High flux polysulfone braided hollow fiber membrane for wastewater treatment role of zinc oxide as hydrophilic enhancer

Peechmani, Prakash; Othman, Mohd Hafiz Dzarfan; Kamaludin, Roziana; Puteh, Mohd Hafiz; Jaafar, Juhana; Rahman, Mukhlis A; Ismail, Ahmad Fauzi; Kadir, Siti Hamimah Sheikh Abdul; Illias, Rosli Md.; Gallagher, Joe; Djuli, Sabreenna Marsya

Published in:
Journal of Environmental Chemical Engineering

DOI:
10.1016/j.jece.2021.105873

Publication date:
2021

Citation for published version (APA):
High Flux Polysulfone Braided Hollow Fiber Membrane for Wastewater Treatment Role of Zinc Oxide as Hydrophilic Enhancer

Prakash Peechmani¹, Mohd Hafiz Dzarfan Othman¹*, Roziana Kamaludin¹, Mohd Hafiz Puteh¹, Juhana Jaafar¹, Mukhlis A Rahman¹, Ahmad Fauzi Ismail¹, Siti Hamimah Sheikh Abdul Kadir³, Rosli Md. Illias⁴, Joe Gallagher⁵, Sabreenna Marsya Djuli³

¹Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor.
²Department of Environmental Engineering, School of Civil Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor.
³Institute of Pathology, Laboratory and Forensic Medicine (I-PPerForM), Universiti Teknologi Mara (UiTM), Cawangan Selangor, Kampus Sungai Buloh, Jalan Hospital 47000 Sungai Buloh, Malaysia
⁴Department of Bioprocess and Polymer Engineering, School of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor.
⁵Institute of Biological, Environmental & Rural Sciences (IBERS), Aberystwyth University, Gogerddan, Aberystwyth, Ceredigion, SY23 3EE United Kingdom.

*Corresponding author: hafiz@petroleum.utm.my

Abstract

Incorporation of zinc oxide (ZnO) nanoparticles has played an important role on the improvement of unique membrane characterization and performance, most notably the hydrophilic modification of the membrane for higher pure water permeability. Additionally, the permeability of the membrane can be improved via introduction of braid support by reducing the thickness of the membrane separation layer. Moreover, the braided hollow fiber membrane (BHFM) is able to perform under higher pressure conditions compared to hollow fiber membranes. In this paper, hybrid polysulfone (PSf)/ZnO BHFM was fabricated via phase inversion method. Hydrophilic 10 ± 1.8nm polycrystalline ZnO nanoparticles synthesized via sol-gel method were incorporated on BHFM to improve the hydrophilicity and increase flux with constant rejection under high pressure and the effect of the ZnO loading on the membrane properties and performance were
thoroughly studied. The fabricated BHFMs with 0.0, 0.5, 1.0 and 1.5 wt.% of ZnO nanoparticles concentration were defined as BHFM1, BHFM2, BHFM3 and BHFM4 respectively. Scanning electron microscopy (SEM), contact angle, mechanical strength, flux performance, rejection with bovine serum albumin (BSA) and fouling of best performed membrane were conducted to achieve the target of this paper. The performance of these hybrid ZnO/PSf BHFMs were compared with neat PSf hollow fiber membrane (HFM) and previous studies. The findings from this research work shows that BHFM4 has the most desired properties for wastewater treatment application. The ZnO nanoparticles in BHFM4 have improved hydrophilicity from 108.79 to 71.02°, and thus BHFM4 has increased flux performance from 36.20 to 919.12 L/m²h at 1.0 bar pressure and 193.48 to 1909.11 L/m²h at 4.0 bar pressure when compared with BHFM1. Constant BSA rejection rates (>90%) were observed in all BHFMs. The improved hydrophilicity and pure flux performance with constant rejection rate in high pressure conditions illustrates the suitability of fabricated ZnO/PSf BHFMs in wastewater treatment applications.

Keywords:
Braided hollow fiber membrane; Zinc oxide; Polysulfone; Water treatment; High flux

1.0 Introduction

The performance of membrane material plays an important role in the membrane application, operational condition, operational cost and effluent quality of the wastewater treatment system [1–3]. The high molecular weight of PSf makes this polymer suitable for use in membrane filtrations particularly for water [4,5], pharmaceutical [6], textile dyeing [7,8], desalination [9], peat water [10] and sewage wastewater[11] treatment systems. The excellent mechanical strength, its stability at pH levels from 2 to 13, excellent resistance to caustic and good resistance to moderate chlorine are qualities of PSf which make it suitable to be used for membrane filtration even though it is hydrophobic in nature [5,11–16]. In detail, the excellent mechanical strength ensures the membranes are able to operate at higher pressure, the capability of PSf which can withstand from low to high pH range allows the filtration process to operate at high temperature [6] and the good tolerance to moderate chlorine makes it very suitable for use in any water and wastewater filtration system. However, the hydrophobic nature of PSf membranes
means that the flux obtained from the filtration is low. Therefore, PSf membranes need some
surface modification to enhance the permeation of water molecules.

From the literature study, high flux rate of the PSf membrane can be improved via
incorporation of hydrophilic nanoparticles [4]. Some examples of nanoparticles are titanium
dioxide (TiO$_2$) nanomaterials, ZnO nanoparticles, silver (Ag) nanoparticles, carbon nanotubes
(CNTs), and graphene oxide (GO) [17–19]. Among them, ZnO nanoparticles are considered to be
a promising metal oxide for PSf membrane modification due to its high hydrophilicity, relatively
inexpensive cost and is non-toxic to humans [20,21]. The hydrophilic nature of the ZnO
nanoparticles can easily absorb hydroxyl (-OH) groups which increases the absorption of water
molecules onto the separation layer of membrane [22]. This water-loving characteristic of ZnO
nanoparticles is able to increase the overall flux performance of membranes. Antifouling of
organic matters by hydrophilic ZnO nanoparticles also adds value for the incorporation of these
nanoparticles in mixed matrix membranes. Organic matters are less susceptible to foul on the
hydrophilic membranes due to the reduced interactions between the hydrophilic membrane surface
with organic matters [23]. Xiong et al. reported ZnO nanoparticles are able to improve
hydrophilicity and porosity of the nanocomposite substrate membranes [24]. Amini et al. [25]
reported that the contact angle values observed were lower as the ZnO nanoparticles loading
increased. Moreover, with increasing amount of ZnO nanoparticles in the membrane matrix, the
reverse salt flux of thin film nanocomposite (TFN) membranes also increased. This can be related
to the soluble permeability or hydrophilicity of the membrane. Kusworo et al.[26] found that 1.5
wt% of ZnO nanoparticle increased the hydrophilic property of PES membrane from 68.33° to
66.17°. They explained that it’s due to the nature of a higher volume of nano-ZnO particles which
have a large surface area on the membrane that can adsorb hydrophilic -OH and therefore increases
the hydrophilicity. Sokhandan et al. [27] reported introduction of hydrophilic agents such as 2.0
wt.% of sodium alginate (C$_6$H$_7$O$_6$Na) in 2 wt.% ZnO improved the flux from 37 to 51 L/m$^2$h,
porosity from 63.00 to 72.00%, antibacterial nature, higher flux recovery from 33.50 to 74.00%
and hydrophilicity from 42.00 to 28.00° for sodium alginate coated zinc oxide in Polyacrylonitrile
(ZnO@SA/PAN) flat sheet membrane.
Apart from the hydrophilic surface modification, a few studies have successfully reported that the introduction of braid support in membrane fabrication has increased flux performance of microfiltration and ultrafiltration membranes by reducing the thickness of the separation layer and its reliability in high pressure conditions compared to hollow fiber membranes [28–31]. From literature, it was also reported that the braid support in hollow fiber membranes is able to improve the overall mechanical strength and can ensure the longer lifetime of the membranes [32–34]. The good flux performance and excellent mechanical strength of BHFMs make them suitable for high pressure submerged filtration systems. Two spinning methods were reported to fabricate defect-free BHFMs, namely non-solvent induced phase inversion (NIPS) [35] and electrospinning [36]. Between these two methods, membranes fabricated via NIPS methods are giving more flux due to their thin separation layers. From the literature, incorporation of the ZnO nanoparticles in braided hollow fiber membranes have not been studied. Hence, this current research aims to prepare high flux PSf BHFMs by incorporating hydrophilic ZnO nanoparticles in hydrophobic PSf BHFMs via NIPS method. The presence of ZnO nanoparticles can be beneficial in absorbing more water molecules into the braided hollow fiber membranes during the filtration process. This valuable attribute makes the ZnO a promising material to be used in membrane surface modification. Polymeric dope solution with 16 wt.% of PSf and 0.0, 0.5, 1.0 and 1.5 wt.% of ZnO nanoparticles were prepared for the fabrication of BHFMs through NIPS and characterized.

2.0 Materials and methods
2.1 Materials

All chemicals used in this work were of analytical reagent grade unless otherwise stated. Commercial 1.3 mm outer diameter of polyester (PET) braid support was purchased from Philos (South Korea). PSf was purchased from Solvay Specialty Polymer (UDEL® P-3500 LCD MB7). N,N-Dimethylacetamide (DMAc) as solvent was purchased from QReC Chemicals. Zinc acetate (Zn (CH₃CO₂)₂), oxalic acid (C₂H₂O₄), ethanol (C₂H₅OH) and BSA were purchased from Sigma-Aldrich.
2.2 Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized by a previously reported sol-gel method \[37,38\]. 0.1 M zinc acetate and 0.1 M oxalic acid mixtures (\(Zn (CH_3CO_2)_2 / C_2H_2O_4\)) were prepared with gentle stirring in ethanol for 30 min at 60 ± 5 °C and 50 ± 5 °C respectively. The oxalic acid solution was added dropwise to the zinc acetate solution at 60 ± 5 °C. The mixture was then left under vigorous magnetic stirring for 90 min to allow for complete reaction in order to obtain a gel-like zinc oxalate. The operating pH of 2.0 ± 0.2 was obtained by initially adding oxalic acid to the zinc acetate mixture. The resulting gel was then dried at 60 °C overnight in an oven to form the precursors for the ZnO nanoparticles which then underwent calcination at temperatures of 400 °C for 3 h. The chemical reactions of the ZnO synthesis with a suitable temperature for the calcination are summarized as below.

\[
\text{Zn(CH}_3\text{COO)}_2 + \text{H}_2\text{C}_2\text{O}_4 \xrightarrow{60^\circ C} \text{ZnC}_2\text{O}_4 + 2\text{CH}_3\text{COOH}
\]

(Equation 1)

\[
\text{ZnC}_2\text{O}_4 \xrightarrow{400^\circ C} \text{ZnO} + \text{CO} + \text{CO}_2 + 2\text{H}_2\text{O}
\]

(Equation 2)

Equation 1 shows the reaction between the starting materials of zinc acetate and oxalic acid to form the zinc oxalate precursor. Equation 2 shows the precursor undergoing calcination to ensure the removal of impurities and excess carbon monoxide, carbon dioxide and water. Hence, a high purity of ZnO nanoparticles was obtained.

2.3 ZnO/PSf dope preparation

The hybrid ZnO/PSf BHFMs were fabricated through phase inversion method \[39\]. The compositions of the dope solutions to fabricated ZnO/PSf BHFMs are as shown in Table 1. In short, ZnO nanoparticles were dissolved in DMAc and stirred vigorously for 30 min at 70 °C until homogenous. The obtained solution was then ultrasonicated under ambient conditions for 2 h to promote dispersion of ZnO nanoparticles in the dope solution. Then PSf pallets were added into the ZnO/DMAc mixture and stirred vigorously for 6 h at 70 °C. The prepared dope solution was degassed for 2 h to remove bubbles formed during stirring and stored in the oven at 60 °C for 24
h to remove any residual bubbles. As shown in Table 1, the ZnO/PSf dope solutions were prepared with various ZnO nanoparticles loading concentration, i.e., 0.0, 0.5, 1.0 and 1.5 wt.%, and labelled as BHFM1, BHFM2, BHFM3 and BHFM4 respectively. Neat PSf HFM was fabricated as a benchmark for the BHFM characterizations.

**Table 1** Formulation of dope solution for BHFM fabrication

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>ZnO nanoparticles (wt.%)</th>
<th>PSf (wt.%)</th>
<th>DMAc (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFM</td>
<td>0.0</td>
<td>16.0</td>
<td>84.0</td>
</tr>
<tr>
<td>BHFM1</td>
<td>0.0</td>
<td>16.0</td>
<td>84.0</td>
</tr>
<tr>
<td>BHFM2</td>
<td>0.5</td>
<td>16.0</td>
<td>83.5</td>
</tr>
<tr>
<td>BHFM3</td>
<td>1.0</td>
<td>16.0</td>
<td>83.0</td>
</tr>
<tr>
<td>BHFM4</td>
<td>1.5</td>
<td>16.0</td>
<td>82.5</td>
</tr>
</tbody>
</table>

2.4 Membrane fabrication

The BHFM s were fabricated via phase inversion method using a tube and orifice spinneret with internal diameter of 2.0 mm and outer diameter of 3.0 mm. Prior to the spinning process, the purchased 1.3 mm outer diameter braid support was pretreated with ethanol for 6 h and the braid surface was functionalized by dipping it in 4% NaOH at 80 °C for 2 h [40]. The supports were cleaned three times with deionized water and dried. The pretreated braid support was collected in a winder roller which was fixed at higher elevation than the spinning system and the braid support was guided through from top to bottom of the spinneret system as shown in Figure 1(a). Unlike the typical spinneret system, this BHFM spinneret system does not require any water to form the lumen as the existing braid support already has the lumen, as shown in Figure 1(b). The prepared ZnO/PSf dope solution was transferred into dope reservoir which was then pumped into the spinneret system and extruded out to the coagulation bath tank once the dope is coated on the braid support. The formed membrane was collected in the winding drum as shown in Figure 1(c). This entire coating and phase inversion process was conducted at room temperature (25 ± 2 °C). The air gap distance and take-up speed were set to 10 cm and 2 m/min respectively. After the fabrication of the ZnO/PSf BHFM, the membrane was collected from collecting drum and stored in water (25 °C) for 24 h to remove the residual solvent and water soluble additives from the membrane [28].
Figure 1  Schematic diagram of the spinning process (a) spinneret, (b) cross-section of PET braid support and (c) Spinning process which consisting of (i) dope solution in reservoir, (ii) gear pump for dope extrusion, (iii) nitrogen gas, (iv) braid support, (v) spinneret, (vi) braid support coated with dope solution, (vii) coagulation bath, (viii) BHFM and (ix) collecting drum.

Meanwhile, self-supported HFM was fabricated via dry-jet wet spinning method using a tube and orifice spinneret with internal diameter of 1.5 mm and outer diameter of 3.0 mm. Reverse osmosis water and tap water were used for internal and external coagulation of the membrane fabrication process respectively. Table 2 shows the spinning parameters that were adopted to fabricate the HFM and BHFM. The fabricated HFM was immersed in water for 24 h to remove the solvent residue. Both HFM and BHFM were post-treated with 30 wt.% glycerol solution prior to characterization.

Table 2  Spinning parameters of PSf HFM and BHFM.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>HFM</th>
<th>BHFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dope extrusion rate</td>
<td>8.00 mL/min</td>
<td>3.6 mL/min</td>
</tr>
<tr>
<td>Air Gap</td>
<td>10 cm</td>
<td>10 cm</td>
</tr>
<tr>
<td>Bore fluid rate</td>
<td>15 ml/min</td>
<td>n.a.</td>
</tr>
<tr>
<td>Coagulation bath temperature</td>
<td>25 °C</td>
<td>25 °C</td>
</tr>
<tr>
<td>Collecting drum speed</td>
<td>12 m/min</td>
<td>2.4 m/min</td>
</tr>
</tbody>
</table>
2.4 Analytical methods

2.4.1 Sample’s characterization

X-ray diffraction (XRD) patterns of synthesized ZnO nanoparticles were investigated in 20° range from 10° to 80° using Bruker diffractometer with Cu_K-beta radiation. The morphologies of the HFM and BHFMs were investigated using Scanning Electron Microscopy (SEM; Model: TM 3000, Hitachi). Prior to the SEM analysis, the HFM was fractured under liquid nitrogen for a clean break, while the BHFMs were cut to clean cross-section by using a surgical scalpel after the BHFMs have been soaked in liquid nitrogen for 5 min. The clean fractured/cut membranes were then sputtered for 5 to 10 min until a thin platinum layer (around 10 nm) coated the surface of the sample to capture high quality cross-sectional images. The SEM images were captured at x60 and x800 magnification. The separating layer thickness of the HFM and BHFMs were measured at 10 selected locations for each cross-section. The outer and inner diameter of the HFM and BHFMs were measured at 3 different randomly selected locations for each cross-section. Surface hydrophilicity was determined via sessile-drop method (Model: OCA 15EC, Dataphysic). The contact angle measurement was taken at 5 randomly selected locations of BHFMs to yield an average result.

2.4.2 Water flux

Water flux experiments were conducted in a membrane module filtration apparatus. For each module, one fibre with 10 cm length was assembled into the filtration module and a pure water flux measurement performed in a cross-flow mode through outside-in configuration. Each membrane sample was tested at 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0 and 6.0 bar trans-pressure in order to get the permeability of the membranes. Compressed distilled water was used as the permeate for pure water flux measurements. The flux permeation of the membranes was calculated according to Equations 3 and 4:

\[ F = \frac{V}{Axt} \]  \hspace{1cm} (Equation 3)

\[ A = \pi d_0 L \]  \hspace{1cm} (Equation 4)
where $F$ is the membrane flux ($L/m^2h$), $V$ is the volume of permeate at time $t$ ($L$), $A$ is the effective filtration area of the membrane ($m^2$), $d_o$ is the outer diameter of hollow fibers (cm) and $L$ is the effective length of hollow fibers (cm).

### 2.4.3 BSA rejection

Rejection test was conducted in membrane module filtration apparatus using bovine serum albumin (BSA: Molecular weight of 66,000 Da). This BSA rejection test was done to confirm the class of fabricated BHFM s are in the ultrafiltration range [41]. Chiam and Rosalam reported that the molecular weight range for testing ultrafiltration membranes is from 20,000 Da to 500,000 Da [42]. The molecule’s radius of 66,000 Da BSA can be calculated by Equation 5:

$$\alpha = 0.33M^{0.46} \quad \text{(Equation 5)}$$

where $\alpha$ represents the molecule radius (nm) and $M$ represent the molecular weight (Da). According to this equation, the molecular radius of this 66,000 Da BSA is 54.4 nm. The molecular radius of BSA is within the ultrafiltration pores range (10 – 100 nm) and smaller than microfiltration pores range (100 – 1000 nm). Thus, BSA was used to evaluate the rejection rate of the fabricated membranes.

2 L of 1000 ppm BSA solution was loaded into the membrane module filtration apparatus and 10 cm of each BHFM s were assembled in the system. The rejection analysis was performed in a cross-flow mode through outside-in configuration. All the loaded membrane samples were tested from 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0 and 6.0 bar trans-pressure, same as the permeability test. The membranes were rinsed with deionized water for 5 min after each circle of the filtration test. The rejection is defined using Equation 6:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad \text{(Equation 6)}$$

where $R$ is the BSA rejection rate ($\%$), and $C_p$ and $C_f$ represent the concentrations of BSA in the permeate and feed solutions respectively. The determination of BSA content in influent and
effluent solutions were measured using UV-Vis spectrophotometer (DR5000, HACH) with absorption wavelength of 278 nm.

2.4.4 Membrane fouling studies
The deposition of foulant material in the bare BHFM and ZnO-incorporated BHFM were studied in this research work. Membrane fouling is an attachment process of foulant particles or impurities present in the treating wastewater in membrane structure. The attachment of the foulant can be on and in membrane’s structure. The deposition of these fouling materials on the membrane surface can disrupt the membrane’s performance in terms of its permeate flux and rejection rate.

Antifouling performance of BHFM1 and BHFM4 in 1000 ppm BSA solution was investigated using cross-flow filtration system in laboratory setup at pressure 1.0 bar. The BHFM were allowed to filter BSA solution for a complete one circle of filtration for a duration of 240 min and volume of flux (ml) was recorded at 30 min intervals to evaluate the fouling behavior. 10 ml of effluent solution was collected at 30 min intervals to evaluate the rejection rate. Upon completion of one cycle of filtration for 240 min, the membranes were detached from the filtration system and rinsed under running water for 30 min without applying any additional pressure on it. After the washing process of the membrane is completed, the membranes were once again subjected to the next cycle of filtration testing. A total of 3 cycles of the filtration process were conducted to evaluate the membrane reusability. Equation 7 was used to evaluate the flux recovery percentage:

\[
FR = \frac{F_i}{F_w} \times 100 \quad \text{(Equation 7)}
\]

where, \(FR\) is the flux recovery percentage, \(F_i\) is initial flux of BSA solution in L/m²h and \(F_w\) is the flux obtained after the membranes were rinsed for 30 min in L/m²h.

2.4.5 Mechanical strength
The mechanical strengths of the braid support and best-performing BHFM were measured using tensile testing apparatus (AG-X Plus). Samples of length 150 mm with clamping distance of 100mm were placed vertically between a pair of pneumatic clamps and stretched at 20 mm/min at
upper clamp. The tensile stress of the samples were recorded at the maximum force on samples to break. Three specimens were tested to get the average tensile stress value.

3.0 Results and discussion

Figure 2 represents the XRD pattern recorded for the synthesized ZnO nanoparticles. The obtained nanoparticles are polycrystalline and the diffraction data agreed well with JCPDS card of ZnO nanoparticles (JCPDS 36-1451) with 20 peaks at t 31.633 (1 0 0), 34.278 (0 0 2), 36.115 (1 0 1), 47.403 (1 0 2), 56.472 (1 1 0), 62.693 (1 0 3), 67.813 (1 1 2), 68.975° (2 0 1) and 72.42 (202). The pattern does not contain any other impurity peaks which proves the pure quality of the synthesized nanoparticles. This result pattern is corresponding to the results obtained by Borker and Desai [43]. They observed major diffraction peaks at 31.73, 34.39, 36.24, 47.51, 56.52, 62.88, 72.54 and 76.89 which assigned as (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), (2 0 1) and (2 0 2) planes respectively. The crystalline size of the nanoparticles were calculated using Hall-Williamson method [38]. The average crystallite size of the synthesized ZnO nanoparticles were 10 ± 1.8 nm.

![XRD pattern of ZnO nanoparticles calcinated at 400 °C for 3 h.](image)

Figure 2
The morphological examination by SEM analysis in Figure 3 shows that the fabricated HFM membrane is highly porous compared to the BHFMs. Finger-like structures were observed in both HFM and BHFMs. Figure 3 (a) and (b) shows the morphology of a neat PSf HFM. The membrane exhibits well-defined structures, i.e. tiny finger-like at its selective outer layers, large and repetitive macro voids underneath the selective layer and well-distributed finger-like structures at bottom layer. Figure 3 (c) and (d) shows the morphology of the BHFM1. The membrane exhibits well-defined membrane structure, i.e., finger-like and micro voids at its outer selective layer, macro voids underneath selective layer, sponge structures underneath the macro voids and a small amount of the PSf coating solution which infiltrated into the braid support. This morphology is corresponding to the result shown by Zho et al. [44]. Two skin layers were observed in the HFM, whereas in BHFMs only one skin layer was observed. Figure 3 (e)-(j) shows the PSf BHFM incorporated with different loadings of ZnO nanoparticles. The loading of the ZnO nanoparticles were increased to 0.5 wt.% (Figure 3 (e) and (f)), 1.0 wt.% (Figure 3 (f) and (g)) and 1.5 wt.% (Figure 3 (h) and (i)).

BHFM2 and BHFM3 exhibits wider finger-like structures with dense skin layer at its outer selective layers, macro voids and sponge structures underneath the selective layer and a small amount of PSf coating solution which infiltrated into the braid support. Meanwhile, BHFM4 exhibits macro finger-like structures and thin skin separating layer at its outer selective layer, macro voids underneath selective layer, thick sponge structures before the braid support and a small amount of PSf coating solution which infiltrated into the braid support. The macro voids and dense sponge structure observed near the braid support are responsible for higher permeation [45]. This was possibly due to the hydrophilic properties of the ZnO nanoparticles which makes the water move faster into the membrane compared to the de-mixing rate between solvent and non-solvent during the phase inversion process [26,45]. In this study the addition of ZnO nanoparticles in the dope solution were believed to delay the de-mixing process between solvent and non-solvent which increased the formation of macro voids. The incorporation of non-solvent material in the dope solution has increased the viscosity, and consequently the kinetic exchange mechanism of the solvent and water in the coagulation bath has become slower. Thus the macro voids structures are formed [46,47]. This mechanism is corresponding to reports by Fan et al., where they detailed that the formation of the macro void pores in the separation layers is due to the transition from
delayed de-mixing to instantaneous de-mixing which mainly happens on the addition of non-solvent materials in the dope solution [35].

From the morphology of the BHFMs, it can be clearly observed that the infiltration of the dope solution was promoted with the introduction of the ZnO nanoparticles. This is due to the hydrophilic property of the doping solution which can easily infiltrate the braid support and accumulate in-between the braid channels during the fabrication process [48]. This infiltration of small amounts of dope solution into braid supports as shown in Figure 4 (b) and (f) promotes a good interfacial bond between the separation layer and braid support. Cheng et al. reported that the intrusion of the dope solution into the braid support increased the mechanical stability of the braided membranes [32]. This is due to the separation layer being tightly bonded with the braids, preventing the delamination of the separation layer from the braid support. Table 4 illustrates the thickness of the separation layer, outer diameter and inner diameter of the fabricated HFM and BHFMs. From the measured thickness of BHFMs, it can be observed that BHFM1 has a thicker separation layer compared to the other BHFMs. Again, this is due to lower infiltration rate of PSf dope solution compared to ZnO/PSf dope solution. Moreover, different thicknesses of separation layer were observed in all BHFMs. This is also closely related to the infiltration rate of the dope solution into the braid support, and the uneven round shape of the braid support during the spinning process due to mechanical stress applied to pull the braid support out from spinneret system. These results correspond to the result obtained by Liu et al. [34]. They explained that this uneven separation layer thickness is due to the pulling force applied during the fabrication of BHFMs, which change the density of braid support and position or angle of the braid in spinneret. Therefore, the infiltration rate of the dope solution into the braid support is not uniform.
Figure 3  Morphology and separation layer of HFM and BHFMs: (a) cross-section morphology of neat PSf HFM, (b) separation layer of neat PSf HFM, (c) cross-section morphology of BHFM1, (d) separation layer of BHFM1, (e) cross-sectional morphology of BHFM2, (f) separation layer of BHFM2, (g) cross-sectional morphology of BHFM3, (h) cross-sectional morphology of BHFM4, (i) cross-sectional morphology of BHFM4 and (j) separation layer of BHFM4.
Figure 4  Typical BHFM structure diagram and morphology of typical separation layer, (a) typical morphology of BHFM, (b) adhesion of dope solution with braid support, (c) surface of braid support, (d) cross-sectional morphology of braid support, (e) cross-section of PET twisted fiber bundle morphology and (f) braid support arrangement before membrane fabrication.

Table 3  Thickness, outer and inner diameter of HFM and BHFM.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (µm)</th>
<th>Thickness of braid support (µm)</th>
<th>Outer diameter (µm)</th>
<th>Inner diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFM</td>
<td>96.66 ± 42.44</td>
<td>n.a.</td>
<td>1250.20 ± 22.70</td>
<td>1075.37 ± 26.17</td>
</tr>
<tr>
<td>BHFM1</td>
<td>89.82 ± 38.38</td>
<td>430.62 ± 35.20</td>
<td>1712.97 ± 78.97</td>
<td>672.10 ± 103.60</td>
</tr>
<tr>
<td>BHFM2</td>
<td>74.73 ± 28.17</td>
<td>290.74 ± 52.36</td>
<td>1576.33 ± 73.77</td>
<td>845.40 ± 89.80</td>
</tr>
<tr>
<td>BHFM3</td>
<td>81.96 ± 44.14</td>
<td>412.53 ± 28.68</td>
<td>1637.57 ± 51.07</td>
<td>648.60 ± 44.60</td>
</tr>
<tr>
<td>BHFM4</td>
<td>84.49 ± 23.81</td>
<td>372.14 ± 37.59</td>
<td>1639.17 ± 10.87</td>
<td>752.90 ± 92.50</td>
</tr>
</tbody>
</table>

The water contact angles of BHFM1, BHFM2, BHFM3 and BHFM4 are 108.79°, 83.54°, 77.04° and 71.02° respectively (Table 4). The presence of ZnO nanoparticles in PSf BHFM has improved its hydrophilicity by at least 37.77°, which can be explained as the large number of
oxidized functional groups on the surface of the membrane after modification, which has a positive
effect on improving the hydrophilicity of the membranes [49]. The contact angle results
correspond to the result shown by Pintilie et al. [50], where they reported that the presence of 1.0
wt.% of ZnO in PSf HFM improved the hydrophilicity by 23.50°. Balta et al. reported that 2.0
wt.% of ZnO nanoparticles in the PES membrane dropped the contact angle significantly from
70.00° to about 57.00°. This shows that the incorporation of the ZnO nanoparticles has
significantly modified the membrane surface to be more hydrophilic.

Table 4  Water contact angle values for fabricated BHFM prepared in various ZnO
nanoparticles concentration.

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>BHFM1</th>
<th>BHFM2</th>
<th>BHFM3</th>
<th>BHFM4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average contact angle (°)</td>
<td>108.79</td>
<td>83.54</td>
<td>77.04</td>
<td>71.02</td>
</tr>
<tr>
<td>Standard error</td>
<td>± 3.207</td>
<td>± 1.535</td>
<td>± 3.209</td>
<td>± 0.926</td>
</tr>
</tbody>
</table>

The tensile stress of the braid support and best-performing membrane BHFM4 were
measured, and the stress-strain data are plotted as shown in Figure 5. The braid support and
BHFM4 exhibited super-high tensile stress at break 118.127MPa and 85.501MPa respectively. It
can clearly be seen that the tensile strength and elongation at break of the BHFM membrane is less
compared to the braid support. The lower mechanical strength of the BHFM is due to the alkaline
pre-treatment of the braid support. The obtained tensile strength of both braid support and BHFM
are corresponding with results reported by Zhou et al., Quan et al., and Liu et al., where they
reported the tensile strength of braided membranes are from 80 MPa to 160 MPa [44,48,52–54].
The obtained tensile stress of BHFM is 4 times higher as compared self-supporting HFM which
are typically from 2 MPa to 22 MPa [44,55,56]. The membrane mechanical strength is one of
factors which is limiting its applications in wastewater treatment systems. Based on the tensile test
result, the BHFM could be an effective membrane in high-pressure wastewater treatment systems.
Based on the other research’s findings, the mechanical strength of the braided membranes is
dependent on the mechanical strength of the selected braid support rather than the mechanical
strength of the coating layers [1,48,52,54]. Along with this, we also can observe that the elongation
of the braided membrane is lower than the braid support; which is 26.910% and 35.815% for
BHFM4 and braid support respectively. This is due to the formed coating layer and infiltrated
separation layers in the braid support limiting the deformation of the braid, and inhibiting the
straining of the braided membrane. Many research studies claims high tensile stress of braided membranes; however, they also placed their concern on the delamination of the coating layers which related to the poor interfacial bonding strength between separation layer and braid surface. The poor interfacial bonding between coating layer and braid support could restrict the lifetime of the membranes [36,44].

![Stress-strain diagram of braid support and braided membrane.](image)

Figure 5

The water flux and BSA rejection rate of neat PSf HFM and all BHFM are depicted in Figure 6. Figure 6 shows that the BHFM4 has a higher flux of 919.12 L/m²h and an average of 97.34 % BSA rejection rate compared to neat PSf HFM (with an average flux of 346.20 L/m²h and BSA rejection of 49.20%) and other ZnO/PSf BHFM at 1.0 bar pressure. The high flux of BHFM4 is due to the -OH of ZnO nanoparticles in the membrane separation layer which absorbs water molecules and the strong electronegativity of ZnO nanoparticles which has hindered the adsorption and deposition of BSA proteins in membrane separation layer.
The braid’s fabric nature to absorb the filtrated water molecules as well as the porous structure of braid support also contributed to the high flux. Despite that, the reduced thickness of the membrane separation layer in BHFM s compared to self-supported HFMs (as shown in Table 3) also contributed to the increase in water flux. Overall, both the thin hydrophilic separation layer and the high water-attracting character of the braid support have played an important role in this high flux achievement.

Initially, at 0.5 and 1.0 bar, neat PSf HFM has shown slightly higher flux then the neat BHFM with 51.07 and 49.20% of BSA rejection rate. Later, the pure water flux observed at pressure ≥1.5 bar from neat PSf HFM was higher than BHFM1 and BHFM2. However, the BSA rejection rate was low. These show that the HFM is collapsed at pressure ≥1.5 bar. At the same moment, the neat PSf BHFM membrane has obtained flux until 6.0 bar with constant rejection rate. The intrusion of 0.5 wt.% ZnO nanoparticles in PSf BHFM has increased flux up to 2.9 times at pressure 6 bar with more than 91.96% of BSA rejection. BHFM3 has obtained its maximum flux 1860.40 L/m²h at 5.0 bar with 96.28% BSA rejection rate and BHFM4 has obtained its maximum flux 1909.90 L/m²h at 4.0 bar with 97.34% BSA rejection rate. This proves that the fabricated BHFM s are able to withstand higher pressures compared to HFMs. Pure water flux trend indicates that the addition of ZnO nanoparticles into the membrane mixed matrix has improved hydrophilicity and flux performance. This is due to the large quantity of -OH present on the ZnO nanoparticles which are contributing to the development of the hydrophilic property, which in turn improves the permeability. This enhanced hydrophilicity of the membrane improved the absorption capability of water molecules within the membrane matrix.

On the basis of BSA rejection, all BHFM s were able to remove more than 90% of BSA. This result indicates that the incorporation of ZnO nanoparticles gives better flux performance than BSA rejection. This result pattern is corresponding to the results obtained by Adilah et al. and Abdi et al. [45][51].
Figure 6  
(a) Water flux permeation and (b) rejection in BSA.

Figure 7 shows the changes in BSA permeate flux over filtration cycles. Both BHFM1 and BHFM4 exhibit drops in flux over time and cycles. The attachment of BSA particles on the braided membranes as fouling materials over time is the reason behind this reduction in flux. Both membranes have shown almost similar flux pattern throughout the three cycles. However, BHFM4 showed a lower flux drop of about 14.30%; while BHFM1 showed major drops in flux of about 28.50% throughout the three cycles. This indicates that BHFM1 experienced a higher fouling rate compared to BHFM4; which can be attributed to its low hydrophilic nature; which allows deposition of protein molecules on the membrane separation layer. The fouling phenomenon on
the membrane surface can be related with the strong interaction of separation particles in wastewater with properties of membrane materials. Hence, the interaction of BSA particles with hydrophilic ZnO/PSf BHFM is the most crucial part in the fouling behaviour study. In this study, the strong electronegativity and excellent hydrophilicity of BHFM4 compared with BHFM1 has hindered the irreversible adsorption and deposition of BSA proteins on the membrane separation layer, which is also believed to improve the antifouling properties of membranes [32].

![Figure 7](image_url)  
**Figure 7**  
BSA flux for five circles of BSA filtration

Table 5 illustrates the flux and rejection performance of the incorporated additive in braided/reinforced braided hollow fiber membranes as reported in the literature. BHFM4 has reasonably high flux permeation rate compared to flux reported by other researchers at pressure 1.0 bar. Hao et al. reported that the incorporation of 0.5 wt % of GE improved the flux permeate from 44.0 to 65.0 L/m²h [57]. Similarly, Wu et al. reported incorporation of 0.3 wt.% of GE were increased the flux performance of BHFM from 350.0 to 1443.0 L/m²h [36]. They reported the highest flux permeate with 99.0% of kerosene rejection. This shows that the incorporation of nanomaterial is able to increase flux performance. Similarly in this study the incorporation of ZnO
nanoparticles in a BHFM mixed matrix has improved flux performance from 32.20 L/m²h to 919.12 L/m²h. From literature, all research works which carried out studies with polymer concentration more than 13.0 wt.% reported more than 90.00% rejection rate. A similar pattern of rejection rate was observed in this study. Additionally, the fabricated BHFMs were successfully operated up to 6.0 bar pressure and high flux with stable BSA rejection rate were obtained. These results have added value for the study of fabricating high flux BHFMs.

Table 5  Flux and rejection of BHFM4 with other braided/reinforced hollow fiber membrane from the published literature.

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Additive (wt.%)</th>
<th>Pressure (bar)</th>
<th>Impurities</th>
<th>Pure water flux (L/m²h) Neat BHFM</th>
<th>Modified BHFM</th>
<th>Rejection (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.0 wt.% PVDF</td>
<td>0.5 wt.% Graphene</td>
<td>1.0</td>
<td>kerosene and water mixture (1:1, v/v)</td>
<td>44.0</td>
<td>65.0</td>
<td>99.7</td>
<td>[57]</td>
</tr>
<tr>
<td>11.5 wt.% PVC</td>
<td>11.5 wt. % poly(ethylene glycol) methyl ether methacrylate</td>
<td>0.5</td>
<td>100ppm latex particle solution</td>
<td>35.0</td>
<td>72.0</td>
<td>76.0</td>
<td>[44]</td>
</tr>
<tr>
<td>12.0 wt.% PVC</td>
<td>10.0 wt.% polyvinylpyrrolidone</td>
<td>1.0</td>
<td>1000ppm BSA solution</td>
<td>n.a.</td>
<td>700.0</td>
<td>71.0</td>
<td>[53]</td>
</tr>
<tr>
<td>20.0 wt.% PIP</td>
<td>1.0 wt.% trimesoyl chloride</td>
<td>1.0</td>
<td>2000ppm NaCl and 2000ppm MgSO₄ solution</td>
<td>17.0</td>
<td>23.0</td>
<td>30.0 65.0</td>
<td>[58]</td>
</tr>
<tr>
<td>16.0 wt.% PU</td>
<td>0.3 wt.% Graphene</td>
<td>1.0</td>
<td>kerosene and water mixture (1:1, v/v)</td>
<td>350.0</td>
<td>1443.0</td>
<td>99.0</td>
<td>[36]</td>
</tr>
<tr>
<td>13.0 wt.% PVC</td>
<td>4.0 wt.% Silicon dioxide</td>
<td>1.0</td>
<td>kerosene and water mixture</td>
<td>30.0</td>
<td>50.0</td>
<td>98.0</td>
<td>[59]</td>
</tr>
<tr>
<td>16.0 wt.% PSf</td>
<td>1.5 wt.% ZnO</td>
<td>1.0</td>
<td>1000ppm BSA solution: 54.4nm particle size</td>
<td>36.2</td>
<td>919.1</td>
<td>96.5</td>
<td>This work</td>
</tr>
</tbody>
</table>
4.0 Conclusion

In summary, the BHFM incorporated with different loadings of ZnO nanoparticles has successfully been fabricated via dry-wet phase inversion technique. The fabricated membrane possessed good morphology with finger-like voids on the outer separation layer, sponge-like structure and good adhesion with braid support. When the ZnO nanoparticles content reached 1.5 wt.%, the morphology of BHFM had good infiltration rate of dope solution into the braid support due to the hydrophilic nature of the ZnO/PSf doping solution, which also promoted a good interfacial bond between the separation layer and braid support. The infiltration rate of dope solution has developed different thicknesses of separation layers in all BHFMs. The incorporation of 1.5 wt.% of ZnO nanoparticles in PSf BHFM membrane also increased the hydrophilic properties of the BHFM from 108.79° to 71.021°. High water permeability and an excellent BSA rejection rate (97.1%) were achieved at 1.5 wt.% of ZnO nanoparticles compared to 0.0, 0.5, 1.0 wt.% BHFMs. Good fouling stability and recovery after three cycles of BSA filtration were observed. The results show that the BHFM exhibit high mechanical strength and remarkable elongation which makes this membrane have a high potential application prospect in wastewater treatments.

Altogether, the hybrid ZnO /PSf BHFM exhibits superior hydrophilicity and higher permeability compared with neat PSf BHFM and PSf HFM. Additionally, it was also observed that the BHFMs are able operate at higher pressures up to 4.0 bar easily with >90% rejection rate, compared to HFM which collapsed at 1.5 bar pressure in this research work. 1.5 wt.% ZnO nanoparticle in 16 wt.% PSf BHFM appears to be the most promising range in improvising hydrophilicity and permeability.

CRediT authorship contribution statement

Prakash Peechmani: Writing - original draft, Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation. Mohd Hafiz Dzarfan Othman: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. Roziana Kamaludin: Validation, Resources, Writing - review & editing, Supervision. Mohd Hafiz Puteh: Validation, Resources,
Writing - review & editing, Supervision. **Juhana Jaafar**: Validation, Formal analysis, Investigation, Writing - review & editing. **Mukhlis A Rahman**: Validation, Formal analysis, Investigation, Writing - review & editing. **Ahmad Fauzi Ismail**: Validation, Resources, Writing - review & editing, Project administration, Funding acquisition. **Siti Hamimah Sheikh Abdul Kadir**: Validation, Writing - review & editing. **Rosli Md. Illias**: Validation, Writing - review & editing. **Joe Gallagher**: Validation, Writing - review & editing. **Sabreena Marsya Djuli**: Validation, Writing - review & editing.

Acknowledgement

The authors gratefully acknowledge financial support from the Ministry of Higher Education Malaysia under the Higher Institution Centre of Excellence Scheme (Project Number: R.J090301.7809.4J430) and Universiti Teknologi Malaysia under the Collaborative Research Grant (Project number: R.J130000.7351.4B418), Award Grant (Project number: R.J130000.7709.5M003) and International and Industry Incentive Grant (IIIG) (Project number: Q.J130000.3009.02M25). The authors would also like to thank Research Management Centre, Universiti Teknologi Malaysia for the technical support.

Reference


[31] J. Yang, D. Sun, N. Hu, H. Ning, J. Zhang, W. Ye, J. Wu, Multi-objective robust design optimization of a two-dimensional tri-axial braided hollow pillar using an evolutionary


[41] M.N. Subramaniam, P.S. Goh, W.J. Lau, Y.H. Tan, B.C. Ng, A.F. Ismail, Hydrophilic hollow fiber PVDF ultrafiltration membrane incorporated with titanate nanotubes for


