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Fabrication of sulfonated polyethersulfone ultrafiltration membranes with an excellent antifouling performance by impregnating with polysulfopropyl acrylate coated ZnO nanoparticles

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ABSTRACT

Sulfonated polyethersulfone/sulfopropyl methacrylate membranes impregnated with the polysulfopropyl acrylate coated ZnO nanoparticles were developed using a non-solvent-induced phase separation recipe. The composite membranes offered much-enhanced hydrophilicity and improved porosity, which are critical for the excellent antifouling performance and high permeate flux. By adding polysulfopropyl acrylate modified ZnO, it achieved the maximum water flux of 420 L m⁻² h⁻¹ while maintained the natural organic matter rejection rate of 99% with an excellent flux recovery ratio up to 99% in the antifouling measurement. The results display that the impregnation of ZnO nanoparticles in the sulfonated polyethersulfone membrane can effectively increase the surface hydrophilicity which is essential for reducing the irreversible fouling with improved long-term performance and excellent recyclability.

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1. Introduction

To supply a growing population with high-quality water, multiple innovative water purification technologies are urgently needed to be developed. Membrane-based water treatment systems have drawn the most recognition in pharmaceuticals (Barbetta et al., 2005), biotechnology (Pan et al., 2017), food (Wu and Bird, 2007) and especially general water purification industries (Song et al., 2016) due to their ease to operate, low cost, high performance, low energy and chemicals consumption, and low secondary contamination. (Burbano et al., 2007; Pruss-Ustun and Organization, 2008; Zhi et al., 2014). Ultrafiltration (UF) membranes are made from either polymeric or ceramic membranes based on the composition of the membranes material (Li et al., 2021; Mahdavi and Bagherifar, 2018; Mavukkandy et al., 2016; Moideen et al., 2016). Because of its tunable structure and easy fabrication approach, the polymeric membrane has become the most versatile option for UF applications. Most of the polymeric membranes offered excellent physicochemical properties with good chemical and mechanical stability. Besides, the polymer mixtures miscibility are of great interest in both industry and academia. The miscibility is primarily determined by the heat of mixing. The beneficial equation-of-state influence

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on blending thermodynamics is outweighed by exothermic mixing (Rana et al., 1996a, 2000, 1996b, 1993). The typical polymeric membranes, however, suffer from rapid fouling due to the adhesion of bio-film or natural organic contaminants (NOM), which results in the plugging of the pores and the development of a surface barrier layer (Hilal et al., 2005). Consequently, the membrane has to be replaced once the water flux is decreased significantly. To develop an antifouling polymeric membrane for long-lasting water filtration performance, it is important to avoid the deposition of bio-film and the accumulation of NOM matter. By improving the surface wettability, a hydrated layer is more likely to be developed on the surface of the polymeric membrane, which minimizes the adhesion of hydrophobic NOMs. In addition, with the surface hydrated layer, contaminants accumulated on the surface of the membrane are easy to be flushed off. Hence, the membrane’s antifouling efficiency can be significantly enhanced using an effective recovering process (Banerjee et al., 2011; Braeken et al., 2006).

To increase the surface hydrophilicity of the polymeric membranes, several technical approaches have been established, including surface grafting and coating, bulk modification, and polymer blending. The physical mixing with hydrophilic nanoparticles (NPs) to improve the hydrophilicity of the polymeric membranes has been increasingly employed due to its simplicity of operation and excellent reproducibility with stable performance (Du et al., 2013; Ouyang et al., 2019; Reddy et al., 2003; Yu et al., 2006). ZnO is well-known for its beneficial properties such as its excellent mechanical, electrical, optical, and chemical characteristic, which make it suitable for a wide range of implementations (Chen et al., 2018; Djurišić et al., 2012). Some studies have used the surface deposition of ZnO NPs on various membranes to manipulate their surface characteristics (Huang et al., 2018). However, such an approach could suffer from the detachment of the coated ZnO NPs, resulting in early failure of the membranes. Hence, many studies have also explored the incorporating of ZnO NPs into the polymeric membranes to improve the hydrophilicity with macro-voids and channels, thereby boosting the water permeability (Balta et al., 2012; Jafarzadeh et al., 2015). However, directly introduce ZnO NPs in the polymer matrix could suffer from the aggregation of ZnO, which could weaken the mechanical strength of the polymer membrane structure. Recently, scientists have shown a strong interest in making breakthroughs in green manufacturing techniques for metal oxide nanoparticles. This is due to the advantages of safety, speed, favorable economics, and environmentally large-scale productive. Alga, enzymes, microorganisms, and plant extracts are employed in the intriguing field of green nanoparticle fabrication. Plant extracts include flavonoid and phenolic components that aid in the fabrication of nanoparticles. The extracts operate as reducing agents, stabilizing, and capping agents respectively (Essawy et al., 2020).

The novelty of this work is to design biogenic ZnO NPs with polysulfopropyl acrylate (PSPA) polymer chains, which was then homogeneously distributed within the sulfonated polyethersulfone (SPES) matrix. Highly porous broccoli-like ZnO NPs were produced under the influence of pomegranate extract. The PSPA coating is essential for reducing the aggregation of ZnO with much more improved dispersion in SPES casting solution. Meanwhile, the additional sulfo group in the PSPA and the OH group on ZnO also increased the hydrophilicity of the modified SPES. The impregnation of the ZnO in the SPES has significantly changed the morphology of the SPES membrane by forming pores and channels during the nonsolvent-induced phase separation process (NIPS). The obtained hydrophilic porous SPES membrane offered combined benefits of excellent permeate flux and outstanding foulant rejection with reduced deposition of the foulants. The used membranes also demonstrated high efficiency of recovery, which is essential for long term performance in UF application. The mechanisms for the high flux, good antifouling property, and excellent recovery were also discussed in association with the morphology and surface property of the ZnO modified SPES membrane.

2. Experimental

2.1. Materials

H₂SO₄ (96%, Fisher Scientific), sodium hydroxide (≥98%, Sigma-Aldrich Co., USA), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, Sigma-Aldrich Co., USA), calcium chloride (CaCl₂·2H₂O; 98%, Sigma-Aldrich Co., USA), sodium chloride (NaCl, ≥99.5%, Sigma-Aldrich Co., USA), ethanol (99%, Sigma-Aldrich Co., USA), 3-sulfopropyl acrylate potassium salt (SPAK, Sigma-Aldrich Co., USA), N-methyl-2-pyrrolidinone (NMP, ≥99%, Sigma-Aldrich Co., USA), N,N-dimethylformamide (DMF, ≥99.5%, Sigma-Aldrich Co., USA), ethylene glycol dimethacrylate (EGDMA, 98%, Sigma-Aldrich Co., USA), polyvinylpyridilone (PVP, Sigma-Aldrich Co., USA), azobisisobutyronitrile (AIBN, 98%, Sigma-Aldrich Co., USA), 3-methacrylate-propyltrimethoxysily (MPS, 98%, Sigma-Aldrich Co., USA), alginic acid sodium salt (SA, ≥99.5%, Sigma-Aldrich Co., USA), humic acid (HA, Sigma-Aldrich Co., USA), bovine serum albumin (BSA, ≥98%, Sigma-Aldrich Co., USA), polyethersulfone (PES, Mw 58,000 g/mol, Goodfellow, USA) were used without further treatment. The NOM solution was prepared based on the literature method by mixing BSA, SA, and HA (10 mg L⁻¹ each) with 1 mM CaCl₂ (1 mM) and NaCl (7 mM) in deionized (DI) water (Kumar et al., 2019). H₂SO₄ was used for the PES sulphonation. A fresh pomegranate fruit, obtained from a local market in Saudi Arabia, was used to extract juice, which was used to control the morphological structure of ZnO nanoparticles. DI water was supplied by a millipore purification system (Milli-Q Direct 8, France).
Table 1
The composition of casting solutions.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>SPES (wt%)</th>
<th>PVP (wt%)</th>
<th>ZnO-g-PSPA (wt%)</th>
<th>NMP (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSZPA0</td>
<td>18</td>
<td>2</td>
<td>0</td>
<td>80</td>
</tr>
<tr>
<td>MSZPA1</td>
<td>18</td>
<td>2</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>MSZPA3</td>
<td>18</td>
<td>2</td>
<td>3</td>
<td>80</td>
</tr>
<tr>
<td>MSZPA5</td>
<td>18</td>
<td>2</td>
<td>5</td>
<td>80</td>
</tr>
</tbody>
</table>

*a The percentage of OH@ZnO-g-PSPA is based on the total fraction of SPES polymer in the casting solution.

2.2. Materials synthesis

2.2.1. Biogenic preparation of ZnO nanoparticles (NPs)

The ZnO NPs was synthesized using a biogenic assisted combustion process with pomegranate arils. Pomegranate arils contain 85% water, 10% total sugars (mostly fructose and glucose), and 1.5% pectin, as well as organic acids like citric acid, malic acid, and ascorbic acid, and bio-active substances comprising primarily anthocyanins, flavonoids, and phenolics. Both the organic acids and sugars can couple with the Zn\textsuperscript{2+} and will significantly affect the kinetics of the ZnO formation. Our previous work has demonstrated a similar technique to control the morphology of the Cu\textsubscript{2}O/CuO NPs with excellent catalytic activity (Alhumaimess et al., 2020). In this work, we use the pomegranate extract to synthesis porous ZnO with a small crystal domain size. 50 mg of the pomegranate juice was added in a crucible (≈100 mL) containing 15.0 mL of DI water. 0.5 g of Zn(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O was dissolved in this solution, which results in a significant color change of the purple color of the pomegranate solution. This suggests that there was a trait of the interaction between the pomegranate juice and the zinc ions. The crucible was then placed in a pre-heated muffle furnace at 300 °C to produce the ZnO nanoparticles after heating for 2 h.

2.2.2. Surface-functionalization of ZnO nanoparticles

The surface of the synthesized ZnO NP was modified with polysulfopropyl acrylate (PSPA) to enhance the dispersion and stability of ZnO in the SPES. The surface modification involves three key steps. First, the surface hydroxyl groups were created by dispersing 0.5 g of ZnO NPs in a 50 mL of 0.5 M NaOH aqueous solution under continuous stirring at 60 °C for 24 h. The formed product was collected by centrifugation, rinsed with water until pH neutral, followed by drying in a vacuum oven at 30 °C for 24 h. Here, we use the low-temperature drying process to preserve the surface OH groups. In the second step, the surface of the hydrolyzed ZnO NPs was grafted with MPS, which formed active functional groups for the in situ polymerization of sulfopropyl acrylate on the ZnO surface. The surface hydrolyzed ZnO (10 mg) NPs were dispersed in 10 mL ethanol and sonicated for 1 h before adding 1.5 mL of MPS. The mixture was vigorously stirred at 30 °C for 16 h. To speed up the sol–gel formation, ammonia solution was added dropwise to increase the pH to 13. The mixture was further heated for 12 h at 50 °C to complete the formation of MPS coated ZnO (ZnO-g-MPS). The resulting product of ZnO-g-MPS was collected by centrifugation. The sample was rinsed with ethanol to remove residual organics before being dried under vacuum for 12 h at 30 °C.

Finally, the PSPA was formed on the surface of ZnO-g-MPS by a free radical initialized polymerization of SPA. 40 mg of ZnO-g-MPS was dispersed in 100 mL acetonitrile in a 500 mL 2-neck round bottom flask fitted with a reflux condenser. The suspension was mechanically stirred for 30 min before adding 0.5 g EGDMA, 0.5 g SPAK, and 20 mg AIBN. The mixture was refluxed at 95 °C for 2 h to complete the polymerization process. The product of PSPA coated ZnO NP (ZnO-g-PSPA) was collected after removing the unreacted materials by thoroughly washing with water and ethanol, followed by drying under vacuum for 24 h at 80 °C (Scheme 1).

2.2.3. Membrane fabrication

The PES was sulfonated using concentrated H\textsubscript{2}SO\textsubscript{4} based on the previously reported procedure (Song et al., 2016). SPES UF membranes were fabricated by the NIPS at room temperature. The typical cast solution contains 18 wt% SPES, 2 wt% PVP, and 80 wt% NMP. The solution was sonicated for 60 min at 50 °C until the SPES was completely dissolved. Different amounts of ZnO-g-PSPA were introduced in the casting solution and the resulting solution was stirred for a further 24 h at 50 °C to obtain a stable composite dispersion. Prior to membrane casting, the composite dispersion was sonicated for 20 min followed by being held at a standstill to eliminate the air bubbles. The solution was cast at a thickness of 250 μm onto a clean sheet of glass with a casting knife. The cast film was submerged in a water bath for a few minutes for phase separation through a complete exchange of solvent and nonsolvent. The membrane was detached from the glass support. To remove the remaining solvent, the obtained membrane was washed with DI water several times. The SPES membranes with ZnO-g-PSPA loadings of 1, 3, and 5 wt% were named as MSZPA1, MSZPA3, and MSZPA5 respectively (Table 1). For comparison, an undoped SPES membrane (MSZPA0) was also fabricated without ZnO-g-PSPA.
2.3. Membrane characterizations

The crystal structures and molecular ordering were investigated using a powder X-ray diffractometer (Optima7000, Shimadzu, Japan) with a Cu Kα radiation (λ = 0.15406 nm). Thermal gravimetric analysis (TGA, STA-449F3, Shimadzu) was carried out in N₂ with the temperature ranging from 50 to 600 °C at a constant heating rate of 10 °C min⁻¹. Molecular structures and the associated functional groups within the polymers were studied with a Fourier transformed Infrared (FTIR) spectrophotometer (IR Tracer-100, Shimadzu) with a scan range from 400 to 4000 cm⁻¹. Field emission scanning electron microscopy (FESEM, Thermo Scientific Quattro ESEM, Thermo Fisher) was used to examine the top surface and cross-section morphologies of the synthesized membranes. To determine the hydrophilicity, the contact angle was measured with a goniometer (SCA20, Data Physics) fitted with a digital camera. Tensile testing was performed with a tensile tester (EZ-S, Shimadzu). The surface zeta potential was measured with an electrokinetic analyzer (SurPASS, Anton Paar).

The membrane’s porosity (ε) was assessed by the absorption of water using Eq. (1):

\[ \varepsilon = \frac{W_1 - W_2}{AT \rho} \]  

where \( W_1 \) and \( W_2 \) are the weight of the wet and dry membranes, respectively. \( A \) is the area of the membrane; \( T \) is the thickness and \( \rho \) is the density of water.

2.4. Ultrafiltration measurements

A stirred dead-end UF cell (Amicon 8050; Millipore) was used to examine the membrane UF performance. The integrity of the membranes was examined by applying 2 bar pressure for 30 min with DI water to ensure there was no cracks or leaks. The UF experiments were operated at 1.0 bar. In 30 min, the weight of permeate was measured to determine the permeate water flux. \( J_w \), calculated in Eq. (2)

\[ J_w = \frac{m}{\rho At} \]  

where \( m \) is the weight of permeate, and \( t \) is the permeation time.

The permeate flux of clean water through the pristine membrane was defined as \( J_{w1} \). Subsequently, the prepared foulant solutions (100 ppm of BSA, HA, and SA, as well as a synthetic NOM) were introduced at 1 bar (Bai et al., 2015). The permeation flux of the foulant solutions \( (J_{fx}) \) was calculated via Eq. (2). The foulant rejection rate, \( R_f \), was determined using Eq. (3)

\[ R_f (\%) = (1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}}) \times 100 \]  

where \( (C_{\text{feed}}) \) and \( (C_{\text{permeate}}) \) are the concentrations of foulant in the feed and permeate. After the measurement, the used membrane was washed with DI water and 0.02M NaOH solution to remove the adsorbed foulants. The permeate flux of clean water through the recovered membrane, \( J_{w2} \), was evaluated for another 30 min filtration. To emphasize the antifouling efficiency, flux recovery ratio (FRR), the total fouling ratio (\( R_t \)), reversible fouling ratio (\( R_r \)) and irreversible fouling ratio (\( R_i \)) were calculated using Eqs. (4)~(7).

\[ \begin{align*} 
\text{FRR} (\%) &= \frac{J_{w2}}{J_{w1}} \times 100 \\
R_t &= \frac{(J_{w1} - J_{fx})}{J_{w1}} \times 100 \\
R_r &= \frac{(J_{w2} - J_{fx})}{J_{w1}} \times 100 \\
R_i &= \frac{(J_{w1} - J_{w2})}{J_{w1}} \times 100 
\end{align*} \]

The foulant concentrations in water were measured with a UV–Vis spectrometer (Cary 60, Agilent). The adsorption capacity per unit area of the membrane \( (q) \) was evaluated using Eq. (8).

\[ q = \frac{(C_o - C_t) V}{A} \]  

where \( V \) and \( A \) are the solution volume and the actual membrane area used in the adsorption experiments; \( C_o \) and \( C_t \) are the initial and final foulant concentrations. 

Figure Scheme 1.
Scheme 1. Schematic illustration of the fabrication of ZnO-g-PSPA polymer.
3. Results and discussion

3.1. Characterization of ZnO nanoparticles

The XRD pattern of the biogenic fabricated ZnO nanoparticles (NPs) is displayed in Fig. 1a. The diffraction peaks at $2\theta = 32.1^\circ$, 34.6$^\circ$, 36.6$^\circ$, 47.8$^\circ$, 56.9$^\circ$, 63.2$^\circ$, 68.1$^\circ$, 69.3$^\circ$, and 77.2$^\circ$ are assigned, respectively, to (101), (002), (102), (110), (103), (112), (201), and (202) planes (Harish et al., 2017) of the ZnO hexagonal structure (JCPDS No. 36-1451). The mean particlesize of ZnO NPs was obtained from the Debye–Scherrer Eq. (9)

$$D = K\lambda/\beta \cos(\theta)$$

where $D$ is the crystallite size (nm), $K$ is the Scherrer’s constant of value 0.9, $\lambda$ is the x-ray wavelength ($\lambda = 1.54$ Å), $\beta$ is the full-width at half maximum of the diffraction peak (FWHM) and $\theta$ is the diffraction angle. The average domain size of our ZnO NPs is 15.3 nm.

The N$_2$ adsorption–desorption isotherm and pore size distribution were carried out to study the textural and morphological characteristics of the ZnO NPs. The N$_2$ adsorption–desorption isotherm is displayed in Fig. 1b. The ZnO features a mesoporous texture with slit-like pores, demonstrated by the type IV isotherm with H3 hysteresis loop (Pudukudy et al., 2013). The surface area of the biosynthesized ZnO is 47.8 m$^2$/g with a pore diameter of 27 Å and pore volume of 0.098 cm$^3$/g. The BJH desorption pore size curve is displayed in the inset in Fig. 1b, which shows the presence of a uniform mesoporous structure.

FESEM was used to examine the shape and structure of the biogenic ZnO NPs for further investigation. The results revealed that the ZnO NPs displayed highly porous broccoli-like morphology, as illustrated in Fig. 1c. The results confirmed that by adding the pomegranate juice, the growth of the ZnO crystal was constrained due to the surface passivation with the organic acids and sugars in the fruit juice. The appropriate juice concentration is essential for the formation of novel nanomorphology and the technique is particularly effective for the synthesis of nanostructured metal oxides. Our previous work (Essawy et al., 2020) demonstrated that without the addition of the pomegranate extract, only solid crystallized nanoparticles can be formed due to its rapid kinetics, which is often accompanied by the Oswald ripening to broaden the particle size distribution.

3.2. Membrane characterization

Fig. 2(a) shows the FTIR spectra of the membranes with various ZnO-g-PSPA concentrations. The O–Si stretching vibrations are assigned to the conspicuous bands at 867 and 1004 cm$^{-1}$. The O=S=O stretching vibrations are associated with the bands at 1110 and 1147 cm$^{-1}$. The -O- group vibration is related to the absorption band at 1237 cm$^{-1}$. The distinctive bands at 1484 and 1569 cm$^{-1}$ are associated with the aromaticity originated from the SPES. The band at 1675 cm$^{-1}$ is related to the C=O stretching, whereas C-H stretching is responsible for the presence of the weak band at 2960 cm$^{-1}$. With the increase of ZnO-g-PSPA, the peaks at 576 and 1147 cm$^{-1}$ were increased accordingly, which are assigned to the Zn-O stretching and the sulfo group in the PSPA. As a result, the FTIR reveals that composite SPES/ZnO-g-PSPA membranes were successfully developed.

The successful impregnation of inorganic NPs in the polymer matrix was also identified using powder XRD, shown in Fig. 2. (b). The MSZPA0 exhibited a large diffraction peak at 18.6$^\circ$, which is characteristic of SPES (Song et al., 2016). By increasing the contents of ZnO-g-PSPA, the intensity was increased. Based on the peak width, other broad weak diffraction peaks at higher diffraction angles were also contributed from the PSPA. The large width of the peak suggests that both SPES and PSPA had limited ordering, possibly due to the intimate interaction between SPES and PSPA.

The thermal stability of the membrane was investigated employing TGA, displayed in Fig. 2. (c). Two weight-loss stages were identified for all the membranes. The first weight-loss peak below 150 °C is associated with the loss of physisorbed water. The second peak in the temperature range of 200–420 °C was attributed to the degradation of the carboxyl groups followed by the degradation of residual polymer chain structures at a higher temperature. Besides, the decomposition temperature of ZnO-g-PSPA is higher than that of the virgin membrane, implying that adding ZnO NPs improves thermal stability.

3.3. Surface charge of the fabricated membrane

The surface charge of the prepared membrane was obtained by measuring the surface potential ($\zeta$) at pH 7, as illustrated in Fig. 3. Due to the presence of a high degree of -SO$_3$H groups in the SPES and the ZnO-g-PSPA, all fabricated membranes had negative surface potentials. Table 2 lists the surface potentials together with other morphological and physical properties for membranes with different ZnO concentrations. The surface potentials became increasingly negative as the amount of ZnO-g-PSPA increased following a pseudo linear relationship, as seen in Fig. 3, due to the increase in the negatively charged hydroxide (-OH) groups around the ZnO NPs as well as the -SO$_3$H in the PSPA. With the highest concentration of ZnO-g-PSPA, the greatest negative surface-potential of $\sim$39 mV was obtained. The consistent behavior of the $\zeta$ as a function of the ZnO-g-PSPA concentration suggests that the surface charge of fabricated membranes can be precisely regulated.
3.4. Morphology and structural characteristics

The membrane morphologies were emphasized using FESEM, with typical top-surface and cross-sectional images displayed in Fig. 4. The membrane surfaces were densely packed and uniform, with no obvious defects. Most of the ZnO-g-PSPA nanofiller was evenly distributed within the membrane, which is critical for the long term antifouling performance of the membrane. The composite membranes (MSZPA1, MSZPA3, and MSZPA5) exhibited substantially higher
surface porosity than the unloaded membrane (MSZPA0). The less porous pristine membrane is expected to have reduced permeability with a greater rejection rate. Conversely, the larger pore diameters of the composite membranes could be originated from the rapid mass transfer between the nonsolvent and the casting solution with the presence of ZnO, which causes the fast break down of the casting solution during the membrane formation, forming porous structures with large diameter channels. The finger-like channels will allow water molecules to pass through rapidly. The porosity measurement results in Table 2 also confirmed that all membranes containing ZnO-g-PSPA offered greater porosities and larger pore radius than the pristine SPES membrane. Hence, the addition of ZnO-g-PSPA can accelerate the phase separation process, which is responsible for creating bigger pores inside the SPES, leading to increased permeability and water uptake. Table 2 summarizes such findings. With the introduction of 3 wt% ZnO-g-PSPA, the greatest porosity with the largest mean pore radius was reached. By increasing the ZnO-g-PSPA concentration further, the porosity was reduced as agreed with the FESEM observation in Fig. 4. This is possibly due to the aggregation of ZnO-g-PSPA at high concentration resulting in a significant increase in the viscosity of the casting solution, which could prevent the rapid penetration, dispersion and exchange of nonsolvent. Furthermore, with the introduction of ZnO-g-PSPA nanofiller, the water uptake was also increased.
Fig. 4. The surface and cross-sectional FESEM images of (a) MSZPA0; (b) MSZPA1; (c) MSZPA3; and (d) MSZPA5 membranes.

with respect to the undoped membrane (MSZPA0). Both the increased porosity and the hydrophilicity could be responsible for this. The increased hydrophilicity is important for a high water flux with a high rejection rate, which will be confirmed with the contact angle measurements below.
3.5. Hydrophilicity of the membrane

The hydrophilicity of the membrane was directly estimated by measuring the contact angle. The results in Fig. 5 demonstrated the effect of ZnO-g-PSPA on the surface hydrophilicity of the SPES membrane. The contact angle of the fabricated membranes decreased when the concentration of ZnO-g-PSPA was increased, indicating that the membrane surface became much more hydrophilic. The ZnO-g-PSPA contains both OH groups and –SO$_3$H. Hence the addition of ZnO-g-PSPA could effectively increase the concentration of –OH and –SO$_3$H. The homogeneous distribution of ZnO-g-PSPA is also essential for the increase of surface hydrophilicity when the bulk ZnO-g-PSPA increases. The increased surface hydrophilicity is consistent with the increase of surface zeta potentials. The high surface hydrophilicity will be helpful for the increased water absorption and permeation through the dipole–dipole attractive interactions and hydrogen bonds with these strongly polarized surface groups. As a result, the magnitude of the membrane surface free energy ($\Delta G_{SL}$) was increased.

3.6. Mechanical characteristics

Table 2 also shows the mechanical characteristics of the produced membranes with different ZnO-g-PSPA content. Young’s modulus, elongation, and tensile strength were measured to evaluate any effects of mixing inorganic NPs on the mechanical stability of the SPES membrane. Such parameters are important for the long term UF performance of the membrane. The results show that by increasing ZnO-g-PSPA content tensile strength, Young’s modulus, and elongation
Table 3

<table>
<thead>
<tr>
<th>Membrane</th>
<th>R_HA (%)</th>
<th>R_HSA (%)</th>
<th>R_SA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSZPA0</td>
<td>98.3 ± 0.3</td>
<td>93.3 ± 0.4</td>
<td>91.9 ± 0.4</td>
</tr>
<tr>
<td>MSZPA1</td>
<td>99.1 ± 0.1</td>
<td>91.2 ± 0.2</td>
<td>90.1 ± 0.2</td>
</tr>
<tr>
<td>MSZPA3</td>
<td>98.7 ± 0.1</td>
<td>93.1 ± 0.2</td>
<td>88.4 ± 0.1</td>
</tr>
<tr>
<td>MSZPA5</td>
<td>97.6 ± 0.2</td>
<td>91.8 ± 0.1</td>
<td>87.3 ± 0.1</td>
</tr>
</tbody>
</table>

were all increased substantially. The results also suggest that the ZnO-g-PSPA was homogeneously dispersed in the SPES polymer matrix as a result of the excellent contact between SPES and PSPA on the surface of ZnO.

3.7. Membrane permeability

The pure water flux for ZnO, ZnO-g-MPS, and ZnO-g-PSPA membrane are shown in Fig. 6a and b, respectively. Obviously, the ZnO, and ZnO-g-MPS membranes had the lowest water flux (188 and 260 Lm⁻² h⁻¹). By adding ZnO-g-PSPA, the water flux was increased monotonically from 270 (MSZPA0) to 420 Lm⁻² h⁻¹ (MSZPA5), which was affected by the increased hydrophilicity and membrane porosity (Zheng et al., 2006). By using foulant solutions (BSA or HA), the permeate water fluxes were reduced with respect to that of the clean water, shown in Fig. 6b, which is expected due to the foulant deposition on the membrane surface or within the pores during the UF treatment at 1 bar pressure. Nonetheless, the flux of foulant solution was increased as the concentration of ZnO-g-PSPA was increased. This suggests that the hydration layer of adsorbed water molecules could effectively prevent the accumulation of foulants. Under similar conditions, the BSA solution flux was lower than that of the HA solution, which is due to the large size of the BSA protein. The MSZPA3 membrane, which has the largest porosity and pore radius, produced the maximum foulant solution flow for BSA. As a result, the reduction in BSA flux is determined by the BSA deposition within the pores. On the other hand, the MSZPA5 membrane produced the maximum foulant solution flow for HA, despite having reduced porosity and a smaller pore radius than MSZPA3. Hence, it can be established that for large molecules like BSA, the pore diameter determines the permeate flux, while for small molecules like HA, the membrane hydrophilicity determines the flow rate. The rejection ratios (RF) for HA, BSA, and SA foulants were quantified for all membranes, summarized in Table 3. In comparison with the hybrid membranes, the undoped membrane (MSZPA0) had the highest rejection ratio, since it has the lowest porosity with a smaller pore radius. Therefore, the foulant rejection by the MSZPA0 followed the exclusion mechanism with sacrificed flow rate.

3.8. Membrane antifouling performance

The foulants adsorption rate on the surface of the membrane is an essential characteristic that determines the membrane’s service life. The adsorptions of BSA, HA, and SA foulants were decreased monotonically as the concentration of ZnO-g-PSPA was increased, shown in Fig. 7a. With the highest surface hydrophilicity, the MSZPA5 membrane has the smallest amount of adsorbed foulant. Hence, the surface hydration layer can effectively reduce the accumulation of organic foulant. Meanwhile, the membranes’ increased negative surface potential could also be responsible for rejecting the negatively charged foulant species (Li et al., 2017).

The flux recovery ratio, FRR, is a measure that indicates regeneration of the UF membrane performance. The FRR of membranes (MSZPA0, MSZPA1, MSZPA3, MSZPA5) was assessed for both HA and BSA solution, shown in Fig. 7b. All of the composite membranes had higher FRR values than the undoped membrane. The FRR values were positively correlated with the ZnO-g-PSPA concentration, although greater FRR values were observed for HA due to its relatively smaller size with respect to BSA. The highest FRR was achieved from MSZPA5 with the highest ZnO-g-PSPA doping. The FRR of 96% and 80% were achieved for HA and BSA foulants, respectively. This suggests that by doping with ZnO-g-PSPA, the high hydrophilicity of the membrane is efficient for reducing foulant deposition with improved membrane recovery. The water flux could be regained following rinsing with distilled water and 0.02M of NaOH, and the membrane UF performance was successfully regenerated.

The fouling resistance of the membranes was also tested using a feed solution containing a combination of NOMs, specified in the experimental section. The UF measurements were carried out for 2 h, after which the membranes were cleaned for 30 min with a mixture of DI water and 0.02M of NaOH. As expected, the NOM solution flux was much lower than that of the pure water, Fig. 8a, due to the deposition of NOM foulant components. The NOM flow did, however, increase with the increase of ZnO-g-PSPA loading up to 3 wt%. Further increase in ZnO-g-PSPA resulted in a modest reduction in NOM flux. The improved flow is due to both the increased hydrophilicity and pore radius when the increase of ZnO-g-PSPA at a low doping level. However, from MSZPA3 to MSZPA5, the pore radius was reduced despite the increased hydrophilicity. Hence, for NOM containing different sizes of foulants, the pore size is more important than the surface hydrophilicity in determining the permeate flow flux. On the other hand, the FRR was increased monotonically from 63% for MSZPA0 to 98% for MSZPA5, shown in Fig. 8b. This implies that the permeate recovery is mainly determined by the
Fig. 7. (a) Adsorbed amount of BSA, HA, and SA per unit area of different membranes and (b) flux recovery ratio (FRR) of the pristine and hybrid membranes.

Fig. 8. (a) Pure water, NOM, and water flux after 30 min washing with DI water and 0.02 M NaOH solution; (b) FFR (%), (c) $R_i$, and $R_e$ values, and (d) Rejection performance of the membrane.
Fig. 9. Reusability test of the ZnO-g-PSPA-based membrane.

surface hydrophilicity, rather than the pore diameter, which suggests that foulant was likely to be accumulated on the surface of the membrane, rather than inside the pore. The binding of NOM on MSZPA5 was substantially less than that on MSZPA0, allowing NOM to be effectively washed off. To emphasize the antifouling qualities of the developed membranes, $R_t$ and $R_{ir}$ parameters were determined using pure water flux, foulants flux, and post-washing pure water flux (Fig. 8c), described in Eqs 6 and 7. The reversible weak adsorption of NOM was further confirmed by the similar trend of the $R_t$ values as the FRR values, accompanied by the reversed trend of the $R_{ir}$ values. Fig. 8d depicts the NOM rejection ratio by the fabricated SPES membranes. It confirms that NOM was successfully removed from the aqueous solution, with the highest removal efficiency of 99% by MSZPA3 membrane.

The MSZPA3 membrane, which exhibited the highest water flux and significantly improved FRR, was selected for further assessment of its long-term flux and fouling resistance via a three-cycle UF test of synthetic NOM solution (Fig. 9). For MSZPA3, the deterioration in $J_w$ and $J_{NOM}$ was significantly weak. The ZnO-g-PSPA induced fouling resistant nature of MSZPA3 prevented the strong surface attachment of NOM, allowing the post-NOM filtration cleaning to effectively remove the loosely attached NOM components from the surface.

4. Conclusion

In this study, ZnO-g-PSPA was successfully fabricated and applied as a nanofiller to modify the morphology and physical property of SPES by the NIPS approach. The structure and performance of a SPES/ZnO-g-PSPA hybrid membrane were investigated in relation to the quantity of the ZnO-g-PSPA nanofiller. The synthesized SPES/ZnO-g-PSPA hybrid membrane achieved the highest pure water permeate flux of 420 Lm$^{-2}$ h$^{-1}$ with the best NOM rejection ratio of 99% when 3 wt% of ZnO-g-PSPA was used in the SPES. The water uptake and porosity were remarkably improved with respect to the unmodified SPES, MSZPA0. The surface hydrophilicity was significantly increased with the water contact angle reduced from 68° to 34°, and the surface energy was increased from 98.9 to 130 mJ m$^{-2}$ for the MSZPA5 sample with respect to the MAZPA0. Furthermore, the adsorption of foulant was gradually reduced as the concentration of ZnO-g-PSPA was increased, due to the increased surface hydrophilicity, which is also responsible for the high-efficiency recovery of the SPES/ZnO-g-PSPA hybrid membrane. The large porous structure within the membrane determined the high permeate flux containing large foulant molecules. Hence, both the flow flux and the antifouling performance of the SPES were successfully improved by modification with ZnO-g-PSPA. This approach offered an advanced high-performance UF membrane technology that could potentially be used in water treatment, oil–water separation, and biological hazard decontamination with minimum environmental impact.

CRediT authorship contribution statement

Eid H. Alosaimi: Conceptualization, Methodology, Investigation, Resources, Formal analysis. Hassan M.A. Hassan: Conceptualization, Methodology, Investigation, Resources, Formal analysis, Writing - original draft, Software, Validation. Ibrahim Hotan Alsohaimi: Conceptualization, Methodology, Investigation, Resources, Formal analysis, Writing - original draft, Software, Validation, Supervision. Qiao Chen: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Software, Validation, Writing - review & editing. Saad Melhi: Investigation, Validation, Formal analysis, Writing - original draft. Ayman Abdelaziz Younes: Investigation, Validation. Walaa H. El-Shwiniy: Investigation, Validation.
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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