

Water transport properties of boron nitride nanosheets incorporated thin film nanocomposite membrane for salt removal

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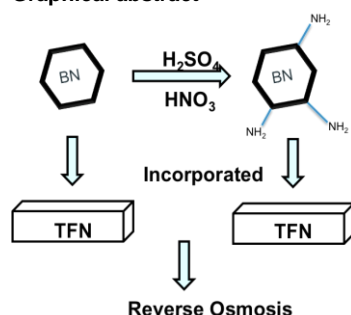
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Graphical abstract



Abstract

This work has focused on the fabrication of thin film composite (TFC) and thin film nanocomposite (TFN) membranes for reverse osmosis (RO) application. Raw boron nitride (BN) and chemically activated boron nitride (A-BN) were used as nanofillers in polysulfone support layer and trimesoyl chloride (TMC) to improve the membrane performance. Different concentrations of BN and A-BN (ranging from 0 to 1 wt %) were added to the polysulfone (PSf) microporous support and polyamide layer was formed on top of PSf support through interfacial polymerization of 1,3-Phenyldiamine and trimesoyl chloride. The fabricated TFN membranes were characterized in terms of membranes structure, contact angle, separation properties, as well as RO performance. According to AFM and SEM images, TFN membranes showed larger average pore size and higher surface roughness as compared with TFC membrane. Thus, TFN membrane showed higher pure water flux but lower NaCl rejection. The addition of BN led to increase in pore size of membrane without increase the selectivity of membrane. The addition of both BN and A-BN into polyamide layer does not aid to improve the properties of membrane. In conclusion, BN nanoparticles showed the potential to be used as nanofillers that aid in formation of larger pore size.

Keywords: Thin film nanocomposite membrane, boron nitride, reverse osmosis

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INTRODUCTION

Human population is increasing day by day and this lead to arise of water scarcity issue. Seawater has become one of the solutions for water scarcity. Seawater has accounted for around 96 % of the water on the Earth. However, seawater cannot be consumed due to the content in the water (Sheikholeslami, 2009). Seawater desalination is a process that is used to demineralize brackish water or desalinate seawater. Among the desalination techniques, membrane filtration by using reverse osmosis (RO) is one of the most known methods to transform seawater into clean water. Reverse osmosis is a water purification technology by using a semipermeable membrane to remove those ions and molecules from potable water (Choi *et al.*, 2017).

In the past two decades, reverse osmosis has become one of the most developed techniques as it is able to provide potable water from the seawater. In the late 1960s, Loeb and McCutchan had developed the first RO plant. Further in the early 1970s, desalination had come to a new era due to the development of new class membrane, thin-film composite (TFC) membrane for reverse osmosis. Cadotte and Rozelle were the founders of the TFC membrane. They synthesized TFC membrane by depositing a thin layer of PA onto finely porous polysulfone membrane through interfacial polymerization reaction. This kind of membrane showed improvement in salt rejection and permeation. Nevertheless, common TFC membrane for desalination application is facing two challenges, which are the selectivity and fouling resistances of the membranes (Cadotte & Petersen, 1980). Polyamide surface membranes are susceptible to fouling especially biofouling and chlorine attack. Those fouling tend to affect the permeate flux and salt rejection capability of membrane. With

technological advancement in nanotechnology, integration of nanomaterials into TFC membranes has been developed to enhance the properties of membranes (Lau *et al.*, 2012).

Nanocomposite membranes are among new membranes that incorporated nanomaterials into the substrate or PA layer of the membrane for the production of thin film nanocomposite (TFN) membrane. With the addition of nanoparticles into membrane has developed to become a promising technology together with novel functionality that aid in rejection performance of membrane. Based on the previous studies, there are a number of nanomaterials such as graphene oxide, silica nanoparticles, zeolite nanoparticles that can be introduced into TFC membranes to enhance the properties and performance of the membranes. TFN membrane incorporated with carbon nanotubes (CNTs) and graphene oxide holds enormous potential in desalination of seawater or brackish water (Goh *et al.*, 2013; Goh *et al.*, 2015, Lai *et al.*, 2016). CNT-membranes have shown outstanding results in desalination application, in terms of water permeability and the selectivity of solutes (Das *et al.*, 2014).

Recently, nanotube-based water purification device have the potential to alter the desalination field by increasing the rejection ability without affecting the flow rate of water molecules. Another nanomaterial that has similar properties with carbon lattice nanoparticles such as CNT and graphene is boron nitride (BN). BN nanoparticles can be categorized as nanosheets and nanotubes. Compared to CNT, the structure of BN nanotube (BNNT) has exactly the same structure with CNT in which the C atoms are fully substituted by boron and nitrogen atoms (Goldberg *et al.*, 2010).

The potential applications of BN have been explored through some theoretical studies and BN show potential in desalination application.

Hilder et al. (2009) stated that BNNT showed superior in water flow properties and 100 % of salt rejection theoretically. In the same experiment, they stated that increasing in the radius of the BNNT would shift the tube become ions selective from cations to anions. In comparison, BN is expected to be more efficient in purifying water than CNT. There is a need to further explore the potential of utilizing newly emerging BN nanoparticles in membrane desalination application. The science behind the performance improvement needs to be elucidated.

The objective of this study was to identify the performance of various type of BN in desalination. A series of characterization were conducted to understand the physical and chemical properties of various types of BN and their effects on the membrane performance. The new type of TFN membrane was determined through the membrane surface hydrophilicity and structural properties as well. Performances of the membrane were further evaluated through salt rejection and pure water permeability.

EXPERIMENTAL

Materials

All chemicals were used as received without further modification. Polysulfone Udel® P-3500 in pellet form (Solvay), 1-methyl-2-pyrrolidinone (NMP, 99 %, Acros Organics) and polyethylene glycol 400 (PEG 400) were used for fabrication of PSf substrate. Trimesoyl chloride (TMC, 98 %, Acros Organics) and m-phenylenediamine (MPD, 99 %, Merck) were used as the monomers to sculpt the PA layer on PSf substrate via interfacial polymerization. n-Hexane (99 %) from RCI Labscan was used as solvent for TMC. Boron nitride powder (<1 µm, Sigma Aldrich) was used as membrane filler for this study. Sodium chloride (NaCl, Merck) was used as solute to determine the performance of membrane in salt rejection.

Chemical activation of BN

BN activation was carried out by adding 3 g of h-BN into 50 w/w % of the activating reagent which is the mixture of 1 M H₂SO₄ aqueous solution and 8 M HNO₃ aqueous solution with a weight ratio of 1:1. The mixture underwent ultrasonication for 30 min at room temperature. The activation procedure end up by stirred the obtained slurry mechanically in an 80 °C water bath for another 2 hours. After activation process, the sample was washed with deionized water until the pH of the rinse in the neutral range (pH 6.8-7.2). To remove the moisture presented, the prepared sample was dried in oven at 105 °C for 24 hours and labeled as activated BN (A-BN) (Li et al., 2015).

Preparation of PSf and PSf/BN substrates

PSf substrates were prepared according to the dope formulation as shown in Table 1. To prepare the PSf/BN membrane, an appropriate amount of PEG and BN / A-BN were added to the NMP solution. The mixture was then undergoes ultrasonication for 30 min to avoid the agglomeration of BN. After that, PSf was slowly added into the mixture under vigorous stirring to produce the casting solution. The solution was then undergoes ultrasonication for another 1 hour to remove the air bubbles trapped within the solution. The PSf substrate was cast on the glass plate by using glass rod. To allow phase immersion process occurred, the cast membrane was immersed into water coagulation bath immediately. After membrane had been peeled off from the glass plate, the membrane was transferred into another water bath for at least 24 hours before used.

Table 1 Dope formulation of the casting solutions.

Membrane	Dope Formulation (wt %)			
	PSf	PEG 400	Nanoparticles	NMP
TFC	15	2	0	83.0
TFN-1	15	2	0.5 BN	82.5
TFN-2	15	2	0.5 A-BN	82.5
TFN-3	15	2	0.5 BN	82.5
TFN-4	15	2	0.5 A-BN	82.5

Preparation of TFC/TFN membranes

Polyamide selective layer was formed on the as prepared mixed matrix membrane via interfacial polymerization between MPD and TMC. Firstly, the substrate was clamped in between a glass plate and Viton frame. 30 ml of 2 w/v% MPD solution was poured into the frame and allowed to contact with the porous PSf for 2 min before those excess MPD solution drained off. A rubber roller was used to remove those residual droplets from the substrates by rolling across the surface of membrane. 20 ml of 0.2 w/v% of TMC in hexane solution was then poured into the frame with 1 min contact time with the substrate surface. Both BN and A-BN was added into the TMC solution and poured onto PSf/BN and PSf/A-BN substrates. A thin active PA layer was formed immediately resulted from the interaction of MPD and TMC monomers. Those excess organic solutions were drained off. The membrane was then cured in oven for 8 min at 60 °C. The resulting membrane was immersed in DI water until used. These membranes were labeled as TFC, TFN-1 (BN in PSf substrate), TFN-2 (A-BN in PSf substrate), TFN-3 (BN in both PSf substrate and PA layer), TFN-4 (A-BN in both PSf substrate and PA layer) as shown in Table 2.

Table 2 Membranes composition.

Membrane	Composition	
	PSf membrane	PA layer
TFC	PSf	PA layer
TFN-1	0.5 % BN in PSf	PA layer
TFN-2	0.5 % A-BN in PSf	PA layer
TFN-3	0.5 % BN in PSf	0.05 % BN in PA layer
TFN-4	0.5 %A- BN in PSf	0.05 %A- BN in PA layer

BN characterization

The structure of BN particle was examined using transmission electron microscopy (TEM Hitachi HT7700) operated at the transmission mode of 100 kV. Fourier transform infrared spectroscopy (FTIR) of BN was investigated by using spectrum One FTIR Spectrometer (PerkinElmer).

Membrane characterization

Functional groups of BN were investigated using Spectrum One Fourier transform infrared spectroscopy (FTIR) Spectrometer (PerkinElmer) in wavelength that range from 400 to 4000 cm⁻¹. The cross-sectional and the surface morphology of the membrane samples were observed using scanning electron microscopy (SEM, Hitachi TM 3000 Tabletop Microscope). Contact angle (CA) measurement was conducted by sessile drop method employing an automated CA goniometer (OCA 15 pro, DataPhysics) using RO water as probe liquid. Ten measurements were collected at different spots of each membrane sample and the mean value was recorded. Topological properties of the membranes were investigated using atomic force microscopy (Hitachi AFM 5100N). The membrane surface (10µm×10µm) was scanned using non-contact mode. The average roughness (R_a), the root mean square of Z data (R_{ms}) and the mean difference between the highest peak and lowest valleys (R_{max}) were measured.

Membrane filtration performance

A dead-end filtration cell (Sterlitech™ HP4750) was used to assess the permeation of the fabricated substrates and membranes under nitrogen atmosphere. The effective surface area of the membrane was 14.6 cm². Prior to any measurement, the membranes were compacted at pressure of 16 bar, respectively for about 30 min to achieve flux steady state condition. The pure water permeability of the substrates was then calculated from the measured permeation flux using pure water at operating pressure of 15 bar. The pure water flux (PWF) of the membranes were operated by using the following equation:

$$J_{WF} = \frac{V}{A\Delta t} \tag{1}$$

where J_{WF} is the water flux (L/m²h), V is the volume of water permeated across the membrane (L), t is the time taken for collecting the permeate (h) and A_m , is the effective membrane area (cm²).

Sodium chloride (NaCl) solution of 1000 ppm was tested for reverse osmosis studies. The rejection efficiency, R (%) was calculated based on the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where C_p and C_f are the solute concentration (ppm) in the permeate and feed respectively. All filtration experiments were operated at 15 bar and at room temperature.

RESULTS AND DISCUSSION

BN and A-BN characterizations

The A-BN was characterized in several ways to compare with the commercial BN. Fig. 1 compares the FTIR spectrum of both BN and A-BN. Both BN and A-BN shows two main peaks at $\sim 1400 \text{ cm}^{-1}$ and 800 cm^{-1} that be in agreement with BN stretching vibrations and B-N-B bending vibrations. There is one new emerging peak that can be observed in A-BN that located at $\sim 3250 \text{ cm}^{-1}$ indicated the present of B-NH₂ group. Besides, A-BN shows an increment in peak intensity of $\sim 1413 \text{ cm}^{-1}$ (B-N). This indicated that the A-BN has increase in polarity. Peak broadening in the range of $\sim 830 \text{ cm}^{-1}$ to 1550 cm^{-1} also indicated that the size of A-BN decreases and aggregation of nanoparticles (Wang *et al.*, 1998). This can be further confirmed in TEM results.

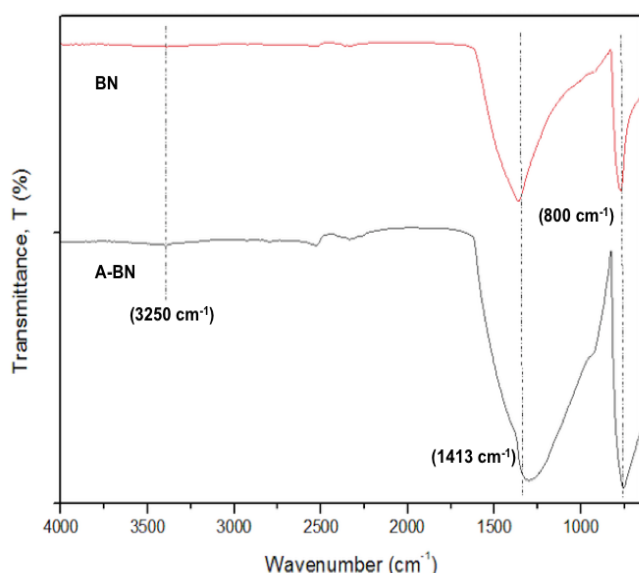


Fig. 1 FTIR spectra of BN and A-BN.

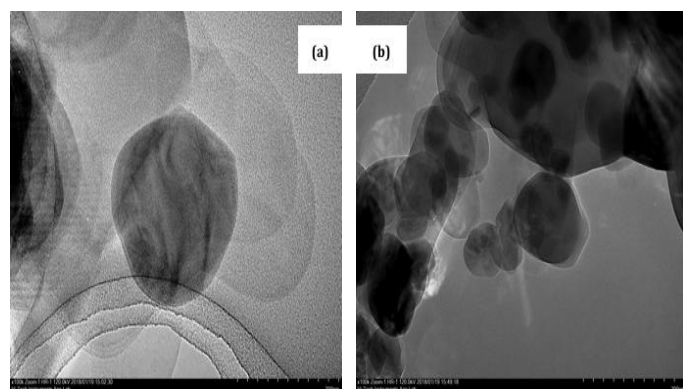


Fig. 2 TEM images of (a) BN and (b) A-BN.

The microstructures of BN and A-BN were investigated by TEM in Fig. 2. Based on the TEM images, the size of the A-BN nanoparticles

is smaller than the BN nanoparticles. It is due to the reaction occurs in between BN nanoparticles and concentrated nitric acid, which creates oxidized radicals on BN and form BN-H⁺ bonds on the surface of BN that might cut and functionalize BN nanoparticles (Ide *et al.*, 2014; Li *et al.*, 2015). This proved that TEM results were in agreement with FTIR results. Besides, the edge of A-BN nanoparticles is found to be rougher as compared to the edge of BN nanoparticles, suggesting that the chemical activation reaction occur on the surface of the A-BN.

Membrane characterizations

Fig. 3 shows the FTIR results of TFC and TFN membranes. Both TFC and TFN membranes show the spectrum at various peaks that corresponding to functional group of the PSf support membranes which, the peaks at the particular wavenumber of 1151 cm^{-1} (symmetric O=S=O stretching), 1242 cm^{-1} (asymmetric C-O-C stretching), 1293 cm^{-1} (asymmetric O=S=O stretching), 1409 cm^{-1} (C=C aromatic ring stretching), and 1503 cm^{-1} (CH₃-C-CH₃ stretching) (Lau, *et al.*, 2014). The formation of PA layer on TFC and TFN membranes can be confirmed through FTIR results at the peak of 1552 cm^{-1} and 1585 cm^{-1} that corresponding to C=O and C-N stretching (Wan Azelee *et al.*, 2017). Moreover, other bands at 1611 cm^{-1} and 1667 cm^{-1} reinforce the formation of PA layer that associated to aromatic amide ring breathing and N-H bending in CO-NH group (Khorshidi *et al.*, 2015). As comparison, the embedment of BN and A-BN into TFN membranes tend to broadening the peak at ~ 795 , ~ 1325 , $\sim 1409 \text{ cm}^{-1}$. This indicated that there is stretching vibration of those functional groups upon the addition of BN and A-BN nanoparticles.

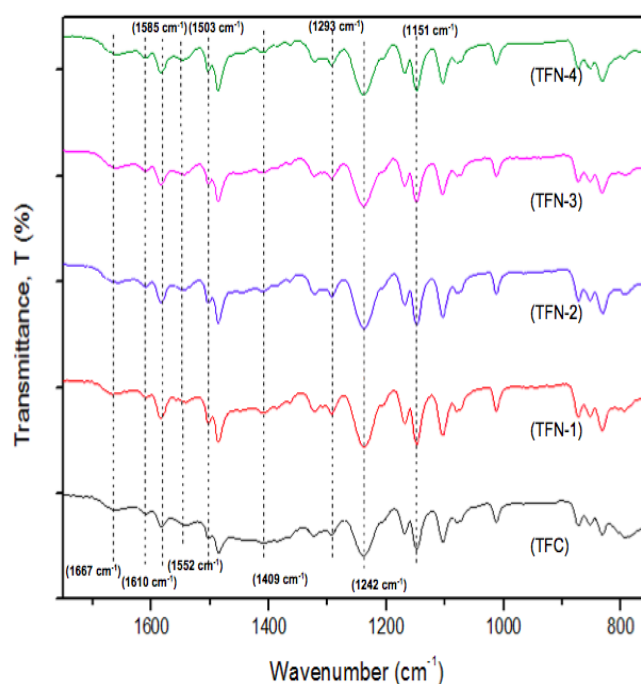


Fig. 3 FTIR of TFC and TFN membranes.

Fig. 4 shows the surface and cross-sectional morphology of the TFC and TFN membranes. The cross-section SEM images of all membranes show that the membranes consist of two layers, which are the PSf support layer and thin-film active layer. All the membranes displayed typically interfacial polymerized characteristic, which consisted of ridge and valley structures. It can be seen clearly in Fig. 4 that those TFN-4 membranes has more ridge and valley structures as compared to other membranes. This observation further confirms the AFM images. Both BN and A-BN were dispersed nicely in both PSf support layer and PA active layer since there is no agglomeration observed in the SEM images.

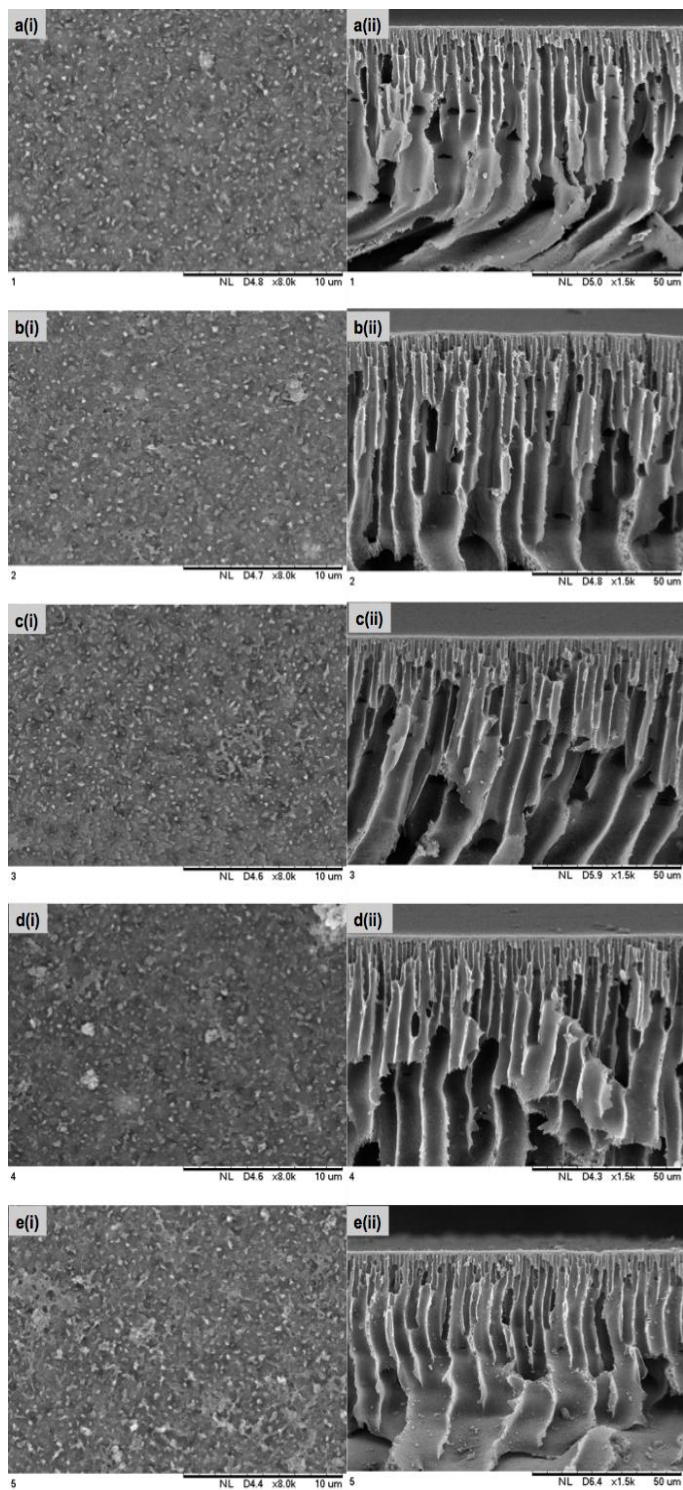


Fig. 4 SEM images for (a) TFC, (b) TFN-1, (c) TFN-2, (d) TFN-3, (e) TFN-4 membranes (i: surface; ii: cross-sectional morphology).

Fig. 5 shows the 3D AFM images of the top surface of TFC and TFN membrane upon addition of BN and A-BN into the PSf substrate and PA surface of membrane. As seen from Fig. 4, both TFC and TFN membranes have ridge and valley structure. The embedment of BN and A-BN into TFN membranes exhibited significant rougher surface compared to TFC membrane. The increase in surface roughness could be due to the enlargement of effective surface area. The increase in surface roughness can be advantageous for water permeability since it provides a higher surface area for water molecules to flow through (Lai et al., 2016). Further surface roughness parameters show in Table 3. R_{ms} values of TFN membranes show distinct increment with the maximum R_{ms} value (113.7 nm) found in TFN-4. From Fig. 5, the embedment of A-BN into TFN-4 has created a higher ridges which indicated increasing in surface roughness of membrane.

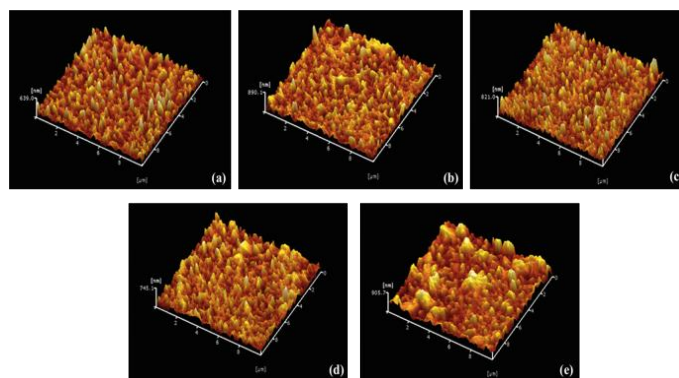


Fig. 5 AFM images for (a) TFC, (b) TFN-1, (c) TFN-2, (d) TFN-3, (e) TFN-4.

Table 3 Surface roughness of TFC and TFN membranes.

Membrane	Surface roughness parameter (nm)		
	Ra	Rms	Rmax
TFC	54.01	70.47	525.6
TFN-1	67.3	85.55	569.1
TFN-2	71.4	93	701.6
TFN-3	64.74	84.48	681.4
TFN-4	90.38	113.7	722.8

Table 4 shows the surface contact angle of TFC and TFN membranes. It is reported that embedment of BN and A-BN into TFN membranes tended to decrease the contact angle. The contact angle decreased from 78.85 to 69.92° for TFN-4. The reduction in contact angle is due to the activation process of BN that facilitates the functional group, B-NH₂ into BN nanosheets. The existence of B-NH₂ group as a polar functional group provides the A-BN hydrophilic behavior by forming hydrogen bonding in between B-NH₂ and water molecules.

Table 4 Contact angle of TFC and TFN membranes.

Membrane	Contact angle (°)
TFC	78.85 ± 4.32
TFN-1	75.38 ± 4.91
TFN-2	75.18 ± 5.16
TFN-3	72.77 ± 3.91
TFN-4	69.92 ± 4.74

Fig. 6 shows the effect of BN on PWP performance and NaCl rejection of TFC and TFN membranes. The TFN membranes that incorporated with BN and A-BN nanoparticles exhibited better performance in water flux property than TFC. In comparison, embedment of A-BN nanoparticles into both PSf substrates and PA layer of TFN showed higher PWP than the TFN membrane that contained pristine BN. TFN-4 exhibited the best water permeability among the membranes with 1.16 L/m² h bar, which was approximately 33.9% higher than TFC membrane. The improvement in PWP TFN-4 membrane was due to the decreasing in surface contact angle and increasing in surface roughness of membrane. The presence of NH₂ group in BN aids in increasing the hydrophilicity of BN by forming hydrogen bonding with water and allowed water molecules to take precedence to flow through (Zhong et al., 2015). The incorporation of nanoparticles into the TFN membranes does not aid in increasing the rejection capability of membranes. TFC control membrane possessed the highest NaCl rejection among the membranes with ~95%. With the embedment of BN and A-BN as nanofillers into both PSf substrate and PA layer, the NaCl rejection of TFN membranes slightly decreases. The NaCl rejection for TFN-1 and TFN-2 was 87% and 93%, respectively. While for TFN-3 and TFN-4, the NaCl rejection was decreased to 81% and 89.84%, respectively. The decrease in NaCl rejection might be due to the lack of functional groups on BN and A-BN. The chemically activated BN possesses B-NH₂ that can aid in increasing water permeability of TFN membranes. Li et al. (2015) had conducted the activation process on BN fibers and the results obtained were slightly different from this

experiment. In comparison, the chemical activation BN fiber possesses B-OH group and a more obvious B-NH₂ group. Meanwhile, the chemical activation method proposed by Li *et al.* was unsuitable to be used on BN (hexagonal shape) due to the properties of BN, which thermal and chemically inertless (Falin *et al.*, 2017). In overall, TFN membranes that incorporated with A-BN nanoparticles show better overall performances as PWF take into consideration.

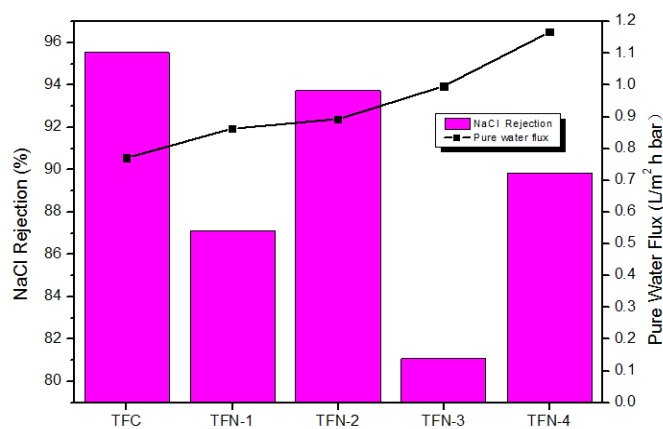


Fig. 6 Pure water flux and NaCl rejection of TFC and TFN membranes.

CONCLUSION

In this experiment, A-BN that was undergoes chemical activation process and incorporated into PSf and PA layer of TFN membranes. The obtained TFN membranes showed improvement in water permeability with a slightly decrease in NaCl rejection capability. Further investigation was needed to identify the chemical activation process on BN. However, BN nanomaterial has the potential to be used as nanofillers in water purification application if the functional group attached can be specifically tailored.

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