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To cite this article: A Benamor *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **634** 012048

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Metal-oxide nanotubes functional material tailored for membrane water/wastewater treatment

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Abstract. Titanium Dioxide Nano-Tubes (TNTs) synthesized by hydrothermal method were used to prepare new polysulfone thin film nanocomposite (TFN) membranes. The TFN membranes contained different TNTs proportions (0.1, 0.3 and 0.5 wt. %). A polyamide selective layer was formed on top of the TFN membrane surface using interfacial polymerization (IP). Nanofiltration experiments were performed using NaCl and MgSO₄ salts solutions. The water flux was found to increase with increased TNT loading in the membrane due to high porosity of embedded nanoparticles and the formation of enlarged pores. The antifouling behaviour of the membrane was tested by bovine serum albumin (BSA) solution and found to improve with increased TNT content in the membrane.

1. Introduction

Membrane technology is considered as one of the most growing technologies for water treatment and desalination of sea and brackish water to solve fresh water scarcity and to cover the increase in drinking water demand in many parts of the world [1, 2]. Among all, TiO₂ is the most extensively studied transition-metal oxides because of its non-toxic, environmentally friendly, inexpensive, commercially available and good corrosion-resistant property. Transition metals embedded in membranes have been applied to counter a large number of environmental problems including those related to water and air purification [3, 4]. Nano materials have its inherent photocatalytic effects that decompose organic chemicals and kill bacteria [5]. Water filtration with composite membrane of TiO₂ particles and photo degradation under ultraviolet (UV) irradiation was investigated by several research groups [6, 7]. Other researchers studied TiO₂/polymer TFC reverse osmosis membrane to reduce biofouling [8, 9]. From previously mentioned outcomes, the incorporation of TiO₂ is a useful approach to improve membrane morphology and inhibit membrane fouling. Preparing TNTs from TiO₂ nanoparticles using hydrothermal method offer larger surface area and larger pore volumes compared to other methods in addition to the hydrophilic properties of TiO₂ [10-12]. These features are the most attractive properties and key features required for the development of high quality membranes [13].

Recently, a new class of nanotube-based membranes (TFN membranes) were synthesized and used for reverse osmosis (RO) operations. These membranes showed excellent performances compared to the usual polyamide (PA) TFC membranes. Based on this concept, titanate nanotubes were produced and functionalized using several amines to produce a new class of TFN RO membranes that showed water permeability up to 93 % with better anti-organic fouling properties [14]. Polyethersulfone blend membrane with incorporated TiO₂ nanotubes used in vacuum membrane distillation showed a permeate



flux of 15.2 kg/m² h and a maximum salt rejection of 98 % for a feed salt concentration of 7000 ppm and a temperature of 65 °C [15]. The addition of TNT to PES membrane for the fabrication of asymmetric PES/TNTs blend membranes resulted in higher porosity, better hydrophilicity, increased permeate flux and higher salt rejection compared to bare PES membrane [16] which can be explained by increased membrane hydrophilicity due to the embedded hydrophilic carbon nanotubes [10, 17, 18] and inner void spaces of nanotubes [19-21]. The gaps existing between the embedded nanomaterials and the polyamide layers enhanced the water diffusion rates [5, 18, 20, 22]. Furthermore, the increased pore volumes of TNTs and their large specific surface area provide a large number of adsorption sites and diffusion channels for water movement, resulting in higher water channeling. Hence, the goal of this study is to synthesize TiO₂ nanotubes by a solution chemical method and use these nanotubes to develop TFN NF membranes for filtration of various salts.

2. Experimental

2.1. Materials

All chemicals employed in this research work are summarised in Table 1. All materials were used as received without further purification. Purified water used in all experiments. Acrylic plastic plates (11×9×0.24 in) were used to support the PSf-TNTs membrane synthesis.

Table 1. Description of materials and their source

Material description	Source
Polysulfone (PSf) Udel P-1700 in pellet	Solvay Advanced Polymers
N-Methyl pyrrolidinone (NMP) anhydrous 99.5%	Sigma-Aldrich St Louis, Ohio, USA
m-Phenylenediamine (MPD) flakes >99%	Sigma-Aldrich St Louis, Ohio, USA
n-hexane (> 99%)	Sigma-Aldrich St Louis, Ohio, USA
1, 3, 5-benzenetricarbonyl trichloride (TMC> 98%,)	Sigma-Aldrich St Louis, Ohio, USA
Sodium hydroxide (NaOH 98%)	Sigma-Aldrich St Louis, Ohio, USA
Sodium chloride (NaCl) > 9.5%	Sigma-Aldrich St Louis, Ohio, USA
Magnesium sulphate (MgSO ₄ 99 %)	Sigma-Aldrich St Louis, Ohio, USA
Titanium dioxide nanoparticles with particle size of < 21 nm (TiO ₂ , Anatase)	Sigma-Aldrich St Louis, Ohio, USA

2.2. Synthesis of TiO₂ nanotubes

Titanium dioxide nanotubes (TNTs) were prepared by hydrothermal method; 3 gm of TiO₂ powder were mixed with 150 ml of 10 molar NaOH solution, and stirred for 60 min at ambient temperature. The resulted suspension was then heated to 170 °C for 24 h in a Teflon-lined autoclave to ensure full dissolution of TiO₂ powder. After that the autoclave was left to cool down until it reached room temperature and a product in the form of white powder was formed. The product was initially washed with an HCl solution of 0.1 molar then washed by deionized water. When the pH of the washing solution approaches 7, cleaning with deionized water was stopped. The product in the form of white powder was then dried under vacuum at 85 °C for 4 h to make sure of complete removal of all water traces. The sample was post-treated again at 500 °C for 3 h with a temperature increase rate of 5 °C/min.

2.3. Composite membrane preparation

2.3.1. Preparation of substrate membrane. To prepare the casting solution, PVP was dissolved in NMP and the solution was stirred for 10 min following the procedure described by Elimelech et al.[23]. Weighed amount of TNT nanotubes was added to NMP/PVP mixture, and ultrasonicated for 30 min to minimize chances of TNT nanotubes agglomeration. Polysulfone (PSF) beads were then added to the solution and stirred vigorously until a homogenous solution was obtained. The obtained homogeneous casting solution was stirred for 8 h at ambient temperature, then ultrasonicated for 1 h to remove trapped

air bubbles and finally stored in a desiccator for 15 h before any use. The solution was then casted at room temperature on a non-woven polyester supported on a glass plate using a 150 μm thickness casting knife. The whole composite was immediately immersed in a distilled water coagulation bath containing 3 wt. % NMP for phase inversion to take place. The substrate was kept in the coagulation bath for 10 min where the membrane was obtained and then transferred to another water bath and kept for at least 24 h to remove the solvent and water-soluble polymer (PVP) residuals. The membrane was washed repeatedly with distilled water and stored in water. The produced substrates are designated as TFC-0, TFC-1, TFC-3, and TFC-5 corresponding to the Nanotubes loading percentage of 0, 0.1, 0.3 and 0.5% respectively.

2.3.2. Preparation of Polyamide selective layer. The polyamide (PA) selective layer was casted on top of the prepared PSF substrate surface by interfacial polymerization (IP) process. To make sure that MPD solution penetrates into the substrate pores, thirty mL of MPD aqueous solution 2 wt. % was poured and held for two minutes on top of the substrate membrane. The excess MPD solution was drained and the remaining residuals were removed by air knife. Another thirty mL of TMC 0.1 wt. % dissolved in n-hexane was poured on the substrate surface and kept for 1 min after which the excess organic solution was drained off. As a result, an ultra-thin PA layer was formed. The synthesised TFC membrane was kept at ambient condition for one min to dry then kept in an oven at a temperature of 70 $^{\circ}\text{C}$ for another eight min for complete drying. The new TFC membrane was stored in DI water at 4 $^{\circ}\text{C}$ until further use [24].

3. Results and discussions

3.1. Morphology of TiO_2 nanotubes

The morphology of TNTs are directly analyzed by SEM (Philips model XL30E, USA) using direct applying nanotubes on copper plate with sputtering at 2 mints. Also TNT were analyzed by transmission electron microscope (Phillips CM12 with motor driven stage and SIA L3C Digital Camera, The Netherlands). The TNTs are dispersed in water using an ultrasonic bath (Branson 3800 ultrasonic cleaner-M3800, USA) for 1 h. A few drops of each suspension were deposited onto 3-mm diameter carbon-coated grids. 120 kV acceleration voltage were used for the TEM analyses. The obtained images as shown in figure 1 reveal that the synthesized nanotubes are open ended nanotubes of narrow size distribution. The average inner diameter was found to be in the range of 3-5 nm while the outer diameter of 10-13 nm. The observed length of TNTs nanotubes was found to be greater than 300 nm. The TEM images revealed that the TNTs are single wall nanotubes.

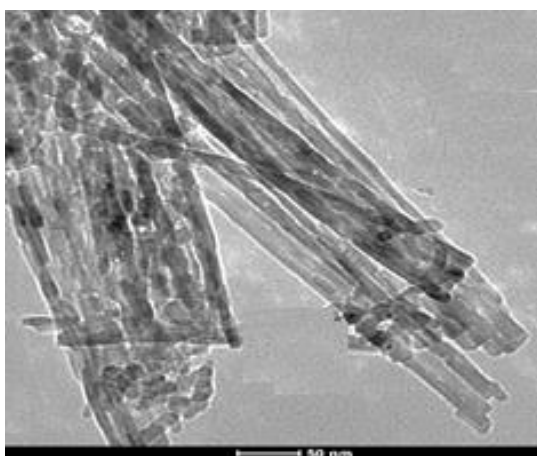


Figure 1. TEM images of synthesized TNTs.

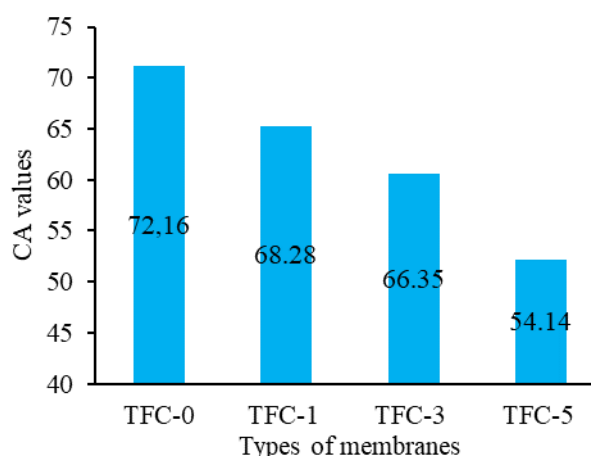


Figure 2. Contact angles of the different membranes.

3.2. Membrane contact angle

Contact angle measurement is an important parameter in membrane characterization as it indicates the membrane's hydrophilicity and flux behavior. For each membrane, the contact angles was measured at least three times and the average value was considered and shown in figure 2. The contact angle results indicate that TNTs content membranes exhibited a higher hydrophilicity than control TFN-0 membrane. In addition, the CA decreases from $72.16 \pm 2^\circ$ to $54.14 \pm 2^\circ$ as TNTs percentage increased from 0.1 to 0.5 wt. % due to increase of hydrophilicity. Therefore, it was expected that the TNTs content membranes absorb more permeate into the membrane and thus enhance the flux rate. The lowest CA of TFN-5 (54.14 ± 2) indicates that this membrane exhibited a more hydrophilic surface due to a superior ultra-hydrophilic property of the TiO_2 nanotubes deposited, which was well distributed over the surface compared to other TFN membranes [25].

3.3. Membrane performance study

3.3.1. Permeation experiments. Two different experimental set ups were used in this work, the first one consist of a dead end cell while the second one is a cross-flow module both supplied by Sterlitech. Applying varying trans-membrane pressures (4 to 10 bars) at ambient temperature, permeation experiments at were performed using a dead-end filtration cell l equipped with magnetic stirrers set at a constant rotation speed of 500 rpm. The effective membrane surface area was 14.6 cm^2 . For each experiment around 300 millilitres of deionized water was used. To ensure reproducibility, all measurements were performed using at least three different membrane samples. Before any measurement, membrane was compacted for about 30 min under a pressure of 15 bar. The permeate flux (J_w) was calculated by Eq. (1):

$$J_w = (V/A.\Delta t) \quad (1)$$

Where,

V: volume of permeated water (L)

A: membrane area (cm^2)

Δt : permeation time (min).

The experimental permeability results of the synthesized TFN membranes are presented in figure 3.

The permeance was defined to be the ratio of the water flux over the membrane pressure difference (Δp):

$$\text{Permeance} = J_w/\Delta P = (V/A.t.\Delta P) \quad (2)$$

The average permeance of the pristine TFN-0 membrane was $1.06 \text{ L/m}^2.\text{h}.\text{bar}$. Compared to the TFN membrane, the addition of 0.3 wt. % TNT resulted in an increased permeance of $1.468 \text{ L/m}^2.\text{h}.\text{bar}$. The permeance slightly increased up to $1.518 \text{ L/m}^2.\text{h}.\text{bar}$ when 0.5 wt. % TNTs was added, which is one time and half the value of the pure PA membrane ($1.06 \text{ L/m}^2.\text{h}.\text{bar}$)

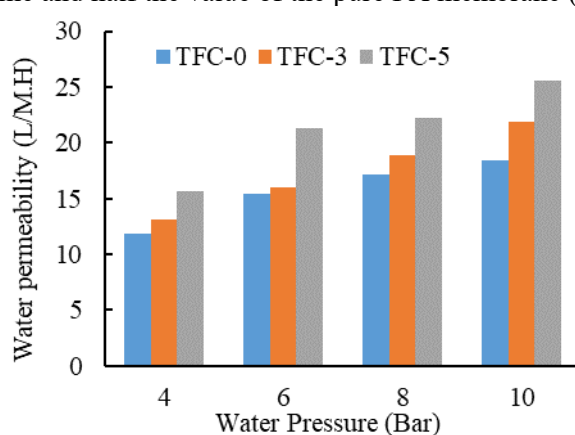


Figure 3. Water permeation results.

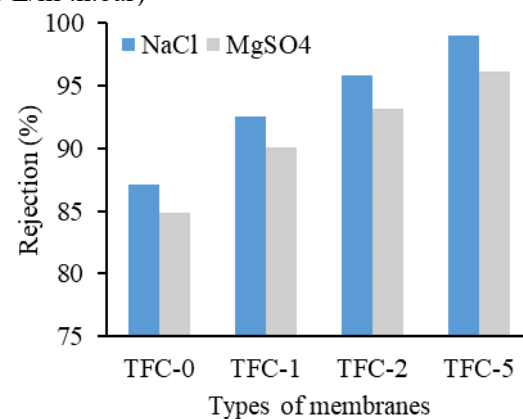


Figure 4. Membrane salt rejection as function of membrane TNT content.

3.3.2. *Salt rejection.* Membrane performances in term of salt rejection, as shown in figure 4 were measured in a lab scale Sterlitech™ CF042P stainless steel cross-flow module with an effective membrane area of 42 cm² and 18 L volume capacity tank [26]. For performance tests, 1,500 mg/L NaCl (1500 mg/L MgSO₄) solution were fed at a flowrate of 1.7 litre per minute at 25°C. The permeate flux was measured under 10 bar for 2 h after membrane compaction for 30 min under 15 bar. Permeate flux (J_w) was calculated by Eq. (1). Salt rejection was calculated by measuring the conductivity of the feed (C_f) and the permeate (C_p) using (HACH, HQ14 portable) conductivity meter as expressed in Eq. (3).

$$\%R = \left(1 - C_p / C_f\right) \times 100 \quad (3)$$

4. Conclusions

Titanate Nanotubes were successfully synthesized and characterized. The average inner diameter was found to be in the range of 3-5 nm while the outer diameter of 10-13 nm. The observed length of TNTs nanotubes was found to be greater than 300 nm. The TEM images revealed that the TNTs are single wall nanotubes. The TNT-incorporated polysulfone TFC membranes were developed. The prepared membranes showed improved permeation properties. The results of the performance evaluation tests recommend that the addition of TNT improved the pure water, compared to pristine PSf membrane. Both salts rejection using NaCl and MgSO₄ calculated by measuring the conductivity of the feed and the permeate showed improved salt rejection with increased TNT content in the membrane.

Acknowledgments

This paper was made possible by an NPRP10-0127-170270 and NPRP8-1115-2-473 from the Qatar National Research Fund (a member of Qatar Foundation). The statements made herein are solely the responsibility of the authors.

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