranes.

Table 4.1. Turbidity, color and total soluble solid values of the apple juice samples clarified using dead-end filtration system

Membrane	**Turbidity (NTU)**	**Color (PtCo)**	**Total soluble solid (°Brix)**
UF1	12.2	424	11.4
UF2	7.4	628	12.8
UFT1	0.5	820	15.0
UFT3	1.0	802	14.6
UFT5	0.6	726	14.2
UFA1	1.8	704	14.8
UFA3	2.8	716	14.6
UFA5	4.1	655	14.4
UFS1	7.6	640	12.6
UFS3	9.5	634	12.4
UFS5	8.9	652	13.0
S2 (Döhler Inc.)	0.34	754	16.2
S1 (Döhler Inc.)	478	-	16.5

UF1:20%PSF; UF2:20%PSF/2%PEI; UFT1:20%PSF/2%PEI/0.01%TiO_2; UFT3:20%PSF/%2PEI/0.03%TiO_2; UFT5:20%PSF/2%PEI/0.05% TiO_2;UFA1: 20%PSF/2%PEI/0.01%Al_2O_3; UFA3:20%PSF/%2PEI/0.03%Al_2O_3; UFA5:20%PSF/2%PEI/0.05%Al_2O_3; UFS1:20%PSF/2%PEI/0.01%SiO_2; UFS3:20%PSF/%2PEI/0.03%SiO_2; UFS5:20%PSF/2%PEI/0.05%SiO_2; S2 (Döhler Inc.): clarified apple juice sample supplied from Döhler Inc.; S2 (Döhler Inc.) turbid apple juice sample supplied from Döhler Inc.

4.1.2. Cross-Flow Filtration Experiments for Apple Juice Clarification Using UF Membranes

According to the dead-end filtration experiments, it was found that the performance of the UF membranes prepared with SiO_2 nanoparticles, in terms of both pure water flux and fruit juice clarification, were lower than those of the ones prepared with TiO_2 and Al_2O_3 nanoparticles (Fig. 4.1, 4.2, 4.3 and Table 4.1). Therefore, the nanocomposite membranes prepared with the addition of SiO_2 nanoparticles were excluded and only TiO_2 and Al_2O_3 nanoparticle incorporated UF membranes were preferred in cross-flow experiments to reflect real applications. TiO_2 and Al_2O_3 nanocomposite UF membranes were re-fabricated for cross-flow experiments and anti-fouling property, membrane characterization experiments and apple juice clarification performance of the membranes were determined.

4.1.2.1. Membrane Characterization

4.1.2.1.1. Apple Juice Flux

The effect of nanomaterial (TiO_2 and Al_2O_3) addition on the performance of PSF/PEI UF membrane was analyzed in terms of apple juice flux using cross-flow filtration system. The apple juice flux results of nanocomposite UF membranes prepared with the addition of TiO_2 and Al_2O_3 nanoparticles (0.01, 0.0.3, 0.05%) are shown in Figure 4.4 and 4.5, respectively. As can be seen from the figures, all nanocomposite UF membranes had higher apple juice flux values than the PSF/PEI membrane (UF2). Among the TiO_2 incorporated UF membranes, the one prepared with 0.01% of TiO_2 nanoparticle (UFT1) had the highest apple juice flux (steady state at 120. min; 44.6 L/m^{2}h). On the other hand, while using Al_2O_3 incorporated membranes, the highest apple juice flux (steady state at 120. min; 43.4 L/m^{2}h) was achieved with the UF membrane prepared with 0.05% Al_2O_3 nanoparticle (UFA5). However, these calculated flux value were lower when compared to the commercial membranes [143], [144].

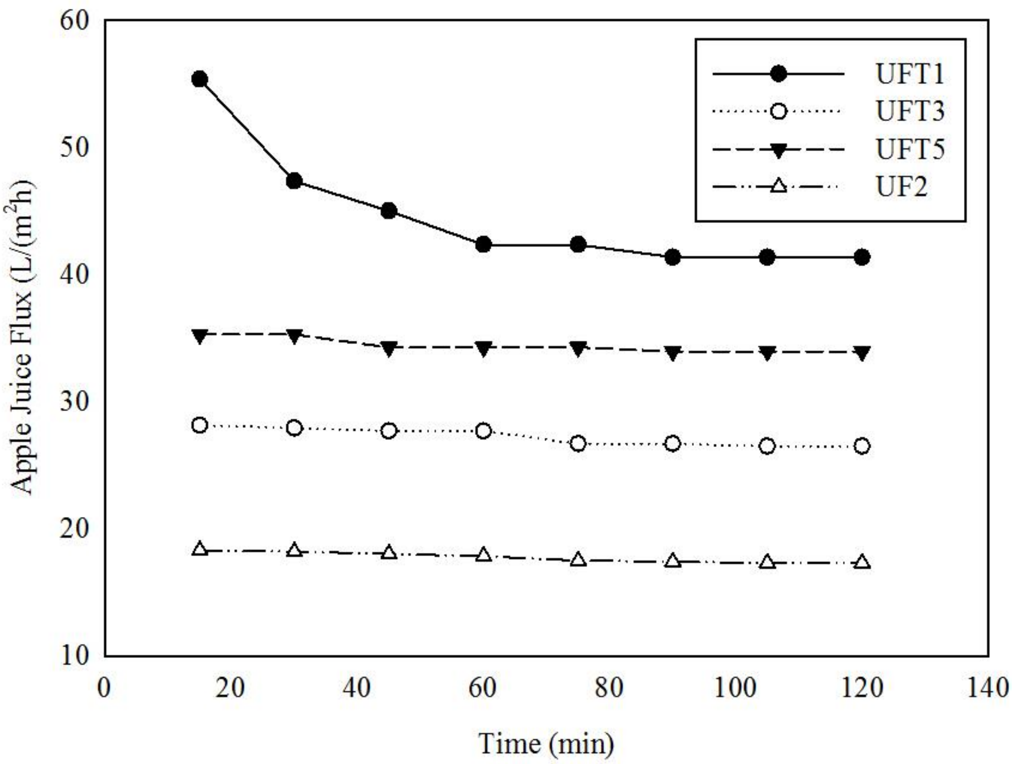

Figure 4.4. Apple juice flux values of PSF/PEI and TiO_2 added nanocomposite UF membranes. TMP=5.4 bar, T= 25±5°C. UF2: 20%PSF/2%PEI; UFT1: 20%PSF/2%PEI/0.01%TiO_2; UFT3: 20%PSF/%2PEI/0.03%TiO_2; UFT5: 20%PSF/2%PEI/0.05%TiO_2.

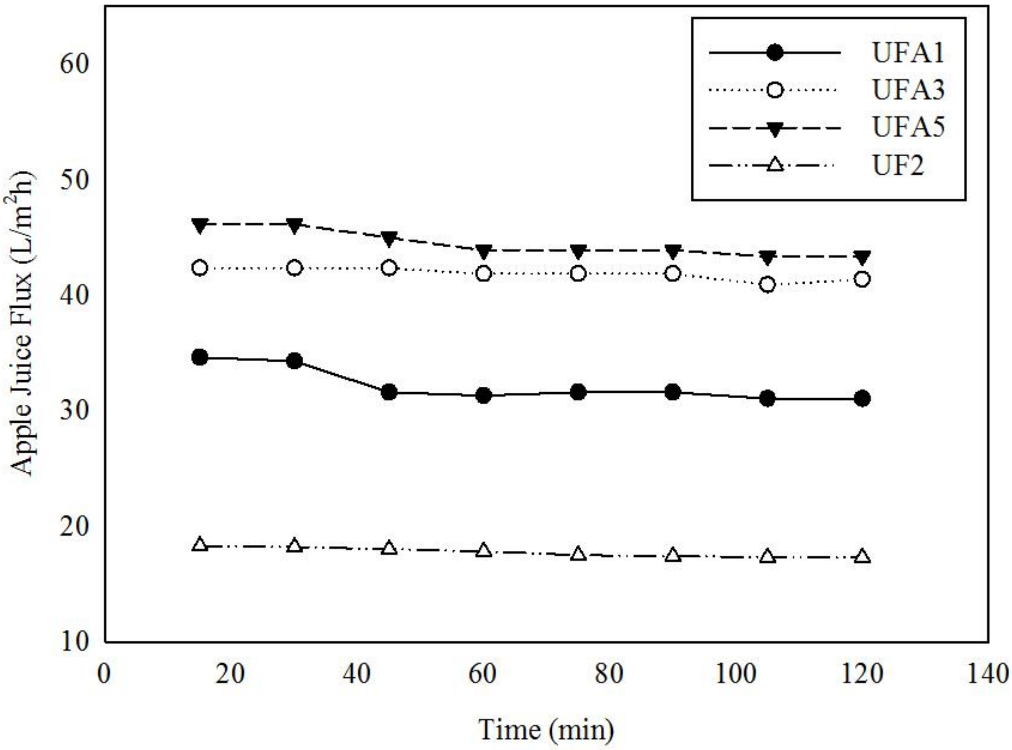

Figure 4.5 Apple juice flux values of PSF/PEI and Al_2O_3 added nanocomposite UF membranes. TMP=5.4 bar, T= 25±5°C. UF2: 20%PSF/2%PEI; UFA1: 20%PSF/2%PEI/0.01%Al_2O_3; UFA3: 20%PSF/%2PEI/0.03%Al_2O_3; UFA5: 20%PSF/2%PEI/0.05%Al_2O_3 .

4.1.2.1.2. Fouling

In membrane processes, the permeate flux decline is related directly to fouling. To determine anti-fouling properties of the membranes, decay ratio (DR), flux recovery ratio (FRR) and relative flux reduction (RFR) of the membranes were calculated and the results were shown in Table 4.2. The pure water flux before apple juice filtration using PSF/PEI membrane (UF2) was 18.9 L/m^{2}h. After the filtration of apple juice, the pure water flux decreased to 11.4 L/m^{2}h as a result of fouling. Similar decreases were also achieved with the other membranes. The higher difference between the pure water flux values before (J1) and after (J2) the filtration of the feed indicates the higher fouling of the membrane. All nanocomposite UF membranes modified by addition of TiO_2 and Al_2O_3 nanoparticles had higher DR (%) values than unmodified PSF/PEI membrane (UF2). The DR (%) value of UF2 membrane was 13.8%, whereas the DR (%) values of TiO_2 incorporated UF membranes (UFTs) and Al_2O_3 incorporated UF membranes (UFAs) were between 30.4%-74.0% and 24.9%-39.6%, respectively. Similar to DR (%) values, FRR values of the TiO_2 incorporated UF membranes (UFTs) and Al_2O_3

incorporated UF membranes (UFAs) were higher than that of UF2 (60.3%). The FRR (%) value of TiO_2 (UFTs) and Al_2O_3 (UFAs) incorporated UF membranes were between 90.9%-94.0% and 79.6%-97.6%, respectively. On the contrary, the RFR (%) values of the nanocomposite UF membranes were lower than that of PSF/PEI membrane (UF2). The RFR (%) value of UF2 was 39.7%, whereas nanocomposite membranes had RFR (%) values less than 10%, except the one prepared with 0.03% Al_2O_3 nanoparticles (UFA3). The high FRR and DR values and low RFR values show the anti-fouling characteristic of the nanoparticle incorporated membranes.

There are several studies investigating the anti-fouling effect of TiO_2 nanoparticle addition to the membrane matrix. Similar to our results, TiO_2 addition improved the antifouling properties of polyethersulfone (PES), polyacrylonitrile (PAN), polysulfone (PSF) and polyvinylidenefluoride (PVDF) membranes [20], [94], [145], [146]. There are also some studies investigating the anti-fouling effect of Al_2O_3 nanoparticle incorporation to the membrane matrix. Garcia-Ivars et al. [110], Maximous et al. [111], Yan et al. [108] examined the effect of Al_2O_3 nanoparticles on the performance of polyethyleneglycol (PEG), polyethersulfone (PES) and and polyvinylidene fluoride (PVDF) membrane, respectively. Similar to our results, they also showed that Al_2O_3 nanoparticles improved the anti-fouling performance of the membranes. The improving effect of nanoparticles on the anti-fouling property of the membranes can be associated with the increase in efficient filtration area of membrane and the surface hydrophilicity by the addition of nanoparticles [108].

Table 4.2. Pure water flux values before (J1) and after (J2) apple juice filtration, apple juice flux values (J), decay ratio (DR), flux recovery ration (FRR), relative flux reduction (RFR)

Membrane	**J1 (Lm^2/h)**	**J (Lm^2/h)**	**J2 (Lm^2/h)**	**DR (%)**	**FRR (%)**	**RFR (%)**
UF2	18.9	16.3	11.4	13.8	60.3	39.7
UFT1	171.4	44.6	160.0	74.0	93.3	6.7
UFT3	38.1	26.5	35.8	30.4	94.0	6.0
UFT5	80.0	34.9	72.7	56.4	90.9	9.1
UFA1	41.4	31.1	38.7	24.9	93.5	6.5
UFA3	68.5	41.4	54.5	39.6	79.6	20.4
UFA5	61.5	43.4	60.0	29.4	97.6	2.4

UF2:20%PSF/2%PEI; UFT1:20%PSF/2%PEI/0.01%TiO_2; UFT3:20%PSF/%2PEI/0.03%TiO_2; UFT5:20%PSF/2%PEI/0.05%TiO_2; UFA1:20%PSF/2%PEI/0.01%Al_2O_3; UFA3:20%PSF/%2PEI/0.03%Al_2O_3; UFA5:20%PSF/2%PEI/0.05% Al_2O_3

Among the UF membranes prepared with TiO_2 nanoparticles (UFTs), the one with 0.03% TiO_2 (UFT3) had the superior performance in terms of DR (30.4%), FRR

(94.0%) and RFR (6.0%), which are indicators of anti-fouling property (Table 4.2). On the other hand, among the Al_2O_3 incorporated UF membranes, the highest FRR value (97.6%) and lowest RFR value (2.4%) was achieved while using the one containing 0.05% Al_2O_3 nanoparticles (UFA5) (Table 4.2). Apple juice flux (J) and pure water flux values before (J1) and after (J2) apple juice filtration obtained using UFT3 and UFA5 are shown in Figure 4.6 and 4.7, respectively.

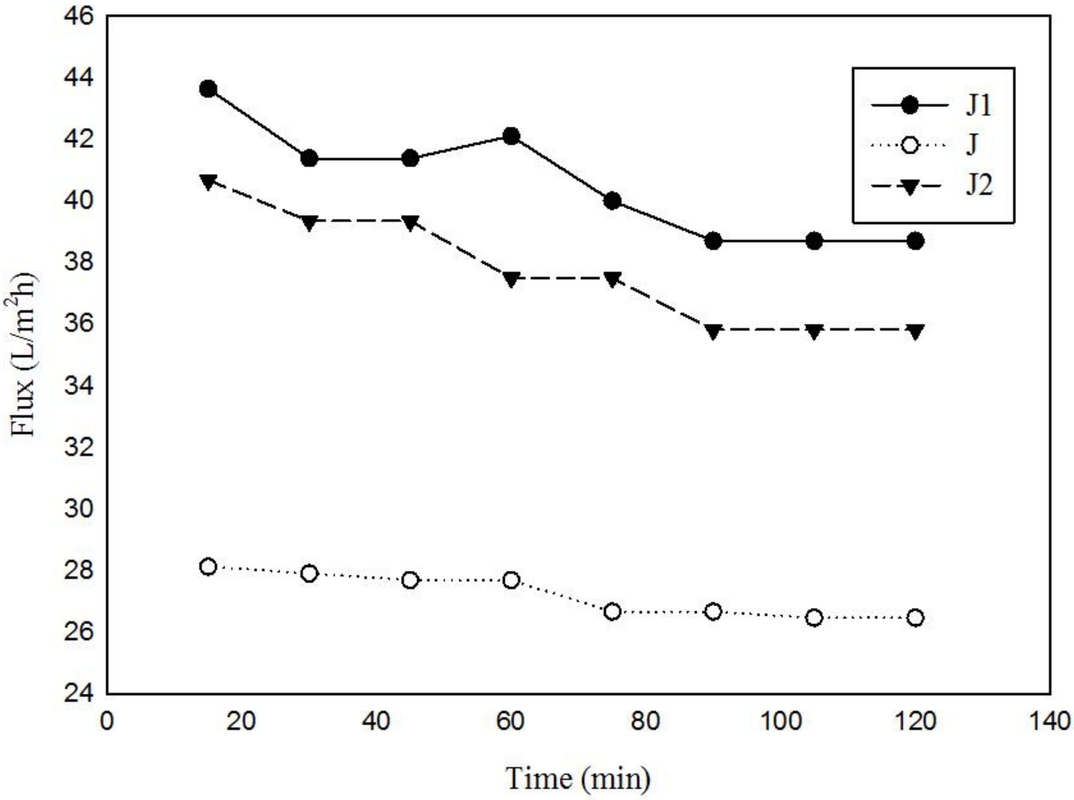

Figure 4.6. Pure water flux values before (J1) and after (J2) apple juice filtration and apple juice flux value (J) obtained from cross-flow filtration system using the UF membrane prepared with 0.03% TiO_2 nanoparticle (UFT3).

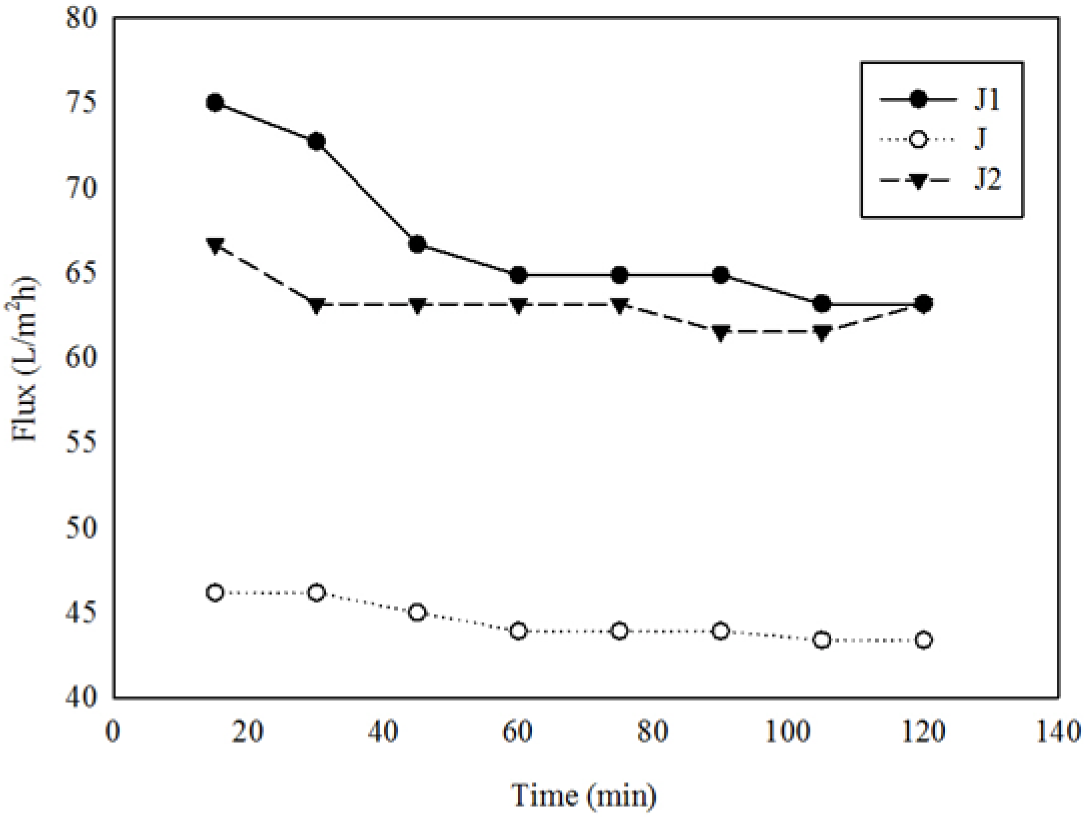

Figure 4.7. Pure water flux values before (J1) and after (J2) apple juice filtration and apple juice flux value (J) obtained from cross-flow filtration system using the UF membrane prepared with 0.05% Al_2O_3 nanoparticle (UFA5).

4.1.2.1.3. FT-IR

FT-IR spectroscopy was used to determine the functional groups of membrane surface and to observe newly formed functional groups with the addition of TiO_2 and Al_2O_3 nanoparticles and the spectrum of the UF membranes are shown in Figure 4.8 and Figure 4.9, respectively. As can be seen from Figure 4.8 and Figure 4.9, the absorption peaks for pure PSF membrane (UF1) were detected as 1150 cm^{-1} and 1167 cm^{-1} (Phenyl-Carbonyl C-C stretching), 1242 (C-H stretching), 1537 cm^{-1} (aromatic ring stretching) and 2965 cm^{-1} (asymmetric and symmetric CH_2 stretching) [147], [148].

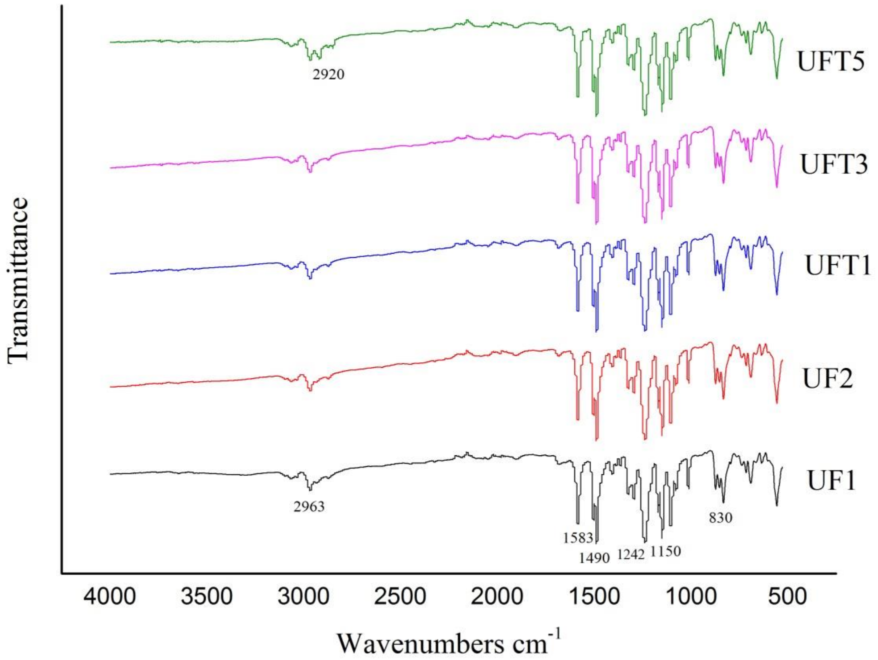

Figure 4.8. FT-IR spectrum of pure PSF membrane, PSF/PEI membrane and TiO_2 added nanocomposite membranes. TMP=5.4 bar, T= 25±5°C. UF1: 20%PSF; UF2: 20%PSF/2%PEI; UFT1: 20%PSF/2%PEI/0.01%TiO_2; UFT3: 20%PSF/%2PEI/0.03%TiO_2; UFT5: 20%PSF/2%PEI/0.05% TiO_2.

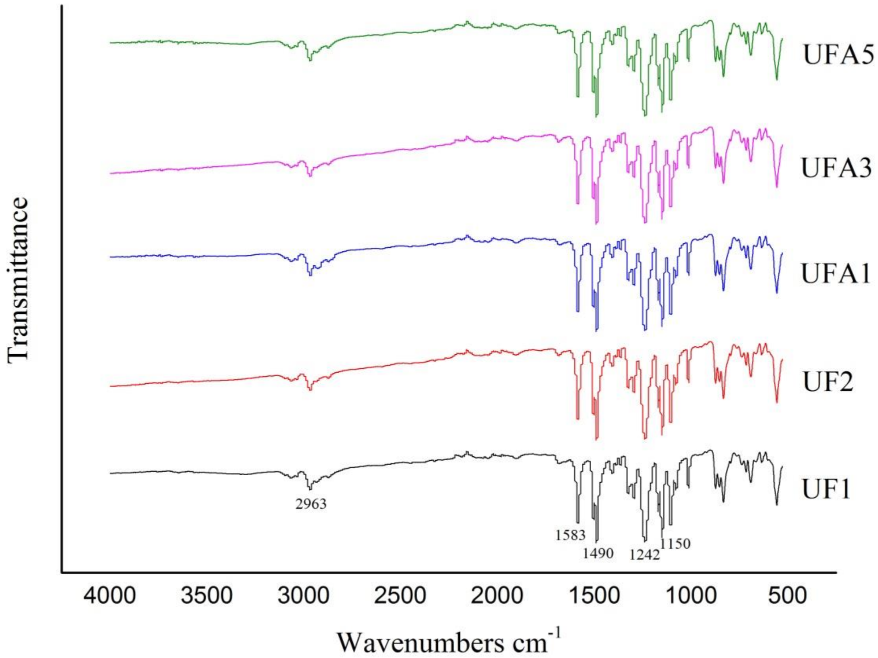

Figure 4.9. FT-IR spectrum of pure PSF membrane, PSF/PEI membrane and Al_2O_3 added nanocomposite membranes. TMP=5.4 bar, T= 25±5°C. UF1: 20%PSF; UF2: 20%PSF/2%PEI; UFA1: 20%PSF/2%PEI/0.01%Al_2O_3; UFA3: 20%PSF/%2PEI/0.03%Al_2O_3; UFA5: 20%PSF/2%PEI/0.05%Al_2O_3.

In order to demonstrate the presence of TiO_2 nanoparticles in the TiO_2 nanocomposite UF membranes, the FT-IR spectra of TiO_2 nanoparticles was also employed. The FT-IR spectrum of PSF/PEI (UF2), TiO_2 nanoparticles and the membrane prepared with 0.05%TiO_2 (UFT5) are shown in Figure 4.10. As can be seen from the figure, TiO_2 nanoparticle had a peak between 2800 and 3500 cm^{-1} which resulted from the stretching vibration of the hydroxyl group of the water molecule [149]. Absorption peak for Ti-O linkages in TiO_2 nanoparticles was recorded between 600 and 400 cm^{-1} by Choudhury and Choudhury [150]. Characteristic peak for TiO_2 nanoparticles was observed between 500-1000 cm^{-1} in Figure 4.10. Similar to our results, Lu et al. [151] described the absorption band between 500-1000cm^{-1} as the absorption peak for the Ti-O-Ti bond in TiO_2 nanoparticles. However, there is no significantly difference between FTIR results between membrane UF2 and UFT5 for this wave number range.

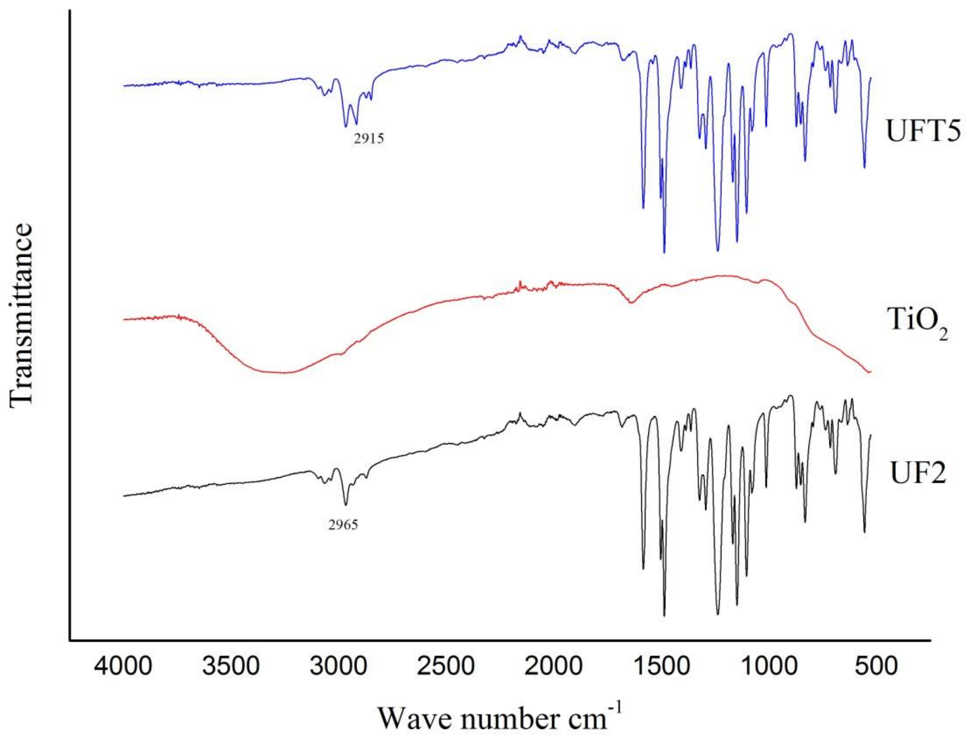

Figure 4.10. FT-IR spectrum of PSF/PEI membrane, TiO_2 nanoparticles added nanocomposite membrane and TiO_2 nanoparticles. UF2: 20%PSF/2%PEI; UFT5: 20%PSF/2%PEI/0.05%TiO_2.

Similar to the TiO_2 incorporated UF membranes, to demonstrate the presence of Al_2O_3 nanoparticles in the nanocomposite UF membranes, the FT-IR spectra of Al_2O_3 nanoparticles was also employed. The FT-IR spectrum of PSF/PEI (UF2), Al_2O_3

nanoparticles and the UF membrane prepared with 0.01% Al_2O_3 (UFA1) is shown in Figure 4.11. As can be seen from the figure, Al_2O_3 nanoparticle had a peak between around 3000 and 3600 cm^{-1} similar to the TiO_2 nanoparticles which resulted from the stretching vibration of the hydroxyl group of the water molecule, [149]. However there is no significant Al_2O_3 peak occurred in the Al_2O_3 incorporated membranes.

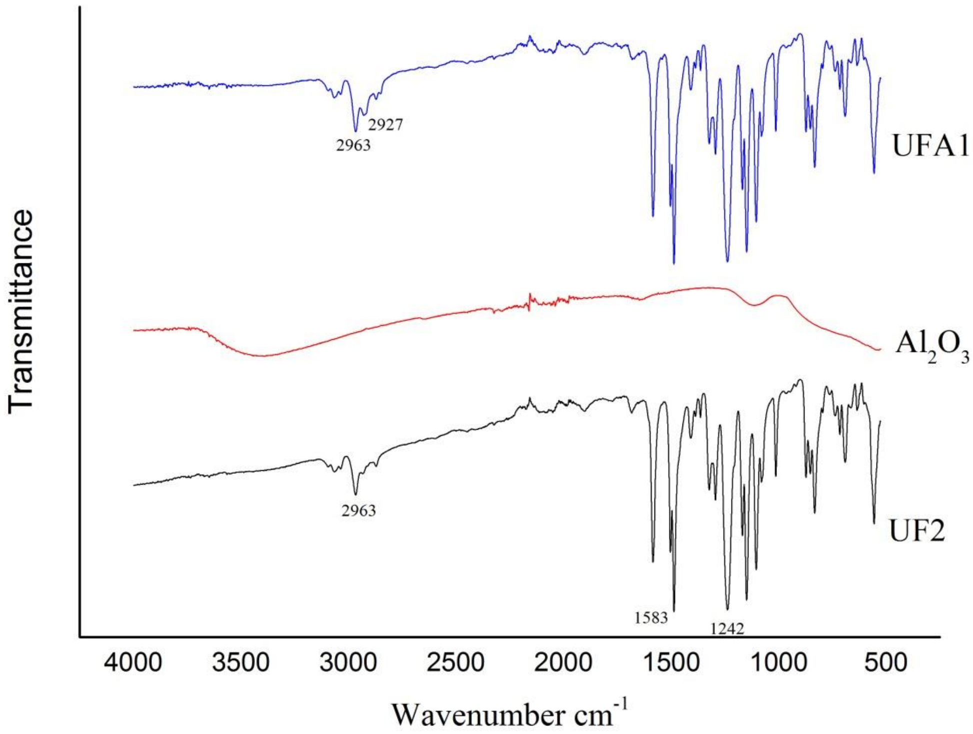

Figure 4.11. FT-IR spectrum of PSF/PEI membrane, Al_2O_3 nanoparticles added nanocomposite membrane and Al_2O_3 nanoparticles. UF2: 20%PSF/2%PEI; UFA1: 20%PSF/2%PEI/0.01%Al_2O_3.

4.1.2.1.4. Membrane Morphology

Membrane morphology analysis is an important tool to evaluate membrane filtration performance. To examine the morphological changes related with the addition of PEI and nanoparticles (TiO_2 and Al_2O_3), the surface and cross-sections of the UF membranes were obtained by SEM. The surface and cross-section images of the PSF (20%, UF1) and PSF/PEI (20%PSF/2%PEI, UF2) UF membranes are shown in Figure 4.12. Pure PSF UF membrane (UF1) has a smooth surface structure (Figure 4.12a) and the membrane surface structure is completely changed by addition of PEI to the membrane matrix (UF2) and small pores are observed (Figure 4.12b). While, PSF UF membrane (UF1) cross-section had porous structure (Figure 4.12c), the membrane cross-section structure was completely altered with the addition of PEI to the membrane matrix (UF2) (Figure 4.12d). Morphologically dense structure of PSF contributes mechanical strength of membranes. In the cross-section of pure PSF membrane, macro-level pores are formed between rigid top and bottom layer and new micro-level pores are observed due to the ability of PEI to form pores.

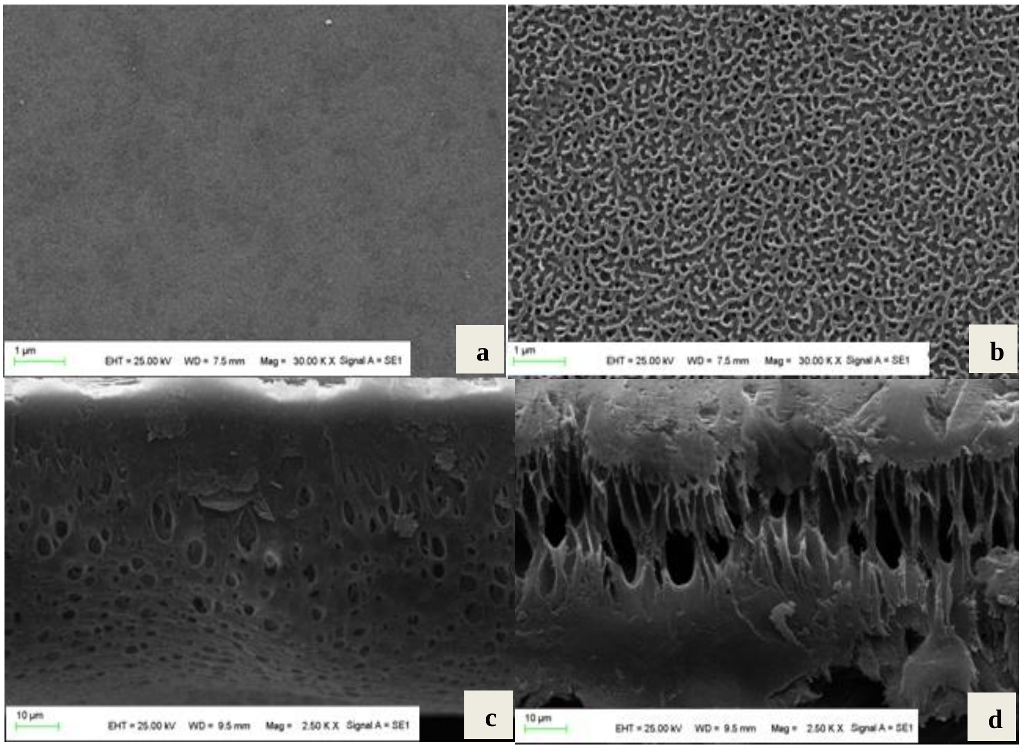

Figure 4.12. SEM images of PSF and PSF/PEI membranes. (a) Surface image of UF1 (20% PSF), (b) Surface image of UF2 (20%PSF/2%PEI), (c) Cross-section image of UF1 (20% PSF), (d) Cross-section image of UF2 (20%PSF/2%PEI)

Surface and cross-sectional SEM images of nanocomposite UF membranes prepared with the addition of TiO_2 nanoparticles to the PSF/PEI matrix are given in Figure 4.13. As can be seen from the figure, with the addition of TiO_2 nanoparticles, finger-like pores are occurred and elongated between top surface and bottom surface of the UF membranes. Similar to our results Razmjou et al. [105] observed finger-like pores in the membranes modified with TiO_2 nanoparticles.

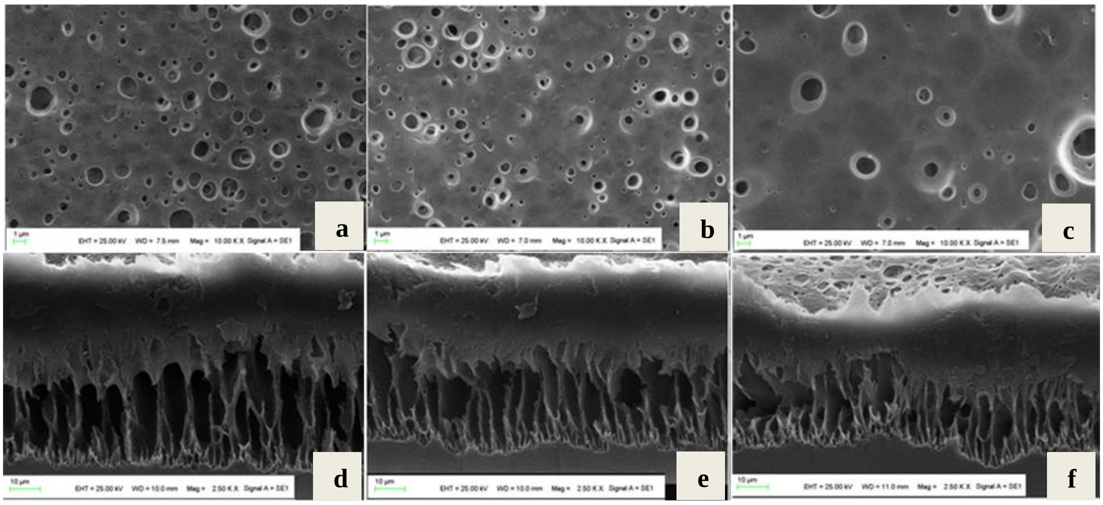

Figure 4.13 SEM images of PSF/PEI/TiO_2 membranes. (a) Surface image of membrane UFT1 (20%PSF/2%PEI/0.01%TiO_2), (b) Surface images of UFT3 (20%PSF/2%PEI/0.03%TiO_2), (c) Surface images of UFT5 (20%PSF/2%PEI/0.05%TiO_2), (d) Cross-section image of UFT1 (20%PSF/2%PEI/0.01% TiO_2), (e) Cross-section image of UFT3 (20%PSF/2%PEI/0.03%TiO_2), (f) Cross-section image of UFT5 (20%PSF/2%PEI/0.05%TiO_2).

Surface and cross-sectional SEM images of nanocomposite UF membranes prepared with the addition of Al_2O_3 nanoparticles to the PSF/PEI matrix are given in Figure 4.14. As can be seen from the figure, the increase in the concentration of Al_2O_3 nanoparticles resulted in more uniformly dispersed micro and macropores on the membrane surface. The cross-sections of Al_2O_3 nanocomposite UF membranes also varied depending on the Al_2O_3 nanoparticle concentration. A dense structured lower and upper layer were observed for the UF membrane prepared using 0.01%Al_2O_3 (UFA1), whereas a finer pore structure was observed with thinner upper layer and finger-like pores when the Al_2O_3 ratio is increased to 0.05%.

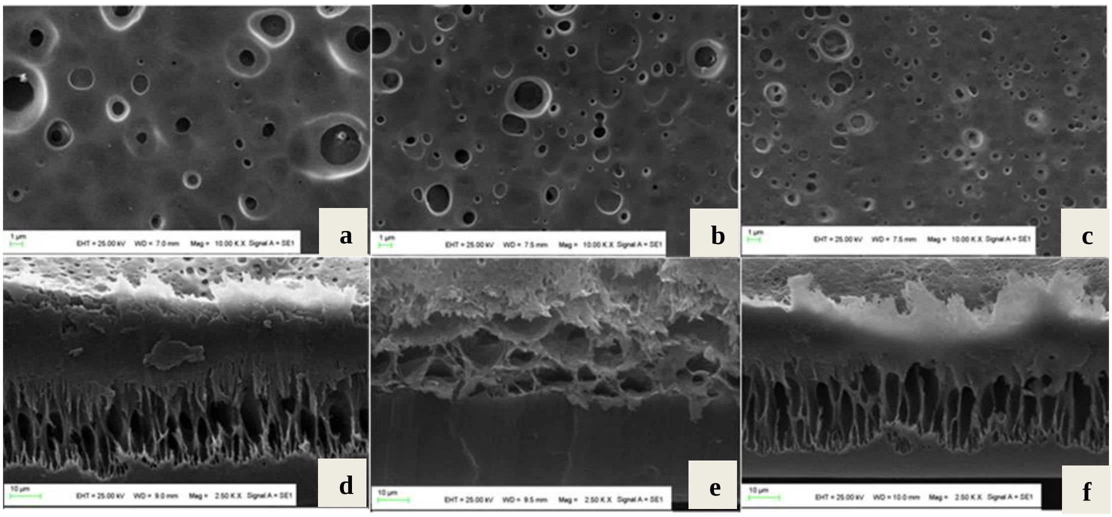

Figure 4.14. SEM images of PSF/PEI/Al_2O_3 membranes. (a) Surface image of membrane UFA1 (20%PSF/2%PEI/0.01%Al_2O_3), (b) Surface images of UFA3 (20%PSF/2%PEI/0.03%Al_2O_3), (c) Surface images of UFA5 (20%PSF/2%PEI/0.05%Al_2O_3), (d) Cross-section image of UFA1 (20%PSF/2%PEI/0.01%Al_2O_3), (e) Cross-section image of UFA3 (20%PSF/2%PEI/0.03%Al_2O_3), (f) Cross-section image of UFA5 (20%PSF/2%PEI/0.05%Al_2O_3).

4.1.2.1.5. Porosity

Porosity values of the nanocomposite UF membranes are shown in Table 4.3. The pure PSF membrane (UF1) had the lowest porosity (60.2%) which is an indicator of its dense structure. Porosity of the UF membranes significantly increased with the addition of nanoparticles and the highest porosity was achieved in the membrane prepared with 0.01% TiO_2 nanoparticle (UFT1). Similar to our results, Razmjou et al. [105] also investigated an increase in the pore size and porosity of the membrane with the addition of TiO_2 nanoparticles. In addition, Uzal et al. [109] observed an increase in the porosity ratio of modified nanocomposite membrane with the addition of Al_2O_3 nanoparticles. Moreover, similar to the SEM images results, porosity values of the membranes also indicated that nanoparticle incorporation led to increase in porosity of the membrane.

Table 4.3 Porosity and contact angle results of pure PSF membrane, PSF/PEI UF membrane and nanocomposite UF membranes

Membrane	Porosity (%)	Contact Angle (°)
UF1	60.2±2	96±6
UF2	69.9±3	88±4
UFT1	75.8±4	74±3
UFT3	70.1±5	79±5
UFT5	71.7±3	75±2
UFA1	72.3±3	81±2
UFA3	70.5±3	83±3
UFA5	74.7±2	80±3

UF1: 20% PSF; UF2: 20%PSF/2%PEI; UFT1: 20%PSF/2%PEI/0.01%TiO_2; UFT3: 20%PSF/%2PEI/0.03%TiO_2; UFT5: 20%PSF/2%PEI/0.05%TiO_2; UFA1: 20%PSF/2%PEI/0.01%Al_2O_3; UFA3: 20%PSF/%2PEI/0.03%Al_2O_3; UFA5: 20%PSF/2%PEI/0.05% Al_2O_3

4.1.2.1.6. Membrane Hydrophilicity

Hydrophilicity of the nanocomposite UF membranes was determined by contact angles and results are given in Table 4.3. According to these results PSF membrane (UF1) has the highest contact angle value (96±6°). With the addition of PEI and nanoparticles, contact angle value decreased which is an indicator of the increase in the hydrophilicity of membranes. The addition of PEI and nanoparticles caused decreases in the contact angle values and TiO_2 incorporated UF membranes had lower contact angle values than that of Al_2O_3 incorporated ones. Due to its high content of amine, PEI causes increases in the hydrophilic property and positive charge of the membranes [152], [153]. Among the UF membranes, the one prepared with 0.01% TiO_2 (UFT1) has the lowest contact angle (74±3°) and therefore highest hydrophilicity. Similar to our results, Bae and Tak [93] also reported that TiO_2 nanoparticles caused decreases in the contact angle values of the PSF membranes from 87.6° to 73.1°. There are some other studies investigating the effect of Al_2O_3 nanoparticle addition on the contact value of membranes. Al_2O_3 nanoparticles caused decreases in the contact angle value of PVDF (Polyvinylidene fluoride) UF membranes [108] and PSF membranes [109].

4.1.2.2. Clarified Apple Juice Characterization

4.1.2.2.1. Color

Color is an important parameter of apple juice because of the quality perception of the consumers. Color results of the clarified apple juice samples obtained using nanocomposite UF membranes are indicated in Table 4.4. The apple juice sample clarified by Döhler Inc. (S2, Figure 3.1) was also analyzed for comparison. However, the turbid apple juice sample (S1, Figure 3.1) obtained from Döhler Inc. was excluded from color analysis, because of its high suspended solids content which can cause misleading results. Color of the clarified apple juice sample of Döhler Inc. (S2) was 754 Pt-Co. Most of the clarified apple juice samples using nanocomposite membranes (UFTs and UFAs) had higher color intensity than that of S2. The sample clarified using the UF membrane prepared with 0.01% TiO_2 nanoparticles had the highest color intensity (1232 Pt-Co) among the samples. According to the results, it can be said that the color of clarified apple juice was generally improved by using TiO_2 and Al_2O_3 nanoparticle incorporated UF membranes. This can be associated with the increase in porosity, pore size and anti-fouling characteristics of the membranes with the addition TiO_2 and Al_2O_3 nanoparticles. Since, increasing porosity and pore-size led to increase in permeability of the membrane, more color pigment in the turbid apple juice can pass through the nanoparticle incorporated membranes. Also, anti-fouling property enables membranes to enhance permeability because membrane fouling lead to decrease in pore size. Moreover, when the color results of the apple juice samples clarified with cross-flow system were compared to those of the ones clarified with dead-end filtration system, it can be seen that the color of the clarified apple juice sample were improved by using cross-flow filtration system. Accumulation of feed on the membrane surface in dead-end filtration system causes decrease in color pigment permeability of the membrane. Therefore, cross-flow filtration system was much better than the dead-end filtration system in terms of not only reflecting real industrial system, but also providing to determine real membrane performance.

Table 4.4 Color, turbidity and total soluble solid results of apple juice samples clarified using cross-flow filtration system

Membrane	Color (PtCo)	Turbidity (NTU)	Total soluble solid (°Brix)
UF2	910	0.11	13.0
UFT1	1232	0.02	16.2
UFT3	887	0.1	12.5
UFT5	740	0.07	13.5
UFA1	623	0.02	12.5
UFA3	785	0.09	14.2
UFA5	868	0.01	14.2
S2 (Döhler Inc.)	754	0.34	16.2
S1 (Döhler Inc.)	-	478	16.5

UF2: 20%PSF/2%PEI; UFT1:20%PSF/2%PEI/0.01%TiO_2; UFT3: 20%PSF/%2PEI/0.03%TiO_2; UFT5:20%PSF/2%PEI/0.05%TiO_2; UFA1:20%PSF/2%PEI/0.01%Al_2O_3; UFA3:20%PSF/%2PEI/0.03%Al_2O_3; UFA5:20%PSF/2%PEI/0.05%Al_2O_3; S2 (Döhler Inc.): clarified apple juice sample supplied from Döhler Inc. S1 (Döhler Inc.): turbid apple juice sample supplied from Döhler Inc.

4.1.2.2.2. Turbidity

Clarification is applied as a pretreatment process of concentration to attain low viscous product with less turbidity. Turbidity results of the apple juice samples clarified using nanocomposite UF membranes (UFTs and UFAs) are shown in Table 4.4. The turbid apple juice (S1, Figure 3.1) and clarified apple juice (S2, Figure 3.1) of Döhler Inc. was also analyzed for comparison. Turbidity of turbid apple juice samples (S1) was measured as 478 NTU. As expected the turbidity of the apple juice samples decreased with membrane filtration. The clarified apple juice of Döhler Inc. (S2, Figure 3.1) had a turbidity value of 0.34 NTU, whereas the turbidity values of the sample clarified using PSF/PEI (UF2) and nanomaterial incorporated UF membranes (UFTs and UFAs) were lower. According to the commercial specification of apple juice, the turbidity should be less than 5 NTU [143]. Nanomaterial incorporated UF membranes resulted less turbid apple juice samples than the unmodified PSF/PEI membrane (UF2). This can be associated with the improvement in the retention capacity of the nanomaterial incorporated membranes. Similar to our results Ngo et al. [154] reported that the addition of TiO_2 nanoparticles improved the retention capacity of the UF membranes. The UF membrane prepared with 0.01% TiO_2 (UFT1) has the highest performance in terms of turbidity (0.02 NTU) among the UF membranes prepared using TiO_2 nanoparticles (UFTs). Among the samples, clarified apple juice obtained using the UF membrane prepared with 0.05% Al_2O_3 (UFA5) has the lowest turbidity (0.01 NTU). There are some studies investigating the effect of clarifying agents and membrane filtration on the turbidity of apple juice. Baysal [155] clarified apple juice by applying chitosan as clarifying agent and the turbidity of apple juice decreased to 9.36 NTU. He et al. [144] obtained clarified juice with low turbidity (0.13 NTU) by using membrane filtration. In another study, the turbidity of clarified apple juice was found to be 1.8 NTU by using a commercial membrane (Carbosep®) [143]. The turbidity values obtained in this thesis using nanomaterial incorporated UF membranes (UFTs and UFAs) was lower than the results found in the literature and Döhler Inc.'s results as well. These results show that clarification with new generation nanocomposite membranes is more sufficient than done with the commercial ones. Moreover, these turbidity results are lower than those of samples clarified with dead-end filtration system. Cross-flow filtration system has more selectivity in terms of water insoluble molecules which caused turbidity [154]. However, feed accumulation on membrane surface in dead-end system leads to decrease in membrane selectivity.

4.1.2.2.3. Total Soluble Solid Content

Total soluble solid content of the apple juice samples are indicated in Table 4.4. The turbid apple juice sample supplied from Döhler Inc. (S1) had a total soluble solid content of 16.5 °Brix. The total soluble solid content of the clarified apple juice sample of the company (S2) was found to be 16.2 °Brix. Most of the samples clarified using nanomaterial incorporated UF membranes (UTFs and UFAs) had lower total soluble content when compared to the S2 sample. However, they all fulfilled the commercial specification in terms of total soluble solid content (≥10 °Brix) [143]. The total soluble solid content of the sample clarified using the UF membrane prepared with 0.01% TiO_2 (UFT1) was comparable with the one clarified by Döhler Inc. (S2). This shows that UFT1 showed similar performance with the commercial membrane used by Döhler Inc. in terms of total soluble solid content.

4.1.2.2.4. Total Phenolic Content

Phenolic compounds are substantial ingredients of apples as they contribute color and flavor of both fresh fruit and processed product [156]. In addition, phenolic compounds is beneficial in promoting human health with protecting against numerous diseases occurred oxidative events [157]. The concentration of phenolic compounds in apple juice is reported to be affected by enzyme treatment, clarification, concentration and storage conditions [138], [158], [159]. Total phenolic content of the apple juice samples clarified using nanomaterial incorporated UF membranes (UFTs and UFAs) are shown in Table 4.5. The turbid apple juice (S1, Figure 3.1) and clarified apple juice of Döhler Inc. (S2, Figure 3.1) was also analyzed for comparison. The total phenolic content of the turbid apple juice (S1) was 312.3 mg GAE/L, however the clarified apple juice sample of Döhler Inc. (S2) had a lower total phenolic content of 147.4 mg GAE/L. The commercial membrane used by Döhler Inc. caused 52.8% loss in terms of total phenolic content. In addition, unmodified PSF/PEI membrane (UF2) leads to the most total phenolic content loss (107.1 mg GAE/L). However, when the UF membranes prepared with TiO_2 and Al_2O_3 nanoparticles (UFTs and UFAs) were used, the loss in total phenolic content was lower. The total phenolic content of the samples clarified with TiO_2 incorporated UF membranes (UFTs) and Al_2O_3 incorporated UF membranes (UFAs) were between 169.3-176.8 mg GAE/L and 108.2-110.4 mg GAE/L, respectively. The apple juice samples clarified with TiO_2 incorporated membranes (UFTs) had higher total phenolic content than those of the ones clarified with Al_2O_3 incorporated membranes (UFAs). TiO_2 incorporated UF membranes (UFTs) performed better performance than Al_2O_3 incorporated UF membranes (UFAs) in terms of total phenolic substance preservation. The loss in total phenolic content of the samples clarified with the TiO_2 and Al_2O_3 incorporated membranes were between 43.4%-45.8% and 64.7%-65.4%, respectively. Among the UF membranes, the one prepared with 0.01%TiO_2 (UFT1) exhibits superior performance with leading 43.4% loss in total phenolic content.

There are some studies related to the clarification of apple juice using membrane filtration. The total phenolic content of the clarified apple juice sample found to be as 88.4±2.22 mg GAE/L and 112.9±5.76 mg GAE/L when 10 kDa and 100 kDa cut-off commercial membranes were used for clarification, respectively. The loss in total phenolic content was calculated as 46% and 31%, respectively [160]. In another study, the apple juice was clarified using Nylon-6 nanofibrous membrane and a polyamide membrane and total phenolic content decreased from 327±3 mg GAE/L to 83±3 mg GAE/L (74.6% loss) and 150±5 mg GAE/L (54.1% loss), respectively [161]. Verma and Sarkar [162] determined a decrease in total phenolic content of the apple juice from 455±10 mg GAE/L to 225±5 mg GAE/L (50.6% loss) after clarification by UF (100 kDa cut off) [162].

Table 4.5. Total phenolic content and antioxidant activity values of the apple juice samples

Membrane	Total Phenolic content (mg GAE/L)	ABTS (mmol TEAC/L)	DPPH (mmol TEAC/L)
UF2	107.1±1.8	0.68±0.032	0.57±0.003
UFT1	176.8±1.22	1.56±0.031	0.67±0.030
UFT3	169.3±1.38	0.89±0.010	0.50±0.001
UFT5	172.5±0.8	0.97±0.011	0.49±0.003
UFA1	108.2±2.6	1.03±0.010	0.42±0.003
UFA3	108.2±1.8	1.08±0.040	0.47±0.003
UFA5	110.4±2.01	0.93±0.060	0.51±0.004
S2 (Döhler Inc.)	147.4±2.54	1.16±0.010	0.44±0.001
S1 (Döhler Inc.)	312.3±0.49	2.58±0.017	1.17±0.001

UF2: 20%PSF/2%PEI; UFT1: 20%PSF/2%PEI/0.01%TiO_2; UFT3: 20%PSF/%2PEI/0.03%TiO_2; UFT5: 20%PSF/2%PEI/0.05% TiO_2; UFA1: 20%PSF/2%PEI/0.01%Al_2O_3; UFA3: 20%PSF/%2PEI/0.03% Al_2O_3; UFA5: 20%PSF/2%PEI/0.05%Al_2O_3; S2 (Döhler Inc.): clarified apple juice sample supplied from Döhler Inc.; S1 (Döhler Inc.): turbid apple juice sample supplied from Döhler Inc.

4.1.2.2.5. Total Antioxidant Content

In biological system, reactive oxygen species (ROS) and reactive nitrogen species (RNS), such as superoxide, hydroxyl, and nitric oxide radicals, can damage the DNA and lead to the oxidation of lipid and proteins in cells [163]. Therefore, intake of exogenous antioxidants would prevent the damage by acting as free radical scavengers[164]. The total phenolics and flavonoids contribute to total antioxidant capacity significantly in apple juice [162], [165], [166]. Total antioxidant activities of the samples were analyzed with ABTS and DPPH radical scavenging methods and results are shown in Table 4.5. The ABTS antioxidant activity of the turbid apple juice (S1) was measured as 2.58 mmol TEAC/L whereas clarification decreases the antioxidant activity. The clarified apple juice sample of Döhler Inc. (S2) has an ABTS antioxidant activity of 1.16 mmol TEAC/L. The commercial membrane used by Döhler Inc. caused 55.0% loss in terms of ABTS antioxidant activity. The samples clarified with TiO_2 and Al_2O_3 incorporated UF membranes had ABTS antioxidant activity values between 0.89-1.56 mmol TEAC/L and 0.93-1.08 mmol TEAC/L, respectively. The lowest ABTS antioxidant activity was achieved at the sample clarified with unmodified PSF/PEI membrane (UF2), indicating that nanoparticle addition caused less antioxidant activity loss during clarification. The loss in ABTS antioxidant activity of the samples clarified with the TiO_2 and Al_2O_3 incorporated UF membranes were between 39.5%-65.5% and 58.1%-63.9%, respectively. Among the clarified samples, the one clarified using the UF membrane prepared with 0.01%TiO_2 nanoparticle (UFT1) had the highest ABTS antioxidant activity (1.56 mmol TEAC/L) and the lowest ABTS antioxidant activity loss (39.5%). Ozmianski et al. [167] clarified apple juice by using clarifying agent and characterized the clarified apple juice samples. The loss in ABTS antioxidant activity (35.6%) was found to be comparable with our lowest ABTS antioxidant activity loss (39.5%).

The DPPH antioxidant activity values of the turbid (S1) and clarified (S2) apple juice samples supplied from Döhler Inc. were 1.17 and 0.44 mmol TEAC/L, respectively. The samples clarified with TiO_2 and Al_2O_3 incorporated UF membranes had DPPH antioxidant activity values between 0.49-0.67 mmol TEAC/L and 0.42-0.51 mmol TEAC/L, respectively. Similar to the results of ABTS antioxidant activity, clarification caused decreases in the DPPH antioxidant activity. The commercial membrane used by Döhler Inc. caused 62.4% loss in terms of ABTS antioxidant activity. The loss in DPPH antioxidant activity of the samples clarified with the TiO_2 and Al_2O_3 incorporated UF membranes were between 42.7%-45.8% and 64.7%-65.4%, respectively. Similar to antioxidant activity results, among the clarified samples, the one clarified using 0.01%TiO_2 nanoparticle incorporated UF membrane (UFT1) had the highest DPPH antioxidant activity (0.67 mmol TEAC/L) and the lowest DPPH antioxidant activity loss (42.7 %).

There are some studies investigating the DPPH antioxidant capacity of the clarified apple juice. In a study the DPPH antioxidant capacity loss was found to be 55.4% 56.9% after clarification with Nylon-6 nanofibrous membrane and a polyamide membrane, respectively [161]. Ozmianski et al. [167] clarified apple juice by using clarifying agent and loss in DPPH antioxidant activity was found to be 56%.

As polyphenolic compounds have the ability to act as antioxidant compounds [157], similar trend was achieved with the total phenolic content and antioxidant activity of the samples. Similar to the total phenolic contents of the clarified apple juice sample obtained using the membrane prepared with 0.01% TiO_2 (UFT1), highest total antioxidant content achieved in the sample obtained using UFT1. In addition, clarified apple juice samples obtained using the unmodified membrane (UF2), had the lowest phenolic content as well as the total antioxidant content.

4.2. Pomegranate Juice Clarification

The clarification process for pomegranate juice was only conducted by using dead-end filtration system and cross-flow filtration system could not been applied due to the corrosion problem caused by the low pH of pomegranate juice.

4.2.1. Dead-End Filtration Experiments for Pomegranate Juice Clarification Using UF Membranes

For the preliminary experiments, the pomegranate juice samples were clarified with the same UF membranes prepared for the clarification of apple juice (Table 3.1) using dead-end filtration system. The clarified pomegranate juice samples were characterized in terms of color, turbidity and total soluble solid content and the results are given in Table 4.6. As can be seen from the Table 4.6, the color intensity of the pomegranate juice supplied from Döhler Inc. (S1) was 5111.3 Pt-Co. However the color intensity of the clarified juices obtained using unmodified PSF/PEI membrane (UF2) and nanoparticle incorporated UF membranes (UFTs and UFAs) are much lower. This can be associated with very dense structure of the UF membranes. UF membranes have smaller pores than microfiltration (MF) membranes. The pore size of MF membranes is between 0.1-10 μm [81], whereas the pore size of UF membranes is between 0.1-0.01 μm [168]. It is reported that, the pores found in UF membranes are too small to prevent the migration of color pigment and soluble solid in pomegranate juice [123]. In addition, UF membranes can foul easier than MF membranes [169]. When the size of suspended solid particles in pomegranate juice are larger than the size of pores of the membrane, during clarification process these particles lead to partial or complete pore blocking [170]. Fouling of pore channel leads to decrease in pore size, therefore color pigment and soluble solids in pomegranate juice cannot pass through the channel. To obtain clarified pomegranate juice with a similar quality of the sample clarified by Döhler Inc. (S2), it is decided to fabricate MF membranes rather than using UF ones. For this purpose PSF concentration in membrane matrix was decreased from 20% to 17% (Table 3.2).

Table 4.6. Color, turbidity and total soluble solid values of pomegranate juice samples clarified with Uf membranes

Membrane	Color (PtCo)	Turbidity (NTU)	Total soluble solid (Brix)
UF2	884	0.09	2.0
UFT1	998	0.03	2.1
UFT3	959	0.05	2.2
UFT5	965	0.05	2.1
UFA1	1005	0.04	2.1
UFA3	998	0.06	2.2
UFA5	1204	0.07	2.3
S2 (Döhler Inc.)	5111.3	1.40	16.5
S1 (Döhler Inc.)	-	785	14.0

UF2: 20%PSF/2%PEI ;UFT1: 20%PSF/2%PEI/0.01%TiO_2; UFT3: 20%PSF/%2PEI/0.03%TiO_2; UFT5: 20%PSF/2%PEI/0.05% TiO_2; UFA1: 20%PSF/2%PEI/0.01% Al_2O_3; UFA3: 20%PSF/%2PEI/0.03% Al_2O_3; UFA5: 20%PSF/2%PEI/0.05% Al_2O_3; S2 (Döhler Inc.): clarified pomegranate juice sample supplied from Döhler Inc.; S1 (Döhler Inc.): turbid pomegranate juice sample supplied from Döhler Inc.

4.2.2. Dead-End Filtration Experiments for Pomegranate Juice Clarification Using MF Membranes

4.2.2.1. Membrane Characterization

4.2.2.1.1. Pure Water Flux

The effect of nanoparticle addition on the performance of PSF/PEI membrane is analyzed in terms of pure water flux using dead-end filtration system. The pure water flux results of nanocomposite microfiltration (MF) membranes prepared with the addition of TiO_2 and Al_2O_3 nanoparticles (0.01, 0.03, 0.05%) are shown in Figure 4.15 and 4.16, respectively. Pure water flux of the membrane prepared with only 17% PSF (MF1) was 135 L/m^{2}h (not shown in Figure 4.15 and 4.16), whereas pure water flux of the PSF/PEI MF membrane (MF2) was measured as 959.3±34 L/m^{2}h. As can be seen from Figure 4.15 and 4.16, the addition of nanoparticles generally caused increases in pure water fluxes of the UF membranes. Among the MF membranes prepared with TiO_2 nanoparticles (MFTs), the one prepared with the addition of 0.01% of TiO_2 (MFT1) had the highest performance in terms of pure water flux (2776.4±32 L/m^{2}h) (Figure 4.15). There are some studies investigating the effect of nanoparticle addition on the membrane performance. Similar to our results, Li et al. [171] investigated that the addition of TiO_2 nanoparticles improved the performance of microporous PES membrane in terms of pure water flux. In addition, Wang et al. [172] demonstrated that modification with TiO_2 nanoparticles leads an increase in pure water flux from 70 L/m^2hbar to 190 L/m^2hbar.

The pure water fluxes of the MF membranes prepared with Al_2O_3 nanoparticles (MFAs) were increased as the nanoparticle concentration increased. The highest pure water flux was achieved with the MF membrane prepared with the addition of 0.05% of Al_2O_3 (MFA5). Our results are comparable with available literature. Yan et al. [173] modified PVDF (polyvinylidene fluoride) membrane with alumina (Al_2O_3) at nano-scale and reported that the increase in Al_2O_3 concentration caused an increase in the water flux.

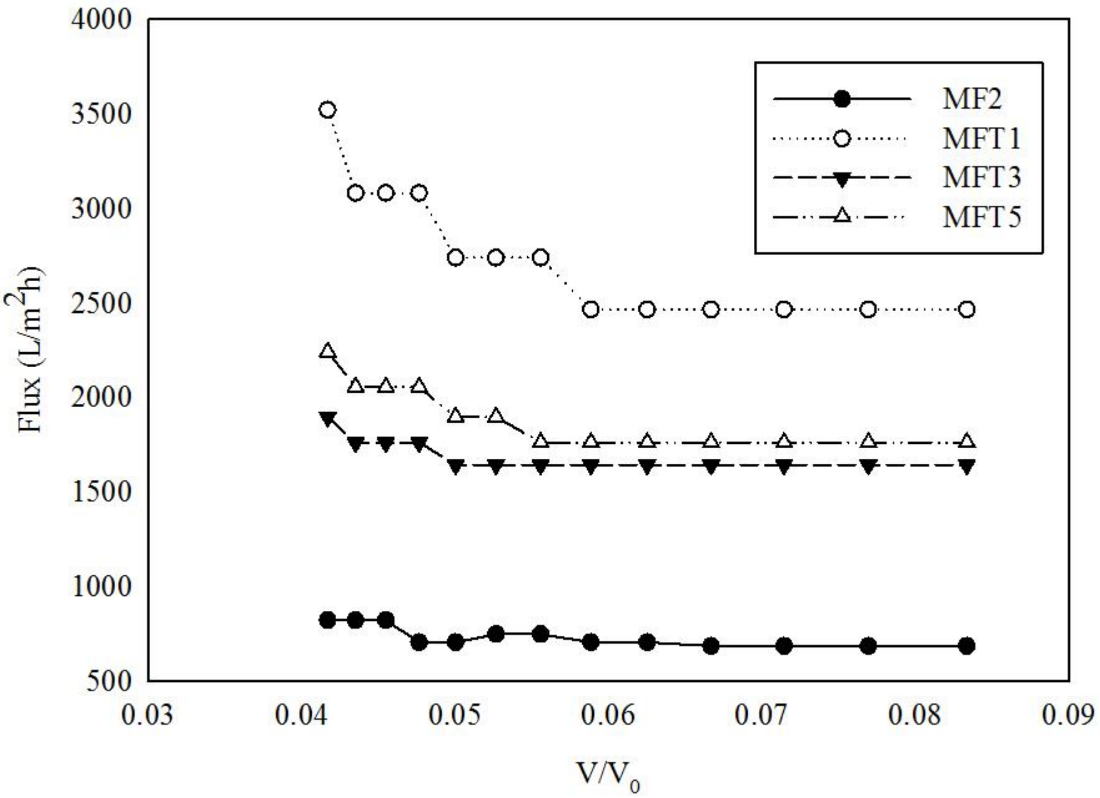

Figure 4.15. Pure water flux values of PSF/PEI and TiO_2 added nanocomposite MF membranes. TMP=5.4 bar, T=25±5°C. MF2: 17%PSF/2%PEI; MFT1: 17%PSF/2%PEI/0.01%TiO_2; MFT3: 17%PSF/2%PEI/0.03%TiO_2; MFT5: 17%PSF/2%PEI/0.05%TiO_2. V_0: apple juice volume (L) in the system before sampling; V: apple juice volume (L) in the system after sampling.

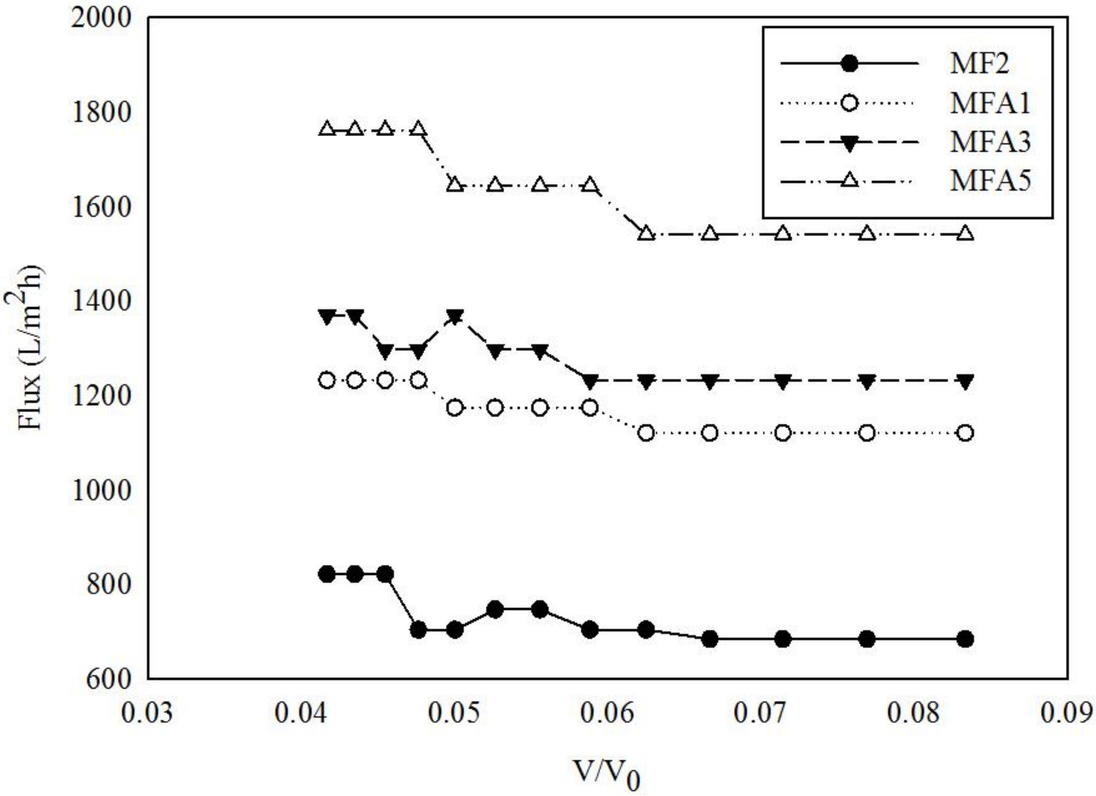

Figure 4.16. Pure water flux values of PSF/PEI and Al_2O_3 added nanocomposite MF membranes. TMP=5.4 bar, T=25±5°C. MF2: 17%PSF/2%PEI; MFT1: 17%PSF/2%PEI/0.01%Al_2O_3; MFT3: 17%PSF/2%PEI/0.03%Al_2O_3; MFT5: 17%PSF/2%PEI/0.05%Al_2O_3. V_0: apple juice volume (L) in the system before sampling; V: apple juice volume (L) in the system after sampling.

4.2.2.1.2. FT-IR

FT-IR spectroscopy was used to determine functional groups found in the membrane surface and to observe new functional groups formed after the addition of TiO_2 and Al_2O_3 nanoparticles. FT-IR spectrum results are shown in Figure 4.17 and Figure 4.18, respectively. The absorption peaks for pure PSF membrane were detected as 1150 cm^{-1} and 1167 cm^{-1} (Phenyl-Carbonyl C-C stretching), 1242 (C-H stretching), 1537 cm^{-1} (aromatic ring stretching), 2965 cm^{-1} (asymmetric and symmetric CH_2 stretching) [147], [148]. As can be seen from Figure 4.17 and Figure 4.18, there is no significant difference between the FT-IR results of pure PSF (MF1) and PSF/PEI (MF2) MF membranes and nanoparticle incorporated MF membranes (MFTs and MFAs). This may be resulted because of very low concentration of nanoparticles.

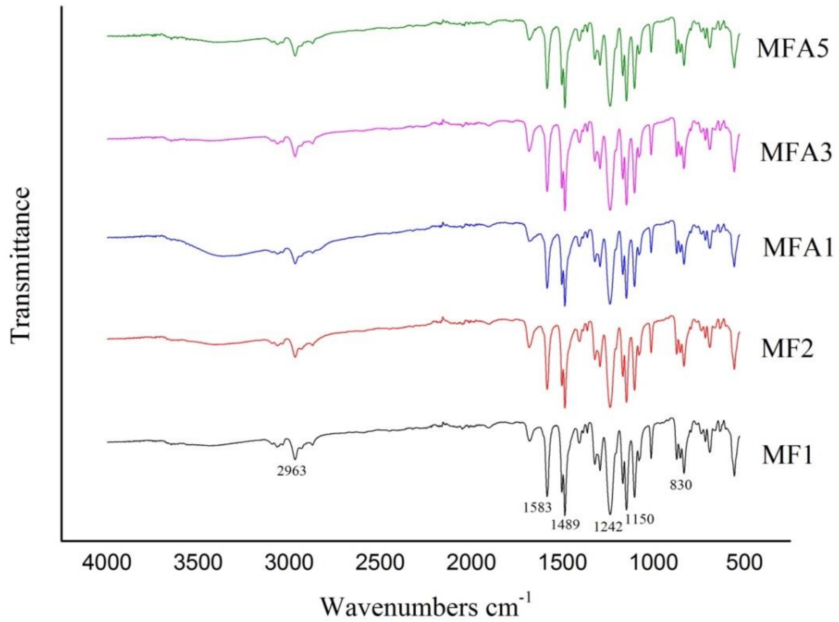

Figure 4.17. FT-IR spectrum of pure PSF membrane, PSF/PEI membrane and TiO_2 added nanocomposite membranes. TMP=5.4 bar, T= 25±5°C. MF1: 17%PSF; MF2: 17%PSF/2%PEI; MFT1: 17%PSF/2%PEI/0.01%TiO_2; UFT3: 17%PSF/%2PEI/0.03%TiO_2; UFT5: 17%PSF/2%PEI/0.05%TiO_2.

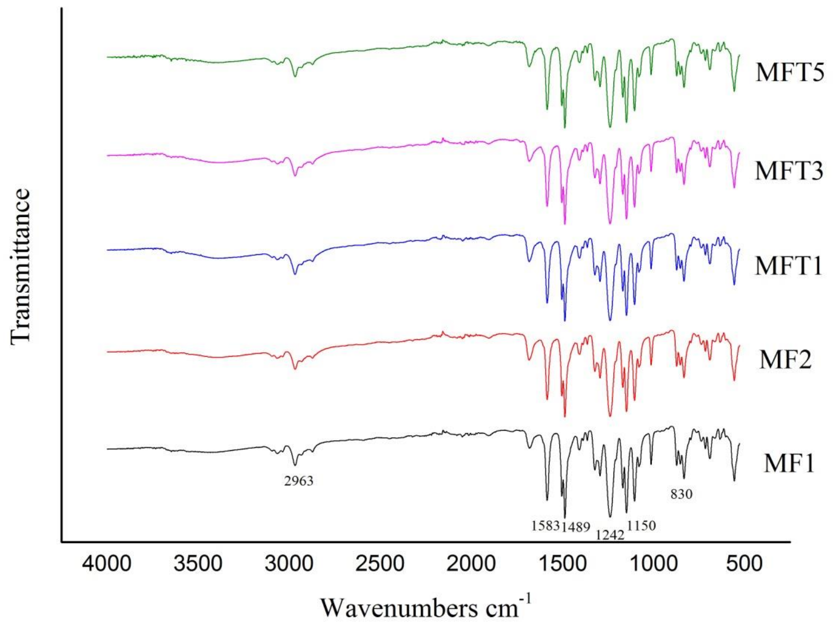

Figure 4.18 FT-IR spectrum of pure PSF membrane, PSF/PEI membrane and Al_2O_3 added nanocomposite membranes. TMP=5.4 bar, T= 25±5°C. MF1: 17%PSF; MF2: 17%PSF/2%PEI; MFA1: 17%PSF/2%PEI/0.01%Al_2O_3; MFA3: 17%PSF/%2PEI/0.03%Al_2O_3; MFA5: 17%PSF/2%PEI/0.05%Al_2O_3.

4.2.2.1.3. Membrane Morphology

The morphological changes related to the addition of PEI and nanoparticles (TiO_2 and Al_2O_3), the surface and cross-section images of the MF membranes were obtained by SEM. The surface and cross-section images of the PSF (MF1) and PSF/PEI (MF2) MF membranes are shown in Figure 4.19. Pure PSF membrane (MF1) has a smooth surface structure (Figure 4.19a) and PSF membrane exhibited asymmetric structure with dense top layer. This is also mentioned by Ganesh et al. [174]. As can be seen from Figure 4.19b, the membrane surface structure is completely changed by addition of PEI to the membrane matrix and macro pores are observed on the surface of the PSF/PEI MF membrane (MF2). Pores on the surface of PSF/PEI MF membrane are much more intensive than those of pure PSF membrane.

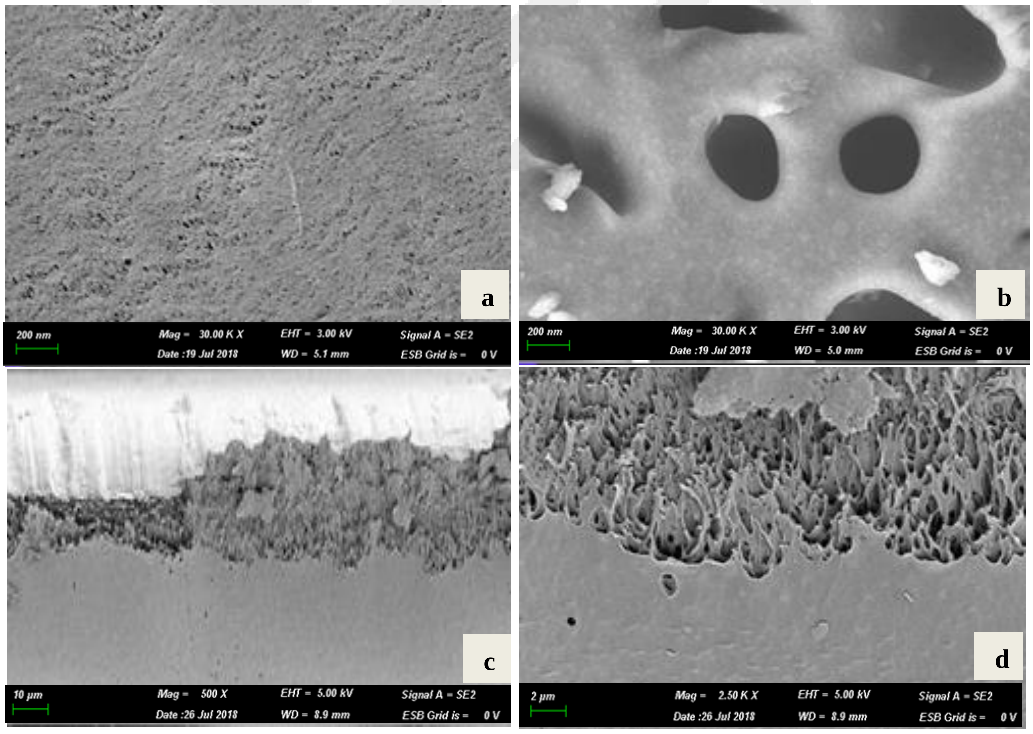

Figure 4.19. SEM images of PSF and PSF/PEI membranes. (a) Surface image of MF1 (17% PSF), (b) Surface image of MF2 (17%PSF/2%PEI), (c) Cross-section image of MF1 (17% PSF), (d) Cross-section image of MF2 (17%PSF/2%PEI).

Surface and cross-sectional SEM images of nanocomposite MF membranes prepared with the addition of TiO_2 nanoparticles to the PSF/PEI matrix are given in Figure 4.20.

As can be seen from the figure, with the addition of TiO_2 nanoparticles, finger-like pores are occurred and elongated between top surface and bottom surface of the MF membranes. Also, pore density of the membranes increased with addition of nanoparticles. Addition of nanoparticles improved porosity, thereby increases pure water flux and permeability. TiO_2 nanoparticles at even low concentration is reported to enhance the inner structure which led to more permeate flux [175]. PSF/PEI MF membrane (MF2) has larger pores but lower pore density than nanocomposite membranes (MFTs and MFAs). The pure PSF membrane (MF1) and PSF/PEI MF membrane (MF2) exhibited less and smaller inner apertures. However, TiO_2 incorporated nanocomposite MF membranes (MFTs) exhibited more and bigger inner apertures. Similar to our results, Cao et al. [175] reported that pure PVDF membrane had less and smaller inner apertures, whereas TiO_2 incorporated PVDF membrane has more and bigger inner apertures. Bae et al. [93] and Yang et al. [146] also investigated that the structure of the PSF membrane became more porous after the addition of TiO_2

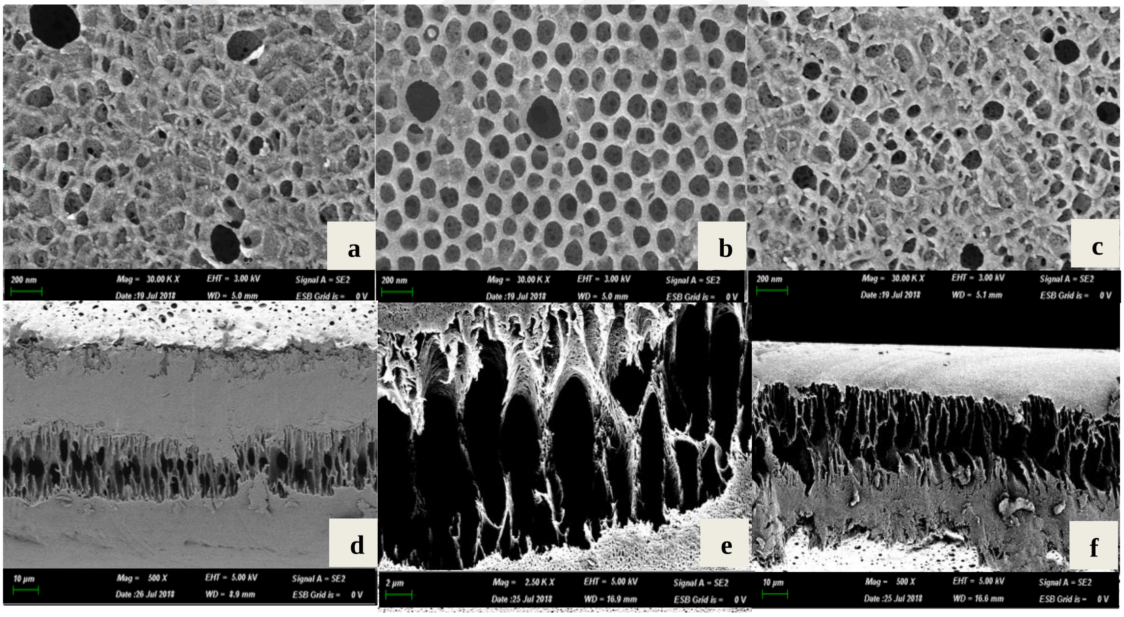

Figure 4.20. SEM images of PSF/PEI/TiO_2 membranes. (a) Surface image of MFT1 (17%PSF/2%PEI/0.01%TiO_2), (b) Surface images of UFT3 (17%PSF/2%PEI/0.03%TiO_2), (c) Surface images of MFT5 (17%PSF/2%PEI/0.05%TiO_2), (d) Cross-section image of MFT1 (17%PSF/2%PEI/0.01%TiO_2), (e) Cross-section image of MFT3 (17%PSF/2%PEI/0.03%TiO_2), (f) Cross-section image of MFT5 (17%PSF/2%PEI/0.05%TiO_2.

Surface and cross-sectional SEM images of the nanocomposite UF membranes prepared with the addition of Al_2O_3 nanoparticles to the PSF/PEI matrix are given in Figure 4.21. Thin microporous top-layer and finger-like pores in sublayer for all nanocomposite membranes are observed in SEM images. According to some researches, this top layer and cross-section structure are indicated as typical asymmetric porous structure [176]–[178]. The morphologies of membrane surfaces indicated that the surface porosity increased with addition of nanoparticles. Also, the addition of nanoparticles leads to form of sponge-like cross-section. These lateral pores of the membranes provides to enhance the pure water fluxes and permeation [178]. As can be seen from Figure 4.21 when Al_2O_3 content increased, the width of finger-like structure increased.

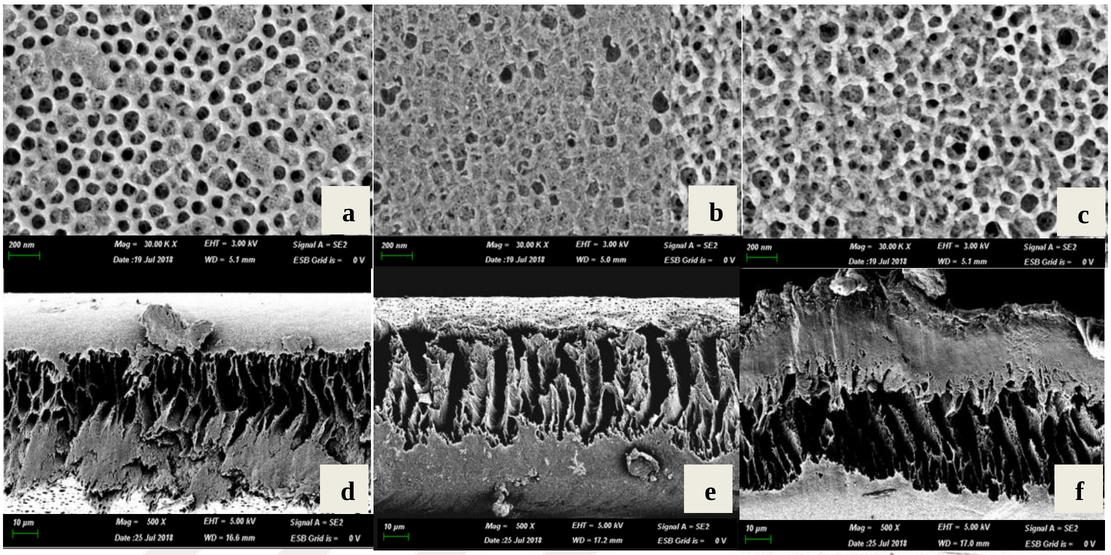

Figure 4.20. SEM images of PSF/PEI/Al_2O_3 membranes. (a) Surface image of membrane MFA1 (17%PSF/2%PEI/0.01%Al_2O_3), (b) Surface images of MFA3 (17%PSF/2%PEI/0.03%Al_2O_3), (c) Surface images of MFA5 (17%PSF/2%PEI/0.05%Al_2O_3), (d) Cross-section image of MFA1 (17%PSF/2%PEI/0.01%Al_2O_3), (e) Cross-section image of MFA3 (17%PSF/2%PEI/0.03%Al_2O_3), (f) Cross-section image of MFA5 (17%PSF/2%PEI/0.05%Al_2O_3).

The finger-like porous structure of the nanocomposite MF membranes was much wider than MF1 and MF2. Larger pore channel can be formed because of the rapid mass transformation during phase inversion [179]. The macro-void structure was altered by the modified with nanoparticles. This can be resulted from hydrophilic nature of the nanoparticles. During phase inversion, hydrophilic nature of nanoparticles leads to increase porosity as well as changes in macro-voids structure [174]. These findings demonstrate that the addition of TiO_2 and Al_2O_3 nanoparticles affect the membrane structure and morphology considerably.

4.2.2.1.4. Porosity

Porosity values of the pure PSF MF membrane (MF1), PSF/PEI MF membrane (MF2) and nanoparticle incorporated MF membranes (MFTs and MFAs) are shown in Table 4.7. The pure PSF membrane (MF1) had the lowest porosity with 69.4±2% because of its dense structure. Similar to our results, Genne et al. [22] calculated porosity for pure PSF membrane (18 wt%) as 79%. Addition of PEI leads to increase in porosity. Also porosity of the membranes significantly increased with the addition of both TiO_2 and Al_2O_3 nanoparticles. This was also seen with the SEM images results (Figure 4.20 and 4.21, respectivetly). The porosity values of the TiO_2 and Al_2O_3 incorporated membranes were between 79.7-83.5% and 77.3-84.8%, respectively. Among the nanoparticle incorporated membranes the one prepared with the addition of 0.05% Al_2O_3 nanoparticle (MFA5) had the highest porosity. There are some studies investigating the effect of TiO_2 and Al_2O_3 addition on the porosity of the membranes. Ayyaru and Ahn [180] modified PES membrane by addition of sulfonated TiO_2 and they observed an increase in the porosity values from 68.4±3% to 87.6±4%. Also, Maximous et al. [181] produced membrane using Al_2O_3 nanoparticles and had higher porosity than unmodified membrane.

Table 4.7. Porosity and contact angle results for pure PSF MF membrane, PSF/PEI MF membrane and nanocomposite MF membranes

Membrane	Porosity (%)	Contact Angle (°)
MF1	69.4±2	94±5
MF2	77.9±3	86±4
MFT1	83.5±3	79±5
MFT3	80.2±3	76±2
MFT5	79.7±4	69±1
MFA1	77.3±3	79±2
MFA3	80.4±3	77±4
MFA5	84.8±4	72±3

MF1:17% PSF; MF2: 17%PSF/2%PEI; MFT1: 17%PSF/2%PEI/0.01%TiO_2; MFT3: 17%PSF/%2PEI/0.03%TiO_2; MFT5: 17%PSF/2%PEI/0.05%TiO_2; MFA1 : 17%PSF/2%PEI/0.01%Al_2O_3; MFA3: 17%PSF/%2PEI/0.03%Al_2O_3; MFA5: 17%PSF/2%PEI/0.05% Al_2O_3

4.2.2.1.5. Membrane Hydrophilicity

Hydrophilicity of the membranes were determined by using contact angle measurement and results are indicated in Table 4.7. According to these results pure PSF membrane (MF1) has the highest contact angle value (94±5°). Similar to the results of UF membranes, with the addition of PEI, TiO_2 and Al_2O_3 nanoparticles contact angle value decreased and thus, hydrophilicity of membranes increased. PEI has been proven to increase the hydrophilic property and positive charge of the membrane due to its to its high content of amine [152], [144]. As the concentration of TiO_2 increase in the membrane matrix, the contact angle value decreased. Among the membranes, the one prepared with 0.05% TiO_2 (MFT3) had the lowest contact angle (69±1°), therefore highest hydrophilicity. Similar to TiO_2 incorporated MF membranes, increase in Al_2O_3 concentration caused decreases in contact angle value. Similar to our result, Uzal et al. [109] also investigated a decrease in the contact angle value of the PSF membrane after Al_2O_3 nanoparticle addition.

4.2.2.2. Clarified Pomegranate Juice Characterization

4.2.2.2.1. Color

Color is an important parameter of pomegranate juice because visual property of the sample is a significant factor in terms of quality perception of consumer. Color, astringency and bitterness of pomegranate juice are derived from the phenolic compounds of pomegranate juice [182]. Producing stable pomegranate juice in terms of color is the main problem required to be solved [183]. Color results of the clarified pomegranate juices obtained from nanocomposite MF membranes are indicated in Table 4.8. The clarified pomegranate juice sample of Döhler Inc. (S2, Figure 3.1) was also analyzed for comparison. As stated before, the spectrophotometric color analysis of turbid juices can cause misleading results due to their high suspended solids content. Therefore, the turbid pomegranate juice sample (S1, Figure 3.1) of Döhler Inc. was excluded from color analysis. The color value of the clarified pomegranate juice supplied from Döhler Inc. (S2) was 5111 PtCo, whereas the sample obtained using pure PSF (MF2) had a lower color value (4879 PtCo). Most of the samples clarified using TiO_2 and Al_2O_3 incorporated nanocomposite MF membranes (MFTs and MFAs) had higher color value than that of S2. The MF membrane prepared with the incorporation of 0.05% Al_2O_3 (MFA5) nanoparticle caused higher color value (5781 Pt-Co) among the others. According to Oziyci et al. [184] color of clear pomegranate juice is easily affected by clarification. Our results showed that the color of clarified pomegranate juice was generally improved by applying TiO_2 and Al_2O_3 incorporated MF nanocomposite membranes.

Table 4.8. Color, turbidity, total soluble solid results of pomegranate juice samples clarified by MF membranes

Membrane	Color (PtCo)	Turbidity (NTU)	Total soluble solid (Brix)
MF2	4879±8	2.06±0.07	10±0.0
MFT1	5475±9	0.28±0.01	16.2±0.1
MFT3	5245±10	0.39±0.01	16.2±0.0
MFT5	5069±4.5	0.27±0.03	15.47±0.1
MFA1	5403±5.1	0.43±0.01	16±0.0
MFA3	5245±6	0.29±0.05	15.5±0.1
MFA5	5781±4	0.69±0.06	16.2±0.0
S2 (Döhler Inc.)	5111±5.8	1.40±0.08	16.3±0.1
S1 (Döhler Inc.)	-	785±4	14.0±0.1

MF2: 17%PSF/2%PEI; MFT1: 17%PSF/2%PEI/0.01%TiO_2; MFT3: 17%PSF/%2PEI/0.03%TiO_2; MFT5: 17%PSF/2%PEI/0.05%TiO_2; MFA1: 17%PSF/2%PEI/0.01%Al_2O_3; MFA3: 17%PSF/%2PEI/0.03%Al_2O_3; MFA5: 17%PSF/2%PEI/0.05%Al_2O_3; S2 (Döhler Inc.): clarified pomegranate juice sample supplied from Döhler Inc.; S1 (Döhler Inc.): turbid pomegranate juice sample supplied from Döhler Inc.

4.2.2.2.2. Turbidity

Turbidity results of pomegranate juice samples clarified using nanocomposite MF nanocomposite membranes (MFTs and MFAs) are shown in Table 4.8. The turbid pomegranate juice (S1, Figure 3.1) and clarified pomegranate juice (S2, Figure 3.1) of Döhler Inc. was also analyzed for comparison. Turbidity of raw pomegranate juice (S1) was measured as 785 NTU. The turbidity values of the clarified samples are lower than that of turbid pomegranate juice, as expected. The pomegranate juices clarified using unmodified PSF/PEI MF membrane (MF2) has the highest turbidity (2.06±0.07 NTU). However, modification of membrane with nanoparticles leads to decrease in turbidity of products. There are some studies investigating the effect of clarifying agent and membranes on the turbidity of pomegranate juice. Turfan et al. [185] clarified pomegranate juice using bentonite as clarifying agent and obtain clarified juice with a turbidity value of 2.23 NTU. Also Erkan et al. [186] used clarifying agents; chitosan and xanthan gum for clarification of pomegranate juice and turbidity of clarified juices were determined as 10.3 NTU and 20 NTU, respectively. According to our results, it can be concluded that, new generation nanocomposite membranes shows superior performance than clarifying agents to clarify pomegranate juice in terms of turbidity removal.

4.2.2.2.3. Total Soluble Solid Content

Total soluble solid content of pomegranate juice samples are indicated in Table 4.8. Total soluble solid content of the turbid pomegranate juice supplied from Döhler Inc. (S1) was measured as 16.3 °Brix. Total soluble solid content of unclarified pomegranate juice was also indicated as 16.09-16.52 °Brix in the literature [187]. After clarification process using the MF membranes prepared in this thesis, total soluble solid content of the samples slightly decreased. Similar reductions was also observed by Erkan-Koç et al. [186]. The total soluble solid content of the clarified pomegranate juice samples were between 16.0-16.2 °Brix, however clarified pomegranate juice obtained from Döhler Inc. (S2) had a lower total soluble solid content (14.0°Brix).

4.2.2.2.4. Total Phenolic Content

Total phenolic content of the clarified pomegranate juices are shown in Table 4.9. The turbid pomegranate juice (S1, Figure 3.1) and clarified pomegranate juice of Döhler Inc. (S2, Figure 3.1) was also analyzed for comparison. The total phenolic content of the turbid pomegranate juice (S1) 3799.7 mg GAE/L, however the clarified pomegranate juice sample of Döhler Inc. (S2) had a lower total phenolic content of 2619.6 mg GAE/L. Commercial membrane used by Döhler Inc. for pomegranate juice clarification caused 31.1% loss in total phenolic content of the sample. The nanocomposite MF membranes fabricated in this thesis showed similar performance with commercial membrane used by Döhler Inc. in terms of total phenolic content of clarified pomegranate juice. The total phenolic content of the pomegranate juice sample clarified using nanocomposite incorporated MF membranes were lower than that of turbid pomegranate juice (S1) and the values were between 1973.3-2642.1 mg GAE/L. Mirsaeedghazzi et al. also demonstrated that applying membrane technology for pomegranate juice clarification caused decreases in total phenolic content [134]. In addition, unmodified PSF/PEI MF membrane (MF2) leads to the most total phenolic content loss (1617.33 mg GAE/L). However, the TiO_2 and Al_2O_3 nanoparticle incorporated MF membranes (MFTs and MFAs) caused less loss in total phenolic content of pomegranate juice. The lowest loss in total phenolic content was achieved when the membrane prepared with 0.05%wt Al_2O_3 was used. This may be resulted from the increase in pore size of the membranes with the addition of Al_2O_3 nanoparticles in membrane matrix [188].

There are some studies related to the clarification of pomegranate juice using clarifying agents and membrane filtration. Mirsaeedghazi et al. [134] applied hydrophilic polyvinyllidenefluoride (PVDF) with 0.22 and 0.45 µm pore size for the clarification of pomegranate juice. The loss in total phenolic content was indicated as 50.5% and 34.9%, respectively. In another study, pomegranate juice was clarified using gelatin and bentonite as clarifying agents and commercial UF membrane and the clarification process led to 25% loss in total phenolic content [189].

Table 4.9. Total phenolic content, antioxidant activity and total monomeric anthocyanin values of the apple juice samples

Membrane	Total Phenolic Content (mg GAE/L)	ABTS (mmol TEAC/L)	DPPH (mmol TEAC/L)	Total Monomeric Anthocyanin (mg/L)
MF2	1617.3±12.8	27.2±0.1	24.2±0.0	50.1±0.3
MFT1	2212.7±14.6	57.4±0.1	36.3±0.1	92.2±0.2
MFT3	2317.5±12.8	55.6±0.1	37.7±0.3	86.2±0.1
MFT5	2062.0±8.1	33.3±0.0	33.7±0.2	75.1±0.2
MFA1	2284.0±32.2	48.8±0.2	40.5±0.1	90.7±0.3
MFA3	1973.3±6.8	42.8±0.2	31.8±0.3	86.7±0.1
MFA5	2642.1±46.4	62.4±0.2	41.3±0.0	100.7±1.7
S2 (Döhler Inc.)	2619.6±66.4	43.0±0.1	30.1±0.3	77.2±0.2
S1 (Döhler Inc.)	3799.7±12.0	67.2±0.3	46.9±0.1	104.5±0.2

UF2: 17%PSF/2%PEI; UFT1: 17%PSF/2%PEI/0.01%TiO_2; UFT3: 17%PSF/%2PEI/0.03%TiO_2; UFT5: 17%PSF/2%PEI/0.05%TiO_2; UFA1: 17%PSF/2%PEI/0.01%Al_2O_3; UFA3: 17%PSF/%2PEI/0.03%Al_2O_3; UFA5: 17%PSF/2%PEI/0.05%Al_2O_3; S2 (Döhler Inc.): clarified pomegranate juice sample supplied from Döhler Inc.; S1 (Döhler Inc.): turbid pomegranate juice sample supplied from Döhler Inc.

4.2.2.2.5. Total Antioxidant Capacity

Total antioxidant activities of the samples were analyzed with ABTS and DPPH radical scavenging methods and results are shown in Table 4.9. Pomegranate juice has the highest antioxidant activity among other fruit juices and beverages [190]. High phenolic compound of pomegranate juice is responsible for high antioxidant capacity in pomegranate juice [191]–[193]. As can be seen from Table 4.9, both ABTS and DPPH antioxidant capacity values of pomegranate juice samples were higher than that of apple juice samples (Table 4.5). The ABTS antioxidant activity of the turbid pomegranate juice (S1) was measured as 67.2 mmol TEAC/L whereas clarification decreases the antioxidant activity. The clarified pomegranate juice sample of Döhler Inc. (S2) has an ABTS antioxidant activity of 43.0 mmol TEAC/L with a loss of 36.9%. In addition clear juice obtained using unmodified PSF/PEI MF membrane (MF2) has the lowest total antioxidant capacity with 27.2 mmol TEAC/L. On the other hand, TiO_2 and Al_2O_3 incorporated nanocomposite MF membranes exhibit superior performance in terms of antioxidant capacity. Among these nanocomposite MF membranes, the one prepared with the addition of 0.05% Al_2O_3 nanoparticle (MFA5) showed the best performance in terms of antioxidant capacity (62.4 mmol TEAC/L; 7.1% loss).

There are some studies investigating the effect of clarifying agents on the antioxidant capacity of pomegranate juice. Koç et al. [186] clarified pomegranate juice using gelatin, casein and albumin as clarifying agents and determined ABTS antioxidant activity loss values as 21.3%, 24.7% and 17.2%, respectively. In another study, (polyether ketone) hollow fiber (HF) membrane clarification caused 17.8% decrease in ABTS antioxidant activity of pomegranate juice [115]. Onsekizoglu [189] clarified pomegranate juice using gelatin and bentonite as clarifying agents and commercial UF membrane (30 kDa cut-off PVDF membrane) and total antioxidant capacity of pomegranate juice decreased by 16% after clarification. As can be seen from these results, clarifying agents leads to more reduction of antioxidant capacity than membrane technology.

The DPPH antioxidant activity values of the turbid (S1) and clarified (S2) pomegranate juice samples supplied from Döhler Inc. were 46.9 and 30.1 mmol TEAC/L, respectively. Similar to the results of ABTS antioxidant activity, clarification caused decreases in the DPPH antioxidant activity. The commercial membrane used by Döhler Inc. caused 35.8% loss in terms of ABTS antioxidant activity. In addition, clear juice obtained using unmodified PSF/PEI MF membrane (MF2) has the lowest total antioxidant capacity (24.2 mmol TEAC/L) and highest loss (48.4%). On the other hand, according to DPPH radical scavenging analysis results TiO_2 and Al_2O_3 nanomaterial incorporated membranes exhibit superior performance in terms of clarifying pomegranate juice with high antioxidant capacity. DPPH antioxidant capacity of clarified pomegranate juices obtained using nanocomposite MF membranes ranges between 31.8-41.3 mmol TEAC/L. Among these fabricated nanocomposite MF membranes, the one prepared with 0.05% Al_2O_3 nanomaterial (MFA5) showed the best performance in terms of antioxidant capacity (41.3 mmol TEAC/L). Moreover, as the polyphenolic compounds act as antioxidant compounds [157], the highest total phenolic content and antioxidant content of the clarified pomegranate juice sample was obtained with the sample clarified using the same membrane (0.05% Al_2O_3, MFA5). In addition, clarified apple juice samples obtained using unmodified membrane (MF2), had the lowest phenolic content as well as total antioxidant content.

4.2.2.2.6. Total Monomeric Anthocyanin

Anthocyanin pigment is responsible for red, purple and blue color quality of many fresh and processed fruits. Color of anthocyanin pigment alters depending on pH, so total monomeric anthocyanin pigment content is determined by using "pH differential method". At pH 1.0 anthocyanin pigments are colored whereas at pH 4.5 anthocyanin pigment are colorless [194]. Total monomeric anthocyanin content contribute to the total antioxidant capacity and total phenolic content of pomegranate juice [195]. Total monomeric anthocyanin content of clarified pomegranate juices determined by pH differential method and shown in Table 4.9. The turbid pomegranate juice supplied from Döhler Inc. (S1) was also analyzed for comparison. After the clarification conducted by Döhler Inc., total monomeric anthocyanin content decreased from 104.46 mg/L (S1) to 77.2 mg/L (S2) with a loss of 26.1%. In addition, clear juice obtained using unmodified PSF/PEI MF membrane (MF2) has the lowest total monomeric anthocyanin pigment with 50.1 mg/L (52.1% loss). On the other hand, TiO_2 and Al_2O_3 nanomaterial incorporated MF membranes exhibit superior performance in terms of clarifying pomegranate juice with high total monomeric anthocyanin pigment content. The antocyanin content of the samples clarified using these membranes were between 75.07-92.20 mg/L and 86.66-100.74 mg/L, respectively. Among the clarified pomegranate juices, the one clarified using 0.05% Al_2O_3 nanomaterial incorporated MF membrane (MFA5) had the highest total monomeric anthocyanin content (100.7±1.7 mg/L) and lowest anthocyanin loss (3.6%).

There are some studies investigating the effect of clarifying agents and membrane filtration in the quality of pomegranate juice in terms of anthocyanin content. Vardin and Fenercioglu [196] used PVPP and gelatin for the clarification of pomegranate juice and total monomeric anthocyanin pigment content was measured as 68.8 mg/L (22.7% loss) and 83.7 mg/L (6.2% loss), respectively. Cassano et al. [115] also indicated that clarification of pomegranate juice by using ultrafiltration leads decrease in total monomeric anthocyanin content at an extent of 11.7%. In another study, after clarification of pomegranate juice using gelatin and bentonite as clarifying agents and commercial UF membrane (30 kDa cut-off PVDF membrane) caused 15% loss in total monomeric anthocyanin content [189].

Chapter 5

5. Conclusion

In this thesis, new generation PSF based nanocomposite UF and MF membranes were fabricated and applied in apple and pomegranate juice clarification processes, respectively. Within this context, PEI used as a pore former in the PSF polymer membrane matrix. Then to enhance membrane performance, membranes were modified with incorporation of TiO_2 and Al_2O_3 nanoparticles. Membrane performance was evaluated by both investigating the structure, physicochemical properties of membranes and clarification of apple and pomegranate juices. Important results for the characterization of membranes and clarified juices are concluded as follows;

Apple juice clarification with TiO_2 incoporated nanocomposite UF membranes;

- Hydrophilicity, porosity, pure water fluxes increased with addition of TiO_2 nanoparticles. Membrane prepared with addition of 0.01% of TiO_2 (UFT1; PES/PEI/0.01%TiO_2) had the highest hydrophilicity, porosity, pure water fluxes among the UF membranes prepared with TiO_2. Contact angle, porosity and pure water flux were measured for membrane UFT1 as 74°, 75.8% and 2241 Lm^2/h, respectively.
- Cross-flow filtration system was applied to clarify apple juice at 5.4 bar. Apple juice fluxes improved with the addition of TiO_2 nanoparticles. UFT1 has the highest apple juice flux (54.9 Lm^2/h).
- Flux recovery experiments carried out to determine anti-fouling properties of F/PEI/ TiO_2 membranes. Addition of TiO_2 nanoparticles led to increase antifouling property, significantly. The FRR and RFR values of TiO_2

incorporated membranes (UFTs) were between 90.9-94.0% and 6.0-9.1%, respectively.

- According to clarified apple juice characterization results, clear juices obtained from modified membrane incorporating TiO_2 nanoparticles had higher quality than clear juice obtained from unmodified membrane (M2). Also, produced clarified juices were compared with clarified juice obtained from Döhler Inc. and results showed that new generation nanocomposite UFT1 membrane exhibited superior performance.

Apple juice clarification with Al_2O_3 incoporated nanocomposite UF membranes;

Hydrophilicity, porosity and pure water fluxes increased with addition of Al_2O_3 nanoparticles. Membranes fabricated with addition of 0.05%wt of Al_2O_3 (UFA5; PSF/PEI/0.05%Al_2O_3) had the highest hydrophilicity, porosity, pure water fluxes among Al_2O_3 incorporated nanocomposite UF membranes. Contact angle, porosity and pure water flux were measured for membrane UFA5 as 80°, 74.7% and 705 Lm^2/h, respectively.

- Flux recovery experiments were carried out to determine anti-fouling properties. Addition of Al_2O_3 nanoparticles led to increase antifouling property, significantly. The FRR and RFR values of Al_2O_3 incorporated membranes (UFAs) were between 79.6-97.6% and 2.4-20.4%.
- Apple juice fluxes increased with the addition of Al_2O_3 nanoparticles. UFA5 (PES/PEI/ 0.05% Al_2O_3) has the highest apple juice fluxes (43.4 Lm^2/h).
- According to clarified apple juice characterization results, clear juices obtained from modified membrane incorporating Al_2O_3 nanoparticles had higher juice quality than juice obtained from unmodified membrane (M2). UFA5 exhibits similar performance with commercial membrane used by Döhler Inc.

Pomegranate juice clarification with UF membranes;

- According to color and total soluble solid results, fabricated new generation nanocomposite membranes were not suitable for pomegranate juice clarification. Because of very dense structure, UF membranes led rejection of color pigments and soluble solid in pomegranate juice.
- Therefore, MF membranes were generated by decreasing PSF concentration in the membrane matrix from 20 wt% to 17 wt % to clarify pomegranate juice.

Pomegranate juice clarification with TiO_2 incorporated nanocomposite MF membrane;

- Hydrophilicity, porosity, pure water fluxes are increased with addition of TiO_2 nanoparticles. MF membrane prepared with addition of 0.01% of TiO_2 (MFT1; PSF/PEI/0.01%TiO_2) had the highest hydrophilicity, porosity, pure water fluxes among the TiO_2 incorporated nanocomposite MF membranes. Contact angle, porosity and pure water flux were measured for membrane MFT1 as 79, 83.5% and 2241 Lm^2/h, respectively.
- Clarified pomegranate juices were analyzed in terms of turbidity, color, total soluble solid content, total phenolic compound, total antioxidant activity and total monomeric anthocyanin and results were compared with literature. Clarified pomegranate juice obtained from membrane MFT1 had the lowest turbidity and highest color, total soluble solid content, total phenolic content and total antioxidant capacity among new generation nanocomposite MF PSF/PEI/TiO_2 membranes.

Pomegranate juice clarification with Al_2O_3 incorporated nanocomposite MF membrane;

- Hydrophilicity, porosity, pure water fluxes increased with addition of Al_2O_3 nanoparticles. MF membrane prepared with addition of 0.05% of Al_2O_3 (MFA5; PES/PEI/0.05% Al_2O_3) had the highest hydrophilicity, porosity, pure water fluxes among Al_2O_3 incorporated nanocomposite MF membrane. Contact angle, porosity and pure water flux were measured for membrane MFA5 as 72, 84.8% and 2241 Lm^2/h, respectively.
- Clarified pomegranate juice obtained from MF membrane including Al_2O_3 nanoparticles had higher quality than unmodified membrane in terms of turbidity, color, total soluble solid content, total phenolic compound, total antioxidant activity and total anthocyanin content.

Results of the thesis demonstrated that there is a great potential to use nanoparticle incorporated new generation nanocomposite membranes with enhanced performance in apple and pomegranate juice clarification process. In conclusion, new generation nanocomposite membranes exhibit similar performance with commercial membrane in terms of fruit juice quality. Especially, UFT1 and MFA5 shows superior performance than other generated membranes and commercial membrane for clarification of apple and pomegranate juice, respectively. UFT1 and MFA5 rejected more molecules causing turbidity; simultaneously allowed more color pigment and soluble solid in juices to pass through into clarified juice. Also, it may be resulted that TiO_2 nanoparticle is more suitable to use as modifying agents for apple juice clarification, whereas Al_2O_3 nanoparticle is more suitable to use as modifying agents for pomegranate juice clarification.

BIBLIOGRAPHY

[1] F. Lipnizki, "Cross-Flow Membrane Applications in the Food Industry," *Membrane Technology*. 26-Nov-2010.

[2] A. Cassano and E. Drioli, "Membrane Contactors in Integrated Processes for Fruit-Juice Processing," *Membrane Technology*. 26-Nov-2010.

[3] K. Schroën, A. M. C. van Dinther, S. Bogale, M. Vollebregt, G. Brans, and R. M. Boom, "Membrane Processes for Dairy Fractionation," *Membrane Technology*. 26-Nov-2010.

[4] C. P. Kechinski, P. V. R. Guimarães, C. P. Z. Noreña, I. C. Tessaro, and L. D. F. Marczak, "Degradation Kinetics of Anthocyanin in Blueberry Juice during Thermal Treatment," *J. Food Sci.*, vol. 75, no. 2, 2010.

[5] S. Timoumi, D. Mihoubi, and F. Zagrouba, "Shrinkage, vitamin C degradation and aroma losses during infra-red drying of apple slices," *LWT - Food Sci. Technol.*, vol. 40, no. 9, pp. 1648–1654, 2007.

[6] P. Nisha, R. S. Singhal, and A. B. Pandit, "The degradation kinetics of flavor in black pepper (Piper nigrum L.)," *J. Food Eng.*, vol. 92, no. 1, pp. 44–49, 2009.

[7] R. C. De Oliveira, R. C. Docê, and S. T. D. De Barros, "Clarification of passion fruit juice by microfiltration: Analyses of operating parameters, study of membrane fouling and juice quality," *J. Food Eng.*, vol. 111, no. 2, pp. 432–439, 2012.

[8] F. Vaillant, E. Jeanton, M. Dornier, G. M. O'Brien, M. Reynes, and M. Decloux, "Concentration of passion fruit juice on an industrial pilot scale using osmotic evaporation," *J. Food Eng.*, vol. 47, no. 3, pp. 195–202, 2001.

[9] A. W. Mohammad, C. Y. Ng, Y. P. Lim, and G. H. Ng, "Ultrafiltration in Food Processing Industry: Review on Application, Membrane Fouling, and Fouling Control," *Food Bioprocess Technol.*, vol. 5, no. 4, pp. 1143–1156, 2012.

[10] T. Urošević, D. Povrenović, P. Vukosavljević, I. Urošević, and S. Stevanović, "Recent developments in microfiltration and ultrafiltration of fruit juices," *Food Bioprod. Process.*, vol. 106, pp. 147–161, 2017.

[11] J. E. Yoo, J. H. Kim, Y. Kim, and C. K. Kim, "Novel ultrafiltration membranes prepared from the new miscible blends of polysulfone with poly(1-vinylpyrrolidone-co-styrene) copolymers," *J. Memb. Sci.*, vol. 216, no. 1–2, pp.

95–106, 2003.

[12] M. Mulder, *Basic Principles of Membrane Technology*. Dordrecht: Kluver Academic Publishers, 1996.

[13] J. S. Louie, I. Pinnau, I. Ciobanu, K. P. Ishida, A. Ng, and M. Reinhard, "Effects of polyether-polyamide block copolymer coating on performance and fouling of reverse osmosis membranes," *J. Memb. Sci.*, vol. 280, no. 1–2, pp. 762–770, 2006.

[14] Y. Zhou, S. Yu, C. Gao, and X. Feng, "Surface modification of thin film composite polyamide membranes by electrostatic self deposition of polycations for improved fouling resistance," *Sep. Purif. Technol.*, vol. 66, no. 2, pp. 287–294, 2009.

[15] P. Ramesh Babu and V. G. Gaikar, "Membrane characteristics as determinant in fouling of UF membranes," *Sep. Purif. Technol.*, vol. 24, no. 1–2, pp. 23–34, 2001.

[16] D. Rana and T. Matsuura, "Surface Modifications for Antifouling Membranes," *Chem. Rev.*, vol. 110, pp. 2448–2471, 2010.

[17] P. Le-Clech, V. Chen, and T. A. G. Fane, "Fouling in membrane bioreactors used in wastewater treatment," *J. Memb. Sci.*, vol. 284, no. 1–2, pp. 17–53, 2006.

[18] F. Meng, S. R. Chae, A. Drews, M. Kraume, H. S. Shin, and F. Yang, "Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material," *Water Res.*, vol. 43, no. 6, pp. 1489–1512, 2009.

[19] L. Q. Shen, Z. K. Xu, Z. M. Liu, and Y. Y. Xu, "Ultrafiltration hollow fiber membranes of sulfonated polyetherimide/polyetherimide blends: Preparation, morphologies and anti-fouling properties," *J. Memb. Sci.*, vol. 218, no. 1–2, pp. 279–293, 2003.

[20] C. Wu, A. Li, and L. Li, "Treatment of oily water by a poly(vinyl alcohol) ultrafiltration membrane," *Desalination*, vol. 225, no. 1–3, pp. 312–321, 2008.

[21] S. P. Nunes, M. L. Sforça, and K. V. Peinemann, "Dense hydrophilic composite membranes for ultrafiltration," *J. Memb. Sci.*, vol. 106, no. 1–2, pp. 49–56, 1995.

[22] I. Genné, S. Kuypers, and R. Leysen, "Effect of the addition of ZrO2to polysulfone based UF membranes," *J. Memb. Sci.*, vol. 113, no. 2, pp. 343–350, 1996.

[23] D. Lu, W. Cheng, and T. Zhang, "Hydrophilic Fe2O3 dynamic membrane mitigating fouling of support ceramic membrane in ultrafiltration of oil/water

emulsion," *Sep. Purif. Technol.*, vol. 165, pp. 1–9, 2016.

[24] E. Yuliwati and A. F. Ismail, "Effect of additives concentration on the surface properties and performance of PVDF ultrafiltration membranes for refinery produced wastewater treatment," *Desalination*, vol. 273, no. 1, pp. 226–234, 2011.

[25] K. A. DeFriend, M. R. Wiesner, and A. R. Barron, "Alumina and aluminate ultrafiltration membranes derived from alumina nanoparticles," *J. Memb. Sci.*, vol. 224, no. 1, pp. 11–28, 2003.

[26] S.-H. Zhi, R. Deng, J. Xu, L.-S. Wan, and Z.-K. Xu, "Composite membranes from polyacrylonitrile with poly(N,N-dimethylaminoethyl methacrylate)-grafted silica nanoparticles as additives," *React. Funct. Polym.*, vol. 86, pp. 184–190, 2015.

[27] A. Higuchi, K. Shirano, and M. Harashima, "Chemically modified polysulfone hollow fibers with vinylpyrrolidone having improved blood compatibility," *Biomaterials*, vol. 23, no. 13, pp. 2659–2666, 2002.

[28] W. Edwards, W. D. Leukes, P. D. Rose, and S. G. Burton, "Immobilization of polyphenol oxidase on chitosan-coated polysulphone capillary membranes for improved phenolic effluent bioremediation," *Enzyme Microb. Technol.*, vol. 25, no. 8–9, pp. 769–773, 1999.

[29] D. Wu, Y. Huang, S. Yu, D. Lawless, and X. Feng, "Thin film composite nanofiltration membranes assembled layer-by-layer via interfacial polymerization from polyethylenimine and trimesoyl chloride," *J. Memb. Sci.*, vol. 472, pp. 141–153, 2014.

[30] C. Ba, J. Langer, and J. Economy, "Chemical modification of P84 copolyimide membranes by polyethylenimine for nanofiltration," *J. Memb. Sci.*, vol. 327, no. 1–2, pp. 49–58, 2009.

[31] M. K. Sinha and M. K. Purkait, "Increase in hydrophilicity of polysulfone membrane using polyethylene glycol methyl ether," *J. Memb. Sci.*, vol. 437, pp. 7–16, 2013.

[32] A. Sotto, A. Boromand, and R. Zhang, "Effect of nanoparticle aggregation at low concentrations of TiO2on the hydrophilicity, morphology, and fouling resistance of PES-TiO2membranes," *J. Colloid Interface Sci.*, vol. 363, no. 2, pp. 540–550, 2011.

[33] M. Baghbanzadeh, D. Rana, C. Q. Lan, and T. Matsuura, "Effects of Inorganic

Nano-Additives on Properties and Performance of Polymeric Membranes in Water Treatment," *Sep. Purif. Rev.*, vol. 45, no. 2, pp. 141–167, Apr. 2016.

[34] T. A. Saleh and V. K. Gupta, "Synthesis and characterization of alumina nano-particles polyamide membrane with enhanced flux rejection performance," *Sep. Purif. Technol.*, vol. 89, pp. 245–251, 2012.

[35] M. Elimelech and W. A. Phillip, "The Future of Seawater Desalination: Energy, Technology, and the Environment," *Science (80-.).*, vol. 333, no. 6043, p. 712 LP-717, Aug. 2011.

[36] M. M. Pendergast and E. M. V Hoek, "A review of water treatment membrane nanotechnologies," *Energy Environ. Sci.*, vol. 4, no. 6, pp. 1946–1971, 2011.

[37] Y. Zhang, J. Sunarso, S. Liu, and R. Wang, "Current status and development of membranes for CO2/CH4 separation: A review," *Int. J. Greenh. Gas Control*, vol. 12, pp. 84–107, 2013.

[38] C. Charcosset, "Preparation of emulsions and particles by membrane emulsification for the food processing industry," *J. Food Eng.*, vol. 92, no. 3, pp. 241–249, 2009.

[39] F. Zaviska, P. Drogui, A. Grasmick, A. Azais, and M. Héran, "Nanofiltration membrane bioreactor for removing pharmaceutical compounds," *J. Memb. Sci.*, vol. 429, pp. 121–129, 2013.

[40] R. D. Ambashta and M. E. T. Sillanpää, "Membrane purification in radioactive waste management: a short review," *J. Environ. Radioact.*, vol. 105, pp. 76–84, 2012.

[41] P. C. Wankat, *Rate Controlled Separations*. Blackie Academic & Professional, 1994.

[42] P. C. Wankat, *Separation process engineering*. Pearson Education, 2006.

[43] R. W. Baker, *Membrane Technology and Applications*. Wiley, 2004.

[44] J. H. Jhaveri and Z. V. P. Murthy, "A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes," *Desalination*, vol. 379, pp. 137–154, 2016.

[45] Q. Chaudhry, L. Castle, R. Watkins, and R. S. of Chemistry (Great Britain), *Nanotechnologies in Food*. RSC, 2010.

[46] J. Mulder, *basic principles of membrane tehnology*. Springer Science&Business, 2012.

[47] R. van Reis and A. Zydney, "Bioprocess membrane technology," *J. Memb. Sci.*,

vol. 297, no. 1–2, pp. 16–50, 2007.

[48] Z. F. Cui, Y. Jiang, and R. W. Field, "Chapter 1 - Fundamentals of Pressure-Driven Membrane Separation Processes," Z. F. Cui and H. S. B. T.-M. T. Muralidhara, Eds. Oxford: Butterworth-Heinemann, 2010, pp. 1–18.

[49] V. D. B. Bart, V. Carlo, V. G. Tim, D. Wim, and L. Roger, "A review of pressure-driven membrane processes in wastewater treatment and drinking water production," *Environ. Prog.*, vol. 22, no. 1, pp. 46–56, Apr. 2004.

[50] K. V Peinemann, S. P. Nunes, and L. Giorno, *Membranes for Food Applications*. Wiley, 2011.

[51] Z. F. Cui and H. S. Muralidhara, *Membrane Technology: A Practical Guide to Membrane Technology and Applications in Food and Bioprocessing*. Elsevier Science, 2010.

[52] M. B. El-Arnaouty, A. M. Abdel Ghaffar, M. Eid, M. E. Aboulfotouh, N. H. Taher, and E.-S. Soliman, "Nano-modification of polyamide thin film composite reverse osmosis membranes by radiation grafting," *J. Radiat. Res. Appl. Sci.*, 2018.

[53] K. Scott and R. Hughes, *Industrial Membrane Separation Technology*. Springer Netherlands, 2012.

[54] J. K. Bungay, *Synthetic Membranes:: Science, Engineering and Applications*, vol. 181. Springer Science & Business Media, 2012.

[55] H. Strathmann, *Introduction to Membrane Science and Technology*. Wiley, 2011.

[56] L. Y. Ng, A. W. Mohammad, C. P. Leo, and N. Hilal, "Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review," *Desalination*, vol. 308, pp. 15–33, 2013.

[57] M. L. Sforça, I. V. P. Yoshida, and S. P. Nunes, "Organic–inorganic membranes prepared from polyether diamine and epoxy silane," *J. Memb. Sci.*, vol. 159, no. 1, pp. 197–207, 1999.

[58] V. C. Souza and M. G. N. Quadri, "ORGANIC-INORGANIC HYBRID MEMBRANES IN SEPARATION PROCESSES : A 10-YEAR REVIEW," vol. 30, no. 04, pp. 683–700, 2013.

[59] C. Labbez, P. Fievet, A. Szymczyk, A. Vidonne, A. Foissy, and J. Pagetti, "Analysis of the salt retention of a titania membrane using the 'DSPM' model: effect of pH, salt concentration and nature," *J. Memb. Sci.*, vol. 208, no. 1, pp. 315–329, 2002.

[60] K. W. J., “Gas separation membranes: needs for combined materials science and processing approaches,” *Macromol. Symp.*, vol. 188, no. 1, pp. 13–22, Nov. 2002.

[61] S. Rajabzadeh, T. Maruyama, T. Sotani, and H. Matsuyama, “Preparation of PVDF hollow fiber membrane from a ternary polymer/solvent/nonsolvent system via thermally induced phase separation (TIPS) method,” *Sep. Purif. Technol.*, vol. 63, no. 2, pp. 415–423, 2008.

[62] S. Mei, C. Xiao, and X. Hu, “Preparation of porous PVC membrane via a phase inversion method from PVC/DMAc/water/additives,” *J. Appl. Polym. Sci.*, vol. 120, no. 1, pp. 557–562, Oct. 2010.

[63] T. Kawai, Y. M. Lee, and S. Yamada, “Preparation of asymmetric porous membranes of poly(vinyl chloride),” *Polymer (Guildf).*, vol. 38, no. 7, pp. 1631–1637, 1997.

[64] D. R. Lloyd, S. S. Kim, and K. E. Kinzer, “Microporous membrane formation via thermally-induced phase separation. II. Liquid—liquid phase separation,” *J. Memb. Sci.*, vol. 64, no. 1–2, pp. 1–11, 1991.

[65] D. R. Lloyd, K. E. Kinzer, and H. S. Tseng, “Microporous membrane formation via thermally induced phase separation. I. Solid-liquid phase separation,” *J. Memb. Sci.*, vol. 52, no. 3, pp. 239–261, 1990.

[66] S. S. Kim, G. B. A. Lim, A. A. Alwattari, Y. F. Wang, and D. R. Lloyd, “Microporous membrane formation via thermally-induced phase separation. V. Effect of diluent mobility and crystallization on the structure of isotactic polypropylene membranes,” *J. Memb. Sci.*, vol. 64, no. 1, pp. 41–53, 1991.

[67] G. B. A. Lim, S. S. Kim, Q. Ye, Y. F. Wang, and D. R. Lloyd, “Microporous membrane formation via thermally-induced phase separation. IV. Effect of isotactic polypropylene crystallization kinetics on membrane structure,” *J. Memb. Sci.*, vol. 64, no. 1, pp. 31–40, 1991.

[68] S. S. Kim and D. R. Lloyd, “Microporous membrane formation via thermally-induced phase separation. III. Effect of thermodynamic interactions on the structure of isotactic polypropylene membranes,” *J. Memb. Sci.*, vol. 64, no. 1, pp. 13–29, 1991.

[69] J. A. Prince, G. Singh, D. Rana, T. Matsuura, V. Anbharasi, and T. S. Shanmugasundaram, “Preparation and characterization of highly hydrophobic poly(vinylidene fluoride) – Clay nanocomposite nanofiber membranes (PVDF–

clay NNMs) for desalination using direct contact membrane distillation," *J. Memb. Sci.*, vol. 397–398, pp. 80–86, 2012.

[70] S. Ramakrishna, R. Jose, P. S. Archana, A. S. Nair, R. Balamurugan, and J. Venugopal, "Science and engineering of electrospun nanofibers for advances in clean energy, water filtration, and regenerative medicine," *J. Mater. Sci.*, vol. 45, no. 23, pp. 6283–6312, 2010.

[71] K. Yoon, B. S. Hsiao, and B. Chu, "Functional nanofibers for environmental applications," *J. Mater. Chem.*, vol. 18, no. 44, pp. 5326–5334, 2008.

[72] K. Trommer and B. Morgenstern, *Nonrigid Microporous PVC Sheets: Preparation and Properties*, vol. 115. 2010.

[73] Q. Yang, Z.-K. Xu, Z.-W. Dai, J.-L. Wang, and M. Ulbricht, "Surface Modification of Polypropylene Microporous Membranes with a Novel Glycopolymer," *Chem. Mater.*, vol. 17, no. 11, pp. 3050–3058, May 2005.

[74] L. Dauginet-De Pra, E. Ferain, R. Legras, and S. Demoustier-Champagne, "Fabrication of a new generation of track-etched templates and their use for the synthesis of metallic and organic nanostructures," *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, vol. 196, no. 1, pp. 81–88, 2002.

[75] Y.-Q. Wang, Y.-L. Su, Q. Sun, X.-L. Ma, and Z.-Y. Jiang, "Generation of anti-biofouling ultrafiltration membrane surface by blending novel branched amphiphilic polymers with polyethersulfone," *J. Memb. Sci.*, vol. 286, no. 1, pp. 228–236, 2006.

[76] A. Asatekin, A. Menniti, S. Kang, M. Elimelech, E. Morgenroth, and A. M. Mayes, "Antifouling nanofiltration membranes for membrane bioreactors from self-assembling graft copolymers," *J. Memb. Sci.*, vol. 285, no. 1, pp. 81–89, 2006.

[77] M. Wang, L. Wu, and C. Gao, "The influence of phase inversion process modified by chemical reaction on membrane properties and morphology," *J. Memb. Sci.*, vol. 270, no. 1, pp. 154–161, 2006.

[78] S. Yu, S. Yang, and M. Cho, "Multi-scale modeling of cross-linked epoxy nanocomposites," *Polymer (Guildf).*, vol. 50, no. 3, pp. 945–952, 2009.

[79] W. Zhao, J. Huang, B. Fang, S. Nie, N. Yi, and B. Su, "Modification of polyethersulfone membrane by blending semi-interpenetrating network polymeric nanoparticles," *J. Memb. Sci.*, vol. 369, no. 1, pp. 258–266, 2011.

[80] G.-R. Xu, J.-N. Wang, and C.-J. Li, "Strategies for improving the performance of the polyamide thin film composite (PA-TFC) reverse osmosis (RO) membranes: Surface modifications and nanoparticles incorporations," *Desalination*, vol. 328, pp. 83–100, 2013.

[81] D. Y. Kwon, S. Vigneswaran, A. G. Fane, and R. B. Aim, "Experimental determination of critical flux in cross-flow microfiltration," *Sep. Purif. Technol.*, vol. 19, no. 3, pp. 169–181, 2000.

[82] J. Glater, S. Hong, and M. Elimelech, "The search for a chlorine-resistant reverse osmosis membrane," *Desalination*, vol. 95, no. 3, pp. 325–345, 1994.

[83] M. A. Aroon, A. F. Ismail, T. Matsuura, and M. M. Montazer-Rahmati, "Performance studies of mixed matrix membranes for gas separation: A review," *Sep. Purif. Technol.*, vol. 75, no. 3, pp. 229–242, 2010.

[84] A. C Balazs, T. Emrick, and T. P Russell, *Nanoparticle Polymer Composites: Where Two Small Worlds Meet*, vol. 314. 2006.

[85] X.-F. Sun, J. Qin, P.-F. Xia, B.-B. Guo, and C.-M. Yang, "Graphene oxide–silver nanoparticle membrane for biofouling control and water purification," *Chem. Eng. J.*, vol. 281, pp. 53–59, 2015.

[86] J. Vanneste, A. Sotto, C. M. Courtin, V. Van Craeyveld, K. Bernaerts, and J. Van Impe, "Application of tailor-made membranes in a multi-stage process for the purification of sweeteners from Stevia rebaudiana," *J. Food Eng.*, vol. 103, no. 3, pp. 285–293, 2011.

[87] S. Balta, A. Sotto, P. Luis, L. Benea, B. Van der Bruggen, and J. Kim, "A new outlook on membrane enhancement with nanoparticles: The alternative of ZnO," *J. Memb. Sci.*, vol. 389, pp. 155–161, 2012.

[88] J. Kim and B. Van Der Bruggen, "The use of nanoparticles in polymeric and ceramic membrane structures: Review of manufacturing procedures and performance improvement for water treatment," *Environ. Pollut.*, vol. 158, no. 7, pp. 2335–2349, 2010.

[89] M. Luo, W. Tang, J. Zhao, and C. Pu, *Hydrophilic modification of poly(ether sulfone) used TiO2 nanoparticles by a sol–gel process*, vol. 172. 2006.

[90] G. Wu, S. Gan, L. Cui, and Y. Xu, "Preparation and characterization of PES/TiO2 composite membranes," *Appl. Surf. Sci.*, vol. 254, no. 21, pp. 7080–7086, 2008.

[91] A. Rahimpour, S. S. Madaeni, A. H. Taheri, and Y. Mansourpanah, "Coupling

TiO2 nanoparticles with UV irradiation for modification of polyethersulfone ultrafiltration membranes,” *J. Memb. Sci.*, vol. 313, no. 1–2, pp. 158–169, 2008.

[92] J. Kim, A. Sotto, J. Chang, D. Nam, A. Boromand, and B. Van Der Bruggen, “Microporous and Mesoporous Materials Embedding TiO 2 nanoparticles versus surface coating by layer-by-layer deposition on nanoporous polymeric films,” *Microporous Mesoporous Mater.*, vol. 173, pp. 121–128, 2013.

[93] T. H. Bae and T. M. Tak, “Effect of TiO2 nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration,” *J. Memb. Sci.*, vol. 249, no. 1–2, pp. 1–8, 2005.

[94] T. H. Bae, I. C. Kim, and T. M. Tak, “Preparation and characterization of fouling-resistant TiO2 self-assembled nanocomposite membranes,” *J. Memb. Sci.*, vol. 275, no. 1–2, pp. 1–5, 2006.

[95] R. A. Damodar, S.-J. You, and H.-H. Chou, “Study the self cleaning, antibacterial and photocatalytic properties of TiO2 entrapped PVDF membranes,” *J. Hazard. Mater.*, vol. 172, no. 2, pp. 1321–1328, 2009.

[96] S. Pourjafar, A. Rahimpour, and M. Jahanshahi, “Synthesis and characterization of PVA/PES thin film composite nanofiltration membrane modified with TiO2 nanoparticles for better performance and surface properties,” *J. Ind. Eng. Chem.*, vol. 18, no. 4, pp. 1398–1405, 2012.

[97] S. S. Madaeni and N. Ghaemi, “Characterization of self-cleaning RO membranes coated with TiO2 particles under UV irradiation,” *J. Memb. Sci.*, vol. 303, no. 1, pp. 221–233, 2007.

[98] P. Pandey and R. S. Chauhan, “Membranes for gas separation,” *Prog. Polym. Sci.*, vol. 26, no. 6, pp. 853–893, 2001.

[99] P. Aerts, A. R. Greenberg, R. Leysen, W. B. Krantz, V. E. Reinsch, and P. A. Jacobs, “The influence of filler concentration on the compaction and filtration properties of Zirfon®-composite ultrafiltration membranes,” *Sep. Purif. Technol.*, vol. 22–23, pp. 663–669, 2001.

[100] J. Schaep, C. Vandecasteele, R. Leysen, and W. Doyen, “Salt retention of Zirfon® membranes,” *Sep. Purif. Technol.*, vol. 14, no. 1, pp. 127–131, 1998.

[101] I. Genné, S. Kuypers, and R. Leysen, “Effect of the addition of ZrO2 to polysulfone based UF membranes,” *J. Memb. Sci.*, vol. 113, no. 2, pp. 343–350, 1996.

[102] A. Bottino, G. Capannelli, V. D’Asti, and P. Piaggio, “Preparation and properties

of novel organic–inorganic porous membranes," *Sep. Purif. Technol.*, vol. 22–23, pp. 269–275, 2001.

[103] V. Vatanpour, S. S. Madaeni, A. R. Khataee, E. Salehi, S. Zinadini, and H. A. Monfared, "TiO2 embedded mixed matrix PES nanocomposite membranes: Influence of different sizes and types of nanoparticles on antifouling and performance," *Desalination*, vol. 292, pp. 19–29, 2012.

[104] A. Razmjou, A. Resosudarmo, R. L. Holmes, H. Li, J. Mansouri, and V. Chen, "The effect of modified TiO2 nanoparticles on the polyethersulfone ultrafiltration hollow fiber membranes," *Desalination*, vol. 287, pp. 271–280, 2012.

[105] A. Razmjou, J. Mansouri, and V. Chen, "The effects of mechanical and chemical modification of TiO2nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes," *J. Memb. Sci.*, vol. 378, no. 1–2, pp. 73–84, 2011.

[106] Y. Yang, H. Zhang, P. Wang, Q. Zheng, and J. Li, "The influence of nano-sized TiO2fillers on the morphologies and properties of PSF UF membrane," *J. Memb. Sci.*, vol. 288, no. 1–2, pp. 231–238, 2007.

[107] M. Homayoonfal, M. R. Mehrnia, Y. M. Mojtahedi, and A. F. Ismail, "Effect of metal and metal oxide nanoparticle impregnation route on structure and liquid filtration performance of polymeric nanocomposite membranes: a comprehensive review," *Desalin. Water Treat.*, vol. 51, no. 16–18, pp. 3295–3316, Apr. 2013.

[108] L. Yan, Y. S. Li, C. B. Xiang, and S. Xianda, "Effect of nano-sized Al2O3-particle addition on PVDF ultrafiltration membrane performance," *J. Memb. Sci.*, vol. 276, no. 1–2, pp. 162–167, 2006.

[109] N. Uzal, N. Ates, S. Saki, Y. E. Bulbul, and Y. Chen, "Enhanced hydrophilicity and mechanical robustness of polysulfone nanofiber membranes by addition of polyethyleneimine and Al2O3 nanoparticles," *Sep. Purif. Technol.*, vol. 187, pp. 118–126, 2017.

[110] J. Garcia-Ivars, M. I. Alcaina-Miranda, M. I. Iborra-Clar, J. A. Mendoza-Roca, and L. Pastor-Alcañiz, "Enhancement in hydrophilicity of different polymer phase-inversion ultrafiltration membranes by introducing PEG/Al2O3 nanoparticles," *Sep. Purif. Technol.*, vol. 128, pp. 45–57, 2014.

[111] N. Maximous, G. Nakhla, W. Wan, and K. Wong, "Preparation, characterization and performance of Al2O3/PES membrane for wastewater filtration," *J. Memb. Sci.*, vol. 341, no. 1–2, pp. 67–75, 2009.

[112] G. Daufin, J.-P. Escudier, H. Carrère, S. Bérot, L. Fillaudeau, and M. Decloux, "Recent and Emerging Applications of Membrane Processes in the Food and Dairy Industry," *Food Bioprod. Process.*, vol. 79, no. 2, pp. 89–102, 2001.

[113] H. May-Britt, "Membranes in Chemical Processing a Review of Applications and Novel Developments," *Sep. Purif. Methods*, vol. 27, no. 1, pp. 51–168, Jan. 1998.

[114] J. Guy Woodroof and B. Shiun Luh, *Commercial fruit processing / by Jasper Guy Woodroof and Bor Shiun Luh in collaboration with specialists*. 1986.

[115] A. Cassano, C. Conidi, and E. Drioli, "Clarification and concentration of pomegranate juice (Punica granatum L .) using membrane processes," *J. Food Eng.*, vol. 107, no. 3–4, pp. 366–373, 2011.

[116] L. R. Fukumoto, P. Delaquis, and B. Girard, "Microfiltration and ultrafiltration ceramic membranes for apple juice clarification," *J. Food Sci.*, vol. 63, no. 5, pp. 845–850, 1998.

[117] S. Alvarez, R. Alvarez, F. A. Riera, and J. Coca, "Influence of depectinization on apple juice ultrafiltration," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 138, no. 2, pp. 377–382, 1998.

[118] Y. P. Lim and A. W. Mohammad, "Effect of solution chemistry on flux decline during high concentration protein ultrafiltration through a hydrophilic membrane," *Chem. Eng. J.*, vol. 159, no. 1, pp. 91–97, 2010.

[119] Y. H. Hui, J. Barta, M. P. Cano, T. W. Gusek, J. S. Sidhu, and N. Sinha, *Handbook of Fruits and Fruit Processing*. Wiley, 2008.

[120] F. Vaillant, A. Millan, M. Dornier, M. Decloux, and M. Reynes, "Strategy for economical optimization of the clarification of pulpy fruit juices using crossflow microfiltration," *J. Food Eng.*, vol. 48, no. 1, pp. 83–90, 2001.

[121] K. J. Siebert and P. Y. Lynn, "Haze-active protein and polyphenols in apple juice assessed by turbidimetry," *J. Food Sci.*, vol. 62, no. 1, pp. 79–84, 1997.

[122] P. Onsekizoglu, K. S. Bahceci, and M. J. Acar, "Clarification and the concentration of apple juice using membrane processes: A comparative quality assessment," *J. Memb. Sci.*, vol. 352, no. 1–2, pp. 160–165, 2010.

[123] F. Vaillant, A. M. Pérez, O. Acosta, and M. Dornier, "Turbidity of pulpy fruit juice: A key factor for predicting cross-flow microfiltration performance," *J. Memb. Sci.*, vol. 325, no. 1, pp. 404–412, 2008.

[124] P. Ghosh, S. Rana, S. Kumar C, R. C. Pradhan, and S. Mishra, "MEMBRANE FILTRATION OF FRUIT JUICE - AN EMERGING TECHNOLOGY," vol. 4,

no. 3, pp. 1–4, 2015.

[125] P. E. SHAW, M. Lebrun, M. Ducamp, M. Jordán, and K. Goodner, “Pineapple juice concentrated by osmotic evaporation,” *J. Food Qual.*, vol. 25, pp. 39–49, Mar. 2002.

[126] A. Cassano, “Clarification and concentration of citrus and carrot juices by integrated membrane processes,” vol. 57, pp. 153–163, 2003.

[127] P. Tallarico, S. Todisco, and E. Drioli, “Use of ultarfiltration in preventing of orange juice bitterness and its effect on the aroma compound distribution,” *AgroFood Ind. Hi-Tech*, vol. 33, no. 5, pp. 739–756, 1998.

[128] B. Girard and L. R. Fukumoto, “Membrane processing of fruit juices and beverages: A review,” *Crit. Rev. Food Sci. Nutr.*, vol. 40, no. 2, pp. 91–157, 2000.

[129] Z. Borneman, V. Gökmen, and H. H. Nijhuis, “Selective removal of polyphenols and brown colour in apple juices using PES/PVP membranes in a single ultrafiltration process,” *Sep. Purif. Technol.*, vol. 22–23, pp. 53–61, 2001.

[130] O. S. Lukanin, S. M. Gunko, M. T. Bryk, and R. R. Nigmatullin, “The effect of content of apple juice biopolymers on the concentration by membrane distillation,” *J. Food Eng.*, vol. 60, no. 3, pp. 275–280, 2003.

[131] A. Cassano and E. Drioli, *Integrated Membrane Operations in the Food Production*. Walter de Gruyter GmbH & Company, KG, 2014.

[132] Á. Kozák, S. Bánvölgyi, I. Vincze, I. Kiss, E. Békássy-Molnár, and G. Vatai, “Comparison of integrated large scale and laboratory scale membrane processes for the production of black currant juice concentrate,” *Chem. Eng. Process. Process Intensif.*, vol. 47, no. 7, pp. 1171–1177, 2008.

[133] Á. Kozák, E. Békássy-Molnár, and G. Vatai, “Production of black-currant juice concentrate by using membrane distillation,” *Desalination*, vol. 241, no. 1–3, pp. 309–314, 2009.

[134] H. Mirsaeedghazi, Z. Emam-djomeh, and S. Mohammad, “Clarification of pomegranate juice by microfiltration with PVDF membranes,” *Desalination*, vol. 264, pp. 243–248, 2010.

[135] S. Saki, “Nanocomposite Membranes and Their Applications in Oily Wastewater Treatment,” Abdullah Gül University, 2017.

[136] R. Re, N. Pellegrini, A. Pannala, M. Yang, and C. Rice-Evans, “Antioxidant Activity Applying an Improved Abts Radical,” *Free Radic. Biol. Med.*, vol. 26,

no. 98, pp. 1231–1237, 1999.

[137] A. A. Anton, R. Gary Fulcher, and S. D. Arntfield, “Physical and nutritional impact of fortification of corn starch-based extruded snacks with common bean (Phaseolus vulgaris L.) flour: Effects of bean addition and extrusion cooking,” *Food Chem.*, vol. 113, no. 4, pp. 989–996, 2009.

[138] G. A. Spanos and R. E. Wrolstad, “Influence of Processing and Storage on the Phenolic Composition of Thompson Seedless Grape Juice,” *J. Agric. Food Chem.*, vol. 20, pp. 1565–1571, 1990.

[139] W. D. Wang and S. Y. Xu, “Degradation kinetics of anthocyanins in blackberry juice and concentrate,” *J. Food Eng.*, vol. 82, no. 3, pp. 271–275, 2007.

[140] Y. C. Chiang, Y. Z. Hsub, R. C. Ruaan, C. J. Chuang, and K. L. Tung, “Nanofiltration membranes synthesized from hyperbranched polyethyleneimine,” *J. Memb. Sci.*, vol. 326, no. 1, pp. 19–26, 2009.

[141] A. E. Livari, A. Aroujalian, A. Raisi, and M. F. et al, “The Effect of TiO2 Nanoparticles on PES UF Membrane Fouling in Water-oil Sepration,” *Procedia Eng.*, vol. 44, pp. 1783–1785, 2012.

[142] M. Luo, J. Zhao, W. Tang, and C. Pu, “Hydrophilic modification of poly (ether sulfone) ultrafiltration membrane surface by self-assembly of TiO 2 nanoparticles,” vol. 249, pp. 76–84, 2005.

[143] J. P. F. De Bruijn, A. Venegas, J. A. Martínez, and R. Bórquez, “Ultrafiltration performance of Carbosep membranes for the clarification of apple juice,” *LWT - Food Sci. Technol.*, vol. 36, no. 4, pp. 397–406, 2003.

[144] Y. He, Z. Ji, and S. Li, “Effective clarification of apple juice using membrane filtration without enzyme and pasteurization pretreatment,” *Sep. Purif. Technol.*, vol. 57, pp. 366–373, 2007.

[145] X. Cao, J. Ma, X. Shi, and Z. Ren, “Effect of TiO2 nanoparticle size on the performance of PVDF membrane,” *Appl. Surf. Sci.*, vol. 253, no. 4, pp. 2003–2010, 2006.

[146] Y. Yang, H. Zhang, P. Wang, Q. Zheng, and J. Li, “The influence of nano-sized TiO2 fillers on the morphologies and properties of PSF UF membrane,” *J. Memb. Sci.*, vol. 288, no. 1, pp. 231–238, 2007.

[147] A. Khalid, A. A. Al-juhani, O. C. Al-hamouz, T. Laoui, Z. Khan, and M. Ali, “Preparation and properties of nanocomposite polysulfone / multi-walled carbon nanotubes membranes for desalination,” *DES*, vol. 367, pp. 134–144, 2015.

[148] F. Avilés, J. Cauich, L. Moo-Tah, A. May Pat, and R. Vargas-Coronado, *Evaluation of Mild Acid Oxidation Treatments for MWCNT Functionalization*, vol. 47. 2009.

[149] A. León, P. Reuquen, C. Garín, R. Segura, P. Vargas, and P. Zapata, "FTIR and Raman Characterization of TiO 2 Nanoparticles Coated with Polyethylene Glycol as Carrier for 2-Methoxyestradiol," *Appl. Sci.*, pp. 1–9.

[150] B. Choudhury and A. Choudhury, "Luminescence characteristics of cobalt doped TiO2 nanoparticles," *J. Lumin.*, vol. 132, no. 1, pp. 178–184, 2012.

[151] X. Lu, X. Lv, Z. Sun, and Y. Zheng, "Nanocomposites of poly(l-lactide) and surface-grafted TiO2 nanoparticles: Synthesis and characterization," *Eur. Polym. J.*, vol. 44, no. 8, pp. 2476–2481, 2008.

[152] C. Trimpert, G. Boese, W. Albrecht, K. Richau, and T. Weigel, "Poly(ether imide) membranes modified with poly(ethylene imine) as potential carriers for epidermal substitutes," *Macromol. Biosci.*, vol. 6, no. 4, pp. 274–284, 2006.

[153] W. Albrecht, B. Seifert, T. Weigel, and M. Schossig, "Amination of poly(ether imide) membranes using di- and multivalent amines," *Macromol. Chem. Phys.*, vol. 204, no. 3, pp. 510–521, 2003.

[154] T. Hong, A. Ngo, D. The, K. Dinh, T. Thi, and M. Nguyen, "Journal of Science : Advanced Materials and Devices Surface modi fi cation of polyamide thin fi lm composite membrane by coating of titanium dioxide nanoparticles," *J. Sci. Adv. Mater. Devices*, vol. 1, no. 4, pp. 468–475, 2016.

[155] Ö. Taştan and T. Baysal, "Chitosan as a novel clarifying agent on clear apple juice production : Optimization of process conditions and changes on quality characteristics," *Food Chem.*, vol. 237, pp. 818–824, 2017.

[156] A. Varnam and J. M. Sutherland, *Beverages: Technology, Chemistry and Microbiology*. Springer, 1994.

[157] C. E. Candrawinata, V. I., Golding, J. B.,Roach, P. D. and Stathopoulos, "Total phenolic content and antioxidant activity of apple pomace aqueous extract : effect of time , temperature and water to pomace ratio," *Int. Food Res. J.*, vol. 21, no. 6, pp. 2337–2344, 2014.

[158] M. Cliff, C. M. Dever, and R. Gayton, "Juice Extraction Process and Apple Cultivar Influences on Juice Properties," *J. Food Sci.*, vol. 56, no. 6, pp. 1614–1617, Jul. 2018.

[159] N. Art, J. Acar, N. Kahraman, and E. Poyrazog, "Effects of various clarification

treatments on patulin , phenolic compound and organic acid compositions of apple juice," pp. 194–199, 2001.

[160] P. Onsekizoglu, "Effects of Osmotic and Membrane Distillation Treatment on the Quality of the Product at Apple Juice Production," 2010.

[161] C. Alberto, S. Mengistu, S. Mannino, T. Mimmo, and M. Scampicchio, "Filtration of apple juice by nylon nanofibrous membranes," *J. Food Eng.*, vol. 122, pp. 110–116, 2014.

[162] S. P. Verma and B. Sarkar, "Food and Bioproducts Processing Analysis of flux decline during ultrafiltration of apple juice in a batch cell," *Food Bioprod. Process.*, vol. 94, no. 2012, pp. 147–157, 2015.

[163] Y.-Z. Fang, S. Yang, and G. Wu, "Free radicals, antioxidants, and nutrition," *Nutrition*, vol. 18, no. 10, pp. 872–879, Oct. 2002.

[164] D. P. Xu *et al.*, "Natural antioxidants in foods and medicinal plants: Extraction, assessment and resources," *Int. J. Mol. Sci.*, vol. 18, no. 1, pp. 20–31, 2017.

[165] M. Pinelo, B. Zeuner, and A. S. Meyer, "Juice clarification by protease and pectinase treatments indicates new roles of pectin and protein in cherry juice turbidity," *Food Bioprod. Process.*, vol. 88, no. 2, pp. 259–265, 2010.

[166] B. L. Silvina and B. Frei, "Relevance of Apple Polyphenols as Antioxidants in Human Plasma : Contrasting in Vitro in Vivo Effects," *Free Radic. Biol. Med.*, vol. 36, no. 2, pp. 201–211, 2004.

[167] J. Oszmia, "Effects of various clarification treatments on phenolic compounds and color of apple juice," *Eur. Food Res. Technol.*, vol. 224, pp. 755–762, 2007.

[168] A. P. Echavarría, C. Torras, J. Pagán, and A. Ibarz, "Fruit Juice Processing and Membrane Technology Application," *Food Eng. Rev.*, vol. 3, no. 3–4, pp. 136–158, 2011.

[169] M. Chamchong and A. Noomhorm, "Effect of pH and Enzymatic Treatment on Microfiltration and Ultrafiltration of Tangerine Juice," *J. Food Process Eng.*, vol. 14, no. 1, pp. 21–34, Jul. 2018.

[170] R. W. Field, "Mass transport and the design of membrane systems BT - Industrial Membrane Separation Technology," K. Scott and R. Hughes, Eds. Dordrecht: Springer Netherlands, 1996, pp. 67–113.

[171] J.-F. Li, Z.-L. Xu, H. Yang, L.-Y. Yu, and M. Liu, "Effect of TiO2 nanoparticles on the surface morphology and performance of microporous PES membrane," *Appl. Surf. Sci.*, vol. 255, no. 9, pp. 4725–4732, 2009.

[172] Q. Wang, X. Wang, Z. Wang, J. Huang, and Y. Wang, "PVDF membranes with simultaneously enhanced permeability and selectivity by breaking the tradeoff effect via atomic layer deposition of TiO2," *J. Memb. Sci.*, vol. 442, pp. 57–64, 2013.

[173] L. Yan, Y. S. Li, and C. B. Xiang, "Preparation of poly(vinylidene fluoride)(pvdf) ultrafiltration membrane modified by nano-sized alumina (Al2O3) and its antifouling research," *Polymer (Guildf).*, vol. 46, no. 18, pp. 7701–7706, 2005.

[174] B. M. Ganesh, A. M. Isloor, and A. F. Ismail, "Enhanced hydrophilicity and salt rejection study of graphene oxide-polysulfone mixed matrix membrane," *Desalination*, vol. 313, pp. 199–207, 2013.

[175] X. Cao, J. Ma, X. Shi, and Z. Ren, "Effect of TiO2 nanoparticle size on the performance of PVDF membrane," *Appl. Surf. Sci.*, vol. 253, no. 4, pp. 2003–2010, 2006.

[176] Z. Xu, J. Zhang, M. Shan, Y. Li, B. Li, and J. Niu, "Organosilane-functionalized graphene oxide for enhanced antifouling and mechanical properties of polyvinylidene fluoride ultrafiltration membranes," *J. Memb. Sci.*, vol. 458, pp. 1–13, 2014.

[177] Z. Wang, H. Yu, J. Xia, F. Zhang, and F. Li, "Novel GO-blended PVDF ultrafiltration membranes," *Desalination*, vol. 299, pp. 50–54, 2012.

[178] S. Zinadini, A. A. Zinatizadeh, M. Rahimi, V. Vatanpour, and H. Zangeneh, "Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates," *J. Memb. Sci.*, vol. 453, pp. 292–301, 2014.

[179] Y. Zhao, Z. Xu, M. Shan, C. Min, and B. Zhou, "Effect of graphite oxide and multi-walled carbon nanotubes on the microstructure and performance of PVDF membranes," *Sep. Purif. Technol.*, vol. 103, pp. 78–83, 2013.

[180] S. Ayyaru and Y. Ahn, "SC," *J. Ind. Eng. Chem.*, vol. 2, 2018.

[181] N. Maximous, G. Nakhla, K. Wong, and W. Wan, "Optimization of Al2O3/PES membranes for wastewater filtration," *Sep. Purif. Technol.*, vol. 73, no. 2, pp. 294–301, 2010.

[182] S. Roger, "Bitterness in foods and beverages, edited by Russell L. Rouseff, Elsevier Science Publishers, Barking, Essex, 1990. No. of pages: XVIII + 356, price Dfl. 260.00, US$133.25. ISBN 0–444–88175–1," *Flavour Fragr. J.*, vol. 7, no. 1, p. 53, Jul. 2018.

[183] N. Alper and J. Acar, "Removal of phenolic compounds in pomegranate juices using ultrafiltration and laccase-ultrafiltration combinations," *Nahrung/Food*, vol. 48, no. 3, pp. 184–187, 2004.

[184] H. R. Oziyci, M. Karhan, N. Tetik, and I. Turhan, "Effects of processing method and storage temperature on clear pomegranate juice turbidity and color," *J. Food Process. Preserv.*, vol. 37, no. 5, pp. 899–906, 2013.

[185] Ö. Turfan, M. Türkyilmaz, O. Yemi, and M. Özkan, "Anthocyanin and colour changes during processing of pomegranate (Punica granatum L.; Cv. Hicaznar) juice from sacs and whole fruit," *Food Chem.*, vol. 129, no. 4, pp. 1644–1651, 2011.

[186] B. Erkan-Koç, M. Türkyılmaz, O. Yemiş, and M. Özkan, "Effects of various protein- and polysaccharide-based clarification agents on antioxidative compounds and colour of pomegranate juice," *Food Chem.*, vol. 184, pp. 37–45, 2015.

[187] M. Türkyilmaz, Ş. Taği, U. Dereli, and M. Özkan, "Effects of various pressing programs and yields on the antioxidant activity, antimicrobial activity, phenolic content and colour of pomegranate juices," *Food Chem.*, vol. 138, no. 2–3, pp. 1810–1818, 2013.

[188] M. Reza, Y. Mohades, and M. Homayoonfal, "What is the concentration threshold of nanoparticles within the membrane structure ? A case study of Al2O3 / PSf nanocomposite membrane," *DES*, vol. 372, pp. 75–88, 2015.

[189] P. Onsekizoglu, "Production of high quality clari fi ed pomegranate juice concentrate by membrane processes," *J. Memb. Sci.*, vol. 442, pp. 264–271, 2013.

[190] I. Gil, F. A. Toma, B. Hess-pierce, D. M. Holcroft, and A. A. Kader, "Antioxidant Activity of Pomegranate Juice and Its Relationship with Phenolic Composition and Processing," no. series 1050, pp. 4581–4589, 2000.

[191] N. P. Seeram, M. Aviram, Y. Zhang, S. M. Henning, and L. Feng, "Comparison of Antioxidant Potency of Commonly Consumed Polyphenol-Rich Beverages in the United States," *J. Agric. Food Chem.*, vol. 56, no. 4, pp. 1415–1422, Feb. 2008.

[192] G. Mousavinejad, Z. Emam-Djomeh, K. Rezaei, and M. H. H. Khodaparast, "Identification and quantification of phenolic compounds and their effects on antioxidant activity in pomegranate juices of eight Iranian cultivars," *Food*

Chem., vol. 115, no. 4, pp. 1274–1278, 2009.

[193] Z. Kalaycıoğlu and F. B. Erim, "Total phenolic contents, antioxidant activities, and bioactive ingredients of juices from pomegranate cultivars worldwide," *Food Chem.*, vol. 221, pp. 496–507, 2017.

[194] R. E. Wrolstad, "Characterization and Measurement of Anthocyanins by UV-Visible Spectroscopy," pp. 1–13, 2001.

[195] B. Koroknai, Z. Csanádi, L. Gubicza, and K. Bélafi-Bakó, "Preservation of antioxidant capacity and flux enhancement in concentration of red fruit juices by membrane processes," *Desalination*, vol. 228, no. 1, pp. 295–301, 2008.

[196] H. Vardin and H. Fenercioglu, "Study on the development of pomegranate juice processing technology : Clarification of pomegranate juice," *Nahrung/Food*, pp. 2–5, 2003.