Research Paper

Fabrication and Characterization of PES Based Nanofiltration Membrane Modified by Zeolite Nanoparticles for Water Desalination

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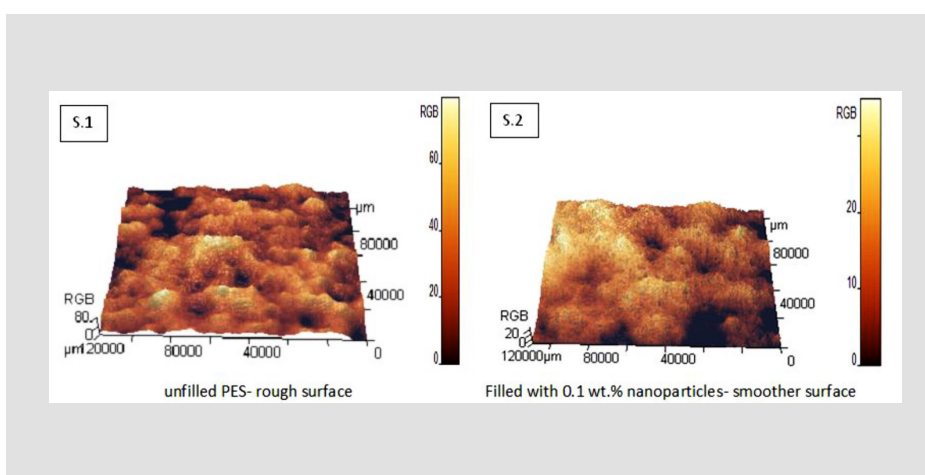
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KEYWORDS

GRAPHICAL ABSTRACT

unfilled PES- rough surface   Filled with 0.1 wt.% nanoparticles- smoother surface

HIGHLIGHTS

• Mixed matrix PES/zeolite nanoparticles nanofiltration membranes were prepared by solution casting technique
• Surface SEM images and SOM images showed nanoparticles agglomeration in the surface in high loading rates
• Membrane roughness was decreased with addition of zeolite into the casting solution
• Water flux and tensile strength were enhanced with added zeolite to 0.1 wt. % and again were decreased whereas the rejection was decreased just in 0.1 wt. % nanoparticles

ABSTRACT

In the present study, mixed matrix PES/zeolite nanoparticles nanofiltration membranes were prepared via the solution casting technique. The effect of zeolite concentration on the PES membrane performance and its properties was studied. Cross-sectional scanning electron microscope (SEM) observations showed that the porosity in the membrane sub-layer was increased with addition of zeolite into the casting solution. Surface SEM images and scanning optical microscope (SOM) images showed the nanoparticles agglomeration in the surface at high loading rates. Membrane roughness was decreased with the addition of zeolite into the casting solution. Results indicated that the membrane water content was improved initially by using 0.05 wt. % zeolite nanoparticles and then was decreased with further increase in additive concentration. Utilizing zeolite nanoparticles in the casting solution also led to decrease of surface contact angle from 62.02° for PES membrane to 36.87° for membrane filled with 0.1 wt.% zeolite. Moreover, water flux and tensile strength were enhanced with addition of the zeolite (up to 0.1 wt. %) and then were decreased whereas the rejection was decreased just in 0.1 wt. % nanoparticles loading rate. The flux reduction ratio of the prepared membranes was also estimated. Mixed matrix PES/zeolite membranes showed better antifouling properties compared to the PES one.

1. Introduction

Nanofiltration (NF), an effective pressure-driven membrane process, has the pore size and cut off ability between reverse osmosis (RO) and ultrafiltration (UF) [1–3]. Compared with RO, it operates not only under lower operating pressures, higher water fluxes, and lower investment, but also with high rejection rates for scale formation bivalent ions, especially anions [4–6]. With these characters, it is gaining its yards quickly in the seawater desalination sector [7]. Pressure driven membranes processes such as NF,

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dominantly are fabricated with various polymers. A number of polymers which widely have been used for fabricating the NF membranes are polyethersulfone (PES), cellulose acetate (CA), polyimide (PA) and polysulfone (PS) [8, 9].

Among above mentioned polymers, the polyethersulfone (PES) is a conventional choice for synthesizing NF membranes, due to its chemical, thermal, and mechanical stability. However, the disadvantage for applying PES is its high hydrophobicity, which increases membrane fouling tendency. The PES membranes always show asymmetric structure, and are prepared by a phase inversion method. The final membrane structure is influenced by the composition (e.g. concentration, solvent, additives) and temperature of the dope solution, the non-solvent (or even the mixture of non-solvents), and the coagulation bath [10].

Increasing the membrane hydrophilicity is a commonly method for modification of PES membranes to optimize their performance and properties [9].

There are three main approaches for midifying the PES membranes, including: (1) bulk modification of PES material, and then to prepare modified membrane; (2) surface modification of prepared PES membrane; and (3) blending, which can also be regarded as a surface modification. The modification procedures allow finding a compromise between hydrophobicity and hydrophilicity, localize the hydrophilic material specifically in the membrane pores, where they have a positive effect on flux and fouling features [11].

In the case of membranes' modification methods, employing different inorganic nanoparticles such as silver, titanium oxide, silica oxide and zirconium oxide embedded into the membrane matrix is a very well-known and interesting method. Utilizing inorganic materials (mostly nanoparticles) into the polymeric matrix can lead to achieve unique physico-chemical properties, such as hydrophilicity, and mechanical, thermal and oxidative stabilities. It can also improve the separation characteristics. In better words, introducing an inorganic filler into an organic polymer matrix contributes a wide range of multifunctional properties which is due to the synergism between the organic-inorganic materials [12].

Zeolite nanoparticles are well-known inorganic particles with great features, such as high adsorption capacity, ion exchange property, sieving characteristic, stable chemical property and safety toward the environment which provides unique physicochemical properties [13–17].

According to the literature [18], a novel mixed matrix (polyvinylchloride/zeolite nanoparticle) electrodialysis heterogeneous cation-exchange membrane was prepared by casting solution technique and the effect of zeolite concentration (as an additive) on the electrochemical properties and its performance was studied. Generally speaking, the results revealed better performance/properties in comparison of bare polyvinylchloride membrane.

To the best of our knowledge, there is no reports have considered the embedding zeolite nanoparticles into the PES nanofiltration membranes and the open literature is silence on performance and properties of PES/zeolite mixed matrix NF membranes.

Preparing a novel mixed matrix NF membrane for desalination and water treatment purposes was the first aim of current research. For this aim, mixed matrix (polyethersulfone/zeolite nanoparticles) NF membranes were prepared by solution casting techniques. The effect of zeolite concentration incorporated into the casting solution on the membrane performance and its properties was studied.

2. Materials and Methods

2.1. Materials

Polyethersulfone (PES) (Ultrason E6020P, M_W= 58,000 g/mol, BASF) was used as the membrane base binder. Polyvinylpyrrolidone (PVP) (M_W= 25,000 g/mol, Merck) was used as the pore former. Zeolite nanoparticles (white powder, average particle size < 100 nm, Germany) were used as the inorganic filler additive. *N,N*-dimethylacetamide (DMAC) (Mw=87.12 g/mol, Merck) and deionized water were used as the solvent and the non-solvent, respectively. All other chemicals were supplied by Merck.

2.2. Preparation of membranes

The conventional casting solution technique and phase inversion method were used for fabricating the membrane samples. The preparation was followed by dissolving of PES and PVP into the solvent (DMAC) in a glassy reactor and then well-mixed using a mechanical stirrer (Model: Velp Scientifica Multi 6 stirrer) for about 4 hr. The stirring was continued by dispersion of various amounts of zeolite nanoparticles into the dope solution.

The prepared solutions were sonicated for 30 min by an ultrasonic cleaner bath (Parsonic11Smodel, S/N PN-88159, Iran) for better dispersion of nanoparticles and breaking up their aggregates into the polymeric matrixes. The obtained homogeneous dope solutions were casted on clean and dry glass plates using a film applicator with constant thickness of 150 µm. Then, they were immediately immersed into deionized water as the non-solvent. The prepared membranes were transferred into the fresh deionized water tanks to remove any soluble components from the membranes' structures. The membranes were then placed between two filter paper sheets and were dried at room temperature (25±2 °C) for one day before testing. The composition of the casting solution is given in Table 1.

Table 1. Compositions of casting solution used in preparation of membranes[a].

Sample No.	Zeolite nanoparticles (wt.%)	Solvent (DMAC) (wt.%)
S.1	0	81
S.2	0.05	80.95
S.3	0.1	80.9
S.4	0.5	80.5
S.5	1	80

[a](PES (18 wt. %), PVP (1 wt. %))

2.3. Morphological studies

Membrane morphologies were investigated using the scanning electron microscopy (SEM) (Seron Technology Inc. Korea). The membrane samples firstly were frozen in the liquid nitrogen and then fractured. The samples were sputtered with a thin gold film and then were scanned.

For SOM imaging, the membrane samples were cut into the small pieces, mounted between two lamellas, then observation was made by the SOM optical microscope.

Surface roughness of the membranes was also measured by analyzing the surface images of the samples to investigate the effect of zeolite nanoparticles addition into the casting solution.

The overall porosity (ε) can be calculated by following expression [19]:

$$\varepsilon\,(\%) = \frac{w_w - w_d}{\rho_f V_m} \times 100 \tag{1}$$

where ρ_f and V_m are the water density (g/cm^3) and membrane small size volume (cm^3), respectively. It should be noted that all of the experiments were repeated three times and the mean values are reported.

2.4. Water content and water contact angle

The water content was measured using the weight difference between the dried and the wet membranes. To measure, the certain weight of membrane pieces was dipped in the distilled water for 24 h. Afterward, the wet membranes quickly were located between two filter paper sheets to remove additional surface water and then were weighed immediately (OHAUS, Pioneer™, Readability: 10−4 g, OHAUS Corp.). The membrane samples then dried in an oven (Behdad Co., Model: O5, Iran) until the constant weight was obtained. The following equation was used for water content calculation [20-23]:

$$\%\mathrm{Water\ content} = \frac{w_w - w_d}{w_w} \times 100 \tag{2}$$

where W_w and W_d are the wet and dry membrane weights (g), respectively. To minimize measuring errors, all measurements were repeated three times for each sample and the average values are reported.

Also water drop contact angle measurement was employed to evaluate the prepared membranes hydrophobicity. Doing so, very small droplets of the deionized water were dropped on the membranes surface in several random places, and the imaging of droplets were taken by using a digital camera. The average values of the measurements were reported to minimize errors. All experiments were carried out in an ambient condition.

2.5. Filtration experiments

The membranes performance was investigated using a dead-end membrane module with the volume of 150 ml and filtration surface area of

11.94 cm^2 at operating pressure of 0.45 MPa (room temperature, 25 °C), according to the schematic diagram which is shown in Figure 1. The experiments were performed after the membranes were pretreated under the pressure of 0.5 MPa for 30 min. The performance of the prepared mixed matrix membranes was evaluated based on two main parameters, including the permeation flux and the rejection (%) of Na$_2$SO$_4$ from its 0.01 mole/L neutral aqueous solution. The feed volume was 150 ml and the permeate volume was 5 ml. The permeation flux, *J*, is calculated as follow [24]:

$$J = \left(\frac{V}{A \times \Delta t} \right)$$ (3)

where *V* is the total amount of the water or solution permeated during the experiment (liter), *A* is the membrane area (m^2), and *t* is the operation time (h). Rejection (R%) was calculated using the conductivity differences between the feed solution and the product solution as follow [25, 26]:

$$\text{Rejection (\%)} = \left(\frac{C_f - C_p}{C_f} \right) \times 100$$ (4)

where C_p and C_f are the concentration of the permeate solution and the feed solution, respectively, and were measured by a conductivity meter (Ohaus Corporation, S/N B143385306, U.S.A).

Furthermore, the antifouling feature of the prepared membranes was measured by recording the flux decreased trend through the filtration time according to the following equation:

$$M\% = \left(\frac{J_0 - J_1}{J_0} \right) \times 100$$ (5)

where J_0 is the initial flux, J_1 is the flux after continuously filtrating for 90 min.
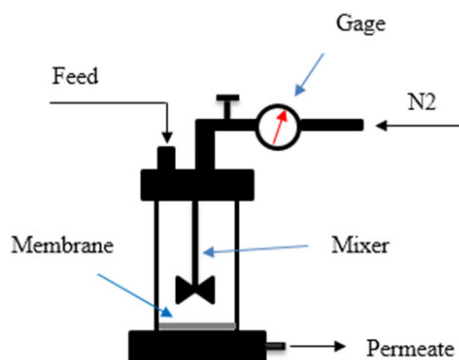

Fig. 1. Schematic diagram of experimental set up.

2.6. Mechanical Strength

The tensile stress of the prepared nanocomposite membranes was investigated according to ASTM1922-03 at ambient temperature. All samples were cut into the standard shapes before to be tested. For each test, three samples were used and the average values were reported [27].

3. Results and discussion

3.1. Morphological characterizations

SEM is carried out for observing the surface and cross-sectional morphologies of the membranes. The SEM images are shown in Figures 2 and 3. In Figure 2, the SEM images of cross-sectional view of the prepared membranes indicate that all the mixed matrix membranes and bare PES membrane have an asymmetric structure with a dense top-layer and a porous sub-layer. As can be seen, the size of the channels and the voids in all PES/zeolite mixed matrix membranes are higher than that of the PES membrane. The SEM images indicate that the membrane's volume fraction was increased by addition of zeolite nanoparticles into the casting solution. Also, the porosity in each mixed matrix membrane obviously is higher than that of the PES one. This may be related to the variable exchange rate between the water and the solvent caused by addition of zeolite nanoparticles into the casting solution.
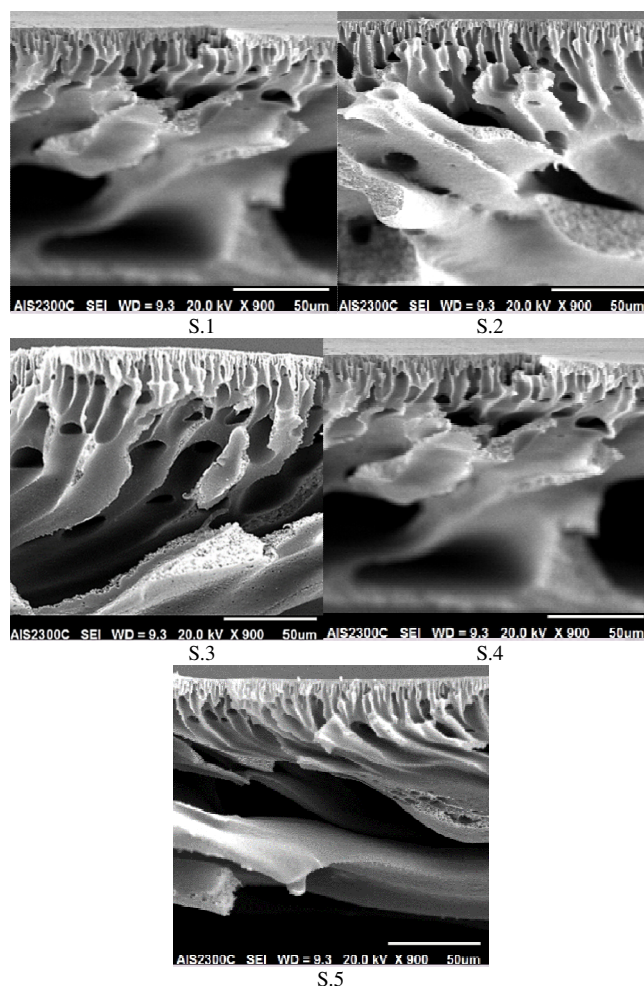

Fig. 2. Cross-section SEM images of prepared membranes filled with different concentrations of zeolite nanoparticles.

Addition of zeolite nanoparticles into the casting solution and the formation of polymer-nanoparticles interactions reduces the polymer interactions and so leads to unstable casting solution formation.

This can be followed by faster exchange of the solvent and the non-solvent during the phase inversion phenomenon. This can consequently result to the formation of the membrane with greater voids, channels and higher volume fraction in its structure. It is very well-known that the effects of the increased pores/channels size and volume fraction value in the membrane structure are favorable for water flux improvement [12].

Figure 3 shows the surface SEM images of the membranes. As can be seen, by increasing the concentration of zeolite nanoparticle into the casting solution, nanoparticles load on the membrane's surface increased. As could be observed, there is no nanoparticles agglomeration on the surfaces of the S.2 and the S.3 membranes and nanoparticles are dispersed homogenously. It can be seen that the nanoparticles agglomerated on the S.4 and S.5 membranes' surfaces and continuously was increased with increasing the nanoparticles concentration. The excessive contents and the agglomeration of zeolite nanoparticles on the membrane surface can cause some of the pores to be blocked. The pores' blockage occurred with excessive nanoparticles on the membrane surface and plays unfavorable role for water flux decline.

SOM was used to observe the zeolite nanoparticles distribution in the prepared membranes' structures. The SOM images are shown in Figure 4. The polymer and the zeolite nanoparticles can be seen in the images, especially for S.4 and S.5. As could be observed, some of the nanoparticles are agglomerated (see S.4 and S.5). It reveals that the loading of nanoparticles in high concentrations (0.5 and 1wt. %) can make increase the nanoparticles interaction and consequently formation of agglomerated spots. Moreover, images show a relatively uniform surface morphology for S.1, S.2 and S.3. As can be seen, a lot of nanoparticles are dispersed on the S.5 membrane's surface which can provide lower pore size with pore blockage phenomenon. This can result in smaller flow channel sizes which leads to lower water flux and higher salt rejection.
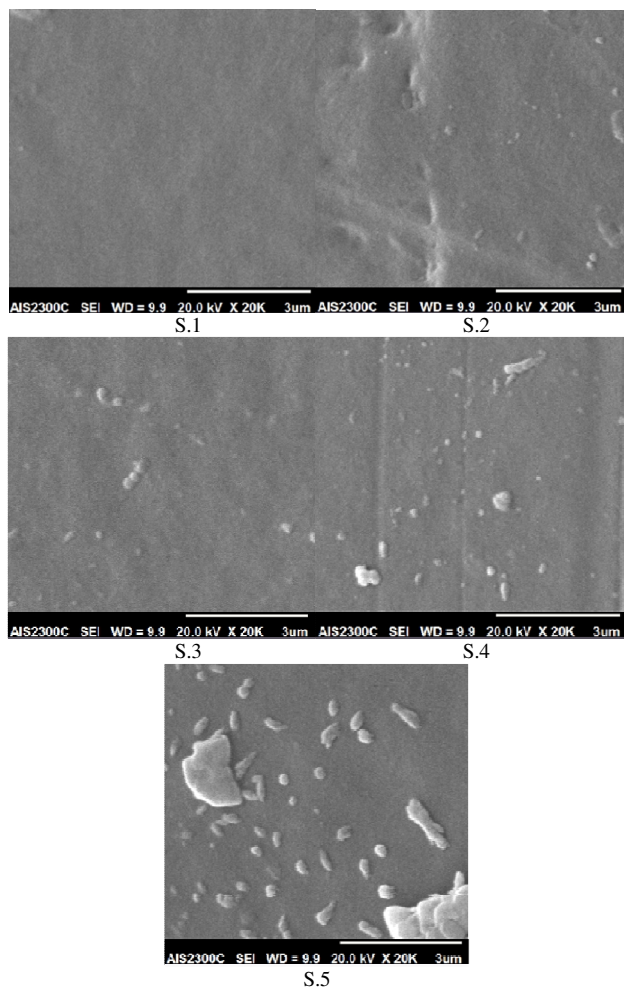
Fig. 3. SEM images of surface of prepared membranes filled with different concentrations of zeolite nanoparticles.
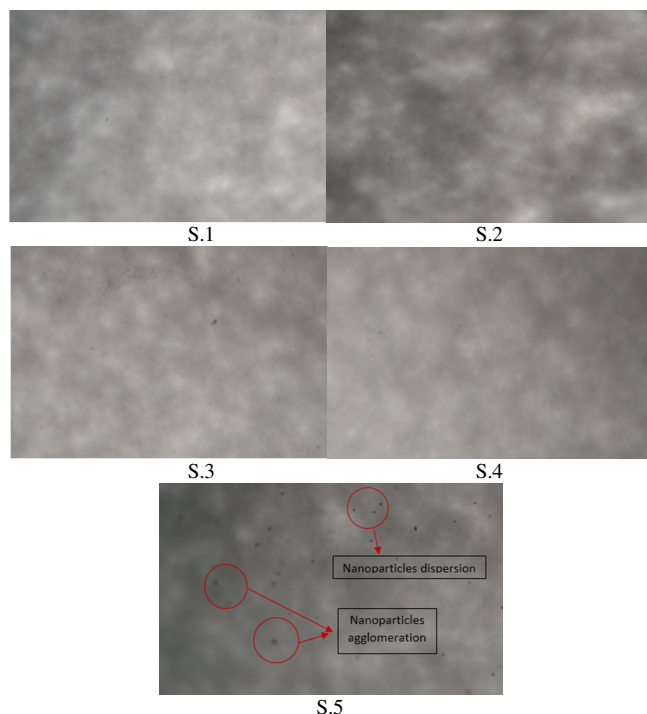

Fig. 4. The SOM images of prepared membranes with various concentrations of zeolite nanoparticle.

Furthermore, 3D surface images of the prepared membranes are demonstrated in Figure 5. According to this figure, the convex parts of the pure PES membrane are sharp which is resulted to the stronger hydrophobicity. After filling the PES membrane by zeolite nanoparticles with various concentrations, the membrane surface roughness (S.1) is obviously modified and smoother surface is obtained (S.2, S.3, S.4 and S.5). This can result in to the higher hydrophilicity of the mixed matrix membranes. Decrease in membrane roughness, can reduce the ions interactions with the membrane surface and also can increase the membrane's flux. In better words, ions trap on the membrane's surface is more thinkable for rougher membranes. Consequently higher ions transport through the membrane can lead to the lower rejection values [28].

Fig. 5. 3D surface images of prepared membranes with various zeolite nanoparticles concentrations.

3.2. Membrane water content and contact angle

Water content and contact angle analysis were used to evaluate the hydrophilicity and wettability of the bare PES membrane and the PES/zeolite mixed matrix membranes. Results for the water content (Figure 6) indicate that the addition of zeolite nanoparticles into the casting solution with various concentrations led to an increase in the membrane's water content, however, just for the S.2 sample which is filled with 0.05 wt. % nanoparticles. On the other hand, addition of higher amounts of nanoparticles into the casting solution resulted to decrease in the water content. The increase of water content for the S.2 membrane is in good agreement with its cross-sectional SEM image, which shows higher porosity for membranes filled with various zeolite nanoparticles concentrations. The higher porosity and wider channels in the S.2 structure which was observed in the SEM image (see Figure 2b), and also the porosity percentage (see Figure 6), compared to S.1, provides more spaces for water to accumulate in the membrane's structure. This led to higher water content for S.2. Both results for water content and porosity in Figure 6 revealed that increase of zeolite nanoparticle concentration into the casting solution led to a decrease of water content for S.3, S.4 and S.5, which is in contrast with the SEM images. This event can be explained with respect to voids occupied by the nanoparticles [29], and pores blockage in the membrane surface/matrix which decreases water molecules embedding into the membrane (as was observed in the SEM images of the membranes' surface and the SOM ones). Based on the obtained results, it can be concluded that with the addition of zeolite nanoparticles higher than that of 0.05 wt.% into the casting solution the voids and pores in the membrane surface and its matrix are surrounded and occupied by the nanoparticles. This results in lower water entrance to the membrane structure.

Contact angle measurement has been widely utilized to characterize the hydrophicility of the membranes' surface. Typically, the smaller contact angle indicates the higher surface hydrophilicity, which can increase the flux and decrease the antifouling tendency [30].

Figure 7 shows the contact angle images of the mixed-matrix membranes containing different concentrations the zeolite nanoparticles. According to the results, contact angle of the PES membrane decreases with addition of zeolite nanoparticle into the casting solution. For the prepared bare PES membrane and the nanoparticle incorporated ones (with 0.05 and 0.1 wt. % zeolite), the membrane contact angle measured at 62.02°, 52.13° and 36.87°, respectively. The bare PES membrane has the largest contact angle due to the hydrophobic nature of the PES raw material. Hydrophilic characteristic of the applied zeolite nanoparticles in this work significantly enhanced the surface hydrophilicity of the bare PES membrane, as well (see S.2, S.3, S.4 and S.5). It is very well-known that the surface hydrophilicity is a favorable feature for enhancing the water flux and the membrane's antifouling ability. As can be seen, a small increase of contact angle was observed for the S.4 and S.5 samples compared to the S.3 one. As mentioned earlier, a few agglomerated nanoparticles were observed in the SEM and the SOM. This led to reduce the active surface area of nanoparticles and their influences on the membrane hydrophilicity and contact angle, as well. In better words, this can be concluded as one of the reasons for the small increase of contact angle value for S.4 and S.5. Another reason can be attributed to the change in the surface roughness which is caused by addition of nanoparticles into the casting solution. In real, presence of further nanoparticles in the membrane surface at S.4 and S.5, further to the agglomerate formations, may lead to a slight increase in surface roughness and consequently slight increase in water contact angle. However, S.4 and S.5 have lower contact angle compared to the bare PES one.
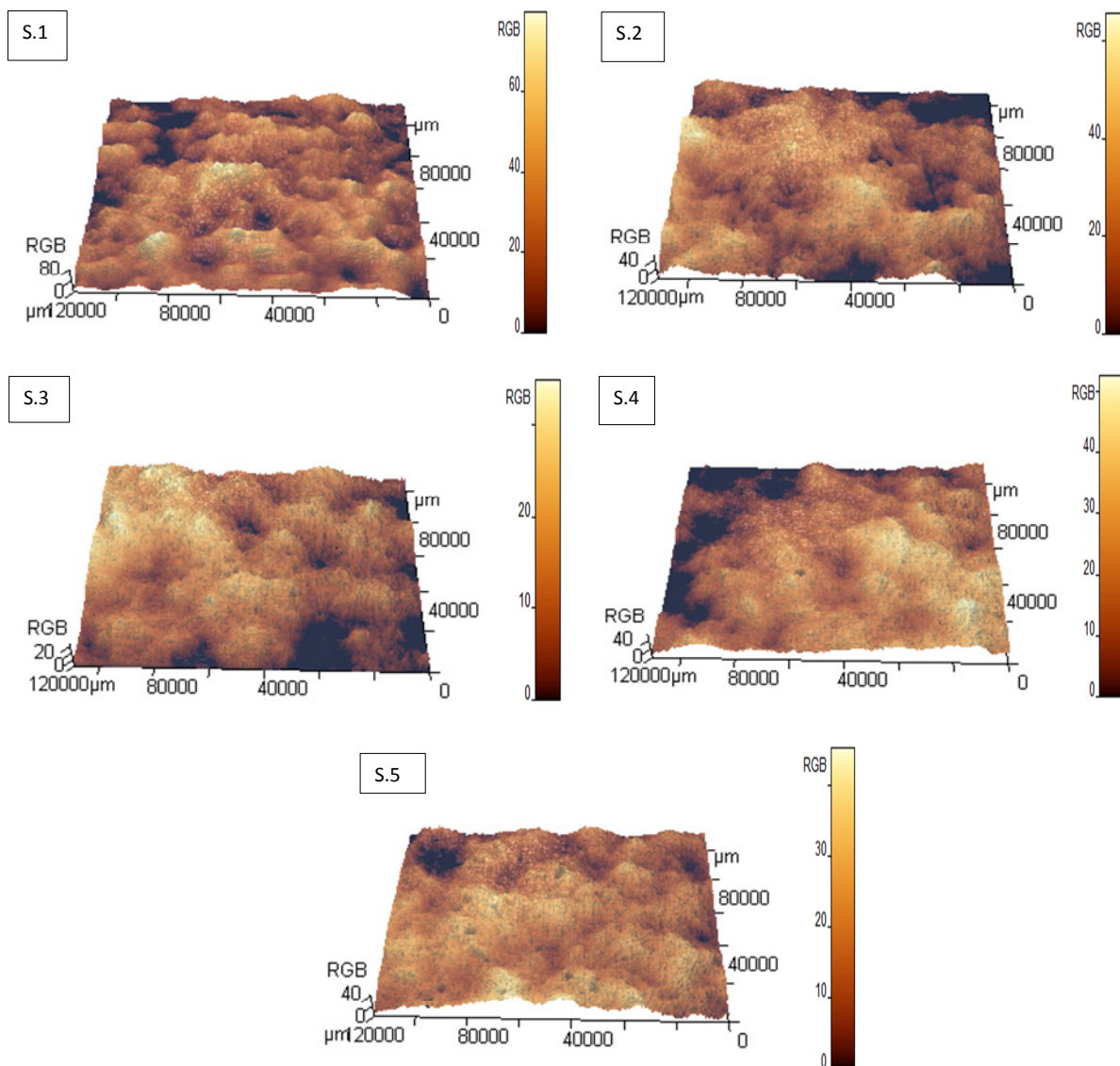
Fig. 6. The effect of zeolite nanoparticles concentrations on water content and porosity.
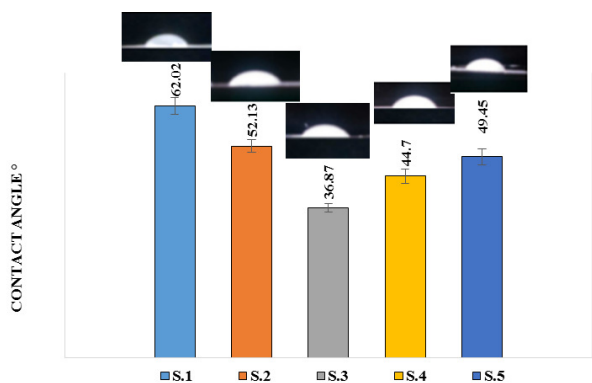

Fig. 7. The effect of zeolite nanoparticles concentrations on contact angle.

prepared membranes also increased, up to a peak value and again decreased with higher nanoparticles loading rates (0.5 and 1 wt. %). The highest water flux was obtained for the mixed matrix membrane filled with 0.1wt.% of the zeolite. It is worth quoting that the surface hydrophilicity and membrane's structure are two main factors for controlling the permeability and the selectivity characteristics [31].
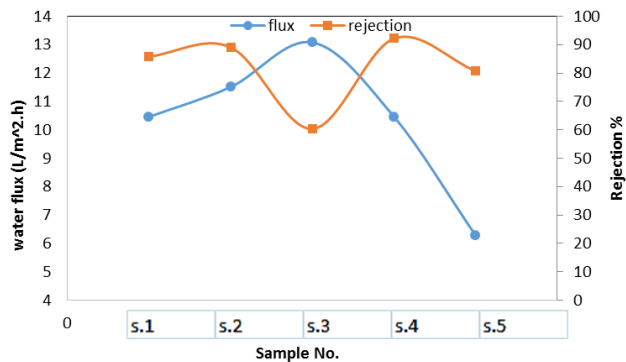
Fig. 8. The effect of zeolite nanoparticles concentrations on water flux and rejection.

3.3. Membrane filtration performance

The water flux of the proposed membranes was measured at the operating pressure of 0.45 MPa. Figure 8 shows the the influence of zeolite nanoparticles concentrations on the performance of PES membrane. As could be observed, the water flux of PES membrane is obviously increased with embedding of 0.05 and 0.1 wt.% zeolite nanoparticles in the membrane matrix. As zeolite nanoparticles concentration increased, the water flux of the
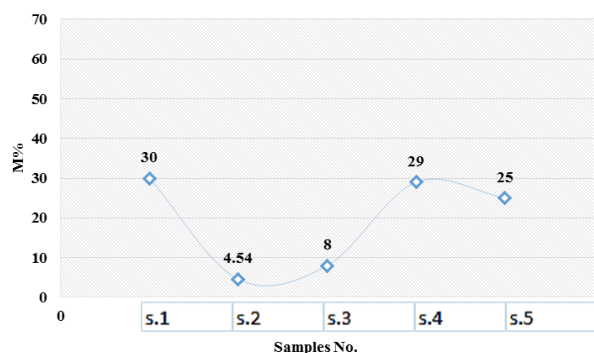
Fig. 9. The effect of zeolite nanoparticle concentrations on tensile strength.
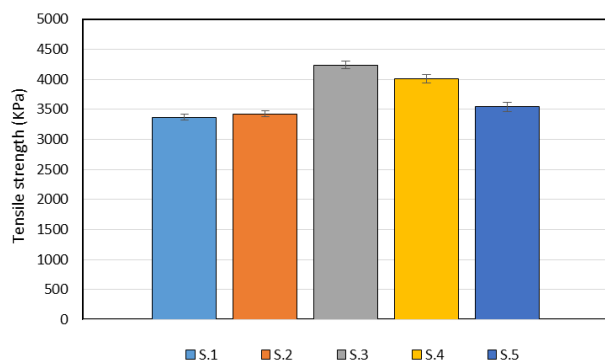

Fig. 10. Decreased flux ratio after 90 min of filtrating for each membrane.

As was seen in the contact angle results, presence of the hydrophilic zeolite nanoparticles with various concentrations into the membrane structure, improved the membranes' hydrophilicity, especially for the S.3 sample, which is favorable factor to improve the water flux. Furthermore, as discussed earlier (see 3D surface images in Figure 5), with decrease in membrane roughness, the ions interactions with the membrane surface declines which can result to increase in the water flux. Therefore, the production of smoother surface caused by addition of zeolite nanoparticles in the casting solution, can also investigate as another reason for the water flux improvement for S.3.

On the other hand, the rejection results show a significant decrease for the zeolite loading rate of 0.1 wt.%. The addition of zeolite nanoparticles into the casting solution increases the rate of demixing process during the phase inversion step, as mentioned earlier. Formation of larger voids and pores, and higher porosity as well, on the membrane's structure (see Figure 2) results in the higher flux and lower rejection for the S.3 membrane, which is filled with 0.1 wt.% of zeolite nanoparticles.

The results of the water flux (see Figure 8) revealed that with increase of zeolite nanoparticles concentration (> 0.1 wt.%, i.e. 0.5 and 1 wt.% for S.4 and S.5), a reductive trend is observed for the water flux, while the salt rejection is improved, again. This result can be explained by the fact of nanoparticles agglomeration and surface pore blocking, which are caused by the high nanoparticles loading rates (see the surface SEM images of S.4 and S.5 and also their SOM images). In this condition, water molecules and ions entrance into the membrane' channels result to the water flux reduction with enhancement of salt rejection.

As reported in open literature [32], permeate flux decreases continually and reach to an almost stable value as the filtration time goes by. Permeate flux trend is a proper measure for evaluating the membrane's antifouling feature. Figure 9 shows that the flux decline ratio of all mixed matrix membranes which are filled with different concentrations of the zeolite nanoparticles is lower than that of the bare PES one. As can be seen (see Figure 9), the flux decline trend for the S.2 membrane (containing 0.05 wt.% zeolite nanoparticle) is 4.54% which is greatly smaller than that of the flux decline of the S.1 membrane (containing 30 wt.% nanoparticles). This figure also indicates that the mixed matrix membranes filled with zeolite nanoparticles have lower fouling tendency. In better words, it can be concluded that the presence of zeolite nanoparticles into the membrane structure improves the antifouling feature of the PES membrane. This can be due to the increase of membrane hydrophilicity (i.e. decreasing of contact angle and smoother surface compared to PES one)

3.4. Mechanical Strength of Prepared Membranes

The effect of zeolite nanoparticles loading rate on the tensile strength behavior of the prepared membranes was studied. Results are shown in Fig. 10. Results (Figure 10) show that the tensile strength of the prepared membranes is improved by increasing the additive concentration to 0.1 wt. %. This can be due to the strong interfacial bonding formed between the polymer and the nanoparticles, which improves the mechanical property [33, 34]. The membrane tensile strength is decreased again with higher zeolite nanoparticles loading (0.5 and 1 wt.%). This reduction can be related to the formation of some nanoparticles agglomeration and clusters into the membrane structure which tends to form discrete phase.

3.5. Comparison of different salts on rejection

The rejection result for different salts is reported in Table 2. The salt rejection mechanism of the NF membranes is very complicated. It depends on some parameters, such as sieving, Donnan exclusion effect and differences in diffusivity and solubility [35]. Donnan exclusion is important in the NF membranes contained charged groups. For the NF membranes without charged groups, rejection controls with the sieving mechanism and is related to the molecular size [36].

Table 2. Effect of different salts on the rejection of membrane (S.4).

Salts	Rejection (%)
Na_2SO_4	92.1
$MgSO_4$	86.3
NaCl	24.1

In the current study, it can be concluded that the main separation mechanism of the zeolite-modified membranes without the charged groups is just of the molecular size and the sieving. So, the rejection of different salts decreased in the order of $Na_2SO_4 > MgSO_4 > NaCl$.

Table 3 shows the comparison between the permeability and the rejection performance of the prepared membrane in this research (S.4) and some previously published literatures. The filled membrane with 0.5 wt. % (in this study) showed higher rejection with comparable/suitable permeability flux compared to the previous relevant literatures.

Table 3. Comparison between the performance of prepared membrane in this research and with some previous relevant literatures.

Membrane	Permeability (l/m².h)	Rejection (%)	reference
Modified membrane (S.4)	10.4	92	This work
S. Ansari and coworkers	10	88	[37]
M. Moochani and coworkers	18	75	[38]
E. Bagheripour and coworkers	5.2	90	[39]

4. Conclusions

In the current study, a PES nanofiltration membrane was filled with various concentrations of zeolite nanoparticles. The membranes were prepared by the phase inversion method and the casting solution technique. Cross sectional SEM images indicates that the addition of zeolite nanoparticles into the casting solution led to higher porosity and bigger macrovoids in the sub-layer. With increase the zeolite concentration, some nanoparticles agglomerations were observed in the SEM surface images and also in the SOM images. 3D surface images showed smoother surface for the membranes filled with the zeolite nanoparticles compared to PES one. The obtained results showed that the water content and the porosity percentage were increased just with addition of 0.05 wt.% zeolite nanoparticles into the casting solution. Membrane contact angles were decreased from 62.02° for bare PES to 36.87° for the S.3 one, which confirmed the improvement of the PES membrane's hydrophilicity. The water flux and also the tensile strength were enhanced with increase the zeolite nanoparticles concentration up to 0.1 wt.% and again were decreased whereas the rejection was decreased just in 0.1 wt.% nanoparticles concentration. The mixed matrix PES/zeolite filled with 0.05 and 0.1 wt.% nanoparticles showed the smallest values for flux decreased ratio which indicated the higher antifouling capability for S.2 and S.3 membranes compared to the PES membrane.

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