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Zirconia nanofibers incorporated polysulfone nanocomposite membrane: Towards overcoming the permeance-selectivity trade-off

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Abstract

Enhancing the properties and structure of the ultrafiltration (UF) membrane via rational manipulation is important to optimize their perm-selectivity performance. To overcome the permeance-selectivity trade-off of nanocomposite membranes, Zirconium dioxide nanofibers (ZrO_2 NFs) was synthesized in nano-micro size and then incorporated into the polysulfone (PSf) membrane. The effect of different concentrations of ZrO_2 NFs on the membrane properties and performance were investigated. Compared to the pristine PSf membrane, the nanocomposite membranes exhibited a remarkable enhancement in the physiochemical properties, mechanical properties, and the overall performance. The results showed that the nanocomposite membrane (M3, 0.5% ZrO_2 NFs) possesses the highest flexibility and tensile strength (43% higher than the pristine PSf). The enhancement of the wettability and enlarge the pore size (2.6 times increase) of this nanocomposite membrane, resulting in a remarkably heightened the pure water permeability (J_{w1} ; $255.8 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$). As a result, it achieved the highest permeability during the filtration of BSA solution with no decline in the BSA rejection. Furthermore, compared to the pristine PSf membrane, all nanocomposite membranes exhibited higher mechanical properties.

This novel strategy of incorporating the nanofibers, instead of nanoparticles, offers significant opportunities to exploit the various inorganic nanofibers in the fabrication of diverse nanocomposite membrane types.

Keywords: Electrospinning; ZrO_2 nanofiber; membrane; nanocomposite; ultrafiltration; antifouling; and high flux.

1. Introduction

Ultrafiltration (UF)-based wastewater treatment is widely considered as a vital, green and effective technology for the production of clean water because of its energy-efficiency, simplicity, easy-integration and scalability, high efficiency, low operating pressure, and environmentally-friendly method [1-3]. UF membranes have been widely used for the separation of macromolecular proteins, suspended solids, dye molecules, oily wastewater, and bacteria [3-7]. Notwithstanding this extensive range of applications; the perm-selectivity trade-off and high fouling tendency are still major obstacles for UF membranes [8]. To address these limitations, designing UF membranes with high perm-selectivity and antifouling property is crucial particularly for the wastewater treatment field.

The hydrophobicity of the polymeric membrane facilitates the hydrophobic interaction between the membrane surface and foulant, resulting in poor permeability and high fouling tendency [9]. So far, various methods were used to mitigate severe fouling problems and achieve excellent UF performance for the polymeric membrane, including surface and/or structure modification [10]. In the current decade, novel various materials developed, especially, the inorganic nanoparticles (NPs) that potentially were incorporated into the polymeric membranes as fillers to enhance the physicochemical properties and performance of the UF membrane [3, 6, 11-13]. The addition of nanofillers into the polymer solution can affect both the kinetic and thermodynamic behaviors in the phase-inversion process, effectively altering the membrane pore structure, surface roughness, and membrane morphology [14]. For instance, the addition of TiO₂ NPs to the polysulfone (PSf) enhanced both the water permeability and antifouling property against different foulant [15-17]. On the other hand, the PSf membrane incorporated with Ag NPs showed high anti-biofouling and virus removal [18, 19]. Also, the performance of

PSf UF membrane was improved by the addition of Fe_3O_4 NPs in the presence of a magnetic field [20]. Recently, we added sulfonated graphene oxide (SGO), which increased the water flux by 125% with no perm-selectivity trade-off [7]. In addition to the single nanoparticles, the nanohybrid materials were also incorporated into PSf to augment its performance, such as SiO_2 -GO [21], ZnO-GO [22], and Ag-GO [23]. In spite of their achievements, the permeability-selectivity trade-off still remains, where an increase of the membrane permeability is accompanied by a decrease in the membrane selectivity (rejection).

It is worth mentioning that all of the previous reports used NPs configuration that makes them easy to be leached out during the phase-inversion and/or filtration process [24, 25], however, the introduction of these materials into nanofiber structure (NFs) would enhance the stability of these materials inside the matrix of the membranes. During the phase-inversion process, when the casted NPs-polymeric solution was immersed in the coagulation bath, some NPs release to the coagulation bath leaving the membrane matrix, while the remaining NPs distribute inside the membrane matrix, on the membrane surface, and/or agglomerated and trapped inside the pores. Both the agglomerated NPs and the trapped NPs would be leached out during the filtration process (especially, during the compaction process). On the contrast, the micro-length of the NFs (micro-sized) would hinder their release during the filtration and/or phase-inversion process, compared to the NPs [26]. Fortunately, NFs can be fabricated easily using the electrospinning technique [27-31], electrospinning can produce continuous nanofibers with nano-sized to submicron diameters and micro-sized length, moreover, sub-nanometer fibers were produced recently [32]. It is important to mention that, unlike the NPs, the orientation of NFs is critical where its micro-sized length can lengthen the water transport path and decrease the pore size if the fibers are oriented horizontally inside the membrane matrix (perpendicular to the cross-section).

Herein, to eliminate the above challenges, ZrO_2 NFs were fabricated using the electrospinning technique and then incorporated as a novel and efficient nanofillers into PSf, aiming to fabricate novel robust nanocomposite membranes with outstanding performance for UF process. The hypothesis was that the diverse nano-micro structure, higher surface area, and adsorptive capability of the ZrO_2 would enhance its stability inside the membrane by restraining, capturing, and confining it inside the polymeric matrix. The influence of the ZrO_2 NFs content on the physicochemical properties, mechanical properties, and UF performance was investigated. To our best knowledge, there is no article which studied or reported the use of ZrO_2 NFs or any NFs in the membrane fabricated by phase inversion.

2. Experimental Section

2.1 Materials

Poly(vinyl alcohol) (PVA, average molecular weight (M_w) 85,000-124,000, 87-89% hydrolyzed, Sigma-Aldrich), Zirconium acetate solution (in dilute acetic acid, Zr, ~16%, Sigma-Aldrich) and deionized water (DI), obtained from a Milli-Q ultrapure water purification system, were used to prepare Zirconium dioxide nanofiber (ZrO_2). Polysulfone (PSf) (BASF, M_w =60,000), N-methylpyrrolidone (NMP, 99% OCI), Polyvinylpyrrolidone (PVP, 10k M_w , Sigma-Aldrich), and N,N-dimethylformamide (DMF, > 99.8%, Sigma-Aldrich) were used to prepare the dope solution of flat sheet membranes. Bovine serum albumin (BSA; 67kDa) were purchased from Sigma-Aldrich to perform ultrafiltration test.

2.2 Preparation

2.2.1 Synthesis the ZrO_2 nanofibers via electrospinning technique

PVA was dissolved into water with vigorous stirring at 60 °C to form a homogeneous solution. Consequently, dropwise of Zirconium acetate solution was added to the prepared solution to form 10 wt.% PVA final concentration (mass ratio of PVA to Zr = 5:3.6). The mixture was mechanically stirred for 4 h at 60 °C, then the solution was transferred into plastic syringes and was then supplied through 23 gauge stainless-steel needle, via a digitally controlled syringe pump, with a feeding flow rate of 1 mL/h. By applying a high voltage of 20 kV between the spinneret (needle tip) and the rotating collector (covered by aluminum foil) with 15 cm distance, the electrospun nanofibers were collected at room temperature. Subsequently, the resulting electrospun nanofibers were dried in an oven at 70 °C for 1 day to remove the residual solvent. Finally, the inorganic ZrO_2 nanofibers were formed by annealing [33, 34] at 800 °C for 5 h at a heating rate of 5 °C/min under air to produce the desired ZrO_2 nanofibers (ZrO_2 -NFs), as shown in Scheme 1(a).

Scheme 1. Schematic diagram of the experimental setup showing (a) the fabrication of ZrO_2 NFs and (b) the fabrication of the nanocomposite membrane via phase inversion.

2.2.2 Fabrication of the PSf-ZrO₂ blended UF membranes via phase inversion

Scheme 1(b) shows the fabrication of pristine and nanocomposite (PSf-ZrO₂) membranes by the phase inversion method (non-solvent induced phase separation). Firstly, an appropriate amount of the synthesized ZrO₂ NFs (as shown in Table 1) were sonicated for 90 min in NMP/DMF bi-solvents, which resulted in a dispersion of short nanofibers [35-38].

After that, 0.5 wt.% of PVP (based on the solution) as a pore-forming agent were added and magnetically stirred for 1 hr. Finally, the PSf was dissolved in the above solution and magnetically stirred for 2 days at 60 °C. Subsequently, the casting solutions were degassed for 90 minutes using sonication. Then the solutions were maintained for 30 minutes before casting on a clean glass plate, using a film-casting knife with the thickness gap set at 120 µm and a constant casting rate. The casted glass plate was put immediately in tap water (a non-solvent) bath and after the membrane was peeled off from the glass plate, the separated membranes were preserved into a DI water bath for 1 day to remove the solvent residue. The pristine (control) membrane was fabricated in the same condition without adding the ZrO₂ NFs. The fabricated membranes were labeled as M0 for the control membrane and from M1 to M5 based on the ZrO₂ NF concentrations in the membrane matrix that is 0.1 to 1 wt.% as shown in Table 1.

Table 1. The composition of the casting solutions

Weight (g)	M0	M1	M2	M3	M4	M5
ZrO ₂ NFs	0.00	0.02	0.05	0.10	0.15	0.20
PVP	0.10	0.10	0.10	0.10	0.10	0.10
PSf	3.20	3.20	3.20	3.20	3.20	3.20
DMF	8.35	8.35	8.35	8.35	8.35	8.35
NMP	8.35	8.35	8.35	8.35	8.35	8.35

2.3 Characterization of ZrO₂ NF and the mixed-matrix UF membranes

The phase structure of the ZrO₂ NFs and mixed-matrix membranes were characterized at range from 10 to 90° with a High-Resolution X-Ray Diffractometer (XRD; X'pert PRO, PANalitical, Netherlands) with Ni-filtered Cu K α radiation. Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer IR 2000 Series, Billerica, MA, US) was used to identify the functional groups on the PSf, ZrO₂ NFs, and PSf-ZrO₂ mixed-matrix membranes. Transmission electron microscopy (TEM, model JEM-2100, JEOL, Japan) was applied to observe the ZrO₂ NFs structure, a high field emission scanning electron microscope (FE-SEM with an EDX spectrometer; S-4700, Hitachi, Japan) and energy-dispersive X-ray spectroscopy (EDX) were employed to characterize the morphology and compositions of the ZrO₂ NFs. The open-access an ImageJ software was used to estimate the mean surface pore size and pore size distribution by analyzing the surface FE-SEM images. The roughness and surface topography of the prepared membranes were analyzed using atomic force microscopes (AFM, XE-100, Park systems, Korea) apparatus.

The theta Attension optical tensiometer (KSV Instruments) was used to measure the membrane wettability (water contact angle; WCA), where 5 μ l water drop was carefully dropped on the membrane surface and the dynamic contact angle was determined. The total monitored time was 40 min with an interval point of 30 s.

The gravimetric method was used to determine the membrane porosity (ϵ), typically, 6 samples of each membrane (4 cm² each) were immersed in isopropanol for 2h. Afterword, the excess isopropanol was removed carefully from the membrane surface using tissue paper, then, the wet membrane was immediately weighed (m_w , g). Then, the membrane was dried overnight in an oven at 80 °C and reweighed to measure the dry weight (m_d , g). The ϵ was calculated using Eq.1.

$$\epsilon = \frac{(m_w - m_d)/\rho_l}{\frac{(m_w - m_d)}{\rho_l} + \frac{m_d}{\rho_p}} \quad \text{Eq.1}$$

where the ρ_l is the density of isopropanol ($\rho_l=0.789 \text{ gcm}^{-3}$) and ρ_p is the polymer density.

The stress-strain and tensile strength of the pristine and nanocomposite membranes were measured using universal mechanical tester (BONGSHIN, Model DB35-10, South Korea), where the 3 to 5 samples of each membrane were measured and the average was taken to decrease the experimental error.

2.4 Evaluation of the membrane performance and antifouling

UF experiments were conducted in a custom lab-scale cross-flow filtration system with an effective membrane area of 7 cm^2 . Before measuring the pure water permeability, the membrane was initially compacted using DI water at 3 bar for 45 min to stabilize the membrane permeability or flux. Once the membrane was pre-compacted, the transmembrane pressure was changed to 1.5 bar and the weight of permeate was continuously recorded using an electronic balance connected to a computer for 1h, to calculate the initial pure water permeability (PWP, $J_{w,i}$, $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) using Eq. 2:

$$J_{w,i} = \frac{\Delta m}{A * \rho * \Delta t * \Delta p} \quad \text{Eq.2}$$

where m, A, ρ , t, and Δp are the mass of permeated water (g), the effective membrane area (m^2), water density (1000 gL^{-1}), the permeation or filtration time (h), and transmembrane pressure (bar), respectively.

After measuring pure water permeability, the DI was replaced with 0.5g/l BSA aqueous solution and the BSA solution was filtrated for 2 h to measure the permeance ($J_{\text{BSA},i}$, $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) and rejection (R%) for the pristine and nanocomposite membranes. Where the BSA rejection was calculated using Eq.3.

$$R\% = \frac{(C_{\text{feed}} - C_{\text{permeate}})}{C_{\text{feed}}} \quad \text{Eq.3}$$

where C_{feed} and C_{permeate} are the concentrations of BSA in feed and permeate solutions (gL^{-1}), respectively. C_{permeate} was measured using a UV–Vis spectrometer (F-2500, Hitachi, Japan) at a wavelength of 280 nm, based on the pre-prepared calibration curve.

After that, the membrane polluted by BSA was washed with DI water for 20 min at a crossflow rate of 300 mLmin^{-1} . Consequently, the pure water permeability of cleaned membranes ($J_{w,i+1}$, $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) was measured again at the same conditions (1.5 bar for 1 h), completing the first cycle. However, two cycles have been conducted.

To assess the antifouling property of the pristine and nanocomposite membranes during each cycle, four fouling indices namely; flux recovery ratio ($\text{FRR}_i(\%)$), total fouling ratio ($R_{t,i}$), reversible fouling ratio ($R_{r,i}$), and irreversible fouling ratio ($R_{ir,i}$) were calculated using the following Eqs. (4-7) [39-41]:

$$\text{FRR}_i(\%) = \frac{J_{w,i+1}}{J_{w,i}} \times 100 \quad \text{Eq.4}$$

$$R_{t,i}(\%) = \frac{J_{w,i} - J_{BSA,i}}{J_{w,i}} \times 100 \quad \text{Eq.5}$$

$$R_{r,i}(\%) = \frac{J_{w,i+1} - J_{BSA,i}}{J_{w,i}} \times 100 \quad \text{Eq.6}$$

$$R_{ir,i}(\%) = \frac{J_{w,i} - J_{w,i+1}}{J_{w,i}} \times 100 \quad \text{Eq.7}$$

Where i is the cycle number; for example, the initial water permeability was $J_{w,1}$, the permeance of BSA solution in the 1st cycle is $J_{BSA,1}$, and the pure water permeability of the cleaned membrane after the 1st cycle is $J_{w,2}$.

3. Results and Discussion

3.1 Characterization of ZrO₂ NFs

The morphology, structure, and compositions of the produced NFs were investigated. FE-SEM images of the ZrO₂ NFs at different magnifications are shown in Fig. 1 (a and b). The produced NFs had an average diameter of 184 ± 46 nm (Fig.S1.(A), supporting information) with a rough surface. The rough surfaces or nanocrystalline is attributed to the small grains of monoclinic (m-ZrO₂) and tetragonal (t-ZrO₂) phases of the ZrO₂. Fig.1(c-1 and c-2) displays TEM images and EDS of the ZrO₂ NFs, which indicates that the NFs are composed of nano-sized Zirconia grains linked to each other. Furthermore, the EDS results showed clear peaks related to Zr and O, while the peak of carbon is attributed to the carbon mesh of the TEM grid (the full EDS image is displayed in Fig. S1(B)). The XRD of the ZrO₂ NFs is shown in Fig.1(d), The strong and sharp diffraction peaks of the m-ZrO₂ at 2θ values of 24.24° , 28.20° , 31.56° , 34.12° , 35.30° , 40.87° , 50.30° corresponding to (011), ($\bar{1}11$), (111), (002), (200), (211), and (220) lattice planes, respectively, were the predominant. While, few low-intensity peaks for t-ZrO₂ at 30.24° (101), and 60.16° (211) were observed [42-44]. In addition, the FT-IR characteristic vibration peaks of ZrO₂ NFs which appeared at bands range of $800\text{--}400\text{ cm}^{-1}$ are corresponding to Zr-O-Zr and Zr-O stretching vibrations, as shown in Fig.1(e) [45, 46].

Fig.1. (a, b) FE-SEM images, (c-1 and c-2) TEM and EDS, (d) XRD patterns, where m and t refer to monoclinic and tetragonal phases of ZrO_2 , and (e) FT-IR spectra of the produced ZrO_2 NFs.

3.2 Characterization of pristine and nanocomposite membranes

3.2.1 Structure and chemical compositions

The chemical compositions and structure of pristine and nanocomposite membranes were analyzed through FTIR and XRD, and the results were presented in Fig.2.

Fig. 2(a) shows the XRD patterns of the pristine and nanocomposite membranes. The pristine PSf reveals a broad reflection peak centered at around 17.80° , which is assigned to its amorphous

structure nature. Importantly, the XRD pattern of the nanocomposite membranes (PSf-ZrO₂NFs) exhibited characteristic peaks of ZrO₂ at around 2 θ values of 24.24° (011), 28.20° ($\bar{1}$ 11), 30.24° (101), 31.56° (111), 34.12° (002), 35.30° (200), 40.87° (211), 50.30° (220), and 60.16° (211) [42-44]. This confirms the inclusion of ZrO₂ NFs in the matrix of nanocomposite membranes. It is worth mentioning that the peak intensity was increased by increasing the percentage of the ZrO₂ NFs in the nanocomposite membranes.

Fig.2. (a) XRD and (b) FT-IR of the pristine PSf and nanocomposite PSf-ZrO₂NFs membranes. The inset (b) shows the specific range of FT-IR from 800 to 400 cm⁻¹, where the peak intensity increased compared to the pristine membrane.

The characteristics bands of FTIR spectra (Fig. 2(b)) were used to investigate the interaction between the PSf chains and ZrO₂ NFs. For the pristine PSf membrane, the aromatic and aliphatic C-H stretching vibrations peaks are positioned between 3090 and 2970 cm⁻¹, and the bands of aromatic C-H bending rocking vibrations are observed at 831, 852, and 872 cm⁻¹, while the peak at 2876 cm⁻¹ assigned to asymmetric stretching of CH₃ group. Furthermore, the peak of the benzene ring (C₆H₆) was observed at 1586 cm⁻¹, whereas the peak of C-SO₂-C asymmetric stretching was noticed at 1321 cm⁻¹, and the peak of C-S-C stretching vibration was positioned at 691 cm⁻¹. The asymmetric and symmetric stretching of O=S=O group was presented at the peak bands of 1294 and 1149 cm⁻¹, respectively, while the absorption bands at 1240 and 1014

cm^{-1} is assigned to asymmetric stretching of C–O–C and C–O, respectively [40, 47, 48]. Moreover, the band at 1170 cm^{-1} referred to etheric stretching vibration between oxygen atoms and aromatic rings. Finally, the broad peak which centered at around 3421 cm^{-1} is attributed to O–H stretching that may be due to the absorption of water [40, 47, 48].

Furthermore, FT-IR spectra of PSf-ZrO₂ nanocomposite membranes were similar to the pristine PSf without the creation of new bands or shifting of the existing bands. This finding suggests that there is no new chemical or covalent bonding between the PSf and ZrO₂ [49]. However, the increase of the peak intensities of the nanocomposite membranes found in the band's range of 800 cm^{-1} to 450 cm^{-1} (Fig.2(b), inset), is assigned to the presence of ZrO₂ NFs in the matrix of the nanocomposite membranes. This points out that no changes in the chemical structure of the membranes, where the zirconia was included physically in the PSf membrane matrix.

3.2.2 Morphology and topography

FE-SEM images of the top, bottom, and cross-section of the pristine and nanocomposite membranes were taken as shown in Fig.3, Fig.S2 and Fig.S3, to examine the morphological alterations associated with the addition of ZrO₂ NFs. It can be seen from Fig.3 that ZrO₂ NFs (marked by magenta color) dispersed inside the top dense layer (1st column) and on the bottom surface (2nd column) of all nanocomposite membranes in different orientations; horizontally, vertically, and with different inclined angles. Moreover, the density of ZrO₂ NFs was increased by increasing the ZrO₂ percent in the nanocomposite membranes.

Fig. 3. FE-SEM images of top surface (column 1, magnification 5kx), bottom surface (column 2, magnification 10kx), and cross-section (column 3, magnification 2kx) of pristine and nanocomposite membranes; (a) M0, (b) M1, (c) M2, (d) M3, (e) M4, and (f) M5. ZrO₂ NFs were marked by magenta false color using ImageJ software and the original images of columns 1&2, and the inset images were presented in Fig. S5.

The cross-section images (3rd column) displayed that all membranes showed asymmetric structure consisting of a thin dense layer supported by a porous sublayer. For the pristine membrane, the sublayer is a finger-like structure, while the nanocomposite membranes exhibited finger-like and macrovoids structures (Fig. S2). Comparing with the pristine membrane, the nanocomposite membranes were found to have wider finger-like cavities. The formation of enlarged finger-like and macrovoids cavity in the nanocomposite membranes attributed to the rapid phase-demixing, where adding of the ZrO₂ NF induced the thermodynamic instability and accelerate the exchange between the solvent and non-solvent [50]. Besides changes of the sublayer structure, more visible ZrO₂ NFs (3rd column) were observed inside the matrix (sublayer) of all nanocomposite membranes at different orientations.

AFM was used to investigate the membrane surface roughness and the 3D AFM images of the membranes, using a scanning area of 5 μm x 5 μm , were presented in Fig.4. Where the surface roughness parameters, such as the mean roughness (R_a), root means square of the Z data (R_q), and the mean difference between the highest peaks and lowest valleys (R_z) are measured and given in Table 2. Compared to the pristine membrane, almost negligible change in the roughness of the M1, M2, and M3 nanocomposite membranes was found with R_a values ranging from 11 to 11.6 nm. However, the M5 exhibited the roughest surface with R_a value of 37.9 nm, this significant increase in the roughness for M5 could increase the membrane fouling propensity.

The increase of the roughness of the nanocomposite membrane having 1% ZrO₂ NFs (M5) is caused by the presence of the agglomerated NFs on the surface, which affects the tip movement in Z-direction, showing high roughness. In detail, when the tip moves up to the top surface of the NFs (on membrane surface), it would be considered as the high Z peak and it is included in the roughness parameter.

Table 2. Surface roughness parameters of the pristine and nanocomposite membranes

Membrane	R_q (nm)	R_a (nm)	R_z (nm)
M0	13.8 ± 0.4	11.0 ± 0.5	118.0 ± 12.0
M1	14.3 ± 0.6	11.3 ± 0.7	169 ± 11.0
M2	14.8 ± 1.0	11.3 ± 1.5	225 ± 24.0
M3	14.2 ± 0.2	11.6 ± 0.2	180 ± 21.0
M4	23.2 ± 3.0	15.4 ± 1.3	212.6 ± 39.0
M5	46.9 ± 10.5	37.9 ± 8.6	277.0 ± 55.8

Fig. 4: Three-dimensional AFM images for pristine and nanocomposite membranes (scan area $25 \mu\text{m}^2$).

3.1.3 The porosity, mean pore size and wettability

The porosity and mean pore size of the pristine and nanocomposites membranes are shown in Fig. 5. As seen in Fig. 5(A), no significant change in the porosity was observed, while the surface pore size was increased by increasing the ZrO_2 NFs content up to some limit. Typically, ImageJ software was used to analyze the pore size and pore size distribution on the membrane surface using FE-SEM images (50k X, Fig. S3) and the results were plotted in Fig. 5(A) and Fig. S4.

It was found that the addition of 0.1% ZrO_2 NFs (M1) increased the mean pore size by approximately 1.7 times in comparison to pristine PSf (M0), while the maximum increase (approximately 2.6 times) was obtained at 0.75% ZrO_2 NFs (M4). Further increase of the ZrO_2 NFs starts to decrease the mean pore size, but still higher than the pristine membrane. This behavior can be explained as follow; ZrO_2 NFs cause two opposites effects; 1) an increase in the viscosity (kinetic effect), and 2) enhancement of the thermodynamic instability due to the high affinity of ZrO_2 NFs to water [51]. At low concentrations of ZrO_2 NF (the thermodynamic

effect is dominant), the presence of ZrO_2 NFs enhances the dope solution instability, hence encouraging fast demixing and forming large pores. As the ZrO_2 NFs percentage increases both of the viscosity (kinetic effect, slow demixing) and the thermodynamic instability (fast demixing) increases, until reach to critical values of ZrO_2 NFs concentration, at which counter-effects of thermodynamic and kinetic effect become equal. Above this value or at high ZrO_2 NFs concentration the kinetic effect becomes dominant, due to the increase of the dope solution viscosity, therefore delaying demixing and forming the denser top layer.

This trade-off relation between the kinetic and thermodynamic behaviors results in an increase of the pore size with increase of ZrO_2 NFs up to 0.5 wt.%, then the increase of pore size becomes negligible at 0.75 wt.%, followed by a decrease in the pore size at 1wt.%. This decrease in the mean pore size at 1% ZrO_2 NFs could be attributed to the agglomeration of the NFs at high concentration, as well as an increase of the viscosity (kinetic effect) which slows the demixing process, resulting in the decrease of the mean surface pore size. These results in agreement with the results of Hong and He [52] who found the same trend when they added ZnO NPs to PVDF. However, all of the membranes have a pore size in the range from 3.6 to 9.24 nm which corresponding to the pore size of the UF membranes.

Fig. 5. (a) Porosity and mean pore size and (b) dynamic water contact angles of the pristine and nanocomposite membranes, and the inset is dynamic WCA for 5 min.

The dynamic WCA measurement was conducted to characterize the change of wettability of the pristine and nanocomposite membranes. As shown in Fig. 5(b), upon addition of the ZrO_2 up to 0.5 wt.%, the nanocomposite membranes exhibited a faster decline rate of WCA in comparison to M0, while M4 showed similar WCA decline rate to M0. On the other hand, M5 depicted the highest WCA and a lower decline rate in WCA even lower than M0. Typically, M0 reached WCA value of 30° after 30 min, meanwhile, M1, M2, M3, M4, and M5 took 26.5, 24.5, 26, 30, 35 min, respectively to reach the same value of 30° .

The faster rate of drawing water through M1, M2 and M3 nanocomposite membranes could be attributed to the high affinity of the ZrO_2 NFs to the water. However, a further increase in the ZrO_2 NFs (M4 and M5) led to a decrease in WCA decline rate. This increment of WCA from M3 to M4 and M5 can be attributed to the increase of their roughness values as shown in Table 2 and Fig. 4. Additionally, during the phase inversion process, ZrO_2 NFs can migrate easily to the membrane surface at low solution viscosity (at low ZrO_2 concentration), while increasing the dope solution viscosity (at high ZrO_2 concentration) could hinder the ZrO_2 movement to the surface. Thus higher ZrO_2 NFs exposure on the surface of M1, M2, and M3 nanocomposite membranes could be obtained, while lower ZrO_2 NFs with poor distribution on the surface of M4 and M5 could be occurred [50].

3.1.4 The mechanical properties of membranes

The mechanical properties of the membranes are very vital for the processing and handling of the membranes. However, Fig. 6 shows the stress-strain curves and tensile strength of the average of three to five samples of the pristine and nanocomposite membranes. Comparing with the pristine membrane, the addition of ZrO_2 NFs improved the tensile strength of the membrane. The pristine PSf membrane has the lowest strength of 4.1 MPa and by adding

a little amount of ZrO₂ NFs (0.1 wt.%) the tensile strength was enhanced by 13%. With a further increase in the ZrO₂ NFs up to 0.5 wt.%, the nanocomposite membrane exhibited more flexibility (Fig. 6 (a)) and the tensile strength augmented by 43% (Fig. 6(b)). When the ZrO₂ NFs concentration was higher than 0.5 wt.% (M4 and M5), the tensile strength was decreased. Overall, all the nanocomposite membranes exhibited higher tensile strength than the pristine membrane, and the membrane having 0.5% ZrO₂ NFs (M3) has the highest flexibility with a maximum tensile strength value of 6.3 MPa. It is worth noting that, the orientations of the ZrO₂ NFs inside the membrane matrix significantly could affect the distribution of the applied stress, as a result, influences the mechanical properties. Thus, the presence of ZrO₂ NFs inside the membrane matrix distributes the applied force (stress), resulting in enhancement of the mechanical properties of the nanocomposite membranes, compared with pristine one (no NFs). Nonetheless, the decrease of the mechanical properties for M5 could be attributed to an increase of the membrane stiffness, which decreases the mobility and anisotropy degree of the polymeric membrane matrix.

Fig. 6. The stress-strain curves (a) and tensile strength (b) of the pristine and nanocomposite membranes.

3.2 Ultrafiltration performance and fouling analysis

The results of pure water permeability (PWP, $J_{w,1}$) of the fabricated membranes at 1.5 bar, are presented in Fig. 7(A). Compared to the pristine membrane, all nanocomposite membranes exhibited higher PWP. Among the nanocomposite membranes, M4 (0.75 wt.% ZrO₂ NFs) revealed the maximum PWP value of 339.3 Lm⁻²h⁻¹bar⁻¹, corresponding to 190 % improvement compared with the pristine membrane. However, a further increase in the ZrO₂ NFs content (higher than 0.75 wt.%; M5) resulted in the decline of the PWP, but still higher than the pristine PSf membrane.

The improvement in the PWP with the addition of the ZrO₂ NFs can be explained as follow. Firstly, the pore size of the membranes increased as the ZrO₂ NFs contents increased up to 0.75wt.% (M4), as shown in Fig. 5(A). This increase in the pore size facilitates water penetration and flow. Secondly, ZrO₂ NFs alters the membrane morphology, where the finger-like morphology of the pristine membrane was changed to finger-like plus macrovoids morphology for nanocomposite membranes, as shown in Fig.S2 and Fig.3. This change in cross-section morphology could decrease the hydraulic resistance, resulting in augmented the water flux. Thirdly, the slight increase in the hydrophilicity as shown in Fig. 5(B). On the other hand, compared to M4, the decrease of the PWP in case of M5 can be attributed to a decrease in its pore size and wettability. Also, it is worth mentioning that, the orientations of ZrO₂ NFs, especially the horizontal orientation, can negatively affect the water permeability by lengthening the path of water transport. Thus more ZrO₂ NFs (at high concentrations) inside the membrane matrix could decrease the water permeability, by decreasing the available water transport path.

Fig. 7. Average permeance of pure water (PWP, $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) (a), and average permeability of BSA solution (J_{BSA1}) and Rejection (b) of the pristine and nanocomposite membranes for the 1st cycle.

Figure 7(B) shows the average permeance of the BSA solution and BSA rejection for the pristine and nanocomposite membranes. As can be observed, the permeability of all the membranes decreased due to the adsorption of BSA on the membrane surface, compared with the PWP.

The M0 membrane showed a permeability of BSA solution of $64.7 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ and with adding ZrO_2 NFs, the permeability of nanocomposite membranes increased considerably to be 78.4, 99.4, 102.0, 99.0, and $89.0 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ for M1, M2, M3, M4, and M5, respectively.

Unlike PWP, the M3 showed maximum permeability during the filtration of BSA solution which is slightly higher than that of M4. This could be attributed to the rough surface of M4 and M5 compared with the other membranes. However, all of the nanocomposite membranes exhibited higher permeability than the pristine membranes during filtration of pure water and BSA solution.

Furthermore, the rejection of the BSA results (Fig. 7(B)) displayed that all the membranes have BSA rejections more than 98%, reflecting an increase of the water permeability of the nanocomposite membranes without a trade-off. This finding can be explained as follow; the existing of some ZrO_2 NFs (inside the nanocomposite membranes matrix) in a horizontal orientation, that perpendicular on the finger-like path (as shown in Fig. 3; FESEM), could adsorb the escaped BSA on its surface, trapping them inside the nanocomposite membranes matrix.

To evaluate the fouling resistance of the pristine and nanocomposite membranes, BSA was used as the model protein foulant and two cycles of UF experiments were conducted. According to the time-dependent normalized permeability results in Fig. 8(A), in the 1st 1 h of pure water filtration, all of the membranes exhibited similar normalized permeability with values of more than 98%. When the DI water was altered to BSA solution in the first cycle, all of the membranes showed a sharp drop in the normalized permeability. The normalized permeability of M0

significantly dropped down to around 32.3% after 2 h filtration of BSA solution. While the normalized permeability of M1, M2, M3, M4, and M5 fell to approximately 34.6, 30.3, 30.4, 27.8, and 33.4%, respectively. This indicated that the fouling took place instantly owing to the interaction between BSA and membrane surfaces. After filtration of BSA solution, the membranes were cleaned with DI water and flux recovery property was studied by filtration of pure water for an hour. Although the pristine membrane showed slower normalized permeability decline rate than the nanocomposite membranes, all of the nanocomposite membranes exhibited higher average permeability during the filtration of pure water and/or BSA solution (Fig. 7).

The flux recovery ratio (FRR) and fouling parameters (R_t , R_{ir} , and R_r) for the 1st cycle were plotted in Fig.8 (B). It was found that the pristine membrane (M0) exhibited an FRR value of 46.7% and with the addition of 0.1 wt.% (M1) and 0.25 wt.% (M2) of ZrO₂ NFs, a negligible or slightly increase in the FRR value was observed, where it became 46.9 and 47.9 % for M1 and M2, respectively. Further increase of ZrO₂ NFs giving rise to decrease the FRR to be 43.8, 39.8, and 44.8% for M3, M4, and M5, respectively. These low FRR values are attributed to fast and irreversible adsorption of BSA protein during the filtration process, where the irreversible fouling (R_{ir}) values were the main part of total fouling (R_t) for all membranes, as shown in Fig. 8(B). Corresponding to 53.3, 53.1, 52.1, 56.2, 60.3, and 55.2 % for M0, M1, M2, M3, M4, and M5, respectively. In contrast, all of the membranes showed small reversible fouling (R_r) values in a range of 7.9 to 13.4 %. It exhibits noteworthy the R_t of the nanocomposite membranes were slightly greater than that of the pristine membrane. However, this finding can be explained as a fellow.

The increase of the hydrophilicity and smoothness of membranes decrease the active sites (valleys/peaks) for accumulation and deposition of BSA, resulted in a decrease of R_{ir} and the deposited BSA protein can be easily eliminated from the surface (R_r) [53, 54]. In contrast, an

increase of their surface pore size and/or initial permeability would result in more fouling as well as a decline of the permeability [55]. Compared to M0, with the addition of ZrO₂ NFs up to 0.25 wt.% (M1 and M2) the hydrophilicity, surface pore size, and initial permeability increased without change in the roughness. The trade-off between these properties resulted in a negligible or slightly increase in FRR and a negligible or slight decrease in R_{ir} values. Further increase in ZrO₂ to 0.5% resulted in a nanocomposite membrane (M3) with same hydrophilicity and roughness to M2, while both of the initial permeability and pore size increased, thus the decrease in FRR and an increase in R_{ir} was obtained. When the ZrO₂ NFs increased to 0.75% (M4) the roughness and initial permeability increased with pore size similar to M3, while the hydrophilicity decreased to be similar to M0, consequently a much decline in FRR and increase in R_{ir} was achieved. Finally, the decrease of initial permeability, hydrophilicity, and pore size as well as increase the roughness of M5 resulted in an increase of FRR value compared with M4, but still lower than M2.

Fig. 8. (A) Normalized permeability (J/J_0) as a function of time for two filtration cycles using 0.5 gL^{-1} BSA solution at 1.5 bar, and fouling parameters (R_t , R_{ir} , and R_r) and FRR of the pristine and nanocomposite membranes (B) 1st cycle and (C) 2nd cycle. Each UF cycle includes 4 steps: measure the PWP, measure the permeance of BSA solution, washing using DI for 20 minutes, and measure PWP of the cleaned membranes. The normalized permeability is defined as the current permeability of the membrane divided by its corresponding initial permeability (J/J_0).

A second run of the fouling test was conducted for another 2 h, after cleaning, and the results revealed that the fouling slightly continued on all of the membranes, as shown in Fig.8 (A). Typically, the normalized permeability of M0, M1, M2, M3, M4, and M5 membranes dropped down to 30.5, 31.6, 26.8, 28.0, 25.8, and 27.0%, respectively. It exhibits noteworthy that there is a slight drop in the normalized permeability compared with the 1st cycle for all of the membranes.

For the 2nd cycle, FRR and fouling parameters (R_t , R_{ir} , and R_r) were plotted in Fig.8 (C) and Fig. S6. For M0, the FRR was 46.7 % in the 1st cycle and it reached 91.6% in the 2nd cycle (Fig.7 (C), or in other words, the FRR slightly decreased after two filtration cycles to be 43.7% (Fig. S6). However, all of the nanocomposite membranes behaved in a similar manner and the M2 showed the highest FRR value of 96.3%. On the other hand, unlike the 1st cycle, the reversible fouling (R_r) was the main part of total fouling (R_t) for all membranes, as shown in Fig. 8(C).

These findings suggest that most of BSA were deposited on the membrane surface in the first 1h (1st cycle) of BSA solution filtration, forming a strong-interacted layer. Consequently, this layer caused the irreversible fouling and it cannot be removed by the hydraulic cleaning (DI washing). Thus these deposited layers of BSA were still on the membrane after the cleaning process in the 1st cycle, and when BSA solution is filtrated through the cleaned membrane, for the 2nd cycle, this BSA layer would hinder the interaction of BSA with the membrane surface. It may be work as an intermediate layer. Though, the BSA in the bulk solution can aggregate and weakly accumulate on this layer, producing reversible fouling. On the other hand, much small amount of BSA in the bulk solution can pass through the available pores and caused the irreversible fouling, as shown in Fig. 8(C) and Fig. S.6.

Overall, based on the above results all of the membranes showed severe irreversible fouling in the first 1 h of BSA filtration and decline in permeability, and after that, the permeability

stabilized even for the 2nd cycle. The hydraulic cleaning is not enough to clean these membrane surfaces, thus the chemical cleaning could be an appropriate solution for these membranes.

Interestingly, although the nanocomposite membranes exhibited low FRR (high R_{ir}) values, the M3 nanocomposite membrane (with mechanical properties) showed higher permeability, during the filtration of BSA, even compared with that of the pure water permeability of the reported nanocomposite membranes [56-59].

It worth mentioning that change of the diameter and length of ZrO_2 NFs could affect the physiochemical properties and performance of the produced nanocomposite membranes, where the decrease of the NFs diameter will not decrease the water transport path (as discussed in the above section). While the shortening of their length will facilitate their movement to the membrane top surface, during the phase inversion process. On the other hand, functionalization of the produced ZrO_2 NFs to increase its hydrophilicity could produce much more hydrophilic nanocomposite membranes, as well as decrease the attachment of the foulant to the surfaces and pores of membranes.

Fig. 9. Comparative performance of flat sheet PSf composite/nanocomposite membranes; comparison between the pure water permeability ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) and BSA rejection (%) in this study (M3; Ref. 0) and literature (the X-axis is the number of Refs. from Table S1).

The comparative performance of PSf flat sheet based composite/nanocomposite membranes is displayed in Fig. 9 and Table S1. The M3 nanocomposite membrane showed higher performance in terms of water permeability and BSA rejection as compared to other nanocomposite membranes. Among the nanocomposite membranes, M3 was chosen because it exhibited the highest mechanical properties, as well as the highest permeance during the filtration of BSA solution in the 1st cycle. Although the nanocomposite membrane No. 10 showed higher water permeability than M3, it exhibited low BSA rejection (~84%) which makes its overall performance less than the M3 nanocomposite membrane.

4. Conclusion

The PSf-ZrO₂ nanocomposite membranes were successfully fabricated. The characterization results display that the ZrO₂ NFs were successfully incorporated and confined in the matrix of the polymeric PSf membrane, producing effective and robust nanocomposite membranes. The nanocomposite membranes possessed an excellent mechanical property, relatively high hydrophilicity, large pore size and superior water permeability without selectivity trade-off. However, the increase of ZrO₂ loading more than 0.75% (M4) resulted in a decrease in the mechanical properties and membrane performance. The results showed that the M3 (0.5wt.%) nanocomposite membrane has the highest tensile strength and flexibility, as well as high water permeability during the BSA solution filtration. This study opens a new avenue for producing high efficient nanocomposite membranes based on the inorganic electrospun NFs additives, instead of the nanoparticles.

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Graphical abstract

Highlights

- ➔ Zirconia nanofibers were fabricated and used to develop nanocomposite membranes.
- ➔ The diverse nano-micro size of ZrO_2 NFs enhanced its stability inside the membrane.
- ➔ Optimum loading of ZrO_2 NFs to maximize flux and BSA rejection was 0.5 wt.%.
- ➔ This efficient nanocomposite membranes overcome the perm-selectivity trade-off.

Conflict of interest

The authors verify that no conflict of interest in this work