

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

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Abstract

Thin film nanocomposite (TFN) membranes containing 0.05 or 0.10 w/v% functionalized titanate nanotubes (TNTs) in polyamide selective layer were prepared 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 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 incorporation of high nanofiller loading tended to interfere with interfacial polymerization and weaken the bonds between monomers blocks, resulting in poor polyamide-nanotubes 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/m².h.bar) and Na₂SO₄ rejection (96.4% vs 86%) while exhibiting higher resistance against the fouling by protein and dye.

Keywords: *thin film nanocomposite; nanofiltration; titanium nanotubes; permeability-selectivity trade-off*

1. Introduction

Thin film nanocomposite (TFN) membrane has been reported for the first time by Hoek's research group in 2007 as a new generation of composite membrane to overcome permeability-selectivity trade-off of thin film composite (TFC) membrane for reverse osmosis application [1]. By embedding a small quantity of zeolite nanomaterials into polyamide (PA) layer of TFC membrane, it was reported that the water permeability of the resultant 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 membrane 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 type 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 [3-6].

Although the potential of PA TFN membrane for water treatment process 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 approach used by researchers to introduce nanomaterials during interfacial polymerization process. 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 [1,5,7-12]. However, owing to the hydrophilic nature of nanomaterials, most research has preferred to introduce nanomaterials in amine aqueous solution. This is because of the difficulties in producing a homogenous mixture in non-polar organic phase. Since removing excess amine solution from the substrate surface (using rubber roller or air knife) is a necessary step during interfacial polymerization process, a large amount of nanomaterials could be removed together with the amine solution (in the case of nanomaterials-aqueous mixture), leaving only a small amount of nanomaterial in the substrate. As a result, the positive features of nanomaterials such as hydrophilicity, anti-fouling property and surface charge density are likely to be reduced in the synthesized PA layer. Nevertheless, many researchers did not take into consideration the inefficiency of this approach in making TFN membrane.

In this work, we reported on synthesis methods for PA TFN membrane by adding inorganic nanomaterials into aqueous or organic solution, respectively. The main objective of the work was to compare the efficiency of approaches used in preparing PA TFN membrane for water/wastewater treatment process. Titanate nanotube (TNT) was selected as the nanofiller owing to its hydrophilic properties and large surface area, as well as the existence of narrow channel that might promote water transport through the membrane [13-14]. To improve the dispersion quality of TNT in organic solution, silane agent was used to modify the surface of TNT. It was also an

Commented [SRG1]: When making nanocomposite UF membranes, we found the addition of nanoparticles was not linearly related to the change in properties. Also loss of some nanoparticles can be compensated by addition of more nanoparticles in the dope, but this is inefficient. Could perhaps approach this from an inefficiency concern rather than just the membrane properties.

Answer: I'm sorry as I might not be able to completely understand your comment. I hope the additional sentence might address your concern.

objective of this work to study how different concentrations of piperazine (PIP) and trimesoyl chloride (TMC) monomer affect the properties of the PA nanocomposite layer, which will in turn alter the performance of the membrane in NF process.

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

^a Membrane	^b Nanofillers used (Loading, w/v%)	Solution that nanofillers are added	^c Solutions for IP process		Approach to remove excess aqueous solution on support surface	Country/Year [Reference]
			Aqueous (w/v%)	Organic (w/v%)		
RO	NaA zeolite (0.04–0.4%)	Organic	2% MPD	0.1% TMC in hexane	Rubber roller	USA/2007 [1] (JMS – 294, 1-7)
RO	Carbon nanotube (0.001–0.1%)	Aqueous	2% MPD	0.1% TMC in hexane	N/A	China/2014 [5] (JMS – 450, 249-256)
RO	MCM-41 SiO ₂ (0–0.1%)	Organic	2% MPD	0.15% TMC in hexane	Rubber roller	USA/2012 [7] (JMS – 423-424, 238-246)
RO	Linde type A zeolite (0.2%)	Organic	2.3–3.2% MPD	0.1–0.13% TMC in Isopar-G	Air knife	USA/2009 [8] (Langmuir– 25(17), 10139-10145)
NF	Ag (0–10%)	Aqueous	2% MPD	0.1% TMC in hexane	Rubber roller	Canada/2012 [9] (JMS – 394-395, 37-48)
NF	SiO ₂ (0–1.0%)	Aqueous	0.2–2% PIP	0.05–0.3% TMC in hexane	Air knife	China/2012 [10] (DES – 301, 75-81)
NF	Mesoporous SiO ₂ (0–0.07%)	Aqueous	1% PIP & 0.2% NaOH	0.15% TMC in hexane	Soft rubber roller	China/2013 [11] (JMS – 428, 341-348)
FO	SiO ₂ (0.01–0.1%)	Aqueous	2% MPD	0.1% TMC in hexane	Rubber roller	Iran/2014 [12] (DES – 343, 140-146)

^a RO – Reverse osmosis, NF – Nanofiltration, FO – Forward osmosis

^b SiO₂ – Silicon dioxide, Ag – Silver

^c MPD – *m*-phenylenediamine, TMC – Trimesoyl chloride, PIP – Piperazine, NaOH – Sodium hydroxide

2. Experimental

2.1 Materials

Polysulfone (PSF, Udel® P-3500) in pellet form purchased from Solvay Specialty Polymers, USA was used to fabricate microporous substrate for TFC/TFN membranes. Polyvinylpyrrolidone (PVP) K29-32 (M_w : 58,000 g/mol) used as a pore forming agent during substrate fabrication was purchased from Acros Organics. Titanium dioxide (TiO_2) Degussa P25 nanoparticles 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 TNTs surface to produce amino-functionalized titanate nanotubes (NH_2 -TNTs). Piperazine (PIP) and trimesoyl chloride (TMC) purchased from Acros Organics and Merck, respectively were used to form PA layer on top of PSF substrate. N-methyl-2-pyrrolidone (purity >99.5%) and cyclohexane supplied by Acros Organics and Merck, respectively were used without further purification. Sodium sulfate (Na_2SO_4 , Riedel-de-Haen), sodium chloride (NaCl, Merck), bovine serum albumin (BSA, Sigma-Aldrich) and Reactive Black 5 (RB5, M_w = 991 g/mol, Sigma-Aldrich) were used as test solutes for membrane flux and rejection determination. The feed solution containing respective test solute was prepared by dissolving the solute in Milli-Q® water. Other chemicals used in this work were 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 TiO_2 nanoparticles was added into 100 mL of 10 M NaOH aqueous solution. After vigorous stirring for 12 h, the milk-like mixture was moved into a 150 mL Teflon-lined hydrothermal 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 centrifugal 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 followed by grinding into fine powders. Surface modification of TNTs was then performed on the fine powder using AAPTS as follows. 1.0 g of TNTs was added into 50 mL toluene containing 1.0 g of AAPTS. The mixture was stirred at 95°C overnight followed by filtration and subsequent washing using toluene, ethanol, ethanol/water (1:1 v/v) and water to produce NH_2 -TNTs. Lastly, modified TNTs were dried at 100°C in an oven to completely remove the residual water. To compare the dispersion quality of TNTs before and after surface modification in organic phase, 0.5% (w/v) TNTs and NH_2 -TNTs were added respectively into cyclohexane and photos were taken to examine the settling behavior of nanomaterials for up to 10 min.

2.3 Preparation of TFC and TFN membranes

All the composite membranes were prepared using in-house made PSF microporous substrate. The substrate prepared via phase inversion method possessed molecular weight cut-off (MWCO) of 47.5 kDa (see [Figure S1](#)) with pure water flux and surface contact angle recorded at ~150 L/m².h.bar and 78.2°, respectively. The MWCO of the substrate prepared was in the range of 30-50 kDa as reported in literature [15-16]. The synthesis of PA layer was performed via interfacial polymerization technique that used PIP and TMC as monomers. [Table 2](#) shows the amounts of NH_2 -TNTs present in the solutions during interfacial polymerization together with the concentration of monomers used in aqueous and organic solutions. A TFC membrane (without NH_2 -TNTs) was also prepared for comparison purpose. Interfacial polymerization process

was initiated by pouring 2% (w/v) PIP aqueous solution to the top surface of substrate. The aqueous solution was then held horizontally on the substrate surface for 2 min to ensure the penetration of aqueous solution into substrate pores. The excess aqueous solution was drained from the substrate surface by 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 contact time. The unreacted monomers were removed from 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. Lastly, the membrane was stored in a pure water container until use.

TFN membranes were cast exactly as described above, except that the amount of 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 ultrasonication process [17-18]. 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), TFN_{aq-0.05}, TFN_{aq-0.10}, TFN_{cyclo-0.05} and TFN_{cyclo-0.10} membrane, respectively. To further study the effect of monomer concentration on the characteristics of PA nanocomposite, the conditions used to prepare TFN_{cyclo-0.05} membrane were further varied by changing the concentration of PIP and TMC without altering the quantity of NH₂-TNTs (see Table 3).

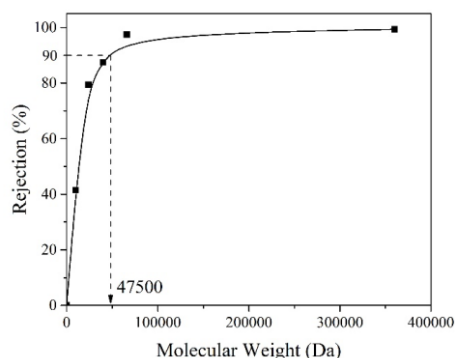


Figure S1. Determination of molecular weight cut-off (MWCO) of PSF substrate based on neutral solute rejection profile

Table 2. Properties of aqueous and organic solutions used for TFC and TFN membranes preparation

Membrane	NH ₂ -TNTs (wt/v%)		PIP (wt/v%)	TMC (wt/v%)
	In aqueous	In cyclohexane		
TFC (control)	–	–		
TFN _{aq-0.05}	0.05	–	2	0.15
TFN _{aq-0.10}	0.10	–		
TFN _{cyclo-0.05}	–	0.05		

TFN _{cyclo-0.10}	–	0.10
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Table 3. Composition of monomer solutions used for preparing TFN membranes

^a Membrane	NH ₂ -TNTs in cyclohexane (wt/v%)	PIP (wt/v%)	TMC (wt/v%)
TFN _{PIP-1.5}		1.5	0.15
TFN _{PIP-2.5}	0.05	2.5	0.15
TFN _{TMC-0.1}		2.0	0.1
TFN _{TMC-0.2}		2.0	0.2

^aTFN_{cyclo-0.05} shown in Table 2 can also be named as either TFN_{PIP-2.0} or TFN_{TMC-0.15}.

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 were then evaluated for water permeability as well as rejection against Na₂SO₄ (1000 ppm), NaCl (1000 ppm), BSA (1000 ppm) and RB5 (1000 ppm) at operating pressure of 6 bar. The volume of permeate (mL) collected over a specified time divided by the membrane area (14.6 cm²) and time to collect the permeate (min) produced the reported value for permeate flux (L/m².h). Observed solute rejections, $R (\%) = (1 - C_f/C_p) \times 100$ were determined from the difference in feed (C_f) and permeate (C_p) solute concentrations. A bench conductivity meter (4520, Jenway) was used to measure conductivity value in the feed and permeate of salt solutions while 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 3-h permeation test using feed aqueous solution containing either BSA or RB5 as model foulant. The flux decline determined from the initial permeate flux, J_i and final permeate flux, J_f 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 TNTs from the PA nanocomposite layer to feed or permeate samples. For each set of feed and permeate samples collected at specific time interval for Ti analysis, the pure water in the permeation cell was withdrawn and refilled again with pure water. The presence of TNTs in the solutions was detected by inductively coupled plasma mass spectrometer (ICP-MS) (ELAN6100, Perkin Elmer) with respect to titanium (Ti) element at $\mu\text{g/L}$ level (equivalent to parts per billion, ppb).

2.5 Characterization

Specific surface measurement of TNTs was performed using a Micromeritics® ASAP 2010 with N₂ at 77.3K. The specific surface area was calculated according to Brunauer-Emmett-Teller (BET) method. Powder XRD analysis was made using D-Max Rigaku

diffractometer at 2θ ranging from 10° to 80° . Transmission electron microscopy (TEM) analysis was performed using Hitachi HT7700 to study the morphological structure of TNTs in 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 $600\text{--}4000\text{ cm}^{-1}$ wavenumber with an average of 16 scans and at a resolution of 4 cm^{-1} . 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 -TNTs-TMC compound was 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 energy-dispersive X-ray (EDX) spectrometer. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo instrument at a rate of $10^\circ\text{C}/\text{min}$ under 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) in a scan size of $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$. The membrane surface hydrophilicity was characterized based on sessile drop technique using a Dataphysics OCA15plus contact angle goniometer.

3. Results and Discussion

3.1 Characteristics of TNTs

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

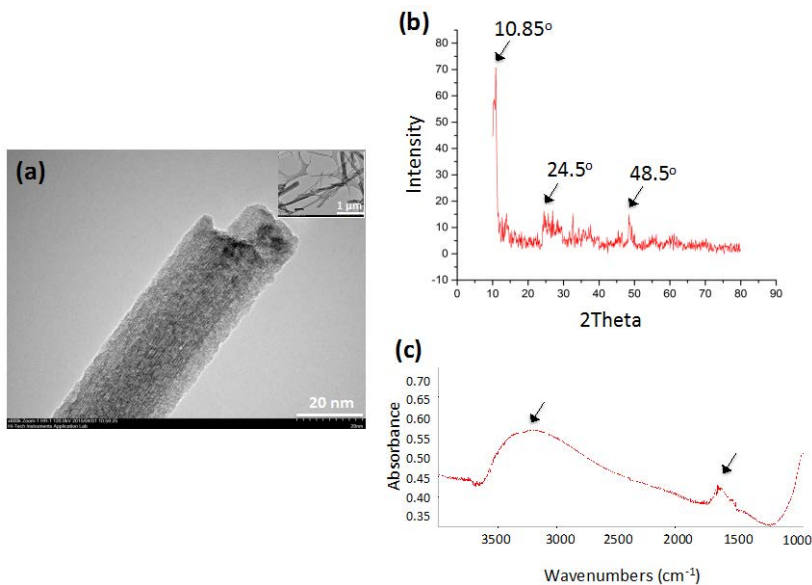


Figure 1. Properties of synthesized TNTs, (a) TEM image, (b) XRD spectra and (c) FTIR spectra

3.2 Comparison between TFN_{aq} and TFN_{cyclo} membrane

FTIR

FTIR spectra of three composite membrane surfaces are shown in Figure 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 organic PA structure, indicating the dominant functional groups do not alter. A similar observation was also reported in the work of Barona et al. [19] in which aluminosilicate single wall nanotubes were incorporated in the PA layer of 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 -OH stretching of carboxylic acid, C=O stretching vibration of amide group and C-N stretching, respectively.

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

However, in order to prove that surface of TNTs has been modified, Figure 2 compares the dispersion quality of TNTs with and without AAPTS modification in cyclohexane. Clearly, the amino functionalized TNTs are dispersed better in non-polar solvent in comparison to the unmodified TNTs. Owing to the improved surface

Commented [SRG2]: Please check as I think the C-N is the amide group and C=O is the carboxylic acid.

Answer: Peak assignment has been re-checked. The original statement is correct. C=O belongs to -NHCO- bond and is generally named as Amide I (Amide II is for C-N stretching).

Commented [SRG3]: If TNT's react with TMC then they can act as cross linkers.

Answer: If TNTs do react with TMC, it is likely to induce end-capping effect on polymerization and reduces degree of cross-linking.

properties, modified TNTs take a longer time to settle. Similar surface modification was conducted by Namvar-Mahboub et al. [20] and Rajaeian et al. [21] on UZM-5 zeolite and TiO₂ nanoparticles, respectively, but both research groups did not demonstrate the dispersion quality of amino-functionalized nanomaterials in the organic solvent.

Commented [LW4]: Does this charge repulsion also occur in non-polar mediums such as cyclohexane? Requires protonation of the amine group which usually arises from water.

Answer: I have removed the statement (together with reference). I agree that protonation occurs only in aqueous medium.

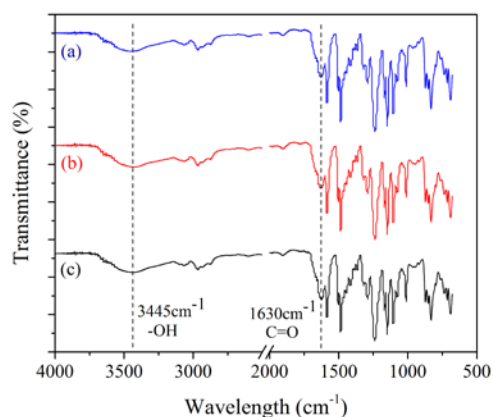


Figure S2. FTIR spectra of (a) TFC, (b) TFN_{aq-0.05} and (c) TFN_{cyclo-0.05}

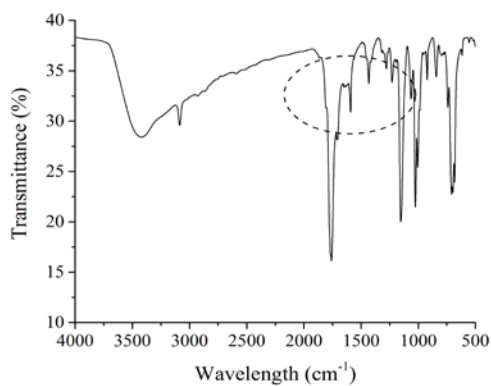


Figure S3. FTIR spectra of the interaction between NH₂-TNTs and TMC monomer

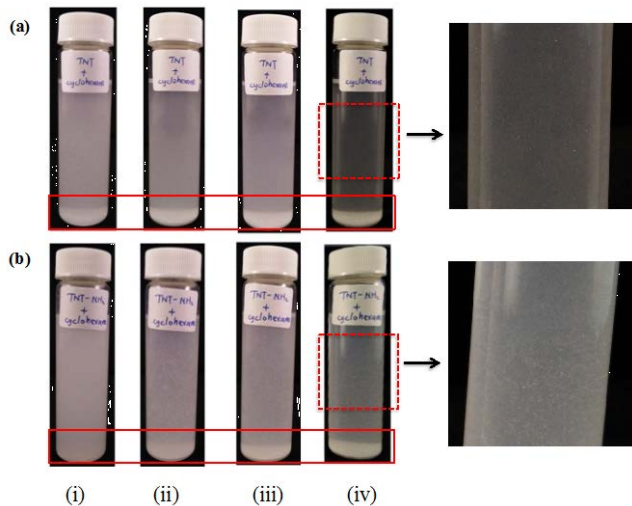


Figure 2.
Dispersion

quality of (a) TNT and (b) NH₂-TNT in cyclohexane at different time, (i) 5 s, (ii) 2 min, (iii) 4 min and (iv) 10 min

FESEM-EDX-AFM

Figure 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 structure confirms that PA active layer is successfully formed over PSF substrate. However, as can be clearly seen, the addition of NH₂-TNTs into either aqueous or organic solution has altered the structure of PA leading to more peaks being formed on the TFN_{aq-0.05} and TFN_{cyclo-0.05} membrane. Particularly for TFN_{aq-0.05} membrane, obvious irregular nodules are formed which affect the integrity of PA layer. The observation can be explained by the approach used in removing excess aqueous solution containing NH₂-TNTs. The use of rubber roller to remove aqueous solution from the substrate surface has negatively affected the distribution of nanofillers on substrate surface. Compared to the TFN_{cyclo-0.05} membrane, in which the nanofillers are introduced from the organic solution after excess aqueous solution being removed, the formation of ridge-and-valley like structure is more even. Besides, it was also experienced that a significant amount of NH₂-TNTs was lost in TFN_{aq-} membrane during excess aqueous solution removal process. This is further supported by TGA results (see Figure S4) in which the residue for TFN_{aq-0.05} membrane at 700°C is lower than the TFN_{cyclo-0.05} membrane, indicating less TNTs are embedded in the TFN_{aq-} membrane. TNT is a high melting point material and does not decompose at temperature less than 700°C as polymeric membrane.

The EDX data on the other hand showed that TFN_{cyclo-0.05} membrane surface exhibits significantly higher weight percent of Ti and O element compared to TFN_{aq-0.05} membrane, suggesting greater amount of nanotubes embedded in PA layer. Meanwhile, no Ti element was detected in the TFC control membrane. With respect to contact angle, it is found that TFC control membrane displays lower value than those

Commented [SRG5]: Evidence for loss of integrity? Expand on this idea.

Answer: I have included Rq, Ra and Rz value in Figure S5 to support the irregular nodules on TFN_{aq-0.05} membrane. Highest Rz value can indicate obvious irregular nodules.

Commented [SRG6]: Is there data to support this? Will you use TGA data to verify the amount of inorganic phase in the membranes?

Answer: TGA results for two membranes (with 0.05% TNTs) made of two different approaches are included to support the statement. But, since the TGA analysis was performed using membrane samples (with microporous substrate), quantification on the actual amount TNTs is difficult to perform.

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 [22].

Correlation between membrane hydrophilicity and water contact angle might not be established in this case as the increase in surface roughness of TFN membranes might affect the contact angle according to the Cassie's model. The 3D AFM images (see Figure S5) indicate that TFN_{aq-0.05} membrane displays higher R_z value (1074.85 nm) compared to TFN_{cyclo-0.05} (741.7 nm) and TFC (419.8 nm). The highest R_z value shown by the TFN_{aq-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 TFN_{cyclo-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 PA layer are increased upon introduction of zeolite nanoparticles [17]. 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 water flux and salt rejection will be provided in the following section.

Commented [SRG7]: Contact angle can also be a function of polymer crystalline phase and incorporation of nanoparticles can alter the phase of the polymer.

Answer: The DSC curves (analysis done by Marlene) did not show significant difference for TFC, TFNaq and TFNcyclo membrane.

I think that DSC analysis might not suitable for TFC/TFN membrane that consists two different polymers, unless PSF substrate is removed.

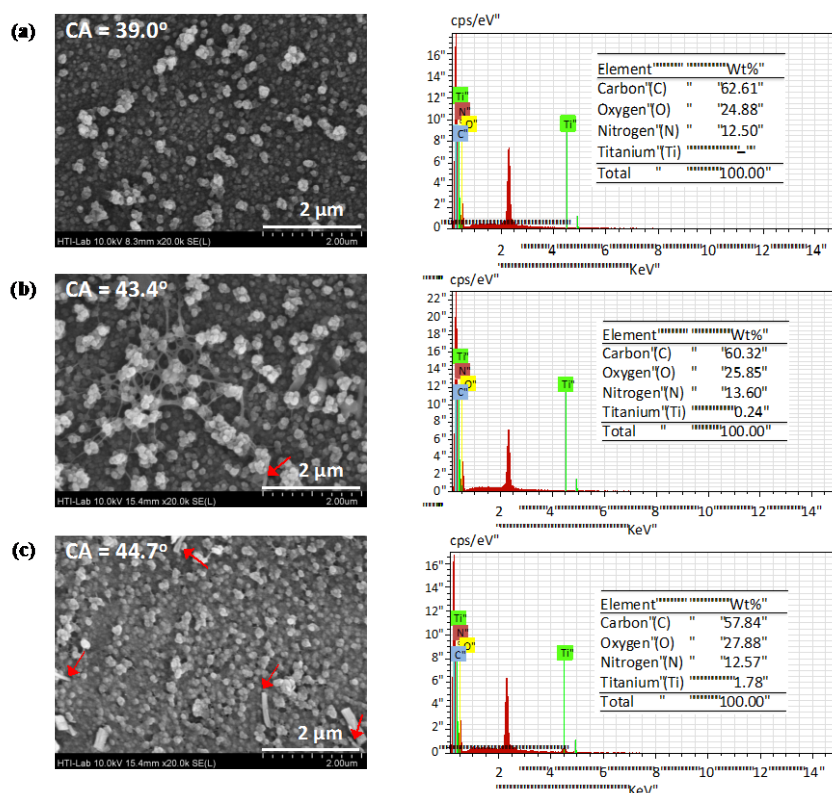


Figure 3. SEM images, contact angle and EDX results on membrane top surface, (a) TFC, (b) TFN_{aq-0.05} and (c) TFN_{cyclo-0.05}. The red arrows indicate the presence of TNTs in the membrane.

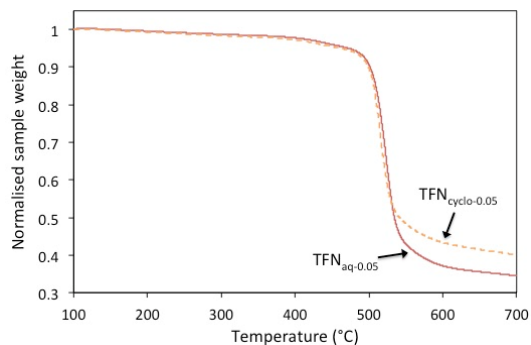


Figure S4. TGA curves of TFN_{cyclo}- and TFN_{aq}-membrane

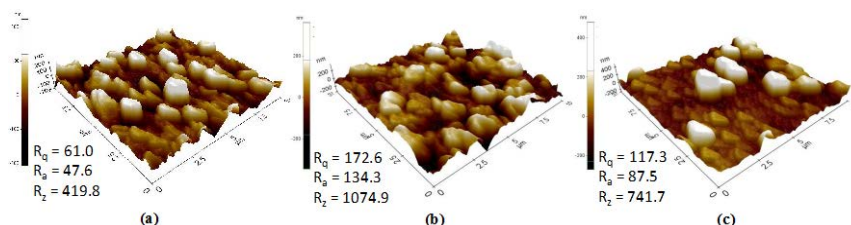


Figure S5. 3D AFM images of the membrane top surface together with surface roughness values, R_q (root mean square of z data), R_a (mean roughness) and R_z (mean difference in the height between the five highest peaks and the five lowest peaks), (a) TFC, (b) TFN_{aq-0.05} and (c) TFN_{cyclo-0.05}. All surface roughness values are in nm.

Filtration Performance

Figure 4 compares the filtration performance of TFN membranes made from the different approaches with TFC membrane. With respect to pure water flux, it can be observed from Figure 4 (a) that all the TFN membranes exhibit higher water permeability than that of TFC membrane, regardless of the nanofiller used and the fabrication approach. Particularly for TFN_{cyclo}-membranes, they achieve 39.0–40.6% higher pure water flux in comparison to the TFC membrane without NH₂-TNTs incorporation. The results obtained in this work are in line with many previous findings [1,5-7,16,23-24], i.e. TFN membranes always achieve greater water production rate compared to TFC membrane irrespective of the solution that was used to disperse nanofillers. The improved water productivity as observed in TFN_{aq}- or TFN_{cyclo}-membrane might be attributed to the presence of abundant hydroxyl groups (average 5.8 –OH/nm²) at the TNT surface and its narrow channels (several tens of nanometers) that provide smooth transport pathway for water to pass through [14, 25]. FESEM images shown in Figure 3 reveal that some of the incorporated nanotubes would be exposed to the membrane surface which makes the hydrophilic nanotubes accountable for the increased membrane hydrophilicity to some extent. However, possible changes in PA network pores and/or chain packing density upon TNT incorporation cannot be ruled out as factors affecting membrane water flux as the nature of the inorganic filler-PA interaction is still not fully understood.

Commented [SRG8]: This is one possible reason, but incorporation of non-porous nanoparticles also increases flux. Hence, how can we definitively state this? It maybe that the polymer chain packing around the nanoparticles has altered, and thereby change the permeability. We cannot be specific about the mechanism from these results.

Answer: Change in polymer chain packing is also possible upon TNTs incorporation. I have further elaborated the mechanism.

Based on the membrane surface characterization and water filtration results, it is proven that introducing nanofillers into organic solution is much more effective to improve composite membrane water flux, owing to the significant quantity of nanofillers present in the PA layer. As a comparison, the water flux of TFN_{cyclo}-membrane is 31.2% and 27.7% higher compared to TFN_{aq}-membrane at NH₂-TNTs loading of 0.05% and 0.10%, respectively.

Although the TFN membrane water flux is further enhanced with increasing the NH₂-TNTs loading, one can observe a negative impact of the use of higher loading of nanofillers on salt rejection (Figure 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 loadings 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. Excessive use of nanofillers tends to negatively affect the integrity of organic PA-inorganic nanotubes structure, interfering with the interfacial polymerization reaction. This, as a consequence, leads to formation of defects (bigger pores) that allow ions to pass through. Our statement is well supported by other relevant works that incorporated nanofillers into PA layer. These include the work of Ma et al. [17], Ghanbari et al. [6] and Mollahosseini and Rahimpour [26] in which zeolite, TiO₂/halloysite nanotube nanocomposites and silver nanoparticles were used, respectively, as nanofillers.

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 monomer.

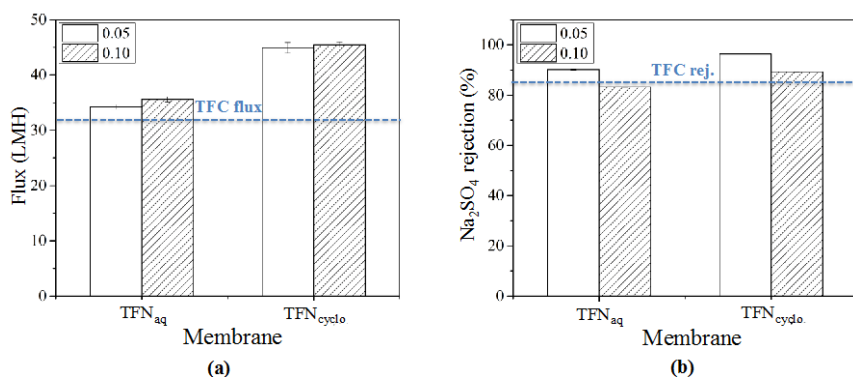


Figure 4. Properties of TFN membranes made of different approaches, (a) pure water flux and (b) salt rejection. (Reference: TFC (control) membrane – Flux: 32.3 L/m².h and rejection: 86.0%)

3.3 Effect of PIP and TMC monomer on TFN membrane properties

Figure 5 presents the effects of PIP and TMC content on the performance of TFN membranes incorporated with 0.5% nanofillers. The effects of both monomers on TFN membrane water flux and salt rejection are found to be very similar, i.e. the

Commented [SRG9]: Is there an indication of membrane reproducibility for these results?

Answer: My student has reproduced the TFN_{cyclo-0.05} membrane last month. We have characterized membrane water flux and salt rejection prior to XPS analysis in UTM. Results showed that flux and rejection (compared to the data in the manuscript) varied within 3.5%.

Commented [SRG10]: Why weakening? Perhaps it just makes bigger holes as the function binding groups are further apart on the TNT.

Answer: I have restructured the sentence.

Commented [SRG11]: TNTs form bigger holes but may not necessarily be weaker. It would be good to have the PALS data.

Answer: I'm sorry to inform that I don't have access to PALS instrument in Malaysia.

Commented [LW12]: Image is not clear. The rejection for TNT_{cyclo} TFN appears higher than TFC. This is not what was stated in the text.

Answer: Image resolution is always a problem whenever I transfer files into Ms Word (MacBook). The image quality somehow changes. I hope the new figure's resolution is better now.

Besides, I have revised the sentences accordingly.

composite membrane achieves optimum values when intermediate PIP (2.0%) and TMC (0.15%) concentration 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 insufficient monomers being available for interfacial polymerization. This concept is supported by the lowest surface roughness values of the $TFN_{PIP-1.5}$ and $TFN_{TMC-0.1}$ membrane as shown in Table 4. The insufficient amount of monomers available for interfacial polymerization might also cause poor interaction between nanotubes and PA layer, leading to the formation of PA surface defects and/or possible nanotubes leaching out. This, as a result, affects both water flux and salt rejection as evidenced.

When the concentration of monomers is the highest, both $TFN_{PIP-2.5}$ and $TFN_{TMC-0.2}$ membranes have significantly lower water flux and salt rejection than that of $TFN_{cyclo-0.05}$ membrane made with intermediate PIP and TMC concentration. The experimental results obtained can be attributed to the formation of denser and thicker PA layer. The increase in surface roughness values of $TFN_{PIP-2.5}$ and $TFN_{TMC-0.2}$ membrane also suggests more ridge-and-valley like structure created by the higher degree of polymerization and cross-linking. Employing higher monomer concentration could produce higher molecular weight polymer and a thicker film [8]. Li et al. [27] further elucidated that a higher PIP and TMC concentration tended to generate a thicker and more compact PA layer that could affect water flux due to increased transport resistance. For the case of PA layer incorporated with nanofillers, thicker surface layer might reduce extent of nanotubes exposure to top PA surface (reduced hydrophilicity) and/or cover the narrow channels of TNTs. Both effects can possibly affect 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 at 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 [28–29].

Commented [SRG13]: Is there experimental evidence of the thicker membrane at higher concentrations?

High concentration will increase the kinetics of polymerisation and reduce concentration will lower the kinetics. It might be better to discuss these effects in terms of kinetics rather than poor interactions etc.

Answer: Relevant references are included. Discussion is also revised accordingly.

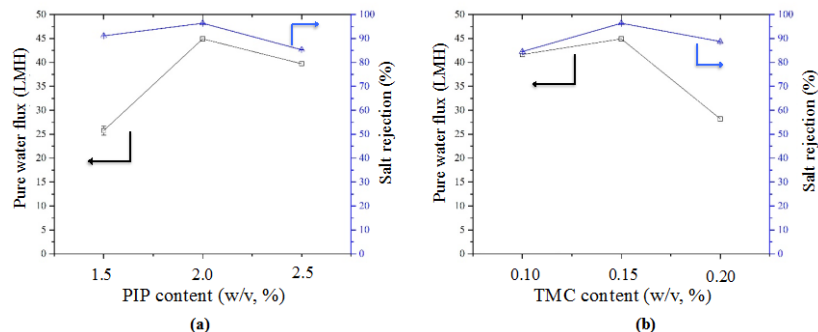


Figure 5. Effect of monomer content on the performance of TFN membranes that contained 0.5 w/v% NH₂-TNTs, (a) PIP content and (b) TMC content

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

Parameter	Membrane	Monomer conc. (wt/v%)	Roughness value (nm)		
			R _a	R _q	R _z
Effect of PIP	TFN _{PIP-1.5}	1.5	74.54	93.69	662.70
	TFN _{PIP-2.0}	2.0	87.51	117.27	741.65
	TFN _{PIP-2.5}	2.5	103.49	126.46	782.96
Effect of TMC	TFN _{TMC-0.1}	0.1	84.34	105.85	746.43
	TFN _{TMC-0.15}	0.15	87.51	117.27	741.65
	TFN _{TMC-0.2}	0.2	99.33	127.16	998.86

^a The properties of TFN_{PIP-2.0} or TFN_{TMC-0.15} membrane is exactly same as TFN_{cyclo-0.05} membrane

Table 5 compares the performances of the best TFN membrane synthesized in our work with other TFC or TFN membranes reported in the literature for the separation of salts. By taking into consideration the pure water permeability coefficient (L/m².h.bar) of the membrane, it is found that our in-house synthesized TFN membrane has achieved greater water permeability than most of the TFC/TFN membranes reported. The higher water permeability of the in-house synthesized TFN membrane does not compromise the high solute separation. It is still able to achieve as high as 96.4% Na₂SO₄ rejection, which is better in comparison to most of the membranes 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 nanofillers with abundant -OH groups. Second, introduction of nanofillers into organic solution. Third, modification of TNTs surface for better dispersion in organic solution and lastly the use of cyclohexane (instead of *n*-hexane) for better diffusivity of PIP and TNTs dispersion. Figure 6 compares the dispersion quality of modified TNTs in cyclohexane and *n*-hexane. It is clearly seen that the modified TNTs disperse better in cyclohexane compared to that of *n*-hexane dispersed nanomaterials, indicating alicyclic hydrocarbon that exhibits higher boiling and flash points a better organic solvent for nanomaterial dispersion.

Commented [SRG14]: Can we compare the aqueous dispersed nanoparticle formulations with those in literature as well? Does our improved performance only occur for the cyclohexane dispersed TNTs?

Answer: Compared with aqueous dispersed nanoparticles, organic dispersed nanoparticles take significantly shorter time to settle. Hydrophilic nanoparticles used for TFN making could never disperse perfectly in organic solvent as aqueous medium due to its hydrophilic nature.

I have included a new figure (Figure 6) to compare the dispersion quality of NH₂-TNTs in cyclohexane and *n*-hexane. It shows that cyclohexane is a better solvent for TNTs dispersion.

Table 5: Performance comparison between TFN membrane synthesized in this work and other TFC/TFN membranes reported for NF application.

^a Flat membrane (Label)	^b Monomers used	^c Nanomaterials added (A/O)	^d Testing conditions		^e PWP (L/m ² .h.bar)	^e Rejection (%)		Reference
			Pressure (bar)	Salt conc. (ppm)		Na ₂ SO ₄	NaCl	
TFN _{cyclo-0.05}	PIP-TMC	Modified TNTs (O)	6	1000	7.48	96.4	18.9	In this work
TFC (control)	PIP-TMC	–	6	1000	5.38	86.0	25.3	In this work
M1 (NF4)	PAMAM-TMC	SiO ₂ (A)	5	1000	2.10	96.4	50.2	[30]
M2 (-)	PIP-TMC	SiO ₂ (A)	6	710.2	5.33	~80	–	[11]
M3 (-)	PIP-TMC	SiO ₂ (A)	6	2000	9.45	97.3	25.6	[10]
M4 (II)	MPD-TMC	Ag NPs (A)	5	2000	~1.50	–	~14.5	[26]
M5 (A-TFN ₃)	MPD-TMC	Modified TiO ₂ (A)	7.5	2000	3.60	–	~33	[21]
M6 (-)	PIP-TMC	Modified MWCNTs (O)	10	2000	~6.98	99	44.1	[31]
M7 (-)	MPD-TMC	H-OMCs (A)	10	2000	1.95	~89	~62	[15]
M8 (TFN)	PIP-TMC	SAPO-34 (O)	3	N/A	~11.0	~85	–	[18]
M9 (-)	TEPA-TMC	–	10	1000	5.10	~80	–	[32]
M10 (N4)	2,2'-OEL-TMC	–	7	2000	5.86	~76	~23	[33]

^aThe designation in the bracket is the membrane designation used in the respective work.

^bPIP: Piperazine, TMC: Trimesoyl chloride, PAMAN: Poly(amidoamine), MPD: *m*-phenylenediamine, TEPA: Tetraethylenepentamine, 2,2'-OEL: 2,2'-oxybis-ethylamine

^cThe 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".

^dPWP: Pure water permeability. PWP was calculated by normalizing the water flux with the applied pressure.

Commented [SRG15]: Can this be converted to permeability rather than flux at different pressures? This would make comparison easier. Better still would be dividing by the net pressure (absolute pressure – osmotic pressure) rather than the absolute pressure.

Answer: I have converted the data to L/m².h.bar. The pressure value shown in the testing condition column is referred to net pressure (shown in pressure gauge).

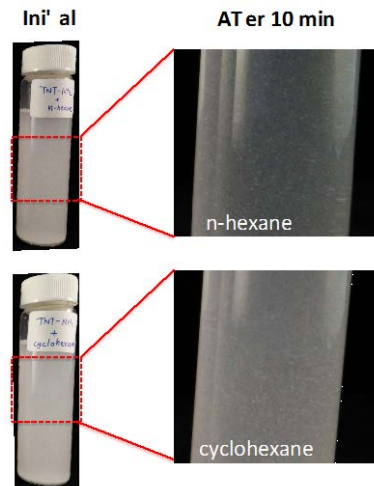


Figure 6. Comparison of dispersion quality of TNTs in *n*-hexane and cyclohexane after 10-min mixing between the 0.05% (w/v) NH₂-

3.4 Antifouling resistance against BSA and dye

The practical applications of TFN membrane have been further studied by subjecting the membrane to solutions containing either 1000 ppm BSA or 1000 ppm RB5. From [Figures 7 and 8](#), it is found that the TFN_{cyclo-0.05} membrane shows much higher water flux than that of 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 TFN membrane declines only 4.95% compared to ~20% of TFC membrane within 180 min, which is ascribed to the improved antifouling resistance against BSA macromolecules of the TFN membrane.

In terms of resistance against RB5, the water flux of TFN membrane declines 10.7% in comparison to 13.6% of TFC membrane. This result is in accordance with the visible observation that the colour stained on TFN membrane surface is obviously less than the TFC membrane after the dye treatment (see inserted photos in [Figure 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 a lower degree of fouling against protein and reactive dye. This, indirectly, might reduce cycles of membrane cleaning and extend membrane lifetime in real field applications such as dairy and textile industry.

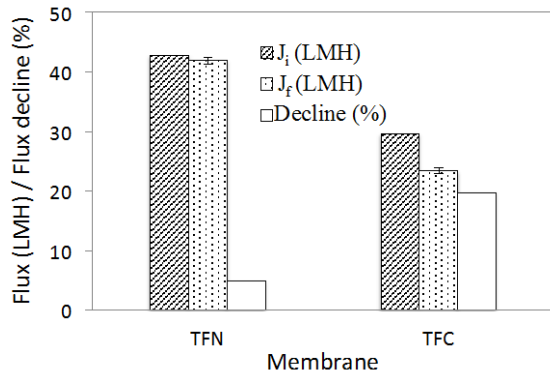


Figure 7. Comparison between the performance of TFC and TFN membrane in filtrating feed solution containing 1000 ppm BSA. The NH_2 -TNTs loading in the tested TFN membrane was 0.05% (w/v).

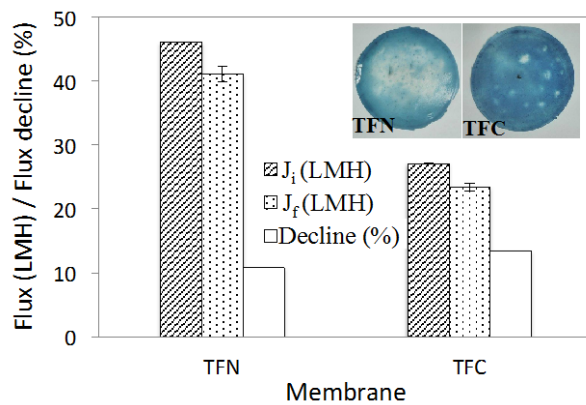


Figure 8. Comparison between the water flux of TFC and TFN membrane in filtrating feed solution containing 1000 ppm RB5. The inserted photos show the top surface of membrane after dye treatment process. The NH_2 -TNTs loading in the tested TFN membrane was 0.05% (w/v).

3.5 Nanofiller leaching test

Figure 9 shows the concentration of Ti element detected in the feed and permeate samples of $\text{TFN}_{\text{cyclo-0.05}}$ membrane as a function of filtration time (up to 8 h). Although 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 concentration of Ti element in the sample solutions could indicate the possible leaching of TNTs from the PA nanocomposite layer to either feed or permeate solution. TNT leaching might be the result of poor interaction of nanofillers with the PA layer during interfacial polymerization, making them unable to be embedded firmly within the PA matrix. Further investigation on this topic is worthy as, at the present, few relevant

works have been conducted on the leaching of nanofillers from PA layer and its impact on long term TFN membrane performance.

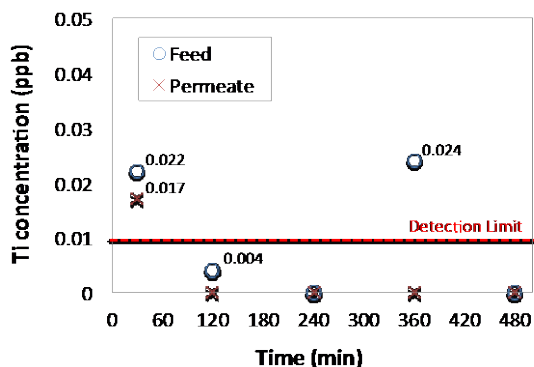


Figure 9. Ti element detected in feed and permeate samples of TFN_{cyclo-0.05} membrane as a function of filtration time.

4. Conclusion

Thin film nanocomposite NF membranes were successfully prepared via two different approaches to introduce modified TNTs into PA layer made of PIP and TMC monomers. Results showed that introducing nanofillers into the TMC organic phase was more effective for synthesis of TFN membrane 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 concentration 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/m².h.bar) and Na₂SO₄ rejection (96.4%). The high hydrophilicity and large surface area of TNTs coupled with their narrow channels are proven to enhance TFN membrane resistance against the fouling by BSA and RB5. However, the possible leaching of nanofillers from the PA nanocomposite matrix needs further attention as, at present, not many relevant works have been conducted on the nanofiller leaching and its impact on long term TFN membrane performance.

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Commented [SRG16]: Did you try it without the rubber roller? I do not think this can be stated definitively. The TNTs may report to the aqueous phase because of the thermodynamics (phase separation has higher TNT concentration in aqueous phase).

Answer: It is rare to prepare TFC/TFN membrane without rubber roller and air-knife. We have previously tried to prepare TFC membrane without rubber roller (solution was removed by gravity force), but salt rejection was poor. Small water droplets or air-bubbles might still present on substrate surface, leading to pin-holes in PA layer. These droplets and bubbles are too small to be seen.

Commented [SRG17]: We are not sure why there was less fouling only that it occurred. It may be because of a change in polymer crystalline phase.

Answer: Since DSC results do not show obvious shift in the peak, I would like to remain the statement (at least the hydrophilicity, large surface area and narrow channel of TNTs are confirmed by FTIR, BET and TEM).

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