A practical approach to synthesize polyamide thin film nanocomposite (TFN) membranes with improved separation properties for water/wastewater treatment†

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Thin film nanocomposite (TFN) membranes containing 0.05 or 0.10 w/v% surface-functionalized titanate nanotubes (TNTs) in a polyamide selective layer were synthesized via interfacial polymerization of piperazine (PIP) and trimesoyl chloride (TMC) monomers. Nanomaterials were dispersed into the monomer solution using two different approaches. In the first one, the functionalized TNTs were dispersed into the amine aqueous solution, while in the second approach the same nanomaterials were dispersed in TMC organic solution. The TFN membranes were characterized and compared with a control thin film composite (TFC) membrane to investigate the effect of nanofiller loadings and the fabrication approach on membrane properties. Results showed that introducing nanofillers into the organic phase was more effective to synthesize a TFN membrane of greater separation performance as the use of a rubber roller to remove aqueous solution from the substrate surface could cause the loss of a significant amount of nanofillers, which further affected the polyamide layer integrity. It was also found that the incorporation of a high nanofiller loading tended to interfere with interfacial polymerization and weaken the bonds between monomer blocks, resulting in poor polyamide–nanotube integrity. Compared to the TFC membrane, the TFN membrane made of 2% PIP and 0.15% TMC with 0.5% nanofiller incorporation could achieve greater water flux (7.5 vs. 5.4 L m⁻² h⁻¹ bar⁻¹) and Na₂SO₄ rejection (96.4% vs. 86%) while exhibiting higher resistance against fouling by protein and dye.

1 Introduction

Polyamide (PA) thin film nanocomposite (TFN) membranes were reported for the first time by Hoek’s research group in 2007 as a new generation of composite membranes to overcome permeability–selectivity trade-off of thin film composite (TFC) membranes for reverse osmosis applications.1 By embedding a small quantity of zeolite nanoparticles into the PA selective layer of TFC membranes, it was reported that the water permeability of the resulting composite membrane could be increased almost by an order of magnitude without compromising salt rejection. The authors attributed the promising membrane performance to the unique characteristics of zeolite that offer preferential flow paths for water molecules through its super-hydrophilic surface and mesoporous structure.

To date, there are more than 100 relevant articles documented in the literature reporting the separation performance of PA TFN membranes for various processes. A recent review authored by Lau et al.2 has summarized the effects of various types of inorganic nanomaterials on the intrinsic properties and performances of PA TFN membranes for separation processes covering not only aqueous-based media like nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO), but also for the treatment of organic solvents as well as pervaporation processes. Depending on the types and characteristics of nanomaterials used, the resultant TFN membrane could show attractive features associated with bacterial, fouling and chlorine resistance, in addition to enhancement in water flux and salt rejection.1–6
Although the potential of PA TFN membranes for water treatment processes in particular has been demonstrated by many researchers over the past 8–9 years, there remain several concerns related to TFN membrane making. One of them is the different approaches used by researchers to introduce nanomaterials during interfacial polymerization processes. As can be seen from Table 1, inorganic nanomaterials could be added either into amine aqueous or acyl chloride organic solution in the process of PA synthesis.\textsuperscript{1,5–7,9} However, owing to the hydrophilic nature of nanomaterials, most research studies have preferred to introduce nanomaterials into amine aqueous solution. This is because of the difficulties in producing a homogeneous mixture in a non-polar organic phase. Since removing excess amine solution from the substrate surface (using a rubber roller or air knife) is a necessary step during interfacial polymerization processes, a large amount of nanomaterials could be removed together with the amine solution (in the case of nanomaterial–aqueous mixture), leaving only a small amount of nanomaterials in the substrate. As a result, the positive features of nanomaterials such as hydrophilicity, anti-fouling properties and surface charge density are likely to be reduced in the synthesized PA layer. Many researchers, however, did not take into consideration the inefficiency of this approach in making TFN membranes.

In this work, we have reported on synthesis methods for PA TFN membranes by adding inorganic functionalized nanomaterials into aqueous or organic solution, respectively. The main objective of the work was to compare the efficiency of approaches used for preparing PA TFN membranes for water/wastewater treatment processes. Titanate nanotubes (TNTs) were selected as the nanofillers owing to their hydrophilic properties and large surface area, as well as the existence of narrow channels that might promote water transport through the membrane.\textsuperscript{13,14} To improve the dispersion quality of TNTs in organic solution, a silane agent was used to modify the surface of TNTs. It was also an objective of this work to study how different concentrations of piperazine (PIP) and trimesoyl chloride (TMC) monomers affect the properties of the PA nanocomposite layer, which will in turn alter the performance of the membrane in NF processes.

2 Experimental

2.1 Materials

Polysulfone (PSF, Udel® P-3500) in pellet form, purchased from Solvay Specialty Polymers, USA, was used to fabricate a microporous substrate for TFC/TFN membranes. Polyvinylpyrrolidone (PVP) K29-32 (M\textsubscript{w}: 58 000 g mol\textsuperscript{-1}) used as a pore forming agent during substrate fabrication was purchased from Acros Organics. Titanium dioxide (TiO\textsubscript{2}) Degussa P25 nanospheres supplied by Evonik Industries were used as received to synthesize TNTs. 1-(2-Amino-ethyl)-3-aminopropyl trimethoxysilane (AAPTS) from Merck was used to modify the TNT surface to produce amino-functionalized titanate nanotubes (NH\textsubscript{2}-TNTs). Piperazine (PIP) and trimesoyl chloride (TMC) purchased from Acros Organics and Merck, respectively, were used to form a PA layer on top of the PSF substrates.

### Table 1. Different approaches used in preparing polyamide thin film nanocomposite (PA TFN) membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Membrane used(^a) (loading, w/v%)</th>
<th>Solution that nanofillers are added</th>
<th>Solution for the IP process(^c)</th>
<th>Approach used to remove excess aqueous solution on the support surface</th>
<th>Country/year (reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO</td>
<td>NaA zeolite (0.04–0.4%)</td>
<td>Aqueous (0.00–0.1%)</td>
<td>2% MPD, 0.1% TMC in hexane</td>
<td>Rubber roller</td>
<td>USA/2009 (ref. 1)</td>
</tr>
<tr>
<td>RO</td>
<td>RO Carbon nanotubes (0.00–0.1%)</td>
<td>Organic (0.00–0.1%)</td>
<td>2% MPD, 0.1% TMC in hexane</td>
<td>Air knife</td>
<td>China/2014 (ref. 5)</td>
</tr>
<tr>
<td>RO</td>
<td>Linde type A zeolite (0.2%)</td>
<td>Aqueous (0.00–0.1%)</td>
<td>2% MPD, 0.1% TMC in hexane</td>
<td>Air knife</td>
<td>Iran/2014 (ref. 9)</td>
</tr>
<tr>
<td>RO</td>
<td>RO Laponite (0.2%)</td>
<td>Organic (0.00–0.1%)</td>
<td>2% MPD, 0.1% TMC in hexane</td>
<td>Air knife</td>
<td>USA/2013 (ref. 11)</td>
</tr>
<tr>
<td>RO</td>
<td>RO Ag (0.05–0.1%)</td>
<td>Organic (0.00–0.1%)</td>
<td>2% MPD, 0.1% TMC in hexane</td>
<td>Air knife</td>
<td>Iran/2013 (ref. 12)</td>
</tr>
<tr>
<td>RO</td>
<td>RO Mesoporous SiO\textsubscript{2} (0.01–0.1%)</td>
<td>Organic (0.00–0.1%)</td>
<td>2% MPD, 0.1% TMC in hexane</td>
<td>Air knife</td>
<td>Iran/2013 (ref. 12)</td>
</tr>
<tr>
<td>RO</td>
<td>RO SiO\textsubscript{2} (0.01–0.1%)</td>
<td>Organic (0.00–0.1%)</td>
<td>2% MPD, 0.1% TMC in hexane</td>
<td>Air knife</td>
<td>Iran/2013 (ref. 12)</td>
</tr>
<tr>
<td>NF</td>
<td>RO SiO\textsubscript{2} (0.01–0.1%)</td>
<td>Organic (0.00–0.1%)</td>
<td>2% MPD, 0.1% TMC in hexane</td>
<td>Rubber roller</td>
<td>Iran/2013 (ref. 12)</td>
</tr>
</tbody>
</table>
substrate. N-Methyl-2-pyrrolidone (purity > 99.5%) and cyclohexane supplied by Acros Organics and Merck, respectively, were used without further purification. Sodium sulfate (Na2SO4, Riedel-de-Haen), sodium chloride (NaCl, Merck), bovine serum albumin (BSA, Sigma-Aldrich) and Reactive Black 5 (RB5, Sigma-Aldrich) were used as test solutes for membrane flux and rejection determination. The feed solution containing the respective test solute was prepared by dissolving the solute in Milli-Q water. Other chemicals used in this work were of analytical grade and were used as received without purification.

2.2 Synthesis and modification of TNTs
TNTs were synthesized using the alkaline hydrothermal method. First, 3 g of TiO2 nanoparticles was added into 100 mL of 10 M NaOH aqueous solution. After vigorous stirring for 12 h, the milky-white mixture was moved into a 150 mL Teflon-lined reactor and heated at 180 °C in an oven for 24 h. After the heating process, the reactor was allowed to cool to ambient temperature naturally before the white powder was collected by a centrifugation process. The white product was further washed with 0.5 M HCl solution followed by pure water rinsing until the pH of washing solution became close to 7. The white powder of TNTs was then dried overnight at 100 °C. The white powder of TNTs was then dispersed in 50 mL toluene containing 1.0 g of AAPTS. The mixture was stirred for 2 h. The unreacted monomers were removed onto the same substrate surface followed by draining off after 10 s of contact time. The unreacted monomers were removed from the membrane surface by rinsing the membrane with pure water. The resultant TFC membrane was then post-treated in an oven at 60 °C for 8 min. Finally, the membrane was stored in a pure water container until use.

TNT membranes were synthesized exactly as described above, except that the NH2-TNTs (0.05 or 0.10%, w/v) were dispersed either in aqueous or organic solution (see Table 2). Prior to the interfacial polymerization reaction, the solutions containing nanofillers were ultrasonicated for 30 min and used immediately after the ultrasonication process. Based on the quantity of the used NH2-TNTs and their presence either in aqueous or organic solution, the prepared composite membranes are labeled as TFC (control), TFNaq-0.05, TFNaq-0.10, TFNcyclo-0.05, and TFNcyclo-0.10 membranes. To further study the effect of the monomer concentration on the characteristics of PA nanocomposites, the conditions used to prepare the TFNcyclo-0.05 membrane were further varied by changing the concentration of PIP and TMC without altering the quantity of NH2-TNTs (see Table 3).

2.3 Preparation of TFC and TFN membranes
All the composite membranes were prepared in the in-house made PSF microporous substrate. The substrate prepared via the phase inversion method possessed a molecular weight cutoff (MWCO) of 47.5 kDa (see Fig. S1†) with a pure water flux and surface contact angle recorded to be ~150 L m−2 h−1 bar−1 and 78.2°, respectively. The MWCO of the substrate prepared was in the range of 30–50 kDa as reported in the literature. The synthesis of the PA layer was performed via the interfacial polymerization technique that used PIP and TMC as monomers. Table 2 shows the amounts of NH2-TNTs present in the solutions during interfacial polymerization together with the concentration of monomers used in aqueous and organic solutions. A TFC membrane (without NH2-TNTs) was also prepared for comparison purpose. The interfacial polymerization process was initiated by pouring 2% (w/v) PIP aqueous solution on the top surface of the substrate. The aqueous solution was then held horizontally on the substrate surface for 2 min to ensure the penetration of aqueous solution into the substrate pores. The excess aqueous solution was drained from the substrate surface by using a soft rubber roller. Secondary organic solution that contained 0.15% (w/v) TMC was poured onto the same substrate surface followed by draining off after 10 s of contact time. The unreacted monomers were removed from the membrane surface by rinsing the membrane with pure water. The resultant TFC membrane was then post-treated in an oven at 60 °C for 8 min. Finally, the membrane was stored in a pure water container until use.

2.4 Filtration experiments
The filtration experiments for TFC and TFN membranes were performed using a commercial stirred dead-end permeation cell (HP4750, Sterlitech Corp.). Prior to any measurement, the membranes were washed thoroughly for 30 min under...
a pressure of 7 bar, until the membranes were fully compacted and the flux reached a steady state. The performance of membranes was then evaluated for water permeability as well as rejection against Na$_2$SO$_4$ (1000 mg L$^{-1}$), NaCl (1000 mg L$^{-1}$), BSA (1000 mg L$^{-1}$) and RB5 (1000 mg L$^{-1}$) at an operating pressure of 6 bar. The volume of permeate (mL) collected over a specified time divided by the membrane area (14.6 cm$^2$) and time to collect the permeate (min) produced the reported value for permeate flux (L m$^{-2}$ h$^{-1}$). The observed solute rejections, $R$ (\%), were determined from the difference between feed ($C_0$) and permeate ($C_p$) solute concentrations. A bench conductivity meter (4520, Jenway) was used to measure the conductivity value in the feed and permeate of salt solutions while a UV-vis spectrophotometer (DR5000, Hach) was used to determine the concentration of BSA and RB5 in solutions. To evaluate the membrane fouling resistance, TFC and TFN membranes were subjected to a 3 h permeation test using feed aqueous solution containing either BSA or RB5 as a model foulant. The flux decline determined from the initial permeate flux, $J_0$, and the final permeate flux, $J_t$, was then used to study the extend of membrane fouling.

A prolonged filtration test using pure water (up to 480 min) was also conducted to determine if there was any leaching of the surface-modified TNTs from the PA nanocomposite layer to feed or permeate samples. For each set of feed and permeate samples collected at specific time intervals for Ti analysis, the pure water in the permeation cell was withdrawn and the cell was refilled again with pure water. The presence of nanofillers in the solutions was detected by using a Benchtop ICP Mass Spectrometer (ICP-MS) (ELAN6100, Perkin Elmer) with respect to the titanium (Ti) element at the ng L$^{-1}$ level (equivalent to parts per billion, ppb).

2.5 Characterization

Specific surface measurements of TNTs were performed using a Micromeritics® ASAP 2010 with N$_2$ at 77.3 K. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method. Powder XRD analysis was made using a D-Max Rigaku diffractometer with 2θ ranging from 10° to 80°. Transmission electron microscopy (TEM) analysis was performed using a Hitachi HT7700 to study the morphological structure of TNTs in the nm scale. Fourier transform infrared (FTIR) spectra of TNTs and membranes were recorded on a Thermo Scientific Nicolet 5700. The spectra were collected in the attenuated total reflection (ATR) mode. The spectra were recorded in the 600–4000 cm$^{-1}$ wavenumber range with an average of 16 scans and at a resolution of 4 cm$^{-1}$. The same characterization was performed to analyze the interaction between NH$_2$-TNTs and TMC monomers in the absence of PIP monomers. To confirm the chemical reaction, NH$_2$-TNT-TMC compounds were obtained by directly adding NH$_2$-TNTs into TMC/cyclohexane solution followed by washing and drying.

Surface images of the composite membranes together with elemental analysis were obtained using a Hitachi SU8000 field emission scanning electron microscope (FESEM) equipped with an energy-dispersive X-ray (EDX) spectrometer. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo instrument at a rate of 10 °C min$^{-1}$ under a nitrogen atmosphere from 100 °C to 700 °C. 3D membrane surface images and roughness values were obtained using a Park System XE-100 atomic force microscope (AFM) with a scan size of 10 μm × 10 μm. The membrane surface hydrophilicity was characterized based on a sessile drop technique using a Dataphysics OCA15plus contact angle goniometer.

3 Results and discussion

3.1 Characteristics of TNTs

Fig. 1 shows the properties of TNTs characterized by using different instruments. The morphological structure of TNTs can be evidenced from the TEM image shown in Fig. 1(a). It is found that the synthesized nanotubes are of tubular-shape with open-ended lumens. The inner diameter and length of these nanotubes are in the ranges of 9–14 nm and 0.35–2.25 μm, respectively, with a BET surface area reported to be about 200 m$^2$ g$^{-1}$. The XRD peaks of 10.85°, 24.5° and 48.5° as shown in Fig. 1(b) correspond to the (200), (110) and (020) planes, respectively indexed to TNTs. Meanwhile, the broad FTIR band between 3000 and 3500 cm$^{-1}$ shown in Fig. 1(c) indicates the presence of abundant –OH groups on the surface of TNTs. The peak at 1630 cm$^{-1}$ could be attributed to the characteristic of stretching and bending vibrations of water molecules that adsorbed on the dried TNTs.

3.2 Comparison between TFN$\text{aq}$ and TFN$\text{cyclo}$ membranes

3.2.1 FTIR. FTIR spectra of three composite membrane surfaces are shown in Fig. S2.† Overall, there is no difference between the spectra of the TFC and TFN membranes prepared. The results suggest that the incorporation of small quantities of inorganic nanofillers do not alter the spectra of the organic PA structure, indicating that the dominant functional groups do not alter. A similar observation was also reported in the work of Baroña et al. in which aluminosilicate single wall nanotubes were incorporated into the PA layer of the composite membrane. In general, the peaks originating from the interfacially polymerized layer could be found at 3445 cm$^{-1}$, 1630 cm$^{-1}$ and 1540 cm$^{-1}$. These peaks correspond to the –OH stretching of carboxylic acid, C==O stretching vibration of the amide group and C–N stretching, respectively.

Further FTIR analysis of the interaction between amino functionalized TNTs and TMC monomers (Fig. S3†) in the absence of PIP monomers shows no peak arising from the amide II (N–H) of functionalized TNTs at 1550 cm$^{-1}$. This suggests that the signal of the amino group attached to the TNT surface is weak. The minimum amount of amino groups attached to the TNT surface can be beneficial to interfacial polymerization, avoiding competition with PIP for interaction with TMC monomers and increasing the PA cross-linking degree.

However, in order to prove that the surface of TNTs has been modified, Fig. 2 compares the dispersion quality of TNTs with and without AAPTS modification in cyclohexane. It is found that the amino-functionalized TNTs are clearly dispersed better in
the non-polar solvent in comparison to the unmodified TNTs. Owing to the improved surface properties, modified TNTs take a longer time to settle. Similar surface modifications were conducted by Namvar-Mahboub et al.\textsuperscript{20} and Rajaeian et al.\textsuperscript{21} on UZM-5 zeolite and TiO$_2$ nanoparticles, respectively, but both research studies did not demonstrate the dispersion quality of amino-functionalized nanomaterials in the organic solvent.

3.2.2 FESEM-EDX-AFM. Fig. 3 shows the FESEM image, contact angle and EDX mapping on the PA surface of three different types of composite membranes. In the FESEM images of the top surface, the white parts represent the peaks while the dark areas correspond to the valleys. The formation of ridge and valley structures confirms that the PA active layer is successfully formed over the PSF substrate. However, as can be clearly seen, the addition of NH$_2$-TNTs into either aqueous or organic solution has altered the structure of PA leading to more peaks being formed for the TFNaq-0.05 and TFNcyclo-0.05 membrane. Particularly for the TFNaq-0.05 membrane, obvious irregular nodules are formed which affect the integrity of the PA layer. The observation can be explained by the approach used in removing excess aqueous solution containing NH$_2$-TNTs. The use of a rubber roller to remove aqueous solution from the substrate surface
has negatively affected the distribution of nanofillers on the substrate surface. Compared to the TFNcyclo-0.05 membrane, in which the nanofillers are introduced from the organic solution after excess aqueous solution has been removed, the formation of ridge-and-valley like structures is more even. Besides, it was also experienced that a significant amount of NH2-TNTs was lost in the TFNaq- membrane during the excess aqueous solution removal process. This is further supported by TGA results (see Fig. S4†) in which the residue for the TFNaq-0.05 membrane at 700 °C is lower than that for the TFNcyclo-0.05 membrane, indicating less TNTs are embedded in the TFNaq membrane. Compared to the polymeric materials (PA and PSF), TNTs are high melting point materials and do not decompose at temperatures less than 700 °C.

The EDX data, on the other hand, showed that the TFNcyclo-0.05 membrane surface exhibits significantly higher weight percents of Ti and O elements compared to the TFNaq-0.05 membrane, suggesting the greater amount of nanotubes embedded in the PA layer. Meanwhile, no Ti element is detected in the TFC control membrane. With respect to the contact angle, it is found that the TFC control membrane displays lower values than those of TFN membranes. Its contact angle of 39.0° is acceptable for a typical hydrophilic PA layer and falls within the range of PA made of PIP-TMC.32

A correlation between membrane hydrophilicity and the water contact angle might not be established in this case as the increase in the surface roughness of TFN membranes might affect the contact angle according to the Cassie’s model. The 3D AFM images (see Fig. S5†) indicate that the TFNaq-0.05 membrane displays a higher Rs value (1074.85 nm) compared to TFNcyclo-0.05 (741.7 nm) and TFC (419.8 nm). The highest Rs value shown by the TFNaq-0.05 membrane is in good agreement with the SEM surface image, i.e. obvious irregular nodules are detected in this membrane type. Compared to the TFC membrane, the relatively higher surface roughness values of the TFNcyclo-0.05 membrane could be attributed to the existence of NH2-TNTs within the PA layer. Previous work has also reported that both the contact angle and surface roughness of the PA layer are increased upon the introduction of zeolite nanoparticles.37 In order to understand if the presence of hydrophilic nanotubes do improve PA surface hydrophilicity, detailed discussion on the TFN membrane performance with respect to
Although the TFN membrane water flux is further enhanced with increasing the NH$_2$-TNT loading, one can observe a negative impact of the use of higher loadings of nanofillers on salt rejection (Fig. 4(b)). For two different types of the TFN membranes fabricated (i.e. TFN$_{aq}$ and TFN$_{cyclo}$), it is found that the higher the loading of nanofiller used, the lower the salt rejection and vice versa. It is also found that with increasing the amount of TNTs from 0.05% to 0.10%, the rejection rate of TFN membranes decreases to the level close to the TFC membrane.

Based on the findings, it can be said that the TFN$_{cyclo}$-0.05 membrane is the best performing membrane among the five composite membranes studied by taking into consideration its high water permeability and excellent salt rejection. In the following section, further investigations are conducted on the characteristics of this TFN membrane type by varying PIP and TMC monomers.

### 3.3 Effect of PIP and TMC monomers on TFN membrane properties

Fig. 5 presents the effects of the PIP and TMC content on the performance of TFN membranes incorporated with 0.5% nanofillers. The effects of both monomers on the TFN membrane water flux and salt rejection are found to be very similar, i.e. the composite membrane achieves optimum values when intermediate PIP (2.0%) and TMC (0.15%) concentrations are employed.
At the lowest concentration of PIP and TMC monomer used, both membrane water flux and salt rejection are lower compared to the intermediate concentration of PIP and TMC. The possible reason for the poor membrane performance is due to the lower degree of polymerization and cross-linking in the PA layer that results from the fact that insufficient monomers are available for interfacial polymerization. This concept is supported by the lowest surface roughness values of the TFNPIP-1.5 and TFNTMC-0.1 membrane as shown in Table 4. The insufficient amount of monomers available for interfacial polymerization might also cause poor interaction between nanotubes and the PA layer, leading to the formation of PA surface defects and/or possible nanotubes leaching out during filtration. This, as a result, affects both water flux and salt rejection as evidenced.

When the concentration of monomers is the highest, both TFNPIP-2.5 and TFNTMC-0.2 membranes have significantly lower water flux and salt rejection than the TFNCyclo-0.05 membrane made with intermediate PIP and TMC concentrations. The experimental results obtained can be attributed to the formation of a denser and thicker PA layer. The increase in the surface roughness values of TFNPIP-2.5 and TFNTMC-0.2 membranes also suggests more ridge-and-valley like structures created by the higher degree of polymerization and cross-linking. Normally, employing higher monomer concentrations tends to produce thicker polymeric films with higher molecular weights.\textsuperscript{6} Li \textit{et al.}\textsuperscript{27} elucidated that a higher PIP and TMC concentration tended to generate a thicker and more compact PA layer that could affect the water flux due to increased transport resistance. In the case of the PA layer incorporated with nanofillers, a thicker surface layer might reduce the extent of nanotube exposure to the top PA surface (reduced hydrophilicity) and/or cover the narrow channels of TNTs. Both effects can possibly affect the water flux and salt rejection behaviour.

The findings of this work demonstrate that changes in the conditions of interfacial polymerization are also required when nanofillers are added to the formulation to produce membranes of excellent performance. Addition of nanofillers simply to the monomer solution, either organic or aqueous, does not necessarily guarantee that you are working under the optimal conditions. The above example indicates that the concentrations of the monomer solutions should also be properly adjusted. It must also be pointed out that the changes in other variables such as substrate properties, aqueous/organic solution properties, reaction time and curing time during interfacial polymerization and types of nanofillers could lead to different outcomes.\textsuperscript{28,29}

Table 5 compares the performances of the best TFN membrane synthesized in our work with those of other TFC or TFN membranes reported in the literature for the separation of salts.\textsuperscript{10,11,15,18,21,26,30–33} By taking into consideration the pure water permeability coefficient (L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) of the membrane, it is found that our in-house synthesized TFN membrane has achieved greater water permeability (7.48 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) than most of the TFC/TFN membranes reported (1.5–6.98 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)), except PIP–TMC–SiO\(_2\) (9.45 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) and PIP–TMC–SAPO-34 (11 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) membranes. Its Na\(_2\)SO\(_4\) rejection (96.4%) recorded is also among the highest ones that are summarized in Table 5. The good balance between water permeability and solute selectivity as exhibited by our TFN membrane can be attributed to several factors. First, the use of

![Fig. 5](https://example.com/image5.png) Effect of the monomer content on the performance of TFN membranes that contain 0.5 w/v\% NH\(_2\)-TNTs, (a) PIP content and (b) TMC content.

**Table 4** Effect of the monomer concentration on the surface roughness value of TFN membranes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Membrane(^a)</th>
<th>Monomer conc. (wt/v%)</th>
<th>Roughness value (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(R_s)</td>
</tr>
<tr>
<td>Effect of PIP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TFNPIP-1.5</td>
<td></td>
<td>1.5</td>
<td>74.54</td>
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<tr>
<td>TFNPIP-2.0</td>
<td></td>
<td>2.0</td>
<td>87.51</td>
</tr>
<tr>
<td>TFNPIP-2.5</td>
<td></td>
<td>2.5</td>
<td>103.49</td>
</tr>
<tr>
<td>Effect of TMC</td>
<td></td>
<td></td>
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<tr>
<td>TFNTMC-0.1</td>
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<td>0.1</td>
<td>84.34</td>
</tr>
<tr>
<td>TFNTMC-0.15</td>
<td></td>
<td>0.15</td>
<td>87.51</td>
</tr>
<tr>
<td>TFNTMC-0.2</td>
<td></td>
<td>0.2</td>
<td>99.33</td>
</tr>
</tbody>
</table>

\(^a\) The properties of the TFNPIP-2.0 or TFNTMC-0.15 membrane are exactly the same as those of the TFNCyclo-0.05 membrane.
nanofillers with abundant –OH groups. Second, the introduction of nanofillers into organic solution. Third, the modification of the TNT surface for better dispersion in organic solution and finally, the use of cyclohexane (instead of n-hexane) for better diffusivity of the PIP and TNT dispersion. Fig. 6 compares the dispersion quality of modified TNTs in cyclohexane and n-hexane after 10 min mixing. It is clearly seen that the modified TNTs disperse better in cyclohexane compared to n-hexane dispersed nanomaterials, indicating an alicyclic hydrocarbon that exhibits higher boiling and flash points, a better organic solvent for nanomaterial dispersion.

3.4 Antifouling resistance against BSA and dye

The practical applications of the TFN membrane have been further studied by subjecting the membrane to solutions containing either 1000 mg L\(^{-1}\) BSA or 1000 mg L\(^{-1}\) RB5. From Fig. 7 and 8, it is found that the TFN\(_{cyclo-0.05}\) membrane shows a much higher water flux than that of the TFC control membrane when both membranes are tested under the same conditions. Besides the greater water flux, the flux decline of the TFN membrane is less than the TFC membrane within the studied period, e.g. the initial flux of the TFN membrane declines only 4.95% compared to ~20% of the TFC membrane within 180 min of filtration, which is ascribed to the improved antifouling resistance against BSA macromolecules of the TFN membrane.

![Fig. 6](image1)

![Fig. 7](image2)

Table 5 Performance comparison between the TFN membrane synthesized in this work and other TFC/TFN membranes reported for NF applications

<table>
<thead>
<tr>
<th>Flat membrane (label)a</th>
<th>Monomers usedb</th>
<th>Nanomaterials added (A/O)c</th>
<th>Pressure (bar)</th>
<th>Salt conc. (mg L(^{-1}))</th>
<th>PWPd (L m(^{-2}) h(^{-1}) bar(^{-1}))</th>
<th>Na(_2)SO(_4)</th>
<th>NaCl</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFN(_{cyclo-0.05})</td>
<td>PIP–TMC</td>
<td>Modified TNTs (O)</td>
<td>6</td>
<td>1000</td>
<td>7.48</td>
<td>96.4</td>
<td>18.9</td>
<td>In this work</td>
</tr>
<tr>
<td>TFC (control)</td>
<td>PIP–TMC</td>
<td>—</td>
<td>6</td>
<td>1000</td>
<td>5.38</td>
<td>86.0</td>
<td>25.3</td>
<td>In this work</td>
</tr>
<tr>
<td>M1 (NF4)</td>
<td>PIP–TMC</td>
<td>SiO(_2) (A)</td>
<td>5</td>
<td>1000</td>
<td>2.10</td>
<td>96.4</td>
<td>50.2</td>
<td>30</td>
</tr>
<tr>
<td>M2 (–)</td>
<td>PIP–TMC</td>
<td>SiO(_2) (A)</td>
<td>6</td>
<td>710.2</td>
<td>5.33</td>
<td>~80</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>M3 (–)</td>
<td>PIP–TMC</td>
<td>SiO(_2) (A)</td>
<td>6</td>
<td>2000</td>
<td>9.45</td>
<td>97.3</td>
<td>25.6</td>
<td>10</td>
</tr>
<tr>
<td>M4 (I1)</td>
<td>MPD–TMC</td>
<td>Ag NPs (A)</td>
<td>5</td>
<td>2000</td>
<td>~1.50</td>
<td>—</td>
<td>~14.5</td>
<td>26</td>
</tr>
<tr>
<td>M5 (A-TFN(_3))</td>
<td>MPD–TMC</td>
<td>Modified TiO(_2) (A)</td>
<td>7.5</td>
<td>2000</td>
<td>3.60</td>
<td>—</td>
<td>~33</td>
<td>21</td>
</tr>
<tr>
<td>M6 (–)</td>
<td>PIP–TMC</td>
<td>Modified MWCNTs (O)</td>
<td>10</td>
<td>2000</td>
<td>~6.98</td>
<td>99</td>
<td>44.1</td>
<td>31</td>
</tr>
<tr>
<td>M7 (–)</td>
<td>MPD–TMC</td>
<td>H-OMCs (A)</td>
<td>10</td>
<td>2000</td>
<td>1.95</td>
<td>~89</td>
<td>~62</td>
<td>15</td>
</tr>
<tr>
<td>M8 (TFN)</td>
<td>PIP–TMC</td>
<td>SAPO-34 (O)</td>
<td>3</td>
<td>N/A</td>
<td>~11.0</td>
<td>~85</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>M9 (–)</td>
<td>TEPA–TMC</td>
<td>—</td>
<td>10</td>
<td>1000</td>
<td>5.10</td>
<td>~80</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>M10 (N4)</td>
<td>2,2′-OEL–TMC</td>
<td>—</td>
<td>7</td>
<td>2000</td>
<td>5.86</td>
<td>~76</td>
<td>~23</td>
<td>33</td>
</tr>
</tbody>
</table>

a The designation in the bracket is the membrane designation used in the respective work. b PIP: piperazine, TMC: trimesoyl chloride, PAMAN: poly(amidoamine), MPD: \(m\)-phenylenediamine, TEPA: tetraethylenepentamine, 2,2′-OEL: 2,2′-oxybis-ethylamine. c The alphabet in the bracket is referred to the solution that inorganic nanomaterials are added. “O” stands for organic solution while “A” stands for “aqueous solution”. d PWP: pure water permeability. PWP was calculated by normalizing the water flux with the applied pressure.
In terms of resistance against dye, the water flux of the TFN membrane declines 10.7% in comparison to 13.6% of the TFC membrane. This result is in accordance with the visible observation that the colour stained on the TFN membrane surface is obviously less than that on the TFC membrane after the dye treatment (see inserted photos in Fig. 8). Further analysis shows that the flux decline of the TFN membrane by RB5 (10.7%) is more severe than by BSA (4.95%), which can be possibly explained by the severe nanotube channel blockage owing to the small size of the RB5 dye compound.

Regarding the separation efficiency, both TFC and TFN membranes achieve complete removal of BSA and approximately 97.5% RB5 rejection. Based on the results, it can be said that the TFN membrane can produce not only higher quantity of treated water during operation but also suffers from a lower degree of fouling against protein and reactive dye. This, indirectly, might reduce the cycles of membrane cleaning and extend membrane lifetime in real field applications such as in dairy and textile industries.

3.5 Nanofiller leaching test

Fig. 9 shows the concentration of the Ti element detected in the feed and permeate samples of the TFN_{cyclo-0.05} membrane as a function of filtration time (up to 8 h). Although the Ti concentration is below the detection limit of 0.01 ppb in most cases, the feed/permeate samples at 30 min and the feed sample at 360 min are found to contain 0.022/0.017 ppb and 0.024 ppb Ti, respectively. The detection of very low concentrations of the Ti element in the sample solutions could indicate the possible leaching of TNTs from the PA nanocomposite layer to either the feed or permeate solution. TNT leaching might be the result of poor interaction of nanofillers with the PA layer during interfacial polymerization (especially those exposed at the membrane surface), making them unable to be embedded firmly within the PA matrix. Further investigation on this topic is worthy as, at the present, few relevant studies have been conducted on the leaching of nanofillers from PA layers and its impact on long term TFN membrane performance.

4 Conclusions

Thin film nanocomposite NF membranes were successfully prepared via two different approaches to introduce surface-modified TNTs into the PA layer made of PIP and TMC monomers. Results showed that introducing nanofillers into the TMC organic phase was more effective for the synthesis of TFN membranes with greater separation performance than the introduction of nanofillers into the PIP aqueous phase. It is because the use of the rubber roller to remove aqueous solution from the substrate surface has caused the loss of a significant amount of nanofillers from the substrate surface, which negatively affected the PA integrity as proved by instrumental analyses. Moreover, when the nanofillers are added, monomer concentrations should be properly adjusted to produce TFN membranes of improved performance. For example, at an optimum nanofiller loading (0.05 w/v%), manipulating the PIP and TMC concentrations to 2 and 0.15%, respectively, is required in order to produce a PA TFN NF membrane with a good combination of water flux (7.5 L m^{-2} h^{-1} bar^{-1}) and Na_2SO_4 rejection (96.4%). The high hydrophilicity and large surface area of TNTs coupled with their narrow channels are proven to enhance the TFN membrane resistance against fouling by BSA and RB5. However, the possible leaching of nanofillers (at µg L^{-1} or ng L^{-1} level) from the PA nanocomposite matrix needs further attention as, at present, not many relevant studies have been conducted on the nanofiller leaching and its impact on long term TFN membrane performance.

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