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# Effect of $TiO_2$ nanoparticles on antifouling and separation properties of PVDF/PAN blend membrane

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## ABSTRACT

Recently, membrane fouling has been one of the most important issues in the field of membrane technology. In this regard, $TiO_2$ nanoparticles blended with polymeric membranes have shown to improve fouling performance. In this study, a new PVDF/PAN/$TiO_2$ ultrafiltration blend membrane was prepared via phase inversion by dispersing $TiO_2$ nanoparticles in the PVDF/PAN casting solutions. The effect of different concentrations of $TiO_2$ on the characteristics of membranes (i.e., morphology, hydrophilicity, permeation performance, and antifouling properties) was investigated. Results of scanning electron microscopy analysis showed the finger-like pores and macrovoids decrease due to the presence of $TiO_2$ in the membrane matrix. Concurrently, contact angles results showed that the membranes hydrophilicity was enhanced by the addition of $TiO_2$ nanoparticles. Cross flow filtration of pure water flux and buffered bovine serum albumin solution were used to investigate performance of the membranes in the presence of $TiO_2$ nanoparticles. The experimental results indicated that PVDF/PAN/$TiO_2$ membranes exhibited improved pure flux (398.5 L/$m^2$ h) as well as antifouling properties (flux recovery ratio 93.64%) due to the addition of 1 wt.% $TiO_2$. However, greater concentrations of $TiO_2$ decreased improvement of antifouling properties.

*Keywords:* PVDF; Blend membrane; $TiO_2$ nanoparticles; Hydrophilicity; Antifouling property

## 1. Introduction

In recent years, membranes have been widely used in many separation processes owing to the development of industries and problem of water pollution. Polymeric membranes are still widely used in membrane separation processes for the advantages of their separation properties, forming ability, and low price [1–3]. The surface properties of the membranes such as pore size, porosity, and hydrophilicity play an important role in membrane separation processes. A suitable membrane must have high permeability, good antifouling property, and a good chemical resistance to the feed [4].

Among all polymer materials to fabricate membranes, PVDF is one of the best due to its antioxidation, thermal, mechanical, and membrane forming properties. Because of all the mentioned properties, PVDF is an excellent polymer used to prepare UF membrane materials [5–10]. However, the hydrophobic nature of PVDF is responsible for its fouling by proteins and some other pollution in water and wastewater treatment plants. Therefore, this property of PVDF results in membrane fouling and permeability decline, which has become an obvious disadvantage for its

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application in separation processes [11]. Many techniques including physical blending, chemical grafting, and surface modifying have been studied to improve the hydrophilicity of membranes. Among such methods, blending with inorganic materials, especially nanoparticles, has drawn great attention because of their easy preparation and good compatibility with the method of phase inversion, which has been widely endorsed as a method for preparation of asymmetric polymeric ultrafiltration membranes [10].

There are many studies which have used inorganic nanoparticles to prepare polymeric membranes such as $SiO_2$ [12], $Al_2O_3$ [13], $Fe_3O_4$ [14], ZnO [15], $ZrO_2$ [16], CdS [17], and $TiO_2$ [18–28]. Among these nanoparticles, $TiO_2$ has gained the most attention because of its stability, availability, high hydrophilicity, and good antibacterial property. Recent studies have shown that $TiO_2$ nanoparticles can mitigate fouling of the PVDF membrane in the membrane bioreactor (MBR) system due to the improvement of the hydrophilicity of PVDF membranes which results in flux enhancement [19,20]. Therefore, it has been used for surface modification of several membranes to improve their antifouling properties.

Bae and Tak [19] discovered that the $TiO_2$ entrapped membrane showed lower flux decline compared with the neat polymeric membrane and membrane fouling was reduced by $TiO_2$ nanoparticles. Yang et al. [21] found out that adding $TiO_2$ to the PSF membrane improved the hydrophilicity and the antifouling ability of the membrane. At the same time, the improvement of membrane hydrophilicity also enhanced the flux rate and increased work efficiency of the membrane in treatment of kerosene emulsified wastewater. In addition, Rahimpour et al. [28] prepared a PVDF/SPES blend membrane with appropriate antifouling and antibacterial properties using $TiO_2$ nanoparticles.

To our best knowledge, the effect of $TiO_2$ addition to the PVDF/PAN blend to prepare ultrafiltration membranes has not been investigated, while its effect on hydrophilicity and antifouling property is significant according to our results.

In the previous work [29], we prepared a PVDF/PAN blend membrane, in which PAN was used as a hydrophilic polymer in order to increase hydrophilicity of PVDF membrane, in the presence of polyvinylpyrrolidone (PVP) as a pore former in the casting solution. PAN was added to the casting solution as a blending polymer to PVDF for improvement of antifouling properties as a result of PAN's considerable hydrophilicity. Despite the significant improved antifouling properties of PVDF/PAN blend membrane, the increment of permeate flux was still low that approves the requirement of applying a suitable additive [30]. PVP has been used as a competent additive to improve the permeate flux. Even though, the PVP is a typical hydrophilic agent, its effect on the antifouling property is almost constant since the formation of larger pores and increase of hydrophilicity neutralize each other, and no net difference has been detected in the total fouling resistance [29]. Therefore, in order to obtain relatively high pure water flux (PWF) along with antifouling properties, it is essential to apply PAN and PVP into PVDF casting solution [29,30]. Results demonstrated that hydrophilicity, permeability, surface pore size, and sub-layer porosity were significantly improved by adding 10 wt.% PAN [30] and 4 wt.% PVP [29]. In this study, the effect of $TiO_2$ nanoparticles on the performance of blend polymeric membrane has been studied. The concentrations of $TiO_2$ nanoparticles were 0, 0.5, 1, 1.5, 2 wt.% in the casting solution. The effects of different compositions of $TiO_2$ on the structure morphology, and hydrophilicity of the PVDF/PAN membranes were investigated by scanning electron microscopy (SEM) and contact angles measurement. The performance of prepared membranes was investigated by pure water flux, retention efficiency, bovine serum albumin (BSA) flux, and determination of the fouling resistances of membranes. Energy dispersion of X-ray (EDX) analysis was also carried out to investigate the distribution of $TiO_2$ nanoparticles on the membrane structure.

## 2. Experimental

### 2.1. Materials

Polyvinylidene fluoride (PVDF with MW = 573,000 Da) and polyacrylonitrile (PAN, MW = 150,000 Da) were supplied from Solvay (France) and Sigma-Aldrich (Germany), respectively. The solvent N,N-dimethylacetamide (DMAc) was obtained from Merck (Germany). Polyvinylpyrrolidone (PVP, MW = 25,000 Da) as a pore former in the casting solutions was purchased from Merck (Germany). The main non-solvent in the coagulation bath was de-ionized water. $TiO_2$ nanoparticles (with average size of 20–30 nm) were purchased from Sigma-Aldrich (Germany). In order to evaluate membrane rejection, BSA (MW = 67,000 g/mol) was used which was obtained from Merck (Germany). In addition, PEO (MW = 100,000 Da) and PEG (MW = 35000 Da) were purchased from Sigma-Aldrich (Germany).

### 2.2. Membrane preparation

Polymers were placed in an oven for 2 h at 80°C to remove their humidity. $TiO_2$ nanoparticles were added to the solvent and to avoid aggregation, ultrasound homogenizer was used. Based on our previous work [29], the best composition of PVDF/PAN/PVP was obtained 90/10/4. Different ratios of $TiO_2$ (0, 0.5, 1, 1.5, 2 wt.%), as shown in Table 1, were added to the solution. Hence, different ratios of PVDF/PAN/PVP/$TiO_2$ were mixed with DMAc for 48 h at 50°C. For bubble removal of prepared casting solutions, they were put in a stagnant place for a day. A Polyvisc digital rheometer (Anton paar, UK, model Physica MCR 5, 1) was used to measure the viscosity of the prepared casting solutions (shown in Table 2). Then, the casting solution was casted on a flat glass and submerged in DI water bath at room temperature. The prepared membranes were kept in deionized water.

Table 1
Composition of casting solutions

| Membrane Code | PVDF/PAN (wt.%) | PVP (wt.%) | $TiO_2$ (wt.%) | DMAC (wt.%) |
|---|---|---|---|---|
| | 90/10 | | | |
| PAP4 | 18 | 4 | 0 | 78 |
| PAT0.5 | 18 | 4 | 0.5 | 77.5 |
| PAT1 | 18 | 4 | 1 | 77 |
| PAT1.5 | 18 | 4 | 1.5 | 76.5 |
| PAT2 | 18 | 4 | 2 | 76 |

Table 2
Porosity, viscosity, and equilibrium water content of PVDF/PAN/PVP/$TiO_2$ membranes

| Membrane | ε (%) | Viscosity (Pa.s) | EWC (%) |
|---|---|---|---|
| PAP4 | 93.97 | 58.2 | 76.1 |
| PAT0.5 | 85.23 | 63.4 | 78.99 |
| PAT 1 | 89.61 | 65.1 | 80.1 |
| PAT1.5 | 83.54 | 68.2 | 82.2 |
| PAT 2 | 77.73 | 78.5 | 82.95 |

### 2.3. Membrane characterization

#### 2.3.1. SEM and EDX analysis

In order to observe the cross-sectional and surface area of the dry membranes, a model VEGA3 (TESCAN, Czech republic) SEM was used. Energy dispersion of X-ray device EDX (VEGA3, TESCAN, and Czech Republic) was used for detection of the presence and dispersion quality of $TiO_2$ on the membrane surface.

#### 2.3.2. Contact angle measurement

Contact angle goniometer (KSV Cam 200 instrument, Finland) was used to measure contact angle between surface of prepared membrane and a droplet of water. The average of four contact angle measurements is reported for each sample.

#### 2.3.3. Porosity and the equilibrium water content determination

Based on gravimetric method, membrane porosity (ε, %) can be determined by Eq. (1):

$$\varepsilon = \frac{m_1 - m_2}{\rho_w \times A \times L} \tag{1}$$

In which $m_1$ is the wet membrane weight (g), $m_2$ is the dry membrane weight, $\rho_w$ is water density, $A$ is the effective membrane surface (4 $cm^2$), $L$ is the thickness of membrane (μm) [27].

Equilibrium water content of membrane was calculated by Eq. (2) [23]:

$$\text{EWC\%} = \frac{m_1 - m_2}{m_1} \times 100 \tag{2}$$

### 2.4. Filtration tests and fouling analysis

#### 2.4.1. Permeability of membranes

The permeation flux and rejection of the prepared membranes (effective area of 33.3 $cm^2$) were measured by UF cross flow filtration setup which has been shown in detail in our previous work [29]. The filtration test was performed for 1 h at a transmembrane pressure of 200 kPa for compaction of the prepared membranes. After conditioning of membranes, the permeability measurements were done.

Membrane PWF was calculated at 100 kPa based on Eq. (3):

$$J_{w1} = \frac{V}{A \times \Delta t} \tag{3}$$

where $J_{w1}$: PWF $\left(\frac{L}{m^2h}\right)$, $V$: volume of permeate stream (L), $A$: membrane area ($m^2$), and $\Delta t$: permeability time (h) [28].

#### 2.4.2. Solution rejection and analysis of membrane fouling

In order to investigate membrane fouling, UF experiments were performed by protein solution of BSA (1 g/L) dissolving in DI water. In all experiments, phosphate buffer saline was used to maintain pH of solution at 7.2. Based on Eq. (3), protein solution flux ($J_p$) was obtained. In addition, BSA rejection of membrane was evaluated by Eq. (4) [28]:

$$R(\%) = \left[1 - \frac{C_p}{C_f}\right] \times 100 \tag{4}$$

where $C_p$ is the protein concentration in permeate and $C_f$ is the protein concentration of feed solution. UV spectrophotometer (Shimadzu UVmini-1240, Japan) in 280 nm was employed to determine the protein concentrations. Then, membranes were washed by DI water and PWF of the washed membranes ($J_{w2}$) were measured from Eq. (3). Consequently, flux recovery ratio (FRR) was determined by using Eq. (5) to analyze the membranes fouling:

$$\text{FRR}(\%) = \left(\frac{J_{w2}}{J_{w1}}\right) \times 100 \tag{5}$$

In addition, the fouling resistant potential of blend membranes was calculated using below equations to fouling study in detail. The first ratio was $R_t$ which represents total flux decrease:

$$R_t = 1 - \frac{J_p}{J_{w1}} \tag{6}$$

To evaluate flux reduction due to reversible and irreversible fouling, $R_r$ and $R_{\text{ir}}$ were defined, respectively:

$$R_r = \frac{J_{w2} - J_p}{J_{w1}} \tag{7}$$

$$R_{\text{ir}} = \frac{J_{w1} - J_{w2}}{J_{w1}} \tag{8}$$

where $R_t = R_r + R_{\text{ir}} = \frac{J_{W1} - J_p}{J_{W1}}$ [28].

#### 2.4.3. Molecular weight cut-off measurement

The molecular weight cut-off (MWCO) of membranes, which is the lowest molecular weight with a solute rejection of 80%–100%, was measured by filtration of 1 wt.% PEG solution (molecular weights of 35, 68, and 100 kDa). UV–Vis spectrophotometer at a wavelength of 535 nm was used for the determination of the PEG concentration in feed and permeate solutions [20].

## 3. Results and discussion

The miscibility of the two polymers is a critical parameter for blending membranes since it can affect the morphology of the resulting membranes [19]. Based on our previous study [30], choosing DMAc, as a good solvent for dissolving polar substances, provides miscibility of PAN and PVDF to some extent. In this study, the influence of $TiO_2$ on the fouling property of this blend membrane was evaluated as described in the following sections.

### *3.1. EDX analysis of $TiO_2$*

The presence of $TiO_2$ nanoparticles was investigated by EDX analysis confirming their existence on the top surface of the composite membranes. The surfaces of membranes have been analyzed since it is important to have an estimation of $TiO_2$ nanoparticles on the surface to evaluate its degree of hydrophilicity, which is inversely proportional to the extent of fouling in wastewater treatment. As shown in Fig. 1, the peak observed around 4.5 keV belongs to Ti, the peak around 0.7 keV belongs to Fluorine (which comes from PVDF), and the peak about 0.3 keV represents PAN. The Ti peaks can be observed in the spectrum of the composite membrane as shown in Fig. 1 for each nanocomposite membrane. The EDX quantitative amounts of the elements for each composite membrane are illustrated for comparison in the tables inside. It is obvious that the Ti amounts are relatively in agreement with the added amounts to the base solutions.

### *3.2. Hydrophilicity of $TiO_2$ entrapped PVDF/PAN blend membrane*

Generally, the hydrophilicity is evaluated by measuring contact angle between a small droplet of water and the flat surface of the membrane [23]. It should be noted that the contact angle has reverse proportion with hydrophilicity. As shown in Fig. 2, the addition of $TiO_2$ causes the decrease of contact angle which indicates the significant effect of $TiO_2$ on the hydrophilicity. It can be explained by considering the high affinity of $TiO_2$ nanoparticles to water leading adsorption of more water molecules. Therefore, more water molecules will be attracted to the membrane surface in the presence of $TiO_2$ which leads to high hydrophilicity.

### *3.3. Morphological studies*

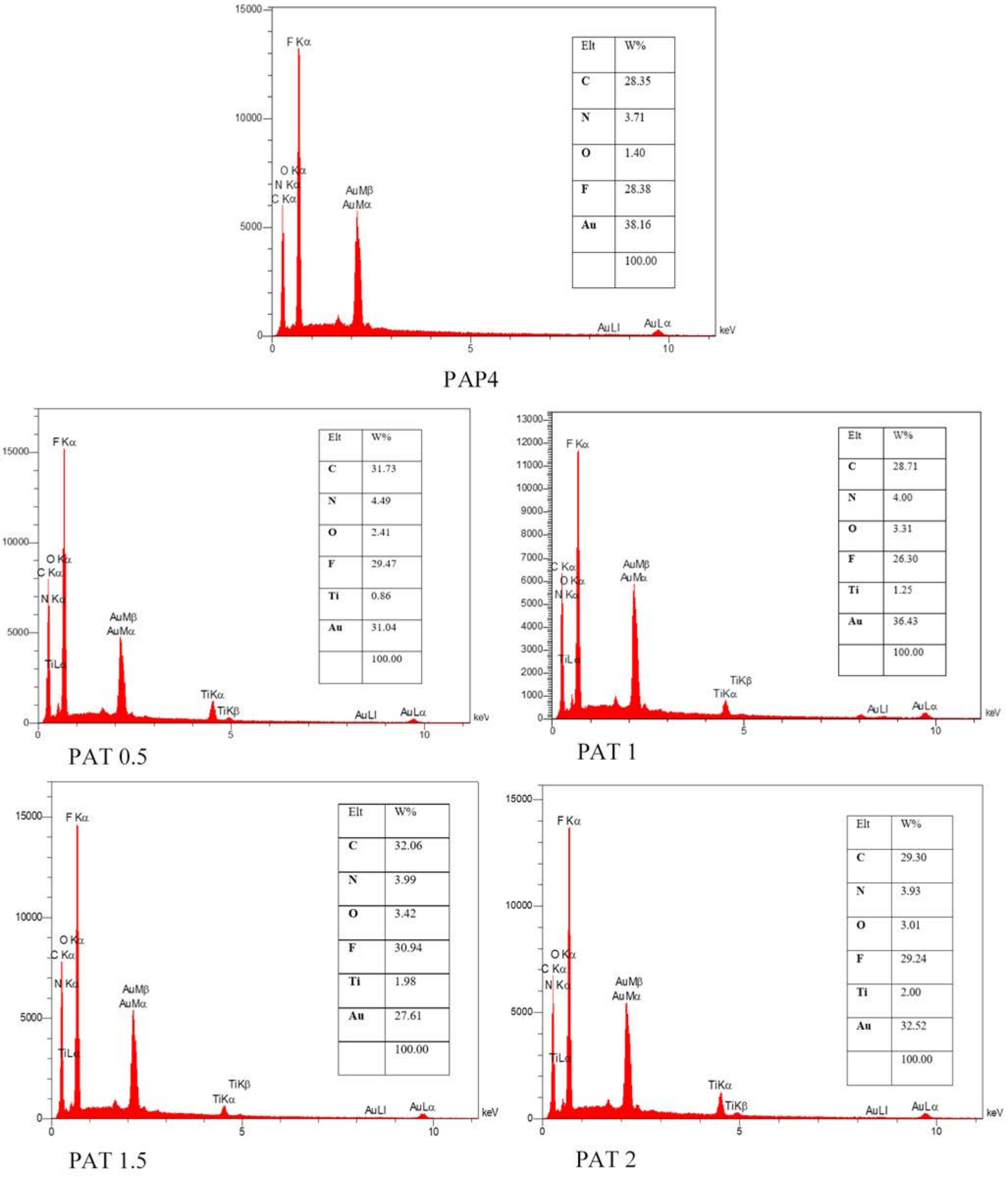
In order to understand the influence of $TiO_2$ concentration on the final membrane structure, the cross-section of the prepared membranes, with the film thickness of 250 ± 20 μm was observed using SEM and shown in Fig. 3. As it is clear, all the membranes are finger-like and have large macrovoids in the sub layer. However, the cross-sectional morphology of the prepared membranes with the addition of 1, 1.5, and 2 wt.% of $TiO_2$ is slightly different from the membrane without nanoparticles. A comparison between images in Fig. 3 shows that the finger-like and macrovoids decrease due to $TiO_2$ presence in the membrane matrix, which creates the smaller voids into the polymeric membrane matrix and so decreases the porosity which is in agreement with porosity results in Table 2.

Based on the porosity amounts in Table 2, by increasing $TiO_2$ concentration up to 1.5 wt.% no significant porosity changes have occurred. However, increase of $TiO_2$ concentration to about 2 wt.%, the porosity decreases because of increasing of the casting solution viscosity and subsequently delay of phase inversion. However, the inherent hydrophilic character of $TiO_2$ favors the water penetration into the polymer matrix which is the reason of the higher hydrophilicity observed for the modified membranes as shown in previous section.

To study the effect of $TiO_2$ nanoparticles on microstructure of the membranes, top surface SEM photographs of the PVDF/PAN membranes without and with different concentrations of $TiO_2$ in the casting solution are depicted in Fig. 4. The existence of $TiO_2$ particles on the surface has been obviously seen. As the concentration of $TiO_2$ in the coagulation bath increases, as it is obvious, more agglomeration of $TiO_2$ nanoparticles would be formed on the top surface of the membranes. It is indicated that better distribution of $TiO_2$ nanoparticles formed on the surface of the membrane with 1 wt.% $TiO_2$ in the casting solution.

### *3.4. Performance and antifouling properties of the membranes*

The effect of $TiO_2$ nanoparticles on the permeability and rejection capacity was investigated through UF experiments. As shown in Fig. 5, the flux of PVDF/PAN membranes in the presence of $TiO_2$ increased notably compared with the blend membrane without nanoparticles. Increment of flux was obtained as a result of higher hydrophilicity with $TiO_2$ addition leading to attraction of water molecules into the membrane matrix and promoted to pass through the membrane. In addition, the BSA rejection of membranes with $TiO_2$ reduced comparing with the neat blend membrane. However, the increase of flux and decrease of rejection continued up to 1 wt.% $TiO_2$ and then flux decreased and rejection increased as the added $TiO_2$ composition reached to 2 wt.%. The maximum flux was 398.5 L/m$^2$ h for pure water and the minimum rejection was 56% at 1 wt.% $TiO_2$. Due to significant influence of $TiO_2$ on the hydrophilicity, membrane flux increased; although by adding $TiO_2$ up to 1 wt.% membrane porosity and pore size decreased. In other words, the increase of hydrophilicity because of adding $TiO_2$ up to 1 wt.% has the dominant effect on flux and rejection compared with obstruction of pores due to the increase of viscosity, which causes decrease of membrane porosity. On the other hand, by addition of $TiO_2$ more than 1 wt.%, membrane flux decreased and rejection increased owing to the aggregation tendency of nanoparticles so that pores would be obstructed. It can be concluded that there is no specific and identical trend for effect of adding $TiO_2$ on membrane performance as the different trend has been observed in the other research which investigated the effect of $TiO_2$ to PVDF/SPES blend membrane [28]. Ergo, it is worth evaluating



PAP4

| Elt | W% |
|---|---|
| **C** | 28.35 |
| **N** | 3.71 |
| **O** | 1.40 |
| **F** | 28.38 |
| **Au** | 38.16 |
|  | 100.00 |

PAT 0.5

| Elt | W% |
|---|---|
| **C** | 31.73 |
| **N** | 4.49 |
| **O** | 2.41 |
| **F** | 29.47 |
| **Ti** | 0.86 |
| **Au** | 31.04 |
|  | 100.00 |

PAT 1

| Elt | W% |
|---|---|
| **C** | 28.71 |
| **N** | 4.00 |
| **O** | 3.31 |
| **F** | 26.30 |
| **Ti** | 1.25 |
| **Au** | 36.43 |
|  | 100.00 |

PAT 1.5

| Elt | W% |
|---|---|
| **C** | 32.06 |
| **N** | 3.99 |
| **O** | 3.42 |
| **F** | 30.94 |
| **Ti** | 1.98 |
| **Au** | 27.61 |
|  | 100.00 |

PAT 2

| Elt | W% |
|---|---|
| **C** | 29.30 |
| **N** | 3.93 |
| **O** | 3.01 |
| **F** | 29.24 |
| **Ti** | 2.00 |
| **Au** | 32.52 |
|  | 100.00 |

Fig. 1. EDX analysis of PVDF/PAN/PVP/$TiO_2$ blend membranes.

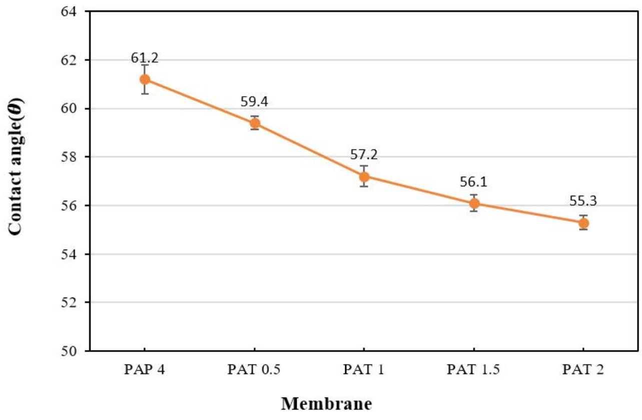


Fig. 2. Contact angle of PVDF/PAN/PVP/$TiO_2$ membranes.

the effect of $TiO_2$ nanoparticles for different types of blend membranes.

The antifouling properties of PVDF/PAN/$TiO_2$ UF membranes could be evaluated by comparing PWF values, before and after BSA solution filtration which are presented in Fig. 6. The PWF of membranes after BSA solution filtration ($J_{w2}$) declined relative to PWF before BSA filtration ($J_{w1}$). This reduction, which happens due to the membrane fouling, is minimum for the membrane with addition of 1 wt.% $TiO_2$ in the casting solution due to the dominant effect of hydrophilicity which increases by adding nanoparticles. In other words, adding $TiO_2$ is the main reason for the improvement of membrane antifouling properties in terms of lower reduction of PWF after BSA filtration ($J_{w2} - J_{w1}$). However, this reduction is obvious up to the adding 1 wt.% $TiO_2$ whereas adding more $TiO_2$ supports the decrease of $J_{w2}$. This is related to the effect

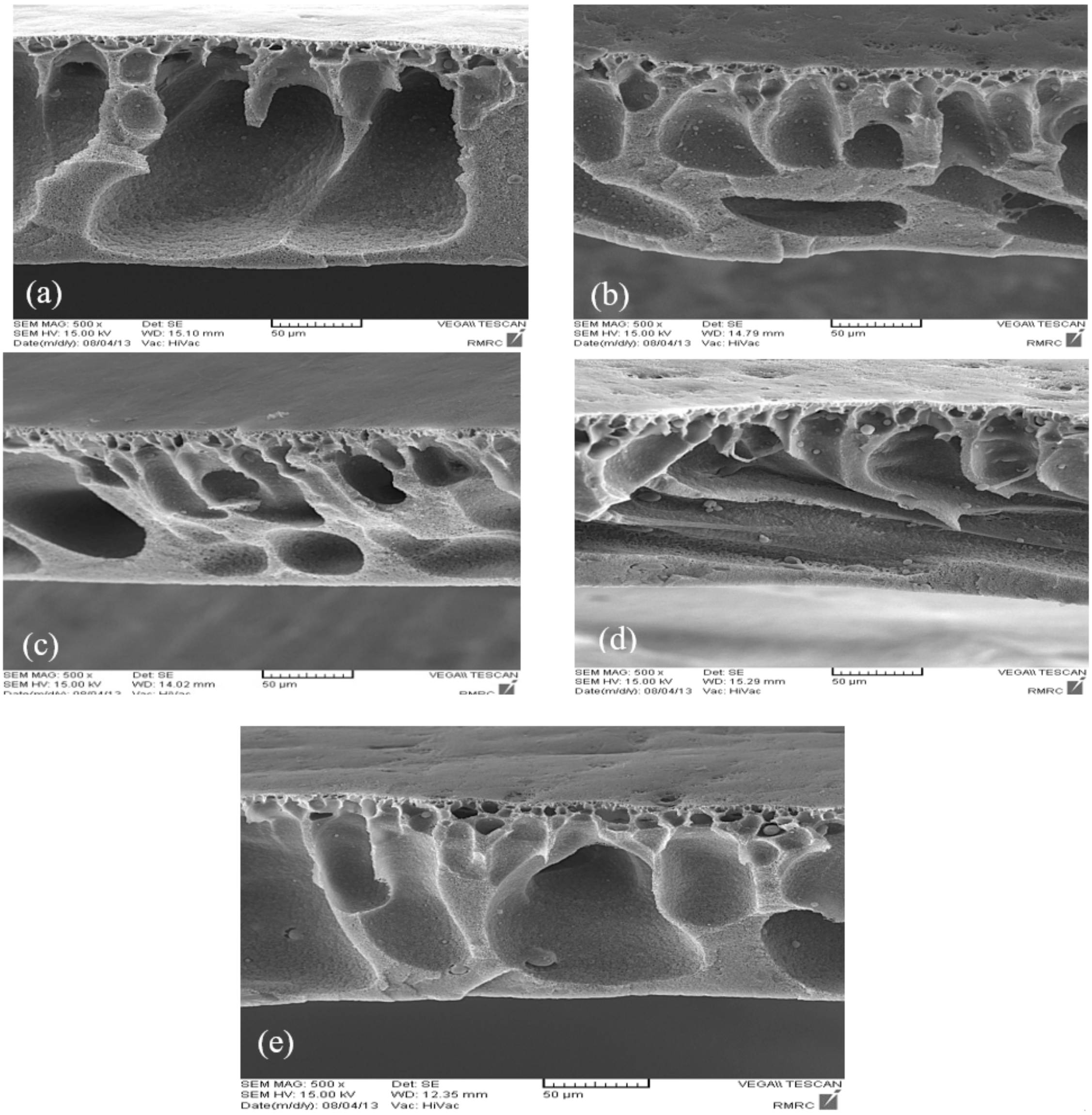


Fig. 3. SEM images of the PVDF/PAN/PVP/$TiO_2$ membranes based on different $TiO_2$ concentration in the casting solution ($TiO_2$ composition in Figs. (a)–(e) is 0, 0.5, 1, 1.5, and 2, respectively).

of high dosage of nanoparticles on viscosity and probable aggregation. High viscosity, which is notable by adding $TiO_2$ more than 1 wt.% (Table 2), drives nanoparticles to aggregate. Therefore, the uniform antifouling effect of nanoparticles on the membrane decreased due to the aggregation of nanoparticles (Fig. 4) by increase of viscosity.

To further investigate the antifouling properties of membranes, reversible ($R_r$) and irreversible ($R_{ir}$) resistances and flux recoveries (FRR) of the prepared membranes were calculated and represented in Table 3. It is displayed that the FRR of $TiO_2$ blended membranes are higher compared with the neat PVDF/PAN membrane due to the enhancement of hydrophilicity as the main effect of $TiO_2$. This indicates that the modified membranes have high recycling property which is maximum for addition of 1 wt.% $TiO_2$. Due to the aggregation of nanoparticles by adding more than 1 wt.%, the effect of nanoparticles on the flux recovery is decreased since the nanoparticles are aggregated in one spot. This prevents the monotonous distribution of nanoparticles (NPs) on the membrane surface and so their uniform and efficient effect on the recycling property of membrane decreased perceptibly. In other words, the aggregated nanoparticles, which is followed by adding more than 1 wt.% of $TiO_2$, resulted in formation of membranes which, have lower FRR values in comparison with the prepared membrane with addition of 1 wt.% $TiO_2$ NPs. The $R_{ir}$ for the PVDF/PAN blend membrane without 1 wt.% nanoparticles is high compared with the other modified membranes with $TiO_2$ because of higher affinity of $TiO_2$ to water which causes more hydrophilicity of the surface of $TiO_2$ entrapped membrane membrane rather than

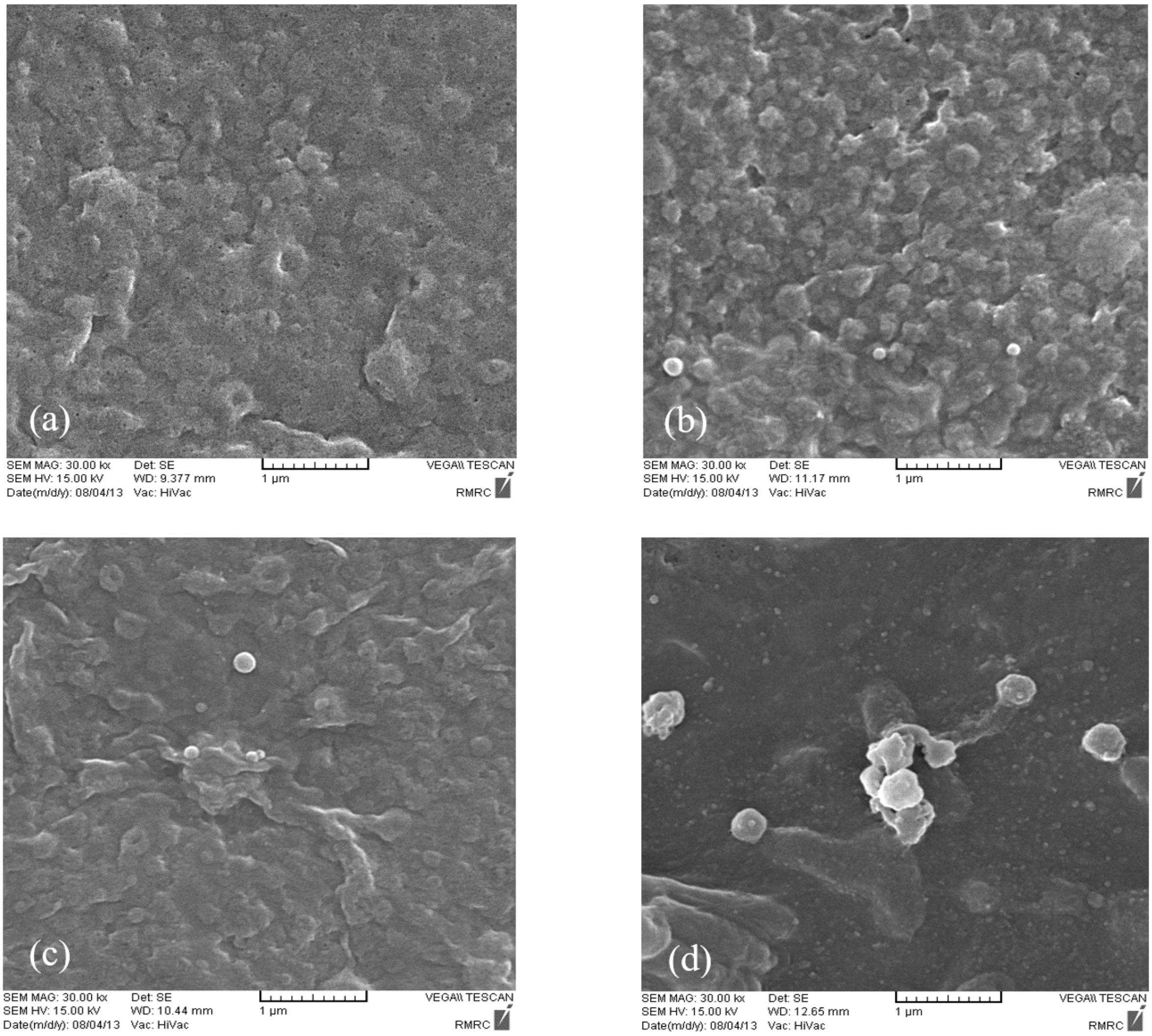


Fig. 4. Top surface SEM photographs of the PVDF/PAN/PVP/$TiO_2$ membranes with different $TiO_2$ concentration in the casting solution ($TiO_2$ composition in Figs. (a)–(d) is 0, 0.5, 1, and 2, respectively).

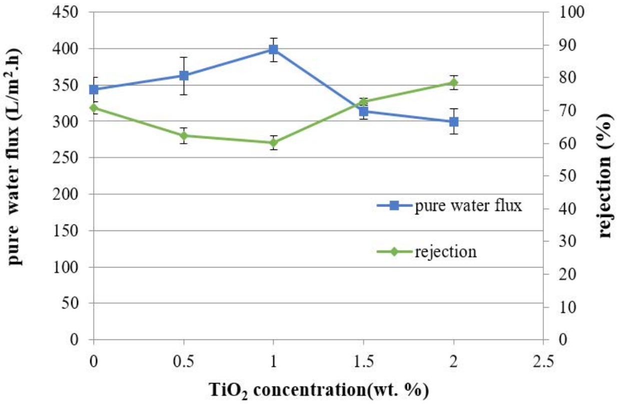


Fig. 5. Pure water flux and BSA rejection of the PVDF/PAN/PVP/$TiO_2$ membranes.

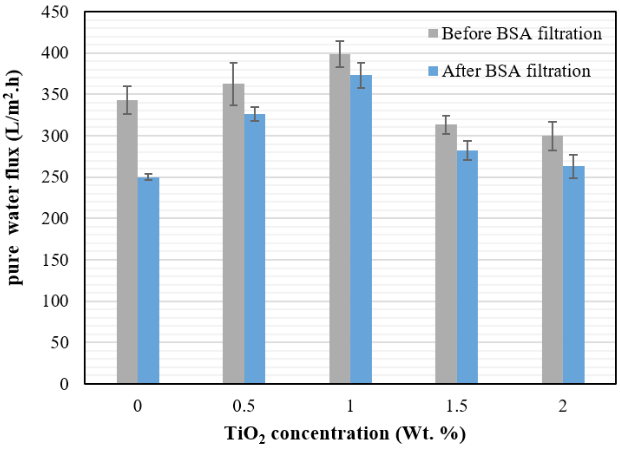


Fig. 6. Effect of $TiO_2$ concentration on pure water flux before and after BSA filtration.

Table 3
Antifouling properties of PVDF/PAN/PVP/$TiO_2$ blend membranes

| Membrane | $R_r$ | $R_{ir}$ | $R_t$ | FRR (%) |
|---|---|---|---|---|
| PAP4 | 0.149 | 0.271 | 0.420 | 72.85 |
| PAT0.5 | 0.290 | 0.0998 | 0.3898 | 90.01 |
| PAT1 | 0.297 | 0.0638 | 0.3608 | 93.64 |
| PAT1.5 | 0.268 | 0.0986 | 0.3663 | 90.13 |
| PAT2 | 0.279 | 0.1218 | 0.4008 | 87.81 |

the neat polymeric membrane. Membrane with 1 wt.% $TiO_2$ has the lowest $R_t$ and $R_{ir}$ which is in consistence with the fact that lower resistance confirms lower tendency of membrane to the fouling [28].

Therefore, the addition of 1 wt.% $TiO_2$ to the PVDF/PAN blend membrane improved the antifouling performance of the membrane owing to the hydrophilicity improvement. By further addition of $TiO_2$ to values higher than 1 wt.%, more aggregation occurred and then by decrease of uniform effect of nanoparticles on the membrane fouling, $R_{ir}$ is increased. This is similar to the other similar works such as the addition of $TiO_2$ to the PVDF/SPES blend membrane, while in that the minimum $R_{ir}$ was obtained by adding 4 wt.% nanoparticles [28]. It can be concluded that the best antifouling properties are obtained for the PAT1 which is in good agreement with the FRR results which obtained for this type of membrane.

### 3.5. MWCO determination

MWCO curves for unmodified and modified $TiO_2$ blend membranes are shown in Fig. 7. It is well known that by determining the MWCOs using PEG, as test solutes, the effect of adding $TiO_2$ on the pore size of the top surface of all membranes can be investigated [31]. Based on the results, addition of $TiO_2$ causes less rejection rate than the PVDF/PAN membrane without $TiO_2$. These results confirm that adding $TiO_2$ leads to the increase of the pore size of the membrane surface which confirms the results of permeability. In addition, PAT1 has the lowest rejection rate between all the membranes due to less aggregation of nanoparticles which obstructs membrane pores. By adding more than 1 wt.% $TiO_2$, due to the increase of viscosity and subsequent increase of aggregation along with more obstruction, rejection increased.

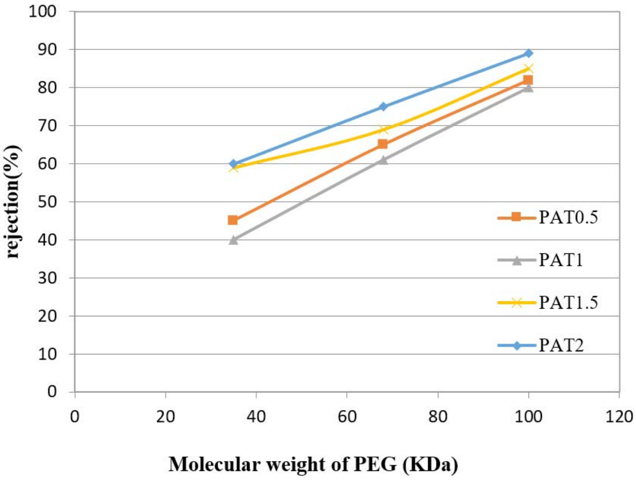


Fig. 7. MWCO determination of PVDF/PAN/PVP/$TiO_2$ membranes.

## 4. Conclusions

A novel PVDF membrane with appropriate antifouling properties was manufactured using blend of PAN polymer along with addition of $TiO_2$ nanoparticles in the presence of PVP in the casting solution via phase inversion. The EDX and SEM studies indicated that the $TiO_2$ nanoparticles were entrapped on the surface of the PVDF/PAN membrane. The hydrophilicity, permeation, and antifouling performance of membranes were improved significantly by addition of hydrophilic inorganic $TiO_2$ nanoparticles. However, it was found out that the effect of $TiO_2$ addition to the cast film solution up to 1 wt.% results in improved performance of membranes. Further addition of $TiO_2$ (from 1 to 2 wt.%) restrains the uniform antifouling effect of nanoparticles due to the increase of aggregation. Ergo, best composition of the casting solution based on the membrane properties and antifouling effect was PAT1 which has maximum permeation flux, FRR, and lower irreversible fouling. The main conclusions were obtained as follows:

- By increasing the $TiO_2$ concentration of the casting solution from 0 to 2 wt.%, the contact angle of the membrane decreases from 61.2 to 55.3 and the porosity of the PVDF/PAN blend membranes decreased from 93.97 to 77.73.
- By increasing the $TiO_2$ concentration, the morphology of the PVDF/PAN blend membrane changes to the smaller finger-like and causes decrease of macrovoids which was in agreement with porosity results.
- PWF of membranes increases by increasing the $TiO_2$ concentration to 1 wt.% due to the dominant effect of hydrophilicity increase. However, due to the aggregation of nanoparticles considering increase of viscosity, further increasing of $TiO_2$ concentration to values more than 1 wt.% causes decrease of permeability.
- The lowest fouling in terms of the maximum FRR (93.64%) and the lowest irreversible resistance ratio (0.0638) was obtained for the membrane with PVDF/PAN/PVP/$TiO_2$ blend ratio of 90/10/4/1.

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