



# Clarification of Apple Juice Using New Generation Nanocomposite Membranes Fabricated with TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> Nanoparticles

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## Abstract

To enhance anti-fouling properties of polymeric membranes during apple juice clarification, PSF/PEI (20/2 wt%) ultrafiltration (UF) membranes were modified with TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles using the phase inversion method. Turbid apple juice samples were clarified using cross-flow membrane filtration system. All fabricated nanocomposite UF membranes had higher apple juice flux values than PSF/PEI membrane. Membrane prepared with 0.01% TiO<sub>2</sub> (UFT1) had the highest apple juice flux (at steady state, 44.6 L/m<sup>2</sup>h). The FRR (%) value of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> incorporated UF membranes was between 90.9–94.0% and 79.6–97.6%, respectively, and these FRR values were higher than that of PSF/PEI membrane (UF2, 60.3%). Porosity and hydrophilicity of the UF membranes significantly increased with the addition of nanoparticles and the highest porosity and hydrophilicity was achieved in the 0.01% TiO<sub>2</sub> incorporated UF membrane (UFT1) membrane. Higher flux recovery ratio (FRR) and lower relative flux reduction (RFR) values of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> incorporated nanocomposite membranes, compared with the unmodified membrane, demonstrated the enhancement in the anti-fouling properties of the PSF/PEI membrane. SEM images of the nanocomposite membranes also proved the nanoparticle incorporation to the PSF/PEI matrix. Color, turbidity, total soluble solid, total phenolic content, and antioxidant capacity of the samples using nanocomposite membranes were better than that of clarified using both commercial and unmodified membranes. TiO<sub>2</sub> incorporated nanocomposite membranes had superior performance than Al<sub>2</sub>O<sub>3</sub> incorporated nanocomposite membranes and among these membranes, the ones prepared with the addition of 0.01 wt% TiO<sub>2</sub> exhibit the best performance in terms of clarification of apple juice.

**Keywords** Nanocomposite membrane · TiO<sub>2</sub> nanoparticle · Al<sub>2</sub>O<sub>3</sub> nanoparticle · Clarification · Apple juice

## Introduction

In the past two decades, using membrane technology in food industry has been increased rapidly to a market volume of

€800–850 million. Although membrane processes are comparatively late technology, food industry has already used remarkably microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) pressure-driven membrane processes. In these processes, UF has the biggest market share. Due to high selectivity and low energy consumption, membrane processes are more desirable in food industry than conventional processes. In addition, when membrane processes are compared with conventional processes, they have significant advantages in terms of saving nutritious components like anthocyanins, carotenoids and vitamins, and sensory parameters like color, aroma, and flavor which are affected negatively from some kinds of treatments like chemical, biological, and heat (Lipnizki 2010). In fruit juice industry, UF membranes are utilized to clarify fruit juice by removing yeast, molds, microscopic organisms, and colloids besides proteins, tannins, and polysaccharides and to concentrate the juice as well (Alberto et al. 2014; Bhattacharjee et al. 2017; De Bruijn et al. 2003;

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Gulec et al. 2017; Mohammad et al. 2012; Onsekizoglu 2010; Oszmianski and Wojdylo 2007; Zhao et al. 2014).

UF 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. 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 (Bhattacharjee et al. 2017; Mulder 1996; Yoo et al. 2003). Fouling of the membrane causes a decrease in flux and rejection of the product while operating and therefore, energy consumption increases (Bhattacharjee et al. 2017; Lipnizki 2010). Modification of membrane surface is one of the ways to improve the anti-fouling characteristics by increasing the hydrophilicity. To overcome fouling problem, membrane surface can be modified using hydrophilic polymers such as polyvinyl pyrrolidone (PVP), polyethylene glycol (PEG), polyvinyl alcohol (PVA), and polyethylenimine (PEI). Among these hydrophilic polymers, PEI is a preferred modifying agent due to its pore forming ability (Saki and Uzal 2018). However, pore former ability of PEI can cause decrease in mechanical strength and selectivity of the membranes (Ba et al. 2009). Researchers are trying to overcome this problem by incorporating nanoparticles to the membrane matrix. Modification with nanoparticles enables PSF/PEI membranes to enhance selectivity, permeability, tensile strength, and thermal and chemical resistance (Baghbanzadeh et al. 2016; Saleh and Gupta 2012). There are some researches investigating the effect of TiO<sub>2</sub> nanoparticle incorporation on the hydrophilicity of polymeric membranes (Madaeni and Ghaemi 2007; Razmjou et al. 2011, 2012; Vatanpour et al. 2012; Yang et al. 2007). Many researchers also modified different polymeric membranes with Al<sub>2</sub>O<sub>3</sub> nanoparticles and demonstrated enhancing anti-fouling property, permeability, and porosity (Garcia-Ivars et al. 2014; Maximous et al. 2009; Uzal et al. 2017; Wang et al. 2006).

There are several studies investigating the effect of membrane filtration on the characteristics of apple juice using commercial membranes (Alberto et al. 2014; De Bruijn et al. 2003; Gulec et al. 2017; Onsekizoglu 2010; Oszmianski and Wojdylo 2007; Zhao et al. 2014). However, to the best of our knowledge, there are no reported data on applying TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> incorporated nanocomposite membranes for clarifying apple juice. Since modification of the polymeric membranes with TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> lead an increase in the anti-fouling properties, we have aimed to investigate the effect of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticle addition to the performance of PSF/PEI membranes for apple juice clarification. The nanocomposite membranes were characterized by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR), contact angle, and porosity experiments. To investigate anti-fouling properties of the membranes, flux recovery ratio (FRR), flux decay ratio (DR), and relative flux

reduction (RFR) values were also calculated. Color, total soluble solid content, turbidity, total phenolic content, and antioxidant capacity of the clarified apple juice samples were also characterized and compared with commercial clarified apple juice to determine the effect of the membranes to apple juice quality.

## Materials and Methods

### Apple Juice Samples

Apple juice samples were supplied from Döhler Inc. (Karaman, Turkey) in December 2017 and stored at  $-18\text{ }^{\circ}\text{C}$  until analysis. Döhler Inc. is one of the major concentrated fruit and vegetable juice producer in Turkey and the capacity reached to process 260,000 tons of fruits and vegetables. The turbid apple juice samples (S1) supplied from Döhler Inc. were subjected to the clarification process using new generation nanocomposite UF membranes to obtain clarified apple juice. Samples clarified with commercial UF membranes (S2) were also provided from the company for comparison. Turbidity of S1 and S2 samples were 478 NTU (nephelometric turbidity unit) and 0.34 NTU, respectively. Total soluble solid content of the samples was 16.5 °Brix and 16.2 °Brix, respectively.

### Membrane Fabrication

Nanocomposite UF membranes were fabricated by using the phase inversion method. PSF (polysulfone, MW 60,000, Acros Organics) and PEI (polyethylenimine, MW 25,000, Sigma-Aldrich, USA) concentrations in the membrane matrix were adjusted from Saki and Uzal's research (Saki and Uzal 2018). For the fabrication of the membranes, 20 wt% PSF, 2 wt% PEI, and TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles (titanium dioxide and aluminum oxide nanoparticles, Nanografi, Turkey) at different concentrations (0.01, 0.03, 0.05 wt%) were mixed and dissolved in a mixture of NMP (1-methyl-2-pyrrolidone, Merck, Germany) and DMF (N,N-dimethylformamide, Merck, Germany) at a ratio of 70:30. Solutions were mixed at 400 rpm using a magnetic stirrer for 12 h to obtain homogeneous mixtures. Then, the solutions were treated in an ultrasonic bath for at least 2 h to remove the bubbles. The composition of the membrane solutions prepared for apple juice clarification is shown in Table 1.

### Membrane Characterization

#### Scanning Electron Microscopy Analysis

Scanning electron microscope (Zeis Evo LS10, Germany) was used at 25 kV to analyze the top surface and cross-

section morphologies of the membranes. The size of membrane pieces was adjusted to approximately 1 cm<sup>2</sup>. 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 to 30,000 and 25,000 for surface and cross-section analyses respectively.

### Porosity

For the porosity measurements, the membranes (4 cm<sup>2</sup>) were immersed in ethanol for 2 h, then were removed from ethanol, and dried in the oven at 50 °C overnight to remove alcohol. The porosity ( $\epsilon$ ) of the membranes was calculated using Eq. (1) (Lohokare et al. 2011);

$$\epsilon = \frac{(W_i - W_f)/d_e}{\left(\frac{W_i - W_f}{d_w} + W_f\right)/d_p} \quad (1)$$

where,  $W_i$  is the weight of membrane (g) before ethanol immersion,  $W_f$  is the weight of membrane (g) after drying, and  $d_e$  and  $d_p$  represents densities of ethanol (0.788 g/cm<sup>3</sup>) and polymer (1.24 g/cm<sup>3</sup>), respectively.

### 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 (4  $\mu$ L) was measured. Measurement was replicated on three different points of membrane and contact angle value was given as average.

### Fourier-Transform Infrared Spectroscopy Analysis

FT-IR spectroscopy was used to determine the functional groups of membrane surface and to observe newly formed functional groups with the addition of PEI and TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles. For this purpose, an FT-IR with ATR crystal was used (Thermo Nicolet Avatar 370, USA). Before analysis, membranes were dried at 50 °C for one night. Measurement was carried out at the interval 400–4000 cm<sup>-1</sup> wavelength. Each spectrum was received after 32 scans.

### Cross-Flow Filtration

Cross-flow membrane filtration system (Sterlitech, Sepa CF, USA) with a filtration area of 150 cm<sup>2</sup> was used to perform filtration tests with 2 L of feed sample (distilled water/raw apple juice). The pressure of cross-flow filtration system was

adjusted to 5.4 bar, which is also used by Döhler Inc. Cross-flow membrane filtration tests was carried out for 120 min and 150 min until reaching steady-state conditions for apple juice filtration and pure water filtration, respectively. Cross-flow membrane 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 min and flux was calculated by using from Eq. (2).

$$J_w = \frac{V}{A \times t} \quad (2)$$

### Flux Recovery

In each cross-flow membrane filtration test, before and after apple 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), and relative flux reduction (RFR) were determined by using the water flux values according to the Eqs. (3), (4), and (5) respectively.

$$DR = \frac{J_1 - J}{J_1} \times 100 \quad (3)$$

$$FRR = \frac{J_2}{J_1} \times 10 \quad (4)$$

$$RFR = \left(1 - \frac{J_2}{J_1}\right) \times 100 \quad (5)$$

where,  $J$  is the flux value of fruit juices at steady-state (L/m<sup>2</sup>h);  $J_1$  is the pure water flux value before fruit juice filtration at steady state (L/m<sup>2</sup>h); and  $J_2$  is the pure water flux value after fruit juice filtration at steady state (L/m<sup>2</sup>h).

## Characterization of the Apple Juice Samples

### Color, Turbidity, and Total Soluble Solid Content

Color of the apple juice samples was determined by the standard ASTM method No: 1209 (ASTM D1209-05 2019) measuring the absorbance at 465 nm, using a spectrophotometer (DR 6000, Hach, UK). Turbidity of the samples was determined using a turbidity meter (Thermo Scientific, Eutech TN-100, Singapore) at room temperature and expressed in nephelometric turbidity units (NTU). Total soluble solid content (°Brix) of the samples was measured using a refractometer (DR-A1, Abbe ATAGO, Japan). All the analyses were repeated three times and the results were given as the average.

**Table 1** Composition of the nanocomposite UF membranes used for apple juice clarification

Membrane	PSF (wt%)	PEI (wt%)	TiO <sub>2</sub> (wt%)	Al <sub>2</sub> O <sub>3</sub> (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

### Determination of Total Phenolic Content

Total phenolic content of the apple juice samples were measured using the Folin-Ciocalteu method described by Spanos and Wrolstad (1990). For this purpose, clarified apple juice (100 µL) was mixed with distilled water (900 µL) in glass tubes and 5 mL of Folin-Ciocalteu phenol solution (0.2 N, Merck, Germany) was added to the tubes. The tubes were capped immediately and incubated in dark at room temperature for 8 min. At the end of the incubation, 4 mL of sodium carbonate (Anhydrous, Merck, Germany) solution (75 g/L) was added to the tubes and the capped tubes were incubated in dark at room temperature for 2 h. After incubation, the absorbance of the solutions was measured at 765 nm (UV-1800, Shimadzu, Japan). Gallic acid (Merck, Germany) was used as calibration reference standard (100–500 mg gallic acid/L methanol). The results were expressed as milligram gallic acid per liter of sample. All the analyses were repeated twice and the results were given as the average.

### Total Antioxidant Capacity

Total antioxidant capacity of the apple juice samples was determined by conducting two different methods: ABTS<sup>•+</sup> radical scavenging and DPPH radical scavenging.

ABTS radical activity was determined according to the method of Re et al. (Re et al. 1999). ABTS (3-ethylbenzothiazoline-6-sulfonic acid, Sigma-Aldrich, USA) solution (7 mM) and potassium persulfate (Merck, Germany) solution (2.45 mM) were mixed and incubated in dark at room temperature for 12–16 h to provide the formation of ABTS<sup>•+</sup> radical cation. Absorbance of ABTS<sup>•+</sup> solution was adjusted to 0.70–0.80 at 732 nm by diluting with 50% ethanol (Merck, Germany) solution (v/v). Diluted apple juice samples (1:2 with EtOH, 50 µL) were mixed with 3 mL ABTS<sup>•+</sup> solution and the absorbance was measured at 732 nm after 6 min (UV-1800, Shimadzu 1601,

Japan). Inhibition percentage was calculated according to Eq. (6)

$$\% \text{Inhibition} = [1 - (A_{\text{sample}} - A_{\text{radical solution}})] \times 100 \quad (6)$$

where  $A_{\text{sample}}$  is the absorbance of the sample 6 min after ABTS<sup>•+</sup> solution addition,  $A_{\text{radical solution}}$  is the absorbance of ABTS<sup>•+</sup> solution. Trolox (6-Hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, Sigma-Aldrich, USA) was used as calibration reference standard (0.5–2.0 mM/50% ethanol). The results were expressed as millimol trolox equivalent per liter of sample (mmol TEAC/L). All the analyses were repeated twice and the results were given as the average.

DPPH radical scavenging was determined according to the method of Anton et al. (Anton et al. 2009). The samples (200 µL) were mixed with 4 mL of DPPH (2,2-diphenyl-1-picrylhydrazyl, Sigma-Aldrich, USA) solution (0.1 mM in methanol) and the tubes were capped immediately and incubated in dark at room temperature for 30 min. The absorbance value of the samples was measured at 517 nm (UV-1800, Shimadzu, Japan) at the end of the incubation. Trolox (Sigma-Aldrich, USA) was used as the calibration reference standard (0.1–0.5 mM in 60% methanol). The results were expressed as millimol Trolox equivalent per liter of sample (mmol TEAC/L). All the analyses were repeated twice and the results were given as the average.

### Statistical Analysis

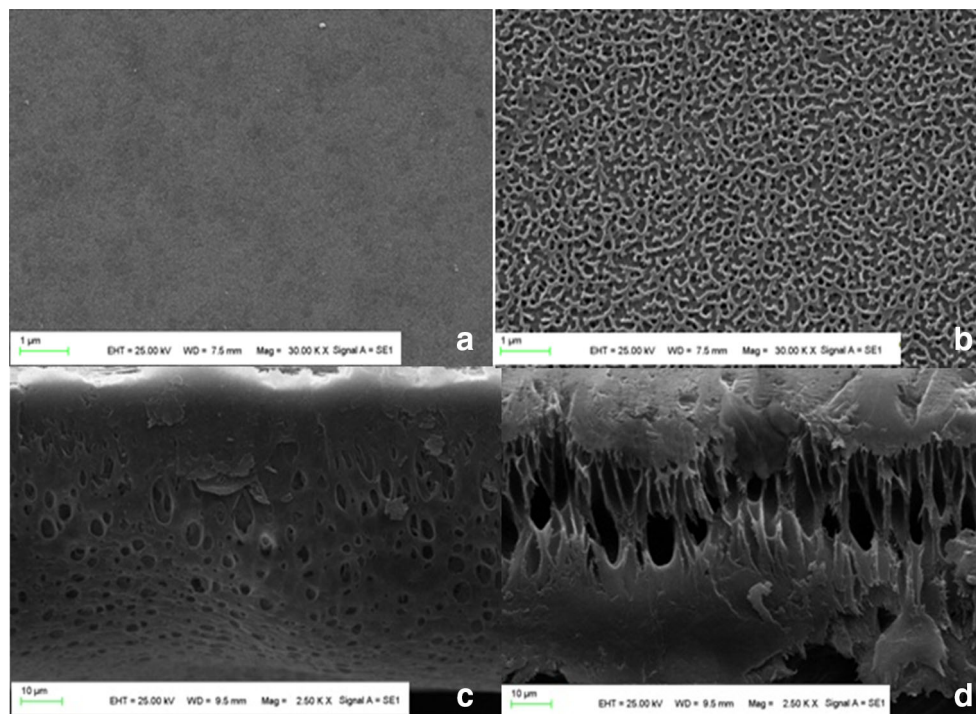
All data were expressed as mean ± standard deviation. Statistical analysis was conducted with one-way analysis of variance (ANOVA) using IBM SPSS Statistics 20 software. Duncan's test was used to detect the differences between the data and  $p < 0.05$  was considered to be statistically significant.

## Results and Discussion

### Membrane Characterization

#### Membrane Morphology

Membrane morphology analysis is an important tool to evaluate membrane filtration performance. To examine the morphological changes related to the addition of PEI and nanoparticles (TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>), the surface and cross-sections of the UF membranes were obtained by SEM. The surface and cross-section images of the UF1 and UF2 are shown in Fig. 1. Pure PSF membrane (UF1) has a smooth surface structure (Fig. 1a) and the membrane surface structure is completely changed by addition of PEI to the membrane matrix (UF2) and small pores are observed (Fig. 1b). While cross-section of



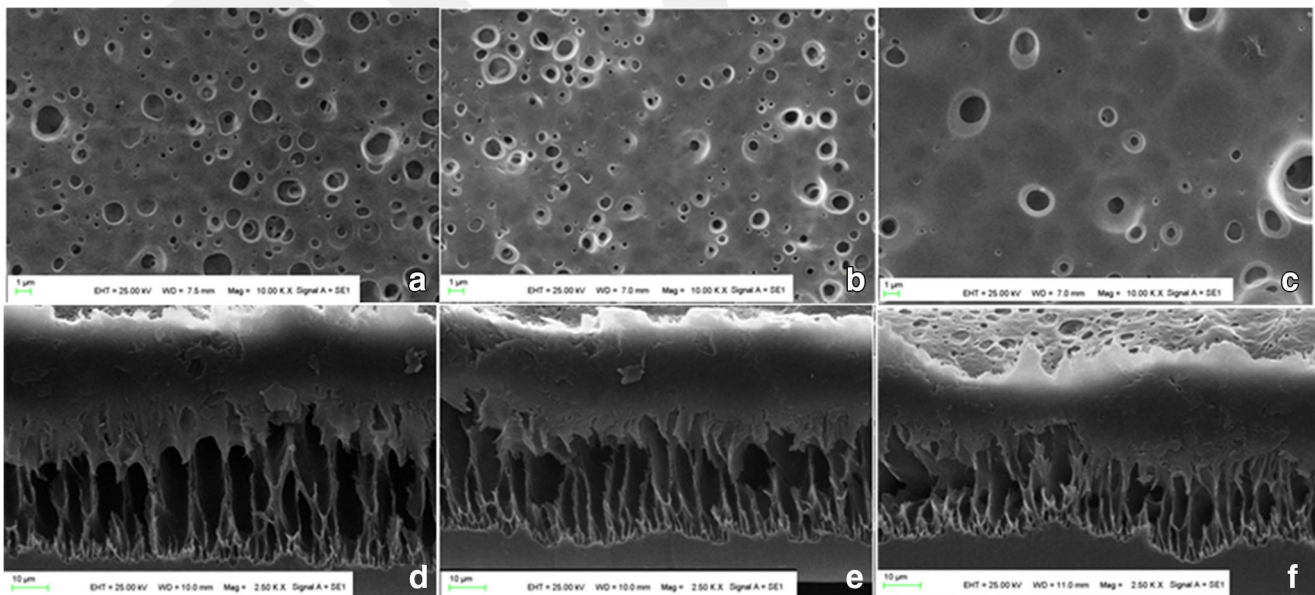
**Fig. 1** FT-IR spectrum of pure PSF membrane, PSF/PEI membrane and  $\text{TiO}_2$  incorporated nanocomposite UF membranes. UF1: 20% PSF; UF2: 20% PSF/2% PEI; T:  $\text{TiO}_2$ ; 1, 3, 5: 0.01, 0.03, 0.05 wt% nanomaterial incorporation ratios

UF1 had a dense structure (Fig. 1c), it was completely altered with the addition of PEI to the membrane matrix (UF2) (Fig. 1d). 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.

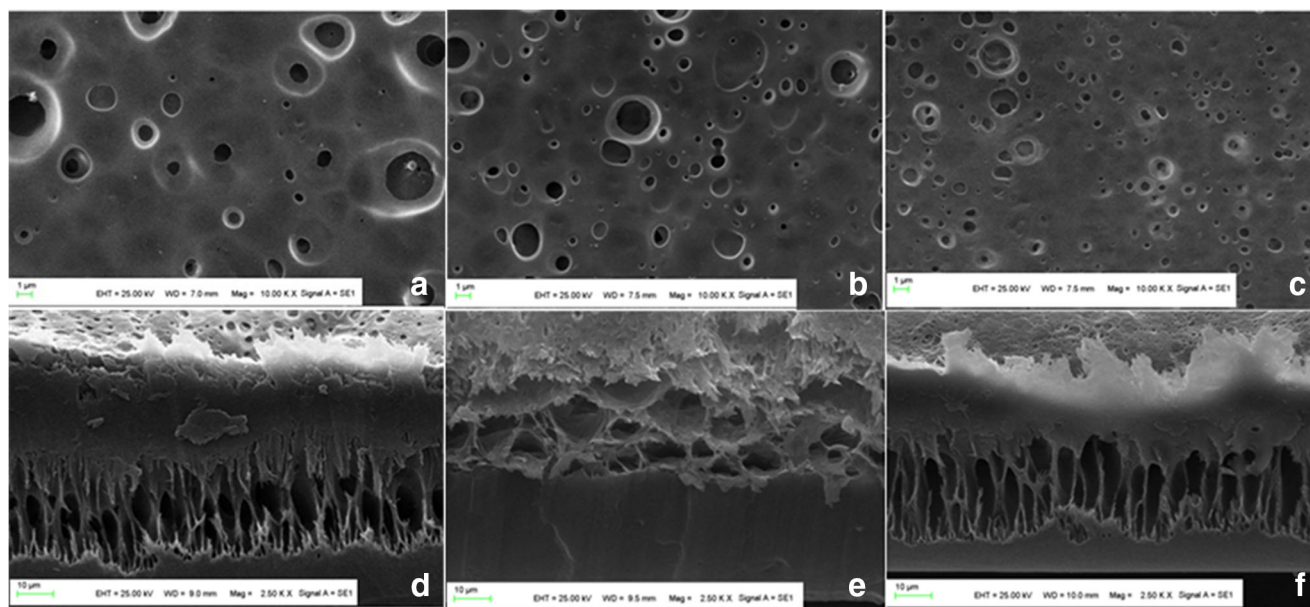
Surface and cross-sectional SEM images of the PSF/PEI/ $\text{TiO}_2$  membranes are given in Fig. 2. As can be seen from the

figure, with the addition of  $\text{TiO}_2$  nanoparticles, finger-like pores occurred and elongated between top surface and bottom surface of the UF membranes. Similar to our results, Razmjou et al. (Razmjou et al. 2011) also observed finger-like pores in the membranes modified with  $\text{TiO}_2$  nanoparticles.

Surface and cross-sectional SEM images of PSF/PEI/ $\text{Al}_2\text{O}_3$  membranes are given in Fig. 3. As can be seen from



**Fig. 2** FT-IR spectrum of pure PSF membrane, PSF/PEI membrane and  $\text{Al}_2\text{O}_3$  incorporated nanocomposite UF membranes. UF1: 20% PSF; UF2: 20% PSF/2% PEI; A:  $\text{Al}_2\text{O}_3$ ; 1, 3, 5: 0.01, 0.03, 0.05 wt% nanomaterial incorporation ratios



**Fig. 3** Apple juice flux values of PSF/PEI and TiO<sub>2</sub> (a) and Al<sub>2</sub>O<sub>3</sub>(b) incorporated nanocomposite UF membranes. UF2: 20% PSF/2% PEI; T: TiO<sub>2</sub>; A: Al<sub>2</sub>O<sub>3</sub>; 1, 3, 5: 0.01, 0.03, 0.05 wt% nanomaterial incorporation ratios

the figure, the increase in the concentration of Al<sub>2</sub>O<sub>3</sub> nanoparticles resulted in more uniformly dispersed micro- and macropores on the membrane surface. The cross-sections of Al<sub>2</sub>O<sub>3</sub> nanocomposite UF membranes also varied depending on the Al<sub>2</sub>O<sub>3</sub> nanoparticle concentration.

### Porosity

Porosity values of the nanocomposite UF membranes are shown in Table 2. 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 UFT1 membrane. Similar to our results, Razmjou et al. (Razmjou et al. 2011) also investigated an increase in the pore size and porosity of the membrane with the addition of TiO<sub>2</sub> nanoparticles. In addition, Uzal et al. (Uzal et al. 2017) observed an increase in the porosity ratio of modified nanocomposite membrane with the addition of Al<sub>2</sub>O<sub>3</sub> nanoparticles. Moreover, similar to the SEM results, porosity values of the membranes also indicated that nanoparticle incorporation led to an increase in porosity of the membrane.

### Membrane Hydrophilicity

Hydrophilicity of the nanocomposite UF membranes was determined by contact angle determination experiment and results are given in Table 2. According to these results, membrane UF1 had the highest contact angle value (96 ± 6°). With the addition of PEI and nanoparticles, contact angle values 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 UFTs had lower contact angle values than that of UFAs. Due to its high content of amine, PEI causes increases in the hydrophilic property and positive charge of the membranes (Albrecht et al. 2003; Trimpert et al. 2006). Among the UF membranes, UFT1 had the lowest contact angle (74 ± 3°) and therefore highest hydrophilicity. Similar to our results, Bae and Tak (Bae and Tak 2005) also reported that TiO<sub>2</sub> nanoparticles caused decreases in the contact angle values of the PSF membranes from 87.6 to 73.1°. Similar to our results, Al<sub>2</sub>O<sub>3</sub> nanoparticles caused decreases in the contact angle value of PVDF (polyvinylidene fluoride) UF membranes (Yan et al. 2006) and PSF membranes (Uzal et al. 2017). As stated in the membrane literature, the presence of inorganic oxide nanoparticles reduces the crystallinity of PSF and increases the amorphous portion (Ng et al. 2013). Therefore, the addition of both TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles improved the hydrophilicity and porosity of PSF/PEI membrane fabricated in this study (Table 2). Besides this, when compared with Al<sub>2</sub>O<sub>3</sub> nanoparticles, TiO<sub>2</sub> nanoparticles are known as their superior performance in generating highly oxidizing hydroxyl radicals, which readily attack and decompose and separate organic molecules (Choi et al. 2009). This could be the reason for improved hydrophilicity with PSF/PEI composite membrane containing TiO<sub>2</sub> compared with Al<sub>2</sub>O<sub>3</sub>. TiO<sub>2</sub> nanoparticles can assemble with the COOH group of the polymer and the surface hydroxyl group of TiO<sub>2</sub> to form hydrogen bond. This newly formed hydrogen bond leads to increase in hydrophilicity of the membrane (Lee et al 2000; Ng et al. 2013).

### FT-IR

The FT-IR spectrum of the pure PSF membrane, PSF/PEI membrane, and TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> incorporated UF membranes

**Table 2** Membrane characteristics of the nanocomposite UF membranes

Membrane	J1 (L/m <sup>2</sup> h)	J (L/m <sup>2</sup> h)	J2 (L/m <sup>2</sup> h)	DR (%)	FRR (%)	RFR (%)	Porosity (%)	Contact angle (°)
UF1	-	-	-	-	-	-	60.2 ± 2	96 ± 6
UF2	18.9	16.3	11.4	13.8	60.3	39.7	69.9 ± 3	88 ± 4
UFT1	171.4	44.6	160.0	74.0	93.3	6.7	75.8 ± 4	74 ± 3
UFT3	38.1	26.5	35.8	30.4	94.0	6.0	70.1 ± 5	79 ± 5
UFT5	80.0	34.9	72.7	56.4	90.9	9.1	71.7 ± 3	75 ± 2
UFA1	41.4	31.1	38.7	24.9	93.5	6.5	72.3 ± 3	81 ± 2
UFA3	68.5	41.4	54.5	39.6	79.6	20.4	70.5 ± 3	83 ± 3
UFA5	61.5	43.4	60.0	29.4	97.6	2.4	74.7 ± 2	80 ± 3

UF1: 20% PSF; UF2: 20%PSF/2%PEI; T: TiO<sub>2</sub>; A: Al<sub>2</sub>O<sub>3</sub>; 1, 3, 5: 0.01, 0.03, 0.05 wt% nanomaterial incorporation ratios

J1: pure water flux values before apple juice filtration; J2: pure water flux values after apple juice filtration; J: apple juice filtration flux values. DR, decay ratio; FRR, flux recovery ratio; RFR, relative flux reduction. Flux values are at the steady state

are shown in Figs. 4 and 5, respectively. As can be seen from the figures, the absorption peaks for pure PSF membrane (UF1) were detected as 1148 cm<sup>-1</sup> and 1168 cm<sup>-1</sup> (phenyl-carbonyl C–C stretching), 1242 (C–H stretching), 1537 cm<sup>-1</sup> (aromatic ring stretching), and 2965 cm<sup>-1</sup> (asymmetric and symmetric CH<sub>2</sub> stretching) (Avilés et al. 2009; Khalid et al. 2015). Due to low concentration of nanoparticles, no significant differences were observed in the FT-IR spectrum results of the membranes.

### Apple Juice Flux

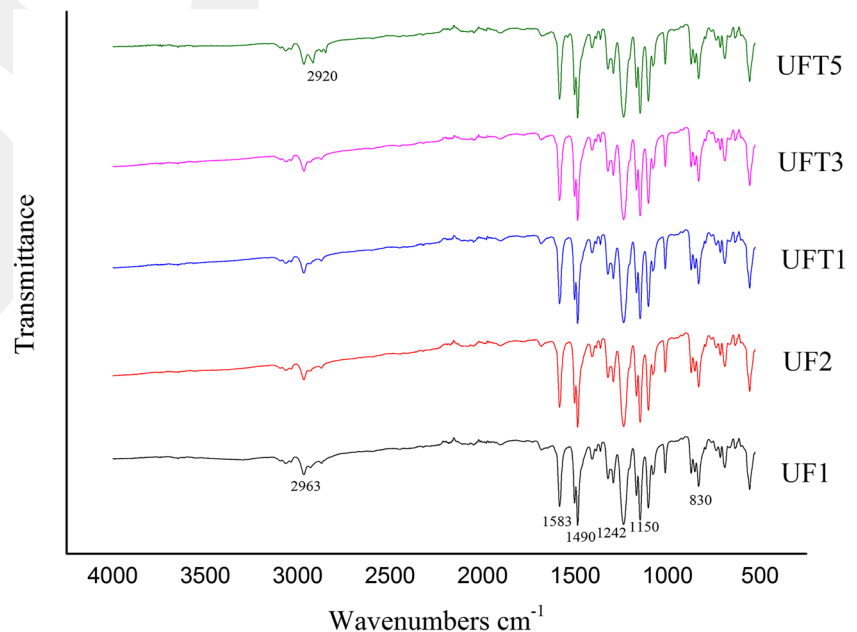
The effect of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticle (0.01, 0.03, 0.05 wt%) addition on the performance of PSF/PEI UF membranes was analyzed in terms of apple juice flux and results are shown in Fig. 6 a and b, respectively. As seen in Fig. 6, all nanocomposite UF membranes had higher apple juice flux values than the PSF/PEI membrane (UF2). Among the TiO<sub>2</sub>

incorporated UF membranes, UFT1 had the highest apple juice flux (steady state at 120 min; 44.6 L/m<sup>2</sup>h) (Fig. 6a). Among Al<sub>2</sub>O<sub>3</sub> incorporated membranes, the highest apple juice flux (steady state at 120 min; 43.4 L/m<sup>2</sup>h) was achieved with the UFA5 (Fig. 6b). Agglomeration of the TiO<sub>2</sub> nanoparticles leads to decrease in the apple juice flux. This agglomeration can be resulted from the increase in concentration of nanoparticles (Ng et al. 2013; Yu, Shen, & Xu, 2009) and ionic strength. The pH of the solution can also induce agglomeration (Gilbert, Ono, Ching, & Kim, 2009; Ng et al. 2013).

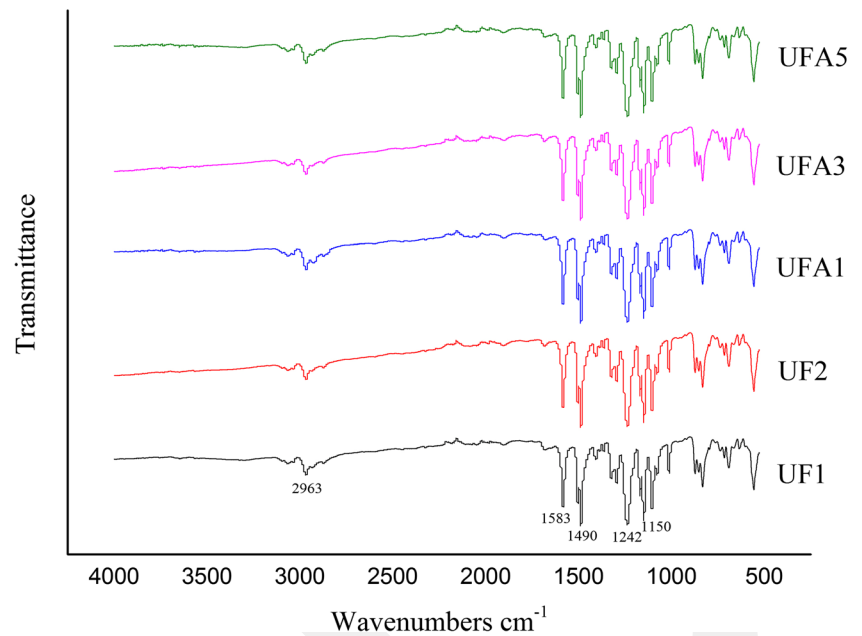
### Fouling

In membrane processes, the permeate flux decline is related directly to fouling. Pure water flux values before (J1) and after (J2) apple juice filtration, and apple juice flux (J) values were measured and decay ratio (DR), flux recovery ratio (FRR), and

**Fig. 4** SEM images of PSF/PEI/TiO<sub>2</sub> membranes. (a) UFT1 (b) UFT3 (c) UFT5 (d) Cross-section of UFT1 (e) Cross-section of UFT3 (f) Cross-section of UFT5. T: TiO<sub>2</sub>; 1, 3, 5: 0.01, 0.03, 0.05 wt% nanomaterial incorporation ratios

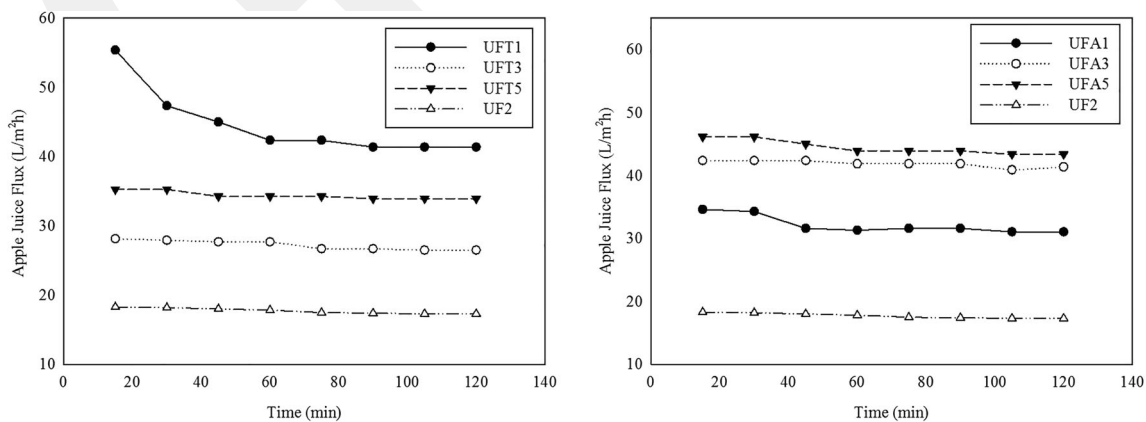


**Fig. 5** SEM images of PSF/PEI/ $\text{Al}_2\text{O}_3$  membranes. (a) UFA1 (b) UFA3 (c) UFA5 (d) Cross-section of UFA1 (e) Cross-section of UFA3 (f) Cross-section of UFA5. A:  $\text{Al}_2\text{O}_3$ ; 1, 3, 5: 0.01, 0.03, 0.05 wt% nanomaterial incorporation ratios



relative flux reduction (RFR) of the membranes were calculated. The results were shown in Table 2. The FRR (%) value of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  incorporated UF membranes were between 90.9–94.0% and 79.6–97.6%, respectively, and these FRR values were higher than that of UF2 (60.3%). On the contrary, the RFR (%) values of the nanocomposite UF membranes were lower than that of UF2. The high FRR values and low RFR values show the anti-fouling characteristic of the nanoparticle incorporated membranes. Similar to our results,  $\text{TiO}_2$  addition improved the anti-fouling properties of polyethersulfone (PES), polyacrylonitrile (PAN), polysulfone (PSF), and polyvinylidene fluoride (PVDF) membranes (Bae and Tak 2005; Cao et al. 2006; Wu et al. 2008; Yang et al. 2007). There are also some studies investigating the anti-fouling effect of  $\text{Al}_2\text{O}_3$  nanoparticle incorporation to the membrane matrix. Garcia-Ivars et al. (2014), Maximous et al. (2009), and Yan

et al. (2006) examined the effect of  $\text{Al}_2\text{O}_3$  nanoparticles on the performance of polyethyleneglycol (PEG), polyethersulfone (PES), and polyvinylidene fluoride (PVDF) membrane, respectively. Similar to our results, they also showed that  $\text{Al}_2\text{O}_3$  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 (Yan et al. 2006). Among the  $\text{TiO}_2$  nanoparticles incorporated UF membranes, 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 2). On the other hand, among the  $\text{Al}_2\text{O}_3$  incorporated UF membranes, the highest FRR value (97.6%) and lowest RFR value (2.4%) were achieved for the membrane UFA5 (Table 2).



**Fig. 6** SEM images of PSF and PSF/PEI membranes (a) UF1 (20%PSF) (b) UF2 (20%PSF/2%PEI), (c) Cross-section of UF1 (20%PSF), (d) Cross-section of UF2 (20%PSF/2%PEI)

## Apple Juice Characterization

Color, turbidity, total soluble solid content, total phenolic content, and total antioxidant capacity results of the apple juice samples, clarified using new generation nanocomposite membranes, are shown in Table 3. Turbid apple juice (S1) and clarified apple juice (S2) samples supplied from Döhler Inc. were also analyzed for comparison and the results were shown in Table 3.

Color is an important parameter of apple juice because of the quality perception of the consumers. The turbid apple juice sample (S1) obtained from Döhler Inc. was excluded from color analysis, because of its high suspended solid content which can cause misleading results. While 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 UFT1 had the highest color intensity (1232 Pt-Co) among the samples. According to these results, it can be said that color of the clarified apple juice was generally improved by using TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> incorporated membranes. 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.

Turbidity of turbid apple juice sample (S1) was measured as 478 NTU. As expected, the turbidity of the apple juice samples decreased with membrane filtration, considerably. The clarified apple juice of Döhler Inc. (S2) 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 (De Bruijn et al. 2003).

Nanomaterial incorporated UF membranes resulted less turbid apple juice samples than the unmodified PSF/PEI membrane (UF2). In addition, UFT1 and UFA5 had the highest performance in terms of turbidity among UFTs and UFAs respectively. Similar to our results Ngo et al. (2016) reported that the addition of TiO<sub>2</sub> nanoparticles improved the retention capacity of the UF membranes. He et al. (2007) 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®) (De Bruijn et al. 2003). The turbidity values obtained in this study 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 UF nanocomposite membranes is more sufficient than done with the commercial counterparts.

Total soluble solid content was measured as 16.5 °Brix and 16.2 °Brix for samples S1 and S2, respectively (Table 3). According to the results, application of UF process leads to decrease in total soluble solid content. Similar to our results, Pap et al. (2012) also observed total soluble solid content of black currant juice decreased from 15 °Brix to 14 °Brix after UF. Most of the samples clarified using nanomaterial incorporated UF membranes (UFTs and UFAs) had lower total soluble content when compared with sample S2. However, they all fulfilled the commercial specification in terms of total soluble solid content ( $\geq 10$  °Brix) (De Bruijn et al. 2003). The total soluble solid content of the sample clarified using the UFT1 membrane 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. Gulec et al. (2017) clarified apple juice using cross-flow filtration unit with three types of commercial UF membranes: US100, UH050, and UC030. They reported that total soluble solid content of apple juice

**Table 3** Color, turbidity, total soluble solid content, total phenolic content, and total antioxidant activity results of apple juice samples

Membrane	Color (Pt-Co)	Turbidity (NTU)	Total soluble solid (°Brix)	Total phenolic content (mg GAE/L)	ABTS (mmol TEAC/L)	DPPH (mmol TEAC/L)
UF2	910 ± 8	0.11 ± 0.07	13.0 ± 1	107.1 ± 1.8	0.68 ± 0.032	0.57 ± 0.003
UFT1	1232 ± 9	0.02 ± 0.05	16.2 ± 0.8	176.8 ± 1.22	1.56 ± 0.031	0.67 ± 0.030
UFT3	887 ± 7	0.1 ± 0.01	12.5 ± 0.7	169.3 ± 1.38	0.89 ± 0.010	0.50 ± 0.001
UFT5	740 ± 5	0.07 ± 0.01	13.5 ± 0.7	172.5 ± 0.8	0.97 ± 0.011	0.49 ± 0.003
UFA1	623 ± 5	0.02 ± 0.01	12.5 ± 1	108.2 ± 2.6	1.03 ± 0.010	0.42 ± 0.003
UFA3	785 ± 8	0.09 ± 0.02	14.2 ± 0.4	108.2 ± 1.8	1.08 ± 0.040	0.47 ± 0.003
UFA5	868 ± 8	0.01 ± 0	14.2 ± 0.5	110.4 ± 2.01	0.93 ± 0.060	0.51 ± 0.004
S2	754 ± 5	0.34 ± 0.01	16.2 ± 0.6	147.4 ± 2.54	1.16 ± 0.010	0.44 ± 0.001
S1	-	478 ± 1	16.5 ± 0.3	312.3 ± 0.49	2.58 ± 0.017	1.17 ± 0.001

UF2: 20%PSF/2%PEI; T: TiO<sub>2</sub>; A: Al<sub>2</sub>O<sub>3</sub>; 1, 3, 5: 0.01, 0.03, 0.05 wt% nanomaterial incorporation ratios

S2 (Döhler Inc.): clarified apple juice from Döhler Inc. S1 (Döhler Inc.): turbid apple juice from Döhler Inc

decreased from 11.9 °Brix to 9 °Brix, 8.8 °Brix, and 9.7 °Brix, respectively.

Phenolic compounds are substantial ingredients of apples as they contribute color and flavor of both fresh fruit and processed product (Varnam and Sutherland 1994). In addition, phenolic compounds are beneficial in promoting human health with protecting against numerous diseases occurred oxidative events (Candrawinata et al. 2014). The concentration of phenolic compounds in apple juice is reported to be affected by enzyme treatment, clarification, concentration, and storage conditions (Cliff et al. 2018; Gokmen et al. 2001; Spanos and Wrolstad 1990). Total phenolic content of the apple juice samples clarified using UFTs and UFAs are shown in Table 3. 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<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles (UFTs and UFAs) were used, the loss in total phenolic content was lower. The total phenolic content of the samples clarified with UFTs and 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 UFTs had higher total phenolic content than those of the ones clarified with UFAs. UFTs performed better performance than UFAs in terms of total phenolic substance preservation. The loss in total phenolic content of the samples clarified with the TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> incorporated membranes was between 43.4–45.8% and 64.7–65.4%, respectively. Among the UF membranes, the one prepared with UFT1 exhibits superior performance with leading 43.4% loss in total phenolic content. 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 cutoff commercial membranes were used for clarification, respectively. The loss in total phenolic content was calculated as 46% and 31%, respectively (Onsekizoglu 2010). 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 to 83 ± 3 mg GAE/L (74.6% loss) and 150 ± 5 mg GAE/L (54.1% loss), respectively (Alberto et al. 2014). Verma and Sarkar (Verma and Sarkar 2015) determined a decrease in total phenolic content of the apple juice from 455 ± 10 to 225 ± 5 mg GAE/L (50.6% loss) after clarification by UF (100-kDa cutoff). In addition, Sagu et al. (2014) used cross-flow filtration system and applied commercial polysulfone membranes with different molecular weight cut-offs to clarify banana juice. Similar to our apple juice flux (J) and total phenolic content results, they reported that maximum polyphenol content was obtained using UF membrane with

highest permeate flux. Since Al<sub>2</sub>O<sub>3</sub> is an amphoteric oxide, Al<sub>2</sub>O<sub>3</sub> incorporated membranes have charge. During apple juice clarification, Al<sub>2</sub>O<sub>3</sub> incorporated membranes will be charged positively due to acidic medium. Therefore, positively charged membranes cause more retention of phenolic compounds. Repulsive force occurs between the charge of membrane and phenolic compounds in the apple juice (Mohammad & Amin, 2013; Schaep, Vandecasteele, Leysen, & Doyen, 1998).

The total phenolics and flavonoids contribute to total antioxidant capacity significantly in apple juice (Pinelo et al. 2010; Verma and Sarkar 2015; Silvina and Frei 2004). Total antioxidant activities of the samples were analyzed with ABTS and DPPH radical scavenging methods and results are shown in Table 3. The ABTS antioxidant capacity of the turbid apple juice (S1) was measured as 2.58 mmol TEAC/L whereas clarification decreases the antioxidant capacity. The clarified apple juice sample of Döhler Inc. (S2) has an ABTS antioxidant capacity of 1.16 mmol TEAC/L. The commercial membrane used by Döhler Inc. caused 55.0% loss in terms of ABTS antioxidant capacity. The samples clarified with UFTs and UFAs had ABTS antioxidant capacity values between 0.89–1.56 mmol TEAC/L and 0.93–1.08 mmol TEAC/L, respectively. The lowest ABTS antioxidant capacity was achieved at the sample clarified with unmodified UF2 membrane, indicating that nanoparticle addition caused less antioxidant capacity loss during clarification. The loss in ABTS antioxidant capacity of the samples clarified with the UFTs and UFAs was between 39.5–65.5% and 58.1–63.9%, respectively. Among the clarified samples, the one clarified using UFT1 had the highest ABTS antioxidant capacity (1.56 mmol TEAC/L) and the lowest ABTS antioxidant capacity loss (39.5%). Oszmianski and Wojdyło (2007) clarified apple juice by using clarifying agent and characterized the clarified apple juice samples. The loss in ABTS antioxidant capacity (35.6%) was found to be comparable with our lowest ABTS antioxidant capacity loss (39.5%).

The DPPH antioxidant capacity 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 UFTs and UFAs had DPPH antioxidant capacity 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 capacity, clarification caused decreases in the DPPH antioxidant capacity. The commercial membrane used by Döhler Inc. caused 62.4% loss in terms of DPPH antioxidant capacity. The loss in DPPH antioxidant capacity of the samples clarified with UFTs and UFAs was between 42.7–45.8% and 64.7–65.4%, respectively. Similar to antioxidant capacity results, among the clarified samples, the one clarified using UFT1 had the highest DPPH antioxidant capacity (0.67 mmol TEAC/L) and the lowest DPPH antioxidant capacity 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% and 56.9% after clarification with Nylon-6 nanofibrous membrane and a polyamide membrane, respectively (Alberto et al. 2014). Oszmianski and Wojdyło (2007) clarified apple juice by using clarifying agent and loss in DPPH antioxidant capacity was found to be 56%. Also, Zhao et al. (2014) used commercial ceramic UF membrane to clarify apple juice and they reported 26.4% loss in DPPH radical scavenging activity.

As polyphenolic compounds have the ability to act as antioxidant compounds (Candrawinata et al. 2014), similar trend was achieved with the total phenolic content and antioxidant capacity of the samples. Similar to the total phenolic content value, highest total antioxidant content achieved in the sample obtained using UFT1. In addition, clarified apple juice samples obtained using UF2 had the lowest phenolic content as well as the total antioxidant content.

## Conclusion

In this study, new generation PSF-based nanocomposite UF membranes were fabricated using TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles and applied in apple juice clarification processes. Within this context, PEI was used as a pore former in the PSF polymer membrane matrix. Then, to enhance membrane performance, membranes were modified with incorporation of TiO<sub>2</sub> (UFTs) and Al<sub>2</sub>O<sub>3</sub> (UFAs) nanoparticles. Membrane performance was evaluated by both investigating the structure, physicochemical properties of membranes and clarification of apple juice. According to the membrane, characterization results such as hydrophilicity, porosity, pure water, and apple juice fluxes increased with the addition of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles. The membranes prepared with 0.01 wt% TiO<sub>2</sub> (UFT1) and 0.05 wt% Al<sub>2</sub>O<sub>3</sub> (UFA5) membrane had the highest hydrophilicity (lowest contact angle), porosity, and apple juice fluxes among the fabricated UFTs and UFAs, respectively. Flux recovery experiments were carried out to determine anti-fouling properties of nanocomposite UF membranes. The FRR value of the nanocomposite UF membranes was higher than that of the unmodified UF membrane (UF2), whereas RFR value of the nanocomposite membranes was lower with demonstrating the enhancement in the anti-fouling property of the membranes. TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticle addition led an increase in the hydrophilicity of the membranes. According to the clarified apple juice characteristics (color, turbidity, total soluble solid, total phenolic content, antioxidant capacity), clarified apple juice samples obtained using the membranes incorporated with TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles had higher quality than the ones obtained from unmodified membrane (UF2). Overall results showed that there is a great potential to use TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> incorporated new generation nanocomposite membranes with enhanced performance in the apple juice

clarification process. Among these nanoparticles, TiO<sub>2</sub> nanoparticle is more suitable than Al<sub>2</sub>O<sub>3</sub> to use as modifying agent for apple juice clarification. Further investigations will be carried out for the clarification process of different fruit/vegetable juices using various nanomaterials such as nanoclay, which is also environment friendly.

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## Compliance with Ethical Standards

**Conflict of Interest** The authors declare that they have no conflicts of interest.

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