Preparation and characterization of new PA-MOF/PPSU-GO membrane for the separation of KHI from water

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HIGHLIGHTS

- A new TFN membrane was developed for the separation of KHI from water.
- The TFN membranes were successfully prepared by incorporating UiO-66-NH2 nanoparticles into the polyamide selective layer.
- The performance of the TFN membrane was improved at optimal UiO-66-NH2 loading.
- The TFN membrane exhibits superior antifouling properties.
- Resultant TFN membrane displays robust longterm stability.

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A BSTRACT

A hydrostable and hydrophilic porous metal-organic framework (MOF)-UiO-66-NH2 was successfully synthesized and characterized. The prepared UiO-66-NH2 nanoparticles were incorporated into the dense selective polyamide (PA) layer over the surface of the polyphenylsulfone (PPSU)-graphene oxide (GO) support layer to make a new thin film nanocomposite (TFN) membrane for the treatment of wastewater containing Kinetic hydrate inhibitor (KHI). Attenuated total reflection infrared (ATR-IR), X-ray diffraction (XRD), and transmission electron microscopy (TEM) analyses of UiO-66-NH2 all confirmed that it was synthesized favorably. The as-prepared membranes were evaluated by ATR-IR, field emission scanning electron microscopy (FESEM), atomic force microscope (AFM), thermal gravimetric analysis (TGA), tensile strength, and contact angle techniques. The results showed that embedment of UiO-66-NH2 nanoparticles notably changes the membrane chemistry and morphology, leading to an improvement of separation performance because of the porous structure and hydrophilic nature of UiO-66-NH2. The incorporation of UiO-66-NH2 enhanced the thermal stability and mechanical strength (26%) of the membrane compared to the unmodified membrane, confirming the formation of a strong nanofiller-polymer matrix interface. The result demonstrated that the leaching out of the incorporated nanoparticles from the membrane was so small that it can be ignored. The surface hydrophilicity of the PA-MOF layer was improved 38% due to the of UiO-66-NH2 nanoparticles loading. The best performing M-TFN2 membrane (incorporated with 0.05% UiO-66-NH2) exhibited an increased permeate flux from 38 L/m2·h to 59.9 L/m2·h compared to the unmodified membrane; while the KHI rejection remained higher than 96%. Besides, the newly developed membrane exhibited remarkable improvement in the antifouling property (FRR of 97.8%) and an excellent long-term stability.

1. Introduction

Kinetic hydrate inhibitors (KHIs) are a well-known tool to overcome the occurrence of gas hydrate problems in gas and oilfield industry [1]. The commercial available KHIs for usage in offshore are typically water-soluble polymers that are added to the produced fluids in hydrocarbon production processes, but the major problem with these commercial inhibitors is that they are toxic to aquatic organisms and are not environmental-friendly, hence there are strict limitations with respect to their use and/or disposal to the environment [2]. Since hydrocarbon production industry generates large volumes of wastewater, “produced water”, discharging this water containing KHIs have a negative impact on the environment, therefore, it is necessary to apply appropriate technology for the removal of these materials from water [3]. The presence of these inhibitors in the produced water may also cause problems in other water management units. Polymers as the
active component in KHI can precipitate at high temperature or in the presence of salt fluids and result in fouling equipment. For example, during re-injection into formations, water containing KHI may mix with high temperature or saline water, which can cause fouling of facilities (storage or pumping) [4].

Various separation methods were studied for KHI removal from water, such as solvent extraction, heated centrifugation, advanced oxidation processes, and membrane filtration [4–11]. However, some of these methods removed only a low content of inhibitors from water, and or suffer from some disadvantages such as complexity and excessively high operational costs. In the course of developing a method for separation of KHI, membrane process has been found as a proper method for KHI removal from water due to efficient, reliable, and selective separation [8,11]. Blumer et al. [9] used the composite ceramic membranes to reject KHI from water. The inorganic membranes achieved a KHI rejection greater than approximately 50% [9,10]. Schrader [12] employed a spirally wound membrane system for separating KHI polymers from an aqueous mixture. According to the results, KHI removal rate was at least 80% [12]. However, the disadvantages of ceramic membranes are their substantial production cost and high weight compared to polymeric membranes [13]. Adham and his group [6,8] used the ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) commercial membranes for removal of the KHI from a synthesis produced water and according to the results, the RO and NF membranes were successful in separation of the KHI with rejection of about 99% and flux of 33.6 and 15 (L/m²·h), respectively. Despite the fact that the NF/RO membranes were successful in the KHI separation, fouling was the major problem of these commercial membranes during the long-time test [6,8].

Recently, water purification technology based on NF process has been widely developed. Thin film composite (TFC) polyamide (PA) membranes are the most successful and energy efficient NF membranes, which is generally fabricated by forming a thin selective PA layer on top of an asymmetric microporous support membrane [11,14]. The PA layer of TFC membrane that plays a main role in the membrane permselectivity, is formed by the interfacial polymerization technique [15] and the support layer is made by the phase inversion method [16]. The advantage of these membranes is that the selective layer and the support layer can be independently designed and optimized to enhance the overall separation performance.

Thin film nanocomposite (TFN) membranes are a new form of membranes, that nanoparticles are incorporated into the TFC membrane to improved membrane properties and performance. Numerous researches have been dedicated to the incorporation of nanomaterials into membrane structure (like titanium dioxide, zeolite, silica, graphene oxide (GO), and carbon nanotubes) in modification of TFC membranes [17–24]. Recently, a combination of organic and inorganic compounds with porous structure, metal-organic frameworks (MOFs) sound attractive for the preparation of TFN membranes because of their high porosity, high specific surface area, distinct pore size and structure and

Fig. 1. Molecular structure of UiO-66-NH₂.
tunable chemical functionality [25–28]. Moreover, the presence of organic linkers in MOFs can increase their compatibility with the PA layer matrix [25].

MOFs with good hydrothermal stability such as MIL-101, ZIF-8, and UiO-66 may impart beneficial characteristics in water treatment. Ma et al. filled UiO-66 into the TFN membrane and by adding 0.1% MOFs to the membrane, the water permeability increased 52%, while the NaCl rejection remained almost the same [25]. Similar outcomes were observed by Xu et al. [26] when embedding MIL-101(Cr) into the dense selective PA layer. Findings showed that the water permeability increased 44% by loading 0.05% MIL-101 to the membrane, while the NaCl rejection remained almost the same [25]. He et al. [28] utilized UiO-66 in the membrane used for removal of selenium and arsenic from aqueous environments. The performance of the TFC membranes enhanced by incorporating 0.15% UiO-66 compared to most conventional NF membrane [28].

In this paper, UiO-66-NH2 nanoparticles were synthesized and then employed as nanofiller in preparation of TFN membranes to separate KHI from water. UiO-66-NH2 an MOF in Zr-based MOF family consists of a cubic framework of Zr6O4(OH)4 cluster (formed in situ via hydrolysis of zirconium chloride) with 2-aminoterephthalic acid linkers (Fig. 1). The hydrophilicity and outstanding chemical stability of UiO-66-NH2 make it appropriate for incorporation into TFn membranes. The thin PA layer was synthesized by the interfacial polymerization process on the top of the polyphenylsulfone (PPSU)-graphene oxide (GO) support layer. As mentioned in the previous work [11], the PPSU support membrane blended with 0.1 wt% GO exhibited the best performance in preparation of the TFN membrane. UiO-66-NH2 nanoparticles were characterized by ATR-IR, XRD, TEM, and DLS tests, and the TFC membranes’ physicochemical properties were examined by ATR-IR, FESEM, AFM, tensile strength, TGA, and contact angle analyses. The fouling resistance of the TFC membrane was also evaluated, and for investigation of the stability of synthesized MOFs in the TFC membrane, the long-term operating performance of the prepared membrane was studied. It was also attempted to study the UiO-66-NH2 nanoparticles leachability from the membrane by using a batch leaching test.

2. Experimental

2.1. Materials

Zirconium chloride (ZrCl4, Sigma-Aldrich), N, N- dimethyl formaldehyde (DMF, Merck), 2-aminoterphthalic acid (NH2-BDC, Sigma-Aldrich), and ethanol (Merck) were employed for the synthesis of UiO-66-NH2. Polyphenylsulfone (PPSU, SOLVAY) was applied as the support layer polymer where N-methyl pyrrolidone (NMP, Merck) and graphene oxide nanoplates (GO, Iranian Nanomaterials Pioneers Company) were used as the solvent and additive/nanofiller for the casting solution. Piperazine (PIP, Merck) and trimesoyl chloride (TMC, Merck) were used as aqueous and organic monomers for synthesizing of the polyamide (PA) selective layer, respectively. n-hexane (Merck) was used as the solvent for the organic monomer. Kinetic hydrate inhibitor (KHI, NOVINCHEM Co.) identified LDHI-10068 was applied for evaluation of filtration performances. Deionized (DI) water was used as a solvent for all aqueous solutions.

2.2. Synthesis and characterization of UiO-66-NH2

The UiO-66-NH2 metal-organic framework was prepared using solvothermal method [29]. In detail, 2.96 g of ZrCl4 was dissolved in 30 mL DMF solution and shacked for 30 min. Meanwhile, 2.12 g of NH2-BDC was dissolved in 133 mL DMF solution and stirred for 40 min. Then, the two synthesized solutions were blended and put in an autoclave of 250 mL. The closed autoclave was then put in an oven at 130 °C for 36 h. Finally, the crystalline crop was extracted from the solution by vacuum filtration. The crystalline crop was activated by plunging in ethanol for 24 h, and then it was filtered and dried.

Attenuated total reflection infrared (ATR-IR) spectroscopy (Thermo Nicolet Avatar 370, USA) was used to confirm the formation of UiO-66-NH2 in the range of 700–4000 cm−1 with spectral resolution of 1 cm−1.
To study the crystalline structure of UiO-66-NH2 nanoparticles, the X-ray diffraction (XRD) analysis was obtained via a Panalytical X’Pert Pro MPD instrument using Cu Ka radiation at 20 ranging between 4° and 30°. The morphological analysis of the nanoparticles was studied using transmission electron microscopy (TEM, CM120 instrument, Philips, Netherlands) at voltage of 100 kV. A dispersion of nanoparticles in methanol was cast onto a TEM grid. The particle size distribution of the synthesized nanoparticles was obtained by dynamic light scattering (DLS, VASCO3, Cordouan, France).

2.3. Fabrication of TFN-NF membrane

The process employed to create a nanocomposite NF membrane in this study is shown in Fig. 2.

2.3.1. Preparation of PPSU-GO support layer

The nanocomposite support layer was fabricated following a procedure reported by Golpour and Pakizeh [11]. The polymer solution was prepared by dissolving 17 wt% PPSU in NMP with 0.1 wt% GO as additive/nanoﬁller at 80 °C. The casting solution was degassed for more than 24 h at room temperature. Next the bubble-free solution was cast on non-woven polyester using an adjustable casting bar (Neurtek2281205). The ﬁlm was immediately immersed in a bath of DI water at room temperature. After coagulation, support membrane kept wet at 5 °C prior to use.

2.3.2. Synthesis of PA-MOF selective layer

The selective layer of NF membranes was synthesized by interfacial polymerization (IP) between PIP and TMC on the top surface of the PPSU-GO support layer (Fig. 2). For the synthesis of PA selective layer, the support layer was initially immersed in the aqueous solution containing 2% PIP for 1 min and excessive PIP solution on the substrate was removed by a ﬁlter. Subsequently, the amine-saturated substrate was immersed in a 0.07% TMC/n-hexane solution for 15 s to perform the IP process over the substrate. Finally, the resultant membrane was cured at 70 °C for 10 min in an oven and then stored in DI water at room temperature. The surface roughness parameters of each membrane sample and the average result was reported. The thermal stability was investigated by thermal gravimetric analysis (TGA, BAHR Thermoanalyse GmbH, Germany) under air ﬂow (20 cm3/min). About 10 mg of each extracted polyamide sample was heated from room temperature to about 800 °C at a heating rate of 10 °C/min.

2.5. Membrane performance evaluation

A cross-ﬂow NF experimental setup was employed to evaluate separation performance of the prepared TFN membranes at 25 ± 1 °C and 8 bar (Fig. 3). The performance was evaluated in terms of ﬂux and KHI rejection. The membranes were pressurized for 1 h with water before each test to reach a steady state. The ﬂux and rejection were calculated by the following equation:

\[ J = \frac{V}{A \cdot t} \]

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

where \( V \) (L) is the permeate volume, \( t \) (h) is the permeate collection time, and \( A \) (m2) is the effective membrane surface area. The effective membrane area was around 20 cm2 in this work. \( C_p \) and \( C_f \) are the permeate and the feed concentrations, respectively. Measurement of the KHI concentrations at the feed and permeate solutions were performed by a UV–Vis spectrophotometer (Optizen POP, Mecasys, South Korea) at a wavelength of 209 nm. The separation performance of the TFN membrane was measured for 80 h at 8 bar for investigation of the long-term operational stability of the membrane. All the prepared membranes were evaluated at least 3 times in different batches.

2.6. Membrane antifouling performance

The three-cycle antifouling experiments of the NF membranes were carried out in a cross-ﬂow ﬁltration system by the KHI solution of 0.5 wt % at 25 ± 1 °C and 8 bar. The membranes fouling behavior was evaluated by calculation of reversible fouling (\( R_f \)), and irreversible fouling (\( IR_f \)) according to the following definition [30]:

\[ R_f = \frac{J_f - J_{o1}}{J_{o1}} \]

\[ IR_f = \frac{J_f - J_{o2}}{J_{o2}} \]

Total fouling=\( R_f + IR_f = \frac{J_f - J_{o2}}{J_{o1}} \)

where \( J_{o1} \) is the pure water ﬂux (PWF) of the initial membranes, \( J_f \) is the permeate ﬂux of the membranes after ﬁltration with the KHI solution, and \( J_{o2} \) is the water ﬂux of the fouled membrane after renewal of the membrane surface by washing with DI water for 10 min. These deﬁnitions were recorded when a stable ﬂux occurred. The ﬂux recovery ratio (FRR) can be calculated as the following equation:

Table 1

<table>
<thead>
<tr>
<th>Membrane name</th>
<th>Aqueous solution</th>
<th>Organic solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPD (w/v%)</td>
<td>TMC (w/v%)</td>
</tr>
<tr>
<td>TFN</td>
<td>2</td>
<td>0.07</td>
</tr>
<tr>
<td>M-TFN1</td>
<td>2</td>
<td>0.07</td>
</tr>
<tr>
<td>M-TFN2</td>
<td>2</td>
<td>0.07</td>
</tr>
<tr>
<td>M-TFN3</td>
<td>2</td>
<td>0.07</td>
</tr>
<tr>
<td>M-TFN4</td>
<td>2</td>
<td>0.07</td>
</tr>
</tbody>
</table>
One of the major issues for industrialization of TFN membranes is leaching out of the incorporated nanoparticles from the membrane due to low adhesion and compatibility between nanoparticles and the PA matrix. For measurement of the amount of UiO-66-NH₂ leached out from the membrane, releases of zirconium (Zr) ions from the membrane was assessed by a batch experiment [31]. For this test, a membrane sample (a circular sheet with the area of 23.5 cm²) was immersed in 100 mL DI water in a container. Then, the batch container was shaken in an incubator at 140 rpm for 60 h. Finally, the water sample collected from the container was acidiﬁed and analyzed for the presence of Zr ions by inductively coupled plasma optical emission spectrometry (ICP-OES, SPECTRO ARCOS, Germany) at wavelength of 343.823 nm.

3. Results and discussion

3.1. Characterization of UiO-66-NH₂

The ATR-IR spectrum of UiO-66-NH₂ was measured and shown in Fig. 4(a). This pattern shows good agreement with that reported in previous studies [32–35]. The characteristic peaks of UiO-66-NH₂ appeared in wavenumbers between 1400 and 1700 cm⁻¹ [35]. Considering that the ligand of amino UiO-66 was an amine-terminated terephthalic acid, it basically included in aromatic carboxylates. So, there are different peaks derived from carboxylic and aromatic groups in the ATR-IR pattern: 1423 cm⁻¹ for C–C vibrational bond, and 1585, and 1397 cm⁻¹ for asymmetric, and symmetric C–O stretching bond of carboxylates, respectively. Since the ligand also possesses a primary amine group linked to the aromatic loop, two specific peaks of the primary amino peaks can be detected at 3337 and 3518 cm⁻¹, ascribing to symmetric and asymmetric vibrational bands of the free-NH₂ group, respectively [34,35]. The linking between nitrogen and aromatic carbon, C–N, could be seen at 1358 and 1254 cm⁻¹, and the peak center at 1618 cm⁻¹ correspond to the N–H bending vibration [36]. The characteristic peaks at 766 cm⁻¹ are also ascribed to the Zr-O mode [25].

Fig. 4(b) shows the XRD patterns of the UiO-66-NH₂ nanoparticles. XRD analysis of UiO-66-NH₂ conﬁrmed that it was synthesized favorably with speciﬁc peaks at 2θ = 7.4°, 8.6° and 25.8° attributed to (1 1 1), (2 0 0) and (6 0 0) crystal planes, respectively. Fig. 4(b) showed thin lines and great crystallinity of the nanoparticles which are consistent with the previous literatures [32,33].

The morphology of UiO-66-NH₂ was further studied by TEM image. According to TEM images (Fig. 5(a)), the as-synthesized UiO-66-NH₂ represent tetrahedron microcrystals with particle size around in 100 nm, corroborating the good crystallized solid mode by solvothermal method. The particle size distributions of UiO-66-NH₂
nanoparticles are shown in Fig. 5(b). The results indicate particle sizes range from 60 to 430 nm that 60% are below 120 nm, and the average size of 87 nm was consistent with the TEM analysis.

3.2. Characterization of TFN membranes

The chemical characterization of the prepared membranes was collected by ATR-IR spectroscopy. The spectra of the PPSU-GO support membrane, TFN membrane, M-TFN membranes incorporated with 0.05% and 0.2% UiO-66-NH₂, and also UiO-66-NH₂ nanoparticles, were illustrated in Fig. 6. The characteristic broad band of polyamide at 1618 cm⁻¹, which corresponds to the C=O band of amide group, was observed in both TFN and M-TFN membranes, indicating the successful IP process over the nanocomposite support membrane. The peaks at 771 and 1360 cm⁻¹ corresponding to UiO-66-NH₂ nanoparticles, were also observed in M-TFN membranes, which is assigned to the Zr-O mode, and the stretching of C-N bond in nanoparticles, respectively.

The morphological structure of the PA-MOF layer was investigated by the FESEM and AFM analyses. The top surface and cross-sectional FESEM images for the support and TFN membranes are shown in Figs. 7 and 8. The surface morphology of PA polymerized by PIP and TMC on the top surface of PPSU-GO support layer shows “nodular” structure. With incorporation UiO-66-NH₂ content to 0.05% into the PA layer, the morphology of the membranes changes to a dense cross-linked.
structure. Forasmuch as by addition of hydrophilic UiO-66-NH₂ in the organic phase, the diffusion of PIP in organic phase may increase during the IP process, UiO-66-NH₂ nanoparticles affect the PA layer structure [37]. This characteristic could be most favorable to obtain membranes with high rejection and stability. The surface morphology of the TFN membranes with 0.025% and 0.05% UiO-66-NH₂ (Fig. 7c and d)
indicates a relatively good dispersion of nanoparticles in the PA layer, but at higher nanoparticles loadings (over 0.05%), nanoparticles aggregations and even larger clusters can be observed for M-TFN3 and M-TFN4. According to the cross-sectional images (Fig. 8), the continuous discrete PA layer was clearly formed over the nanocomposite support. The thickness of the PA layer was measured at four different locations for each TFN membrane sample and the average thickness values of thin film (δ_{film}) are reported in Fig. 7. With increasing UiO-66-NH$_2$ loading in the PA, the thickness of the PA layer increased. The hydrophilic nature of UiO-66-NH$_2$ is also a factor resulting in the increased
layer thickness with increasing nanoparticles loadings [25]. Because by addition of UiO-66-NH2 in the TMC solution, diffusion of PIP in the organic phase is facilitated due to the presence of hydrophilic nanoparticles and a thicker rejection layer is formed.

Fig. 9 shows the AFM topographic images of the TFN and M-TFN membranes, and the surface roughness parameters obtained from the AFM test including the average roughness (Rₐ), and the root mean square of the z data (Rₚ) are listed in Table 2. With the increase of UiO-66-NH2 loading, the membrane surface became rougher and their roughness parameters values increased. The same behavior has been reported in the previous study with MIL-101 (Cr) nanoparticles [26]. At higher UiO-66-NH2 loadings (over 0.05%), the aggregations of the nanoparticles caused bumps on the membranes surface and a considerable increase in roughness, which were in accordance with the FESEM images in Fig. 7.

The hydrophilicity of the TFN membrane was characterized by water contact angle measurements. The results are presented in Table 2. The water contact angle of the membranes decreased with the incorporation of UiO-66-NH2 nanoparticles in the PA layer. This behavior may be attributed to the exposed super-hydrophilic UiO-66-NH2 nanoparticles on the top surface of the M-TFN membranes. However, when the amount of UiO-66-NH2 was increased from 0.05 to 0.1%, the water contact angle increased slightly. This is maybe due to agglomeration and irregular position of nanoparticles in the membrane surface and increasing of the membrane surface roughness [26,28]. Generally, the hydrophilicity of the M-TFN membrane enhanced with the addition of UiO-66-NH2 nanoparticles, which is beneficial for improving the water flux, fouling resistance, and rejection in membrane filtration. As shown in Table 2, the M-TFN membranes interestingly have higher PWF comparing with the TFN membrane. This may be caused by the introduction of additional direct channels for water molecules by the incorporation of hydrophilic and porous UiO-66-NH2 nanoparticles in the PA layer of M-TFN membranes [28]. However, the PWFs of the M-TFN membranes increased first with increasing UiO-66-NH2 content and then decreased (over 0.05%), similar to what was observed with UiO-66 and MIL 125 MOFs nanoparticles [25,27]. This is attributable to the nanoparticles aggregation at higher loadings of nanoparticles, which could block the water transfer through the membrane by the hydrophobic linkers overlapping [27].

The tensile strength at the break of the membranes was determined to study the impact of UiO-66-NH2 nanoparticles amount on the mechanical stability of the M-TFN membranes, and the test results are presented in Table 2. The TFN membrane showed a 6.49 MPa tensile strength and this value increased to 8.22 MPa when 0.2% UiO-66-NH2 was added. Furthermore, when the UiO-66-NH2 content increased from 0.1 to 0.2% no significant difference in tensile strength was observed. The improvement in tensile strength can be credited to strong inter-action between UiO-66-NH2 and polymer matrix owing to uniform dispersion of nanoparticles [38]. Besides, high amount of nanoparticles (0.4%) negatively affects the mechanical properties of the membrane due to agglomeration of nanoparticles [38].

The TGA analyses of UiO-66-NH2 nanoparticles, TFN membrane and M-TFN2 membrane (incorporated with 0.05% UiO-66-NH2) are shown in Fig. 10. Three steps of weight loss were noted for UiO-66-NH2 nanoparticles [39,32]. The weight loss in the first step was about 10 wt% from 140 to 200 °C, attributed to the initial solvent loss, and the second weight loss was about 5 wt% from 204 to 366 °C, attributed to the de-hydration of the Zr6O2(OH)4 nodes to Zr6O5. The last step, the weight loss was about 40 wt% from 380 to 600 °C, corresponding to the decomposition of the organic linkers. Both the PA/PPSU-GO membrane (TFN) and the PA-MOF/PPSU-GO membrane (M-TFN) possessed two major stages in the decomposition process, which is consistent with the results obtained by other researchers for polyamides [40,41]. The first weight loss in the range of 535–630 °C was due to the degradation of functional group from nanoparticles, PA and PPSU. The second weight loss stage from 640 °C was mainly attributed to the decomposition of the substrate backbone. The first decomposition began at 535 °C for TFN membrane and at 538 °C for M-TFN2 membrane and the maximum weight loss was observed in neat PA. Consequently, M-TFN2 exhibited the best stability due to the strength of the interaction between the nanofiller and the polymer during the polymerization [41,42]. The above results were well in agreement with the mechanical properties and indicate that the M-TFN nanocomposite membranes also have good thermal stability.

### 3.3. Performance evaluation of TFN membranes

The impact of incorporating UiO-66-NH2 on the performance of the TFN membranes was investigated using separation of KHI from an aqueous solution contains 0.5 wt% KHI. The permeate flux and KHI rejection of the membranes are shown in Fig. 11. Substantial improvements are observed for the M-TFN membranes by adding UiO-66-NH2 nanoparticles in comparison to the TFN membrane. The permeate flux has minimum value (38.4 L/m² h) for TFN membrane, and by adding 0.05% UiO-66-NH2, permeate flux increased to 59.9 (L/m² h), while the KHI rejection remains almost the same. This increase of flux is probably due to change of structure in the PA layer (e.g. hydrophilicity or cross-linking extent), and also the porous structure of UiO-66-NH2.

### Table 2

The effect of UiO-66-NH2 nanoparticles addition on the surface roughness, hydrophilicity, performance and mechanical properties of the membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Rₛ (°)</th>
<th>Rₚ (°)</th>
<th>θ (°)</th>
<th>PWF (L/m² h)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFN</td>
<td>3.99 ± 0.2</td>
<td>11.02 ± 1.5</td>
<td>34.6 ± 2</td>
<td>44.77 ± 3.7</td>
<td>6.49 ± 0.29</td>
</tr>
<tr>
<td>M-TFN1</td>
<td>5.31 ± 0.4</td>
<td>16.7 ± 2.1</td>
<td>27.4 ± 1.3</td>
<td>59.54 ± 2.9</td>
<td>7.67 ± 0.10</td>
</tr>
<tr>
<td>M-TFN2</td>
<td>8.54 ± 0.6</td>
<td>20.45 ± 4</td>
<td>26 ± 1</td>
<td>64.4 ± 2</td>
<td>8.19 ± 0.15</td>
</tr>
<tr>
<td>M-TFN3</td>
<td>15.26 ± 2</td>
<td>30.1 ± 5.6</td>
<td>28 ± 2</td>
<td>52.2 ± 3.1</td>
<td>8.22 ± 0.25</td>
</tr>
<tr>
<td>M-TFN4</td>
<td>28.27 ± 1.2</td>
<td>59.47 ± 3</td>
<td>25 ± 1.7</td>
<td>45.4 ± 2.4</td>
<td>7.33 ± 0.06</td>
</tr>
</tbody>
</table>

The surface roughness parameters (Rₛ and Rₚ), contact angle (θ), and pure water flux (PWF) of the membranes.
The particle aggregation could also create voids in the PA layer that sage through the membrane, hence decreases the water hand, when a high dosage of UiO-66-NH2 nanoparticles are added to be mainly caused by the FESEM image analysis (Fig. 7). Aggregation may block the water passage of PA layer for percentages higher than 0.05% as shown in the aqueous solution as feed).

However, with further increase in the content of UiO-66-NH2 up to 0.05% a drop in the flux and also rejection happened. This behavior can be mainly caused by the filler aggregation and lower cross-linking extent of PA layer for percentages higher than 0.05% as shown in the FESEM image analysis (Fig. 7). Aggregation may block the water passage through the membrane, hence decreases the water flux [26,27]. The particle aggregation could also create voids in the PA layer that allowed the feed aqueous solution to pass through [43]. On the other hand, when a high dosage of UiO-66-NH2 nanoparticles are added to the organic solution, the viscosity of the solution increases, and diffusion of PIP reduces during IP process, which this leads to the formation of a lower cross-linking PA layer [37]. Thereby, reduction in both flux and rejection at higher nanoparticles loadings and at rejection at higher nanoparticles loadings occurred due to these defects. Overall, incorporation of an optimum concentration of UiO-66-NH2 (0.05%) into PA layer allows a significant increase in membrane flux, which is approximately 56% higher than unmodified TFN membrane with minimal compromise in rejection.

The antifouling properties of the membrane without UiO-66-NH2 nanoparticles (TFN) and the membrane incorporated with 0.05% UiO-66-NH2 (M-TFN2) were investigated in a cross-flow filtration using 0.5 wt% KHI solution as the feed solution at 8 bar and 25 °C. However, fouling is a main limiting factor in efficient application of the membrane separation processes, which negatively affects membrane performance [11]. In Fig. 12, the permeate flux for TFN and M-TFN2 membranes are compared as a function of time. The M-TFN2 membrane always maintained higher flux, which indicates that the performance of the membrane was interestingly improved by the addition of UiO-66-NH2. The flux decline analysis and FRR of the membranes were calculated through Eqs. (3)–(6), and are listed in Table 3. The total fouling of M-TFN2 membrane is obviously lower than the TFN membrane, and the irreversible fouling has a little portion of the total fouling (almost 2%). The FRR of M-TFN2 membrane is also higher than TFN membrane, which means the addition of UiO-66-NH2 nanoparticles into a PA layer not only increases its water permeability but also enhances the fouling resistance of the membrane. The improved antifouling properties of M-TFN2 membrane may be related to the improved hydrophilicity of the membrane surface as shown in Table 2. The surface adsorption properties of TFN membranes depend upon the hydrophobicity of the PA active layer, hence increasing the hydrophilicity of a membrane can enhance antifouling properties [21]. The hydrophilic surface of M-TFN2 membrane could cause to reduce the hydrophobic interaction and reduce the contaminants adsorption.

Table 4 compares the separation performance of the prepared membranes in this study with other membranes reported in the literature for KHI removal. With considering the flux and antifouling properties, the M-TFN membrane exhibits better membrane performance among these reported membranes.

To evaluate the stability of M-TFN2 membrane, a long-time test (70 h) was performed, and the results are illustrated in Fig. 13. Membrane stability is a key factor which significantly determines the Durability and applicability of the membrane [44]. As shown in Fig. 13, both the flux and rejection declined at the first, which can be related to the reversible fouling caused by concentration polarization of solute at the membrane surface [16]. Finally, the membrane reached a relatively stable state, which means M-TFN2 membrane incorporated with 0.05% UiO-66-NH2 was stable in term of the separation performance.

Another major challenge for large-scale application of TFN membranes is leaching out of the incorporated nanoparticles from the membrane due to low adhesion/interaction between nanoparticles and the PA matrix. Leaching out of the nanofillers into the downstream (permeate and retentate) causes degradation of TFN membranes and infringement the strict regulations of drinking water and environmental safety [45]. The leachability of the UiO-66-NH2 from M-TFN2 membrane was studied by shaking the membrane in a batch incubator and measuring the amount of Zr ions leached out from the membrane in the collected water using ICP-OES analysis. The ICP result indicated that a negligible amount of Zr (around 11 ppb) leached out from the membrane during 60 h batch test. The results clearly suggest that there is strong interaction between the UiO-66-NH2 nanoparticles and the PA matrix.

4. Conclusion

In the current study, hydrophilic zirconium-based MOF (UiO-66-NH2) nanoparticles were successfully synthesized, characterized and used as the filler in the TFN membranes. The TFN-NF membranes with high performance have been successfully fabricated through interfacial polymerization using aqueous PIP and organic TMC/UiO-66-NH2.
this study showed that the TFN membranes incorporated with UiO-66-attributed to enhanced the membrane hydrophilicity. The results from

membrane occurred during the batch experiment. A significant improvement of the membrane compared to the unmodified membrane. The performance of the membrane samples was investigated by the rejection of KHI, resulting in a significantly improved water flux and a minor reduction in rejection. The M-TFN2 membrane with 0.05 (w/v%) UiO-66-NH2 loading, exhibits the highest permeate flux, which is almost 56% higher than the unmodified TFN membrane. The M-TFN2 membrane exhibits an excellent operation stability for a long-time NF test. Moreover, the ICP-OES analysis (Zr content, 11 ppb) showed that no leaching out of UiO-66-NH2 nanoparticles from M-TFN2 membrane occurred during the batch experiment. A significant improvement was also observed in antifouling properties of the M-TFN2 membrane by addition of the UiO-66-NH2 nanoparticles and this can be attributed to enhanced membrane hydrophilicity. The results from this study showed that the TFN membranes incorporated with UiO-66-NH2 nanoparticles have an acceptable performance for applications in the water purification field.

Acknowledgements

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Table 4

Benchmarking of the membranes for KHI removal.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Operating pressure (bar)</th>
<th>Permeate flux (L/m²·h)</th>
<th>Total fouling (%)</th>
<th>Rejection (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic membrane (Alumina, Zirconia, Silica, Silicon carbide, and mixed oxides)</td>
<td>3.5–8.5</td>
<td>–</td>
<td>–</td>
<td>50–90</td>
<td>[8]</td>
</tr>
<tr>
<td>Ceramic membrane (Zirconia and Titania)</td>
<td>15–60</td>
<td>–</td>
<td>–</td>
<td>&lt; 80</td>
<td>[9]</td>
</tr>
<tr>
<td>BWRO</td>
<td>41</td>
<td>15</td>
<td>30</td>
<td>99.9</td>
<td>[7]</td>
</tr>
<tr>
<td>Desal-DK</td>
<td>10–12</td>
<td>33.7</td>
<td>66.4</td>
<td>99.4</td>
<td>[7]</td>
</tr>
<tr>
<td>GK</td>
<td>3.4–4.5</td>
<td>13</td>
<td>43.2</td>
<td>84</td>
<td>[7]</td>
</tr>
<tr>
<td>PA/PPSU (TFC)</td>
<td>8</td>
<td>26.4</td>
<td>43.2</td>
<td>97</td>
<td>[10]</td>
</tr>
<tr>
<td>PA/PPSU-GO (TFN)</td>
<td>8</td>
<td>38</td>
<td>16.5</td>
<td>96.2</td>
<td>This study</td>
</tr>
<tr>
<td>PA/PSU/PPSU-GO (M-TFN2)</td>
<td>8</td>
<td>55.5</td>
<td>9.9</td>
<td>96.6</td>
<td>This study</td>
</tr>
</tbody>
</table>

* Commercial membrane.

References


