ORIGINAL PAPER



Fabrication of fullerenol-incorporated thin-film nanocomposite forward osmosis membranes for improved desalination performances

M. Gimhani N. Perera^{1,2} · Yeshan R. Galagedara^{1,2} · Yiwei Ren¹ · Mahesh Jayaweera³ · Yuntao Zhao^{1,2} · Rohan Weerasooriya⁴

Received: 8 March 2018 / Accepted: 8 August 2018 © Springer Nature B.V. 2018

Abstract

Development and use of novel membranes for forward osmosis (FO) applications have gained popularity throughout the world. To enhance FO membrane performance, a novel thin-film nanocomposite membrane was fabricated by interfacial polymerization incorporating Fullerenol ($C_{60}(OH)_n$) nanomaterial, having n in the range of 24–28 into the active layer. Different concentrations of fullerenol loading (100, 200, 400, and 800 ppm) were added to the top skin layer. The structural and surface properties of the pure thin-film composite membrane (TFC) and fullerenol-incorporated thin-film nanocomposite (FTFC) membranes, were characterized by ATR-FTIR, SEM, and AFM. FO performance and separation properties were evaluated in terms of water flux, reverse salt flux, antifouling propensity, water permeability and salt permeability for all TFC and FTFC membranes. Osmotic performance tests showed that FTFC membranes achieved higher water flux and reverse salt flux selectivity compared with those of TFC membranes. The FTFC membrane with a fullerenol loading of 400 ppm exhibited a water flux of 26.1 L m⁻² h⁻¹ (LMH), which is 83.03% higher than that of the TFC membrane with a specific reverse salt flux of 0.18 g/L using 1 M sodium chloride draw solution against deionized water in FO mode. The fullerenol incorporation in FTFC membranes also contributed to a decreased fouling propensity.

Keywords Fouling · Permeability · Salt flux · Water contact angle · Water flux

Introduction

The ever-increasing demand for potable water over the last couple of decades due to rapid population growth and economic development has been attributed to the scarcity of fresh water affecting two-thirds of the global population (four billion people) at least for one month of the year [1]. In addressing this water crisis, membrane-based technologies offer advantages due to their high selectivity, robustness, and reliability.

Yiwei Ren renyiwei@cigit.ac.cn

M. Gimhani N. Perera gimhani_perera@cigit.ac.cn

Yeshan R. Galagedara yeshan galagedara@cigit.ac.cn

Mahesh Jayaweera maheshjayaweera@gmail.com

Yuntao Zhao zhaoyuntao@cigit.ac.cn Forward osmosis (FO) is an emerging membrane technology in this context and has been experimented for a variety of applications, including desalination [2], wastewater treatment [3], osmotic power generation [4], processing of pharmaceutical products [5] and food processing [6]. The driving force in FO process is the osmotic pressure gradient capable of transporting water molecules across the semi-permeable membrane to a high solute concentration of draw solution (DS) from a feed solution (FS) of a relatively low concentration of solute.

Rohan Weerasooriya rohan@uwu.ac.lk

- ¹ Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, China
- ² University of Chinese Academy of Sciences, Beijing 100049, China
- ³ Department of Civil Engineering, University of Moratuwa, Katubedda, Sri Lanka
- ⁴ Environmental Science Program, National Institute of Fundamental Studies Hantana Road, Kandy, Sri Lanka

FO membranes have acquired popularity over reverse osmosis (RO) membranes due to their relatively low operating cost, low fouling propensity, and higher water recoverability [7].

Over the past few decades, the flat-sheet cellulose triacetate (CTA) FO membrane (Hydration Technology Innovations Inc., HTI Co., USA) was the most popular commercialized membrane [8]. However, its relatively low solute rejection, low water flux, and biodegradation tendency have critically narrowed down its wide range of applicability [9]. As a result, new types of membranes have been developed, and among them, polyamide (PA) thin-film composite (TFC) membrane has gained popularity because of its pH stability, high osmotic flux and easy fabrication [10]. To date, much attention has been paid to optimize the chemical and structural properties of the support layer of TFC-FO membranes [11, 12]. In this context, attention is paid towards modifications of the active layer, as it plays a vital role in determining the osmotic performance of TFC-FO membrane [13]. Hence, modification of the active layer by incorporating nanoparticles in the form of thin-film nanocomposite (TFN) has been demonstrated to remarkably enhance the performances of TFC-FO. The thin layer modifications are capable of direct incorporation of nanomaterials on the membrane surface without changing the Interfacial Polymerization (IP) process [14]. Some of the typical nanomaterials used are zeolites, TiO₂, carbon nanotubes (CNTs), and graphene oxide (GO) [14-17]. The incorporation of such nanomaterials has yielded substantial increases in the water flux and salt rejection of membranes. The membranes with nanoparticle-incorporated PA layers have been pronounced more commercially viable than those undergone only substrate modification due to the improved performances of the former membranes [14].

These materials are enriched with a variety of functional groups, e.g., carboxyl, epoxy, and hydroxyls, capable of attracting water molecules. Due to the presence of functional groups with different affinities to water, modified surfaces may, however, exhibit some heterogeneity that limits their efficiency. Search for membranes with the hydrophilic character of homogeneity will, therefore, yield superiority in performance. In this context, due to the abundance of -OH groups, fullerenol nanofillers with excellent hydrophilicity and antifouling propensity show a great promise in the modification of active layer on the membrane. However, only a few studies concerning fullerenol incorporation into polyvinyl alcohol (PVA) and nano-filtration (NF) membranes have been carried out with success [18, 19]. For example, the fouling recoveries were significantly increased in fullerenol $(C_{60}(OH)_{22-24})$ -assimilated TFC membranes [20]. The major drawback of using fullerenol having the molecular structure of $C_{60}(OH)_{22-24}$ is its low solubility in solvents used in the fabrication of membrane substrates. It is, therefore, paramount to modify surface or functionalization of -C₆₀ to improve their performance as required in membrane technology.

In our work, we use fullerenol having the molecular structure of $C_{60}(OH)_{24-28}$ to modify the active layer of TFC-FO membranes. Fullerenol consists of multiple hydroxyl groups attached to the spherical surface. Due to the monotonous nature of functional groups, we envisage homogeneous membrane surface with enhanced hydrophilic character. The high density of -OH functional group on C₆₀ arranged in a ball-shaped cage facilitates more reactive sites, which would invariably increase hydrophilicity [21]. To our knowledge, the use of $C_{60}(OH)_{24-28}$ in membrane technology is scarce; hence this study. In our work, fullerenol-incorporated membranes are characterized by spectroscopic methods to examine the structure, morphology, and roughness of the surfaces. The FO membrane-specific desalination performances are too examined with the optimum fullerenol loading on TFC.

Materials and methods

Chemicals

Fullerenol having –OH functional group of 24–28, with average diameter ~1 nm, made of 99% purity was purchased from Suzhou Tanfeng Graphene Technology Co. Ltd., Suzhou, China. Polysulfone (PSF) beads, dimethylacetamide (DMAc), n-hexane (97%, anhydrous), sodium chloride (NaCl, 99.5%), sodium alginate (SA, MW: 98.11), potassium dihydrogen phosphate (KH₂PO₄, 99.5%), magnesium sulfate (MgSO₄, 99%), sodium bicarbonate (NaHCO₃, 99.5%), calcium chloride (CaCl₂, 96%) and ammonium chloride (NH₄Cl, 99.5%) were obtained from Kelong Co. Ltd., Chengdu, China. The m-phenylenediamine (MPD, 99.5%) and 1,3,5-benzene-tricarbonyltrichloride (TMC, 98%) were stored in a refrigerator until use.

Fabrication of membrane substrate

As described elsewhere [22], the membrane substrates were formulated using non-solvent-induced phase separation. PSF beads were dissolved in DMAc solution with a ratio of 15:85 by weight. The solutions were then stirred constantly with a stirrer at room temperature for one day and desiccated to eliminate air bubbles. The polymer solution was cast onto a pre-cleaned glass plate and immersed immediately in deionized (DI) water bath for 10 min at room temperature to facilitate phase separation. The DI water bath was frequently changed (every 12 h for two days) to eliminate residual tracer solvents attached to the membrane. Subsequently, the membrane substrates were stored at 5 $^{\circ}$ C until further use.

Fabrication of polyamide (PA) and PA-Fullerenol layers

The purpose of the fabrication of these layers is to characterize the functional behavior of fullerenol in polyamide matrix, as fullerenol incorporation into the active layer through IP would not facilitate a conducive environment to identify functional groups due to masking effect. PA layer was, therefore, prepared by mixing MPD aqueous solution (2% wt.) and TMC solution (0.15% wt.) in hexane in a cleaned petri dish. PAfullerenol nanocomposite was made by adding fullerenol (0.08% wt.) into MPD aqueous solution (2% wt.) using ultrasonication and mixing with TMC in hexane (0.15% wt.). Finally, both PA layers were air-dried for 24 h.

Fabrication of polyamide active layer in the substrate

The fullerenol-incorporated thin-film polyamide layer was synthesized on the membrane substrate surface via in-situ IP [17]. The solution of MPD/fullerenol was prepared by adding fullerenol into the MPD aqueous solution (2% wt.) with concentrations ranging from 0 to 800 ppm and ultrasonicated for three hours. The ultrasonicated top surface of membrane substrate was rinsed with DI water for one minute and immersed in it for two minutes for dissolution of impurities. The excess amount of MPD solution was removed by a rubber roller, and the remainder was dried in a fume hood for several minutes. TMC/hexane solution (0.15% wt.) was mixed with the saturated membrane substrate to induce IP. The membrane was first airdried at ambient conditions for one minute and then in an oven at 60 °C for two minutes, and stored in DI water at 5 °C until further use. These control TFC and fullerenol-incorporated TFC membranes were denoted as TFC and FTFC, where FTFC-1 contained fullerenol loading of 100 ppm, and FTFC-8 contained fullerenol loading of 800 ppm, respectively.

Characterization of TFC and FTFC membranes

The membranes were prepared for characterization by storing in a vacuum drying oven, at room temperature for 24 h. Membrane surface morphology was identified by Field emission scanning electro-microscope (FE-SEM) (JSM-7800F, brand, Japan) at 10 kV. The presence of nanomaterials was studied through freeze-dried membrane surfaces whose surface was fractured in liquid nitrogen to protect the pore structure. All the samples were sputtered with a thin layer of gold (SCD 050 BAL-TEC, Germany). The contact angle was estimated by the applied senssile drop method at room temperature under a vacuum. Using tensiometer, membrane surface was kept in contact with tiny droplets of DI water (5–7 μ L); high-resolution images were taken to capture the side elevation of water droplets and analyzed by an image processing method. The roughness of the membranes was determined by Atomic force microscope (TT2 AFM, AFM workshop, USA). For topological and roughness estimations, air-dried membranes were prepared as stripes on the cover-slip glasses. The spectral data of all TFC and FTFC membranes were collected by Fourier Transform Infrared (FTIR) Spectroscopy (Cary 630, Agilent Technologies, USA). Membrane thickness was estimated using a standard method elaborated elsewhere [23].

Determination of water flux, salt rejection, and permeability

The performances of TFC and FTFC membranes at 25 °C such as water flux (J_v) , reverse salt flux (J_s) , and specific salt flux (J_s/J_v) were evaluated by cross-flow FO filtration apparatus. Tests were performed in FO mode (active layer facing to FS) and PRO mode (active layer facing to DS) [24]. FO mode with NaCl concentrations of 0.5 M, 1.0 M, 1.5 M and 2.0 M solutions and PRO mode with concentrations of 1.0 M NaCl solutions as draw solutions were applied with DI water as feed solution, respectively. A cross-flow speed of 6.4 cm/s was maintained across the membranes. Each test was performed for 30 min to reach a stable level, and subsequently, the weight difference of feed solution was measured by a digital balance (BSA6202S-CW, Sartorius) while conductivity changes of FS were recorded by a conductivity meter (DDSJ-308A, INESA Scientific Instrument). Data were acquired every two minutes and the whole procedure was repeated for three times to confirm the stable average levels. The J_{ν} (L m⁻² h⁻¹ or referred to as LMH) was calculated by Eq. 1:

$$J_{\nu} = \frac{\Delta V}{A_m \times \Delta t} \tag{1}$$

Under the predetermined time of Δt (h), ΔV (L) is the volume change of draw solution while the effective surface area of the membrane is A_m (m²). The density of water: 1000 g/L. The J_s (g m⁻² h⁻¹ or referred to as gMH) was calculated by Eq. 2:

$$J_s = \frac{C_t V_t}{A_m \Delta t} \tag{2}$$

Where C_t (g/L) is salt concentration and V_t (L) is the FO feed solution volume. Tiraferrie and co-authors have developed a method to calculate water permeability (*A*) and salt permeability (*B*), which was used in our study [25].

Antifouling test

The fouling test was performed at a constant temperature of 25 \pm 0.5 °C with active layer membrane cells. Two synthetic wastewater solutions having a volume of 1.5 L each were prepared; The 1st solution was prepared by adding 0.45 mM of KH₂PO₄, 9.20 mM of NaCl, 0.61 mM of MgSO₄, 0.5 mM of

NaHCO₃, 0.5 mM of CaCl₂, and 0.93 mM of NH₄Cl to DI water, which was labelled as Solution 1. The other solution with similar compositions plus an organic foulant composed of sodium alginate with a concentration of 250 mg/L was prepared (called Solution 2). These solutions were fed to the membranes with a speed gear pump at 150 rpm having a flow rate of 0.3 L min⁻¹. The set-up was first run for 60 min to clean the membranes using DI water and 2 M aqueous NaCl for FS and DS. The set-up was then run with the FS having the Solution 1 while 2 M aqueous NaCl was deployed as the DS for 1 h to stabilize the water flux, and this initial water flux was recorded as J_{0} . Switching the FS to the Solution 2, the set-up was again run with cross-flow being 2 M aqueous NaCl as the DS for 1080 min, and at the end, J_t , the flux after the accelerated fouling test was estimated. The speed of water flux maintained unchanged for the entire experiment. At a constant speed of 300 rpm with a flow rate of 0.6 L min⁻¹ water flux was circulated together with 2 M NaCl solution for both FS and DS through the membrane cell for 30 min. FO membrane was thoroughly cleaned with FS of DI water and DS of 2 M NaCl for 30 min. The reduction ratio of the flux (FR%) and flux recovery ratio (FRR%) were calculated by Eqs. (3) and (4).

$$FR\% = \frac{J_o - J_t}{J_o} *100\%$$
(3)

$$FRR\% = \frac{J_c}{J_o} *100\%$$
 (4)

Where J_o is the initial flux; J_t is the flux after accelerated fouling test, and final water flux after the physical cleaning stage is J_c .

Results and discussion

Characterization of TFC and FTFC membranes

Fig. 1 shows the FTIR spectra of the TFC and FTFC membrane series. The adherence between amide groups in MPD and acyl chloride groups in TMC was apparent in the FTIR spectra.

The characteristic bands at 1543 cm^{-1} and 1660 cm^{-1} in all spectra of membranes due to the formation of polyamide groups by IP, associated with amide II (C – N stretching and coupling of the in-plane N – H bending vibration) and amide I (carbonyl stretching vibration), respectively [26]. During IP, fullerenol was allowed to react with MPD and TMC molecules in the aqueous solution. The amide groups of MPD may have interacted with hydroxyl groups in fullerenol. Subsequently, this reaction may have led to the formation of new amide bonds and hydrogen bonds during ultrasonication.



Fig. 1 FTIR spectra of TFC and FTFC membranes

When the TMC solution approaches the membrane, the IP takes place, where acyl groups of TMC react with MPD and with hydroxyl groups of fullerenol to form ester and anhydride groups respectively [20]. The possible reaction mechanism using molecular structures is presented in Fig. 2.

We used FTIR spectral data to probe chemical interactions between fullerenol and PA layers. Our results indicate that infrared signatures due to fullerenol and PA interactions are often masked giving monotonous spectral patterns irrespective of fullerenol loadings (details not shown) and FTIR analysis was, therefore, carried out utilizing PA and PAfullerenol composites (Fig. 3). In the region of 3580- 3670 cm^{-1} , there was a transition band due to O-H stretching vibrations (due to free O-H). In addition, due to the intramolecular hydrogen bonded O-H stretching vibrations there was a sharp transition band in the region of 3420-3590 cm⁻¹. The IR bands corresponding to the functional groups of fullerenol at 3000-3500 cm⁻¹ were not readily discernible in all FTFC membranes due to the facts that minute amounts of fullerenol loadings were added so that they could not yield peaks and even if they are pronounced they were not identifiable because of the nearoverlapping effect. Moreover, the vibrations of PA layer formed on the top surface could not be detected due to the intense vibrations of the PSF membrane matrix. In general, the broadband between 3000 and 3500 cm^{-1} is attributed to O-H stretching vibrations of water/hydroxyl groups [27]. According to the proposed molecular structure, multiple peaks appeared in the region of $3030-3080 \text{ cm}^{-1}$ due to the presence of = C–H stretching vibrations. Upon fullerenol addition to PA, the -OH bands show narrowing, which signifies strong interactions between PA and fullerenol indicating a possibility of encapsulation. The bands at 2954 cm^{-1} and 2860 cm⁻¹ are ascribed to the asymmetric and symmetric stretching vibrations of C-H bonds, respectively.



Fig. 2 Schematic representation of chemical interactions between MPD, TMC, and fullerenol during interfacial polymerization

The incorporation of fullerenol may have influenced the formation of amide bands at 1543 cm⁻¹ and 1660 cm⁻¹. In fullerenol, the band at 1560 cm⁻¹ is ascribed to stretching vibration of C=C, the band at 1384 cm⁻¹ due to the in-plane symmetric vibration of C-O-H bond, and the band at 1060 cm^{-1} is due to C–O stretching vibrations [28]. The band at 1300 cm⁻¹ is due to -C-N coupling [29]. The bands at 1063 cm⁻¹ and 1160 cm⁻¹ in PA-fullerenol composite spectrum are due to ester and aromatic ring (Ar-COO) interactions that result in reactions between fullerenol-OH and acyl chloride groups of PA [30]. This evidence substantiates chemical interactions of fullerenol with PA. In the FTIR spectra, due to



Fig. 3 FTIR spectra of PA, fullerenol, and PA-fullerenol composite

the C-O stretching vibrations and O-H in-plane deformations for tertiary alcohols, there were transition bands in the region of 1100–1170 cm⁻¹ and 1310–1410 cm⁻¹, respectively. Due to the absorption of C-C bond of fullerenol, there was a transition band in the region of $530-578 \text{ cm}^{-1}$.

Variations in PA layer thickness of TFC and FTFC membranes upon fullerenol loadings were determined by FTIR data with a standard method [23], using absorbance ratios of – CONH- and -SO₂- bands. According to Table 1, the PA layer thickness decreases with increasing fullerenol loadings up to 400 ppm and increases at 800 ppm-fullerenol loading. The membrane with the thinnest PA layer showed a marked reduction of mass transfer resistance leading to an improved water flux. This observation agreed with SEM and AFM analyses.

All TFC and FTFC membranes depict characteristic ridgeand-valley morphology because of MPD and TMC interactions (Fig. 4). The relevant patterns are leaf-like (characteristics of rough surfaces) and nodule-like structures (characteristics of smooth surfaces), respectively.

Table 1Amide/PSFintensity ratio of the TFCand FTFC membranes	Membrane ID	Intensity ratio (nm)
	TFC	0.86
	FTFC-1	0.73
	FTFC-2	0.63
	FTFC-4	0.59
	FTFC-8	0.68

Fig. 4 SEM images of surface morphologies of TFC and FTFC membranes



In the FTFC membrane series, the FTFC-1 surface was dominated by leaf-like structures giving rise to rough surfaces, whereas in FTFC-8 nodular-like structures were pronounced showing smooth surfaces. This observation could be attributed to the increment of the thickness of the skin layer of FTFC-8 by agglomeration of fullerenol when introduced to the PA layer. The rest of the membranes, including TFC, exhibited different proportions of leaf- and nodular-like structures giving rise to varying morphologies. This phenomenon confirmed the distribution of fullerenol throughout the topskin layer with minimum agglomeration. This scenario also suggested the proper formation of polyamide with the reaction of MPD and TMC together with fullerenol when fabricating membranes. The self-assembly of fullerenol onto the membrane surfaces was, therefore, pronounced through the hydrogen bonding interaction with hydroxyl functional groups in PA layer.

The cross-sectional morphology of TFC and FTFC membrane series across their depth is shown in Fig. 5. The SEM images of cross-sections depict that there are distinct morphologies of corrugated-like structures for TFC and FTFCs of different densities. With higher densities of fullerenol, the corrugated-like structure is pronounced in sandwiched form while the TFT membrane shows many voids. As in the case of FTIR data, however, the minute morphological variations of the SEM images upon fullerenol addition (up to 800 ppm) could not readily be observed due to limitations in measurements. Detailed variations of the membrane surfaces were thus obtained by AFM imaging.

Fig. 6 shows the three-dimensional AFM images of TFC and FTFC membranes. Table 2 displays the statistical data in terms of average surface roughness (R_a) and root mean squared roughness (R_q) for all membranes. AFM analysis also assessed the height of surface lumps that could be further explained as improved surface nodules.



Fig. 5 SEM images of crosssectional morphologies of TFC and FTFC membrane series



Fig. 6 AFM images of surface morphologies of TFC and FTFC membranes

When doubling the concentrations of fullerenol loadings, the roughness (R_a) of FTFC series first increased up to 400 ppm and then decreased. TFC membrane manifested sharp edges, whereas FTFC membranes possessed somewhat smooth edges (Fig. 6). These changes of the surface structure were in a good agreement with SEM images. The increment of surface roughness may have been due to the electronegativity of fullerenol, which would merely act as either acceptor or donor when it reacts with MPD and acyl chloride in TMC and the dynamic nature of the PA layer formation [21]. This phenomenon leads to higher water solubility with a reasonably high-water uptake rate during IP, besides the surface roughness escalated by lengthening the fullerenol loading in the MPD solution [31]. The root mean squared roughness values of TFC and FTFC membranes, suggested the presence of fullerenol-enhanced surface roughnesses. Formation of the thin PA layer yields denser surfaces of the skin-layer with thicker edges (Fig. 6). Further, it was seen that pore orifices became much narrower and more elongated. However, when

Surface roughness of TFC and FTFC membranes Table 2 Membrane ID R_a (nm) $R_q (\text{nm})$ TFC 74.10 ± 1.5 91.25 ± 3.32 FTFC-1 54.06 ± 3.9 67.25 ± 0.63 FTFC-2 79.50 ± 0.10 62.68 ± 3.6 FTFC-4 75.35 ± 2.6 94.85 ± 3.93 FTFC-8 54.50 ± 2.2 69.14 ± 3.18

excess solutes on the fullerenol are present, they tend to agglomerate in the interfacial region affecting the structural integrity of the top surface while reducing the water permeation flux [32]. Incorporation of fullerenol to the PA layer yielded the formation of broad pore orifices due to high polarity and fullerenol agglomeration in the ridges, increasing R_a and R_a . Also, the formation of H-bonds contributed to a more compact chain structure being present despite the concentrated loading.

Intrinsic separation properties of control TFC and FTFC membranes

The separation properties, A and B of TFC and FTFC membranes were summarized in Table 3. Fullerenol loading in active layer influenced the properties of the membranes and hence, altered the transport properties.

These results indicate that FTFC membranes exhibited significantly higher separation properties than TFC membrane;

Intrinsic transport properties of TFC and FTFC membranes Table 3

Membrane ID	A, LMHbar ⁻¹	<i>B</i> ,LMH	B/A, bar
TFC	1.23 ± 0.08	0.729 ± 0.03	0.59
FTFC-1	2.24 ± 0.06	0.685 ± 0.02	0.30
FTFC-2	2.88 ± 0.04	0.638 ± 0.02	0.22
FTFC-4	3.87 ± 0.02	0.590 ± 0.01	0.15
FTFC-8	2.36 ± 0.04	0.655 ± 0.03	0.28



Fig. 7 Water contact angle of TFC and FTFC membranes

the A values of FTFC membranes were much higher than that of TFC (higher than $1.14 \text{ Lm}^{-2} \text{ bar}^{-1}$). On the other hand, a high B value was recorded for TFC membrane $(0.797 \text{ Lm}^{-2} \text{ h}^{-1})$ while FTFCs showed lower values. The FTFC-4 manifested the highest A value (3.87 L m⁻² bar⁻¹) and the lowest B value (0.59 L m⁻² h⁻¹), indicating that it gives the excellent performances with the highest water flux and the lowest salt flux. These results emphasize that the incorporation of fullerenol leads to the enhancement of the passage of water via the interfacial gaps between fullerenol and polyamide, which is attributed to the increasing hydrophilicity due to -OH groups capable of attracting water molecules and facilitating their passage effectively due to the existence of fullerenol in the top layer of the membranes [32]. It is also noted that the better performance of fullerenol was observed for its optimum volumetric density of functional group (hydroxyl group), which is between 24 and 28 to make it more hydrophilic. However, higher loading of fullerenol (800 ppm) may have hindered some of these hydroxyl groups due to agglomeration, yielding somewhat poor performances.

As shown in Table 3, the intrinsic selectivity (B/A) factor directly indicates the FO membrane selectivity. Compared to

the TFC membrane, FTFC membrane series recorded lower B/A value, which led to lower solute reverse diffusion into the feed water. With the initial increment of fullerenol loading, the FTFC membranes manifested higher salt rejection. However, a further increase in fullerenol loading (800 ppm) showed poor salt rejection. This phenomenon could be attributed to the fullerenol agglomeration in the IP process.

The observed trends in water permeability of FTFC membranes were also elucidated in terms of the water contact angle. As shown in Fig. 7, it agreed with published data [14, 17, 20] that the water contact angle of TFC membrane was about 87.64°; however, it was reduced sharply to 68.61° with the fullerenol loading. As shown in Fig. 8, the low water contact angle values indicate that the water spreads on the surface of the membrane while high water contact angle values show poor spreading. Fig. 8 depicts that FTFC membranes have higher hydrophilicity than the pristine TFC membrane. The abundance of oxygen-rich functional groups such as -OH, enhanced the hydrophilicity, reducing the contact angle values. Membranes with higher values of hydrophilicity represented by the presence of active functional groups could form hydrogen bonds with the aqueous solution in contact. Moreover, greater charge density on membrane surface due to –OH group warrants greater membrane hydrophilicity [33]. It was also noted that permeability trends of pure water could not solely be accounted for the contact angle measurements. Our results justified that the FTFC membranes yielded greater water permeability when compared with the TFC membrane did and therefore, exhibited excellent FO performance.

FO performance with fullerenol loading

The FTFC membranes were evaluated under both PRO and FO modes using DI water and 1 M NaCl solution. The TFC and FTFC membranes exhibited high water flux in both AL-DS (active layer facing the DS) and AL-FS (active layer facing the FS) orientations for both PRO and FO modes as shown in Fig. 9.

Compared to AL-FS orientation, AL-DS showed higher water flux (ranging from 14.26–26.1 LMH in AL-FS to 31.35–48.66 LMH in AL-DS). This increase in flux could



Fig. 8 Images of water contact angle of (a) TFC, (b) FTFC-1, (c) FTFC-2, (d) FTFC-4, (e) FTFC-8 membranes

be attributed to the internal concentration polarization (ICP) effect when the active layer faces the FS, as the water passes under low resistance across the channels of the porous substrate due to the pressure applied.

Interestingly, FTFC membranes exhibited excellent water flux and somewhat better solute rejection when compared with those of TFC membrane. Water flux of FTFC-4 membrane was estimated to be 26.1 LMH, which is 83.03% higher than that of the TFC membrane. The incorporation of fullerenol in the thin selective layer increased the surface hydrophilicity of the membranes due to the presence of -OH group so that it could attract water molecules into the membrane matrix and facilitated their transport through the membrane. FTFC membranes possessed the highest water flux due to their controllable nano-level passages created by randomlyoriented fullerenol [21]. Moreover, the assimilation of fullerenol reduces the thickness of the PA layer, contributing to a lower transport resistance and an improved water flux [34]. In the case of a solute diffusion, the solute flux is inversely proportional to the salt rejection coefficient [8]. The lower reverse solute flux is, therefore, accredited to high solute rejection. Initially, in our study, the reverse salt flux decreased from FTFC-1 to FTFC-4 membranes and increased in FTFC-8 (Figs. 6b, c). Therefore, the fullerenol seems to have a favorable influence on the salt rejection of TFC membranes.

As shown in Fig. 9, FTFC-4 and FTFC-8 were evaluated in terms of osmotic water flux (J_v) , reverse salt flux (J_s) , and specific salt flux (J_s/J_w) , respectively. Figure 10 demonstrates the effect of DS concentration on pure water flux and the same on the reverse solute flux. These results indicate the similar trends with the increase in DS concentration in both FO and PRO modes. The increment of DS concentration positively affects the water flux due to a large osmotic pressure developed by high concentrated salt molecules in DS.

Evaluation of antifouling performance of TFC and FTFC membranes

Membrane fouling is an inevitable phenomenon in the FO process, which would adversely affect the membrane degradation, chemical cleaning that lead to a decline of flux and increment of operation and maintenance costs [35]. Therefore, careful attention focused on the improvement of the antifouling capability of membranes, which was investigated by cyclic filtration tests run with the TFC and FTFC membranes under FO mode (Fig. 11). Experiments were carried out with the presence of SA as a foulant containing calcium ions to evaluate the behavior of foulant on the membrane active layer.

During the initial stages, the permeation flux of the TFC and FTFC membranes decreased rapidly due to the direct attachment of protein molecules [36]. However, as displayed in the Fig. 11, the normalized flux was declined for FTFC membranes comparatively slower compared to that of TFC



Fig. 9 (a) Water flux (b) reverse salt flux (c) specific salt flux of TFC and FTFC membranes

membrane. The highest normalized flux after two filtration cycles was observed for FTFC-8. This phenomenon could be attributed to the formation of a thin alginate layer on the surface of FTFC membranes due to their high hydrophilicity and low surface roughness [37]. Figure 12 shows the quantitative reduction of water flux (sodium alginate) over 18 h of operation. As shown in Figs. 11 and 12, the flux was 7 L m⁻² h⁻¹ for the pristine TFC membrane, whereas much higher values for the membranes containing fullerenol



Fig. 10 Water flux and reverse salt flux of FTFC-4 and FTFC-8

(21 L m⁻² h⁻¹ for FTFC-8 and 21.5 L m⁻² h⁻¹ for FTFC-4 membranes). This observation confirms the superior effect of fullerenol in improving the antifouling properties of modified membranes compared with control TFC membrane without fullerenol. In addition, FTFC-8 membrane reached the stable flux, achieving the equilibrium of desorption and adsorption mechanisms of the protein molecules with the membrane active surface. The low surface roughness and low contact angle obtained for FTFC-8 demonstrated high antifouling performances. These roughness characteristics could strongly affect the adsorption/desorption of foulants on the surface. Accordingly, by decreasing the surface roughness of a hydrophilic membrane, the trapping of contaminants in the valleys and adhesion at the top positions of the active layer is restricted [37]. Moreover, FTFC membranes reached a stable flux, which indicates the equilibrium of sorption of the protein molecules to the membrane surface during the period of the run.



Fig. 11 Forward osmosis fouling test of TFC and FTFC membranes (2 M NaCl solution and synthetic wastewater were used as DS and FS, respectively; the $J_w/J_{w,o}$ ratio was taken with a 10-min. Intervals during the fouling test)



Fig. 12 Foulant (sodium alginate) solution flux of TFC and FTFC membranes

To investigate the antifouling propensity of membranes, the flux recovery ratio (*FRR*, %), and flux reduction ratio (*FR*, %) of the membranes were compared (Fig. 13).

The TFC membrane possessed the lowest *FRR* value of 53.4%, while the *FRR* values of the FTFC-4 and FTFC-8 membranes increased up to 87.19 and 97.25%, respectively and the best antifouling performance showed by FTFC-8 membrane. This observation confirmed the superior effect of fullerenol in improving antifouling properties of membranes. This phenomenon was attributed to the increased surface coverage of the hydrophilic –OH group of the membrane resulting in a stable hydration layer. In the case of membrane filtration, adsorption of protein molecules was observed on the surface of the membrane or interfacial pores so that complete restoration was difficult to be achieved by physical washing [38]. However, all FTFC membranes



Fig. 13 The variation of flux over time for a fouling episode (*Jw/Jw,o* ratio was taken before and after cleaning of fouling episode)

possessed higher restoration affinity compared to that of TFC membranes, which suggests that the TFC membrane is affected more by irreversible physical fouling due to its relative hydrophobic nature [39]. However, there was an increase in hydrophilicity of FTFC membranes, which resulted in higher fouling resistance because SA, is hydrophobic. This phenomenon could be understood by increasing the membrane surface hydrophilicity by introducing high volumetric density of –OH group possessed by FTFC membranes, which could then provide better antifouling properties.

Foulants are negatively charged so that when the negative charge on the membrane surface is increased, a strong electrostatic repulsion force could be generated, which will then lead to an enhanced antifouling performance [40]. Accordingly, FTFC membranes rich in -OH group are more negatively charged than the ones in TFC membrane, resulting in higher reversible fouling. Another governing factor is the surface tension/interfacial free energy that is recorded to be high for hydrophilic surfaces and low for hydrophobic surfaces [41]. Hydrophobic particles, therefore, influence to form colloidal particles due to low interfacial free energy. Thus, fouling could be reduced by modifying membranes to become more hydrophilic, which is attributed to a hydroxyl group. The improvement of membrane hydrophilicity (contact angle) reduces membrane fouling by influencing the surface adsorption characteristics of the membrane. Also, the protein adsorption onto the membrane is affected by van der Waals forces, hydrogen bonding, and electrostatic forces [38, 40, 42]. Strongly-bound water molecules could attach to the hydrophilic surface through hydrogen bonding hindering progressively the adsorption of foulants, which is influenced by increased hydrogen bonding force caused by ionized hydroxyl groups on the FTFC membrane surfaces with the removal of foulants as a loose cake layer. Meanwhile, the high electrostatic repulsion forces inhibit protein absorption and also remove the attached foulants.

Conclusions

A novel fullerenol with the molecular structure being $C_{60}(OH)_{24-28}$ was incorporated with TFC membranes by IP process. Introduction of fullerenol to the PA skin-layer yielded an increase of pure water flux and a decrease of salt rejection. The thickness of the PA layer was decreased from 0.86 nm to 0.59 nm when fullerenol concentration reached 400 ppm, which is one of the reasons for the improved pure water flux of FTFC membranes. AFM studies revealed that fullerenol incorporation into the PA skin-layer warranted a significant increase of surface roughness parameters of the membranes. The FTFC membranes possessed surfaces with high surface roughness. The FTFC-4 membrane exhibited a water flux of

26.1 LMH, which is 83.03% higher than that of TFC membrane with the specific reverse salt flux of 0.18 g/L using 1 M sodium chloride draw solution against deionized water in FO mode. FTFC membranes were found to have superior antifouling performance compared to that of TFC membrane.

Acknowledgements This research was funded by the National Natural Science Foundation of China (Grant Nos. 51503205 and 51478452) and the National Research Council of Sri Lanka (Grant No. NRC-TO-16-015).

Nomenclature *A*, water permeability; *AL-DS*, active layer facing draw solution; *AL-FS*, active layer facing feed solution; *A_m*, effective membrane area; *B*, salt permeability; *CNTs*, carbon nanotubes; *V_b* volume of feed solution; *C_b* draw solute concentration; *FO*, forward osmosis; *FR%*, flux reduction ratio; *FRR%*, flux recovery ratio; *FTFC*, fullerenol-incorporated thin-film composite; *GO*, graphene oxide; *IP*, interfacial polymerization; *J_c*, final water flux after the physical cleaning; *J_o*, initial flux; *J_s*, reverse salt flux; *J_s/J_v* specific salt flux; *J_b* flux after accelerated fouling test; *J_v* water flux; *PRO*, pressure retarded osmosis; *PSF*, polysulfone; *TFC*, thin-film composite; Δt , test time; ΔV , volume change

References

- Mekonnen MM, Gerbens-Leenes PW, Hoekstra AY (2016) Future electricity: the challenge of reducing both carbon and water footprint. Sci Total Environ 569–570:1282–1288
- Wang Y-N, Goh K, Li X, Setiawan L, Wang R (2017) Membranes and processes for forward osmosis-based desalination: recent advances and future prospects. Desalination
- Singh N, Petrinic I, Hélix-Nielsen CH, Basu S, Balakrishnan M (2018) Concentrating molasses distillery wastewater using biomimetic forward osmosis (FO) membranes. Water Res 130:271–280
- Yip NY, Tiraferri A, Phillip WA, Schiffman JD, Hoover LA, Kim YC, Elimelech M (2011) Thin-film composite pressure retarded osmosis membranes for sustainable power generation from salinity gradients. Environ Sci Technol 45:4360– 4369
- Yang Q, Wang KY, Chung T-S (2009) A novel dual-layer forward osmosis membrane for protein enrichment and concentration. Sep Purif Technol 69:269–274
- Sant'Anna V, Marczak LDF, Tessaro IC (2012) Membrane concentration of liquid foods by forward osmosis: process and quality view. J Food Eng 111:483–489
- Qasim M, Darwish NA, Sarp S, Hilal N (2015) Water desalination by forward (direct) osmosis phenomenon: a comprehensive review. Desalination 374:47–69
- Cath TY, Childress AE, Elimelech M (2006) Forward osmosis: principles, applications, and recent developments. J Membr Sci 281:70–87
- Li D, Yan Y, Wang H (2016) Recent advances in polymer and polymer composite membranes for reverse and forward osmosis processes. Prog Polym Sci 61:104–155
- Zhang Y, Miao X, Pan G, Shi H, Yan H, Xu J, Guo M, Li S, Zhang Y, Liu Y (2017) Highly improved permeation property of thin-filmcomposite polyamide membrane for water desalination. J Polym Res 24:5
- Zhang X, Shen L, Lang W-Z, Wang Y (2017) Improved performance of thin-film composite membrane with PVDF/PFSA substrate for forward osmosis process. J Membr Sci 535:188–199

- Ren J, O'Grady B, deJesus G, McCutcheon JR (2016) Sulfonated polysulfone supported high performance thin film composite membranes for forward osmosis. Polymer 103:486–497
- Wang X, Wang X, Xiao P, Li J, Tian E, Zhao Y, Ren Y (2016) High water permeable free-standing cellulose triacetate/graphene oxide membrane with enhanced antibiofouling and mechanical properties for forward osmosis. Colloids and Surfaces A: Physicochem Eng A spects 508:327–335
- Shen L, Xiong S, Wang Y (2016) Graphene oxide incorporated thin-film composite membranes for forward osmosis applications. Chem Eng Sci 143:194–205
- Dong H, Zhao L, Zhang L, Chen H, Gao C, Winston HWS (2015) High-flux reverse osmosis membranes incorporated with NaY zeolite nano-particles for brackish water desalination. J Membr Sci 476:373–383
- Alam J, Alhoshan M, Dass LA, Shukla AK, Muthumareeswaran MR, Hussain M, Aldwayyan AS (2016) Atomic layer deposition of TiO₂ film on a polyethersulfone membrane: separation applications. J Polym Res 23:183
- Amini M, Jahanshahi M, Rahimpour A (2013) Synthesis of novel thin film nanocomposite (TFN) forward osmosis membranes using functionalized multi-walled carbon nanotubes. J Membr Sci 435: 233–241
- Penkova AV, Acquah SFA, Dmitrenko ME, Sokolova MP, Mikhailova ME, Polyakov ES, Ermakov SS, Markelov DA, Roizard D (2016) Improvement of pervaporation PVA membranes by the controlled incorporation of fullerenol nano-particles. Mater Des 96:416–423
- Penkova AV, Dmitrenko ME, Ermakov SS, Toikka AM, Roizard D (2017) Novel green PVA-fullerenol mixed matrix supported membranes for separating water-THF mixtures by pervaporation. Environ Sci Pollut Res 25(21):20354–20362
- Plisko TV, Liubimova AS, Bildyukevich AV, Penkova AV, Dmitrenko ME, Mikhailovskii VY, Melnikova GB, Semenov KN, Doroshkevich NV, Kuzminova AI (2018) Fabrication and characterization of polyamide-fullerenol thin film nanocomposite hollow fiber membranes with enhanced antifouling performance. J Membr Sci 551:20–36
- 21. Kramer CN (2007) Fullerene research advances. Nova Science Publishers Inc, New York, p 307
- Ge Q, Ding L, Wu T, Xu G, Yang F, Xiang M (2018) Effect of surfactant on morphology and pore size of polysulfone membrane. J Polym Res 25:21
- Zhao Y, Wang X, Ren Y, Pei D (2017) Mesh-embedded Polysulfone/Sulfonated Polysulfone supported thin film composite membranes for forward osmosis. Appl Mater Interfaces 10:2918– 2928
- Zhao Y, Ren Y, Wang X, Xiao P, Tian E, Wang X, Li J (2016) An initial study of EDTA complex based draw solutes in forward osmosis process. Desalination 378:28–36
- Tiraferri A, Yip NY, Straub AP, Castrillon SRV, Elimelech M (2013) A method for the simultaneous determination of transport and structural parameters of forward osmosis membranes. J Membr Sci 444:523–538

- Fulmer PA, Wynne JH (2011) Development of broad-spectrum antimicrobial latexpaint surfaces employing active amphiphilic compounds. ACS Appl Mater Interfaces 3:2878–2884
- 27. Branca C, D'Angelo G, Crupi C, Khouzami K, Rifici S, Ruello G, Wanderlingh U (2016) Role of the OH and NH vibrational groups in polysaccharide-nanocomposite interactions: a FTIR-ATR study on chitosan and chitosan/clay films. Polymer 99:614–622
- Saviello D, Toniolo L, Goidanich S, Casadio F (2016) Noninvasive identification of plastic materials in museum collections with portable FTIR reflectance spectroscopy: reference database and practical applications. Microchem J 124:868–877
- Yang X, Zhen M, Li G, Liu X, Wang X, Shu C, Li J, Wang C (2013) Preparation of Pd-decorated fullerenols on carbon nanotubes with excellent electrocatalytic properties in alkaline media. J Mater Chem A 1:8105–8110
- Nakanishi K (1962) Infrared absorption spectroscopy. Practical Holden-day Inc and Nankodo company. Tokyo, San Francisco, p 233
- Tasaki K, Gasa J, Wang H, DeSousa R (2007) Fabrication and characterization of fullerene-Nafion composite membranes. Polymer 48:4438–4448
- Zhao C, Xu X, Chen J, Yang F (2013) Effect of graphene oxide concentration on the morphologies and antifouling properties of PVDF ultrafiltration membranes. J Environ Chem Eng 1:349–354
- Tiraferri A, Kang Y, Giannelis EP, Elimelech M (2012) Highly hydrophilic thin-film composite forward osmosis membranes functionalized with surface-tailored nano-particles. ACS Appl Mater Interfaces 4:5044–5053
- Hu M, Mi B (2013) Enabling graphene oxide nanosheets as water separation membranes. Environ SciTechnol 47:3715–3723
- Jhaveri JH, Murthy ZVP (2016) A comprehensive review on antifouling nanocomposite membranes for pressure driven membrane separation processes. Desalination 379:137–154
- Ayyaru S, Ahn YH (2017) Application of sulfonic acid group functionalized graphene oxide to improve hydrophilicity, permeability, and antifouling of PVDF nano-composite ultrafiltration membranes. J Membr Sci 525:210–219
- Rong G, Zhou D, Pang J (2018) Preparation of high-performance antifouling polyphenylsulfone ultrafiltration membrane by the addition of sulfonated polyaniline. J Polym Res 25:66
- Wang P, Ma J, Wang Z, Shi F, Liu Q (2012) Enhanced separation performance of PVDF/PVP-g-MMT Nanocomposite ultrafiltration membrane based on the NVP-grafted polymerization modification of Montmorillonite (MMT). Langmuir 28:4776–4786
- Kim DG, Kang H, Han S, Lee J-C (2012) The increase of antifouling properties of ultrafiltration membrane coated by star-shaped polymers. J Mater Chem 22:8654
- Vatanpoura V, Madaenia SS, Moradian BR, Zinadinia S, Astinchap B (2011) Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite. J Membr Sci 375: 284–294
- Bogler A, Lin S, Bar-Zeev E (2017) Biofouling of membrane distillation, forward osmosis and pressure retarded osmosis: principles, impacts and future directions. J Membr Sci 542:378–398
- 42. Dejardin P (2006) Proteins at solid–liquid interfaces. Springer-Verlag, Berlin