Preparation of graphene oxide incorporated polyamide thin-film composite membranes for PPCPs removal

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Abstract. Incorporating nano-materials in thin-film composite (TFC) membranes has been considered to be an approach to achieve higher membrane performance in various water treatment processes. This study investigated the rejection efficiency of three target compounds, i.e., reserpine, norfloxacin and tetracycline hydrochloride, by TFC membranes with different graphene oxide proportions. Graphene oxide (GO) was incorporated into the polyamide active layer of a TFC membrane via an interfacial polymerization (IP) reaction. The TFC membranes were characterized with FTIR, FE-SEM, AFM; in addition, the water contact angle measurements as well as the permeation and separation performance were evaluated. The prepared GO-TFC membranes exhibited a much higher flux (3.11 ± 0.04 L/m2·h·bar) than the pristine TFC membranes (2.12 ± 0.05L/m2·h·bar) without sacrificing their foulant rejection abilities. At the same time, the GO-modified membrane appeared to be less sensitive to pH changes than the pure TFC membrane. A significant improvement in the anti-fouling property of the membrane was observed, which was ascribed to the favorable change in the membrane's hydrophilicity, surface morphology and surface charge through the addition of an appropriate amount of GO. This study predominantly improved the understanding of the different PA/GO membranes and outlined improved industrial applications of such membranes in the future.

Keywords: graphene oxide; polyamide membrane; thin-film composite; interfacial polymerization; PPCPs

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are intensively used for personal health or cosmetic reasons or even partially for veterinary purposes (Díaz-Cruz and Barceló 2004). The release of PPCPs into the aquatic environment is a potential risk to human health. Since the late 1980s, the occurrence of PPCPs in different environmental matrices, such as domestic effluents, ground water and wastewater, has been reported in many studies (Gros *et al.* 2012, Schultz *et al.* 2010, Ternes 1998). Three PPCPs: Reserpine, norfloxacin and tetracycline hydrochloride are proposed to be of widespread use as an analgesic/antipyretic, as a medication of antibacterial and as an antibiotic, respectively (Chang *et al.* 2012, El-Gendi *et al.* 2016).

Thin-film composite (TFC) membranes have been used as attractive materials for water treatment processes to remove both conventional and emerging contaminants (Rahimpour *et al.* 2010, Sun *et al.* 2012). A typical TFC membrane is made up of a thin selective polymeric layer (i.e., polyamide) on top of a micro-porous support substrate, which is usually fabricated with an interfacial polymerization (IP) reaction (Song *et al.* 2005, Stillman *et al.* 2014, Verissimo *et al.* 2005, Widjojo *et al.* 2011). Recently, nanofiltration (NF) and reverse osmosis (RO)

processes widely employ TFC membranes for their good separation performances and wide pH tolerance ranges and they have been considered effective for the removal of organic micro-pollutants, such as pharmaceutically active compounds (PhACs), PPCPs and endocrine disrupting compounds (EDCs), from aquatic environments (Comerton *et al.* 2008, Kimura *et al.* 2003, Ozaki *et al.* 2008, Radjenovi *et al.* 2008, Tao *et al.* 2015, Verliefde *et al.* 2009). For its inherent comparative advantage, including low power consumption and higher flux, NF is extensively used in many water treatment and purification plants instead of reverse osmosis. The retention of pharmaceutical substances by NF membranes is affected by the physicochemical properties of the membrane characteristics (surface charge, pore size, hydrophilicity), the organic solute (molecular weight, charge), the solution chemistry (ionic environment, pH and concentration) and the process conditions (pressure, permeation rate, cross-flow velocity/stirring rate) (Zazouli *et al.* 2009). Yoon *et al.* suggested that more polar, less volatile and less hydrophobic EDC/PPCPs had relatively low retentions owing to the hydrophobic adsorption governing the retention by NF and UF. Meanwhile, research investigating the removal of twenty-seven EDC/PPCP compounds showed that NF membranes retained EDC/PPCPs better than the UF membranes, implying that retention is affected by the membrane pore size (Mirfarah *et al.* 2017, Yoon *et al.* 2007). The research of Kimura *et al.* suggested that charged compounds were rejected to a great extent (i.e., > 90%) while the rejection of non-charged compounds was found to be influenced mainly by the size of the

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compounds, which indicated that electrostatic interaction played an important role in explaining the membrane rejection rates for negatively charged compounds (Kimura *et al.* 2003, Lin and Lee 2014). Chang *et al.* investigated two membranes fouled with humic acid and humic acid/Ca2+ for PPCPs removal showing that the rejection efficiency of small and neutral-charged target compounds increased in the presence of humic acid and calcium ions as a result of an extra hindrance layer provided by the foulants; meanwhile, the rejection efficiency of larger target compounds decreased due to fouling of the membranes (Chang *et al.* 2012, Verliefde *et al.* 2009).

However, a major problem associated with TFC membranes is fouling, which has restricted their water treatment applications (Gu *et al.* 2012, Mi and Elimelech 2010, Shin *et al.* 2011). At the same time, concerns surrounding their relatively low water flux as well as energy efficiency has also impeded their further advancement in industrial implementation. To solve this problem, modifying TFC membranes with nano-materials (Al-Hobaib *et al.* 2015, Tiwari *et al.* 2015) is a promising approach toward improving the performances of the membranes (i.e., adding GO) (Xia *et al.* 2015). Graphene oxide nanosheets is made of single two-dimensional carbon sheets and has been considered a super material in recent years (Mi 2014). Recently, many studies have described the water permeability of graphene oxide membranes (Hu and Mi 2013, Joshi *et al.* 2014, Nair *et al.* 2012), creating a new era for its application in water desalination and the removal of organic foulants (Filice *et al.* 2015, Hegab and Zou 2015, Liang *et al.* 2015, Nicolaï *et al.* 2014, Xia and Ni 2015, Yeh *et al.* 2013). In particular, modified membranes have an enormous potential to achieve superior chemical stability, strong hydrophilicity and excellent anti-fouling properties due to the oxygen-containing functional groups in graphene oxide (Dikin *et al.* 2007, Dreyer *et al.* 2010, J. Lee *et al.* 2013, Zinadini *et al.* 2014).

Many benefits of adding GO in the active top layer of the TFC membrane compared to using a pure TFC membrane have been highlighted in some of the previous work, suggesting that higher flux and higher anti-fouling abilities were achieved for GO-modified TFC membranes (Xia *et al.* 2015). However, few studies have involved the use of GO in TFC nanofiltration membranes for PPCP removal.

In this study, GO-modified TFC membranes with different GO loadings were prepared via an IP process on polysulfone (PSf) UF membrane substrates for the removal of three target compounds. Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), atomic force microscope (AFM) and water contact angle tests were utilized to evaluate the composition, structure and hydrophilicity of the membranes. The water permeation performance, foulant removal efficiency and anti-fouling properties of these membranes were systematically investigated at different pHs, ionic strengths and fouling conditions.

2. Materials and methods

2.1 Materials

Graphene oxide nanosheets were purchased from Sigma Aldrich. The PSf UF membrane (molecular weight cut-off: 100 kDa) was obtained from XINLIMO Tech Co., Ltd., China. 1, 3-phenylene diamine (MPD) with a 99% purity (supplied by Aladdin) and 1, 3, 5-benzenetricarbonyl trichloride (TMC) (purchased from Sigma Aldrich) were used as interfacial reaction monomers. N-hexane, used as the solvent, was purchased from Sinopharm Chemical Reagent Co., Ltd, China. Deionized (DI) water (18.2 MΩ cm at 25°C) was used in the solution preparation and experiment washing and was provided by a water purification system (Milli-Q, Millipore Corporation, U.S.A). The reserpine, norfloxacin and tetracycline hydrochloride purchased from Aladdin were selected as the target PPCPs compounds. The detailed properties of these three compounds are shown in Table 1.

2.2 Fabrication of the membranes

TFC membranes with PA and GO in the top layer and a PSf UF membrane as the substrate were prepared through an interfacial polymerization reaction. Prior to use, GO nanosheets were dispersed in deionized water by sonication for 20 min to form a 0.1 wt% suspension solution. The PSf UF membranes were immersed in DI water for 24 h before use. Different contents of the 0.1 wt% graphene oxide suspension solution were added into a 2% (w/v) MPD aqueous solution to form solutions with GO (0, 0.004, 0.008 and 0.016wt%). The PSf UF membrane was placed in a frame to allow for coating only on the top surface. An aqueous solution containing MPD/GO with different ratios was poured onto the membrane and sonicated for 2 min and then, the excess solution was removed from the membrane surface using a rubber roller. After drying in air for over 1 min, a 0.1% (w/v) TMC solution in N-hexane was poured onto the membrane and left for 1 min to form the PA layer via interfacial polymerization. The unreacted MPD and TMC were removed from the membrane surface by rinsing the membrane with N-hexane. The membrane was then soaked in a 0.2% (w/v) sodium carbonate solution for 5 min and was thermally treated in a vacuum oven at 60°C for 8 min. All membrane samples were stored in a DI water bath prior to further testing.

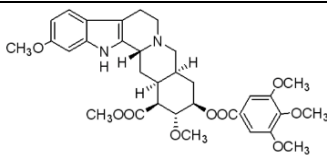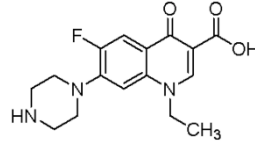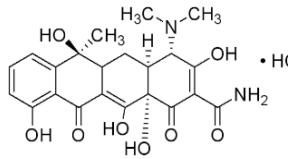### 2.3 Characterizations of the membranes

2.3.1 Morphology and microstructure

The top surface and cross-sectional micromorphology of the prepared membranes were observed by field-emission scanning electron microscope (FE-SEM, Ultra 55, Carl Zeiss Company, Germany). FE-SEM was operated under standard high-vacuum conditions at 5.00 kV and the samples were photographed to obtain micromorphology images of each membrane. The samples were air-dried and sputtered with a thin gold layer to become electrically conductive before analysis.

2.3.2 Chemistry properties

The surface chemistry and composition of the TFC were analyzed by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet iS5, Thermo

Table 1 Characteristics of the organic compounds

Target compound	CAS Number	Molecular formula	Chemical structural formula	Molecular weight
Reserpine	50-55-5	$C_{33}H_{40}N_2O_9$		608.68
Norfloxacin	70458-96-7	$C_{16}H_{18}FN_3O_3$		319.33
Tetracycline hydrochloride	64-75-5	$C_{22}H_{24}N_2O_8$ HCl		480.90

Fisher Scientific Inc., U.S.A). The ATR-FTIR analyses were carried out using a Ge crystal as the background in a wavenumber range from 800 - 4000 cm^{-1}.

2.3.3 Surface hydrophobicity

The dynamic water contact angle was measured using an optical tension meter (Attension Theta Lite, Biolin Scientific Co. Ltd., Sweden) to signify the surface hydrophilicity of the membranes. A deionized water droplet from a micro syringe with a stainless steel needle was dropped onto the smooth, flat and dry membrane surface. A reliable contact angle value was acquired for each membrane by averaging 5 measurements from different positions on the membrane surface.

2.3.4 Surface carboxyl group density

The surface carboxyl group density of the TFC membrane polyamide surfaces was quantified via a Toluidine Blue (TBO) technique developed by Tiraferri *et al.* (Tiraferri and Elimelech 2012). Briefly, to expose only the active layer of the TFC membrane, the support surface was prepared for sealing with waterproof tape. Then, the active layer of the TFC membrane, in contact with a freshly prepared solution of TBO (2 mM) and NaOH (pH 11), reacted with positively charged TBO molecules to deprotonate the carboxylic acid groups on the polyamide surface. The membrane was rinsed with a dye-free NaOH solution (pH 11) to remove any unbound dye molecules and subsequently immersed in a NaCl solution at pH 2 to elute the bonded TBO dye from the polyamide surface. An ultraviolet spectrophotometer at a wavelength of 630 nm was used to measure the absorbance of the eluent to determine the surface carboxyl group density.

2.4 Membrane filtration experiments

The filtration experiments were performed with a nano-filtration cross-flow system using a solution of the three target organic compounds that are shown in Table 1. The cross-flow membrane cell was custom built with an effective membrane area of 46.07 cm^2. The schematic representation of the experimental set-up is shown in Fig. 1.

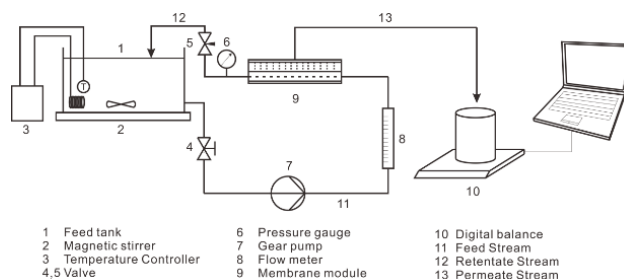|		
1 Feed tank	6 Pressure gauge	10 Digital balance
2 Magnetic stirrer	7 Gear pump	11 Feed Stream
3 Temperature Controller	8 Flow meter	12 Retentate Stream
4,5 Valve	9 Membrane module	13 Permeate Stream

Fig. 1 Schematic representation of the bench-scale NF set-up

A 3 L vessel was used as the feed tank and the feed solution was pumped into the membrane module via a gear pump (Longer Pump, WT3000-1JB). An aqueous 2000 ppmNaCl solution was used as the feed solution for the desalination study and the experiments were carried out at 6 bar gauge and ambient temperature. The membranes were compacted at 6 bars with a feed solution of DI water for 1 h to obtain a stable flux. The flux was calculated using the following Eq. (1)

$$J = \frac{V}{S \times t} \tag{1}$$

Where J is the flux (L m^{-2}h^{-1}), V is the permeate volume (L), S is the membrane effective area (m^2) and t is the time (h).

2.5 Analysis of the permeate water samples

The concentration of the target compounds was analyzed with ultra-performance liquid chromatography (ACQUITY UPLC, Waters Corporation, U.S.A) equipped with an ultraviolet detector and fluorescence detector. The mobile phase consisted of a mixture of acetonitrile and water acidified with 0.1% formic acid. The wavelength was 268 nm for norfloxacin and tetracycline and E_x 280 nm and E_m 360 nm for reserpine. The chromatographic column temperature was 35°C and the sample temperature was 30°C.

3. Results and discussion

Four series of TFC membranes with different GO loadings in the PA active layer (0, 0.004, 0.008 and 0.016wt%) were prepared in this study via the interfacial polymerization reaction on top of commercial PSf UF membranes and these samples were labeled as TFC, 4-GO-TFC, 8-GO-TFC and 16-GO-TFC, respectively.

3.1 Membrane characterization

Fig. 2 presents a comparison of the FTIR spectra of the PSf, TFC and GO-modified TFC membranes (ranging from 4000 cm^{-1} to 800 cm^{-1}). The characteristic peaks (1663,1609 and 1541 cm^{-1}) of polyamide formed by MPD and TMC appeared conspicuously with strong intensities (Oh *et al.* 2001, Tang *et al.* 2009a). The peak at 1663 cm^{-1}, which can be assigned to the amide I band, was attributed to the C=O stretching, C-N stretching and C-C-N deformation vibration in a secondary amide group (Kwon and Leckie 2006, Skrovanek *et al.* 1985). The amide II band (1541 cm^{-1}) was representative of the N-H in-plane bending and N-C stretching vibration of a -CO-NH-group (Kwon and Leckie 2006). The peak at 1609 cm^{-1} was associated with aromatic amide, which had been previously assigned to the N-H deformation vibration (Kwon and Leckie 2006) and C=C ring stretching vibration. Fig. 2 shows an enhancement in absorbance at 1663 cm^{-1} for the GO-modified TFC membranes, confirming that the formation of some new amide linkages of the -COOH group of GO reacted with the -NH2 group of MPD, further suggesting the incorporation of GO into the polyamide structure during interfacial polymerization (Bano *et al.* 2015). Compared to the PA membrane without GO, the peak at 3367 cm^{-1} for the GO-modified PA membrane was more intense, which is mainly ascribed to the hydroxyl stretching vibration. With the presence of hydroxyl groups, the improved hydrophilicity of the membrane is assumed with the addition of GO, which was later confirmed with the results of the water filtration tests and water contact angle measurements.

A higher contact angle is related to the relatively hydrophobic nature of the polyamide TFC membranes. Table 2 shows that the contact angle decreased with increasing GO content, which suggests the hydrophilicity increased. The contact angle was the smallest at 8-GO-TFC (57.99 ± 0.89°) at 4-GO-TFC and 16-GO-TFC, the contact angles were consistently larger. Meanwhile, the 8-GO-TFC membrane appeared to have a higher carboxyl group density value (22.96 ± 3.66 nm^{-2} vs. 19.24 ± 6.17 nm^{-2}) compared to the TFC membrane, which indicated that the GO-modified TFC membrane exhibited a higher hydrophilicity again. The presence of oxygen-containing functional groups in GO is thought to promote hydrophilicity in the membrane, which in turn is expected to result in greater water flux. Nevertheless, it must be noted that excessive loading of GO leads to agglomeration on the surface, compromising the structural integrity of the top surface and reducing the water permeation flux (Xia *et al.* 2015).The carboxyl or hydroxyl groups in GO can interact with the acylchloride in TMC and then form anhydride or ester bond during IP process. It was reported that GO nanosheets was cross-linked by TMC. The aggregation of the GO particles might affect the reaction between TMC and GO, thus impact the membrane
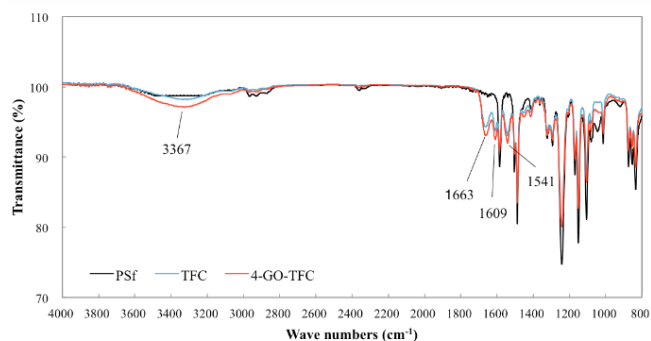

Fig. 2 FTIR spectra of PSf and TFC membranes

Table 2 The water contact angles and flux of the pure PA TFC and GO-modified TFC membranes

| | Pure water | | Desalination | |
	Flux (L/m2·h·bar)	Contact angle (deg)	Flux (L/m2·h·bar)	Rejection
TFC	2.12±0.05	71.63±0.67	1.46±0.04	81.30%
4-GO-TFC	2.34±0.04	62.55±0.75	1.63±0.03	62.63%
8-GO-TFC	3.11±0.04	57.99±0.89	2.22±0.04	52.83%
16-GO-TFC	2.54±0.03	62.64±0.63	1.87±0.02	64.16%

hydrophilicity. That might explain the higher contact angle and lower flux of 16-GO-TFC compared with 8-GO-TFC.

The surface morphology and surface roughness of the pure PA TFC and GO-modified TFC membranes were analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surface and cross-sectional SEM images of the pure PA TFC and GO-modified TFC membranes were shown in Figs. 3a-3f. Both the pure PA TFC and GO-modified TFC membranes had typical ridge-valley structures on their surfaces, corresponding to the peculiar feature of the PA membrane surface (Jeong *et al.* 2007, H. S. Lee *et al.* 2008, S. Y. Lee *et al.* 2007, Tang *et al.* 2009b, Taurozzi *et al.* 2008). The brighter and darker parts on the surface SEM images (Figs. 3a-3d) were believed to be ridges and valleys, respectively (Chae *et al.* 2015). Compared with the pristine PA TFC membrane in Fig. 3a, it was observed that the GO-modified TFC membrane (Figs. 3b-3d) had a denser structure throughout the plane. After embedding GO nano-sheets into the active layer, the size of leaf-like structures increased and some were connected with each other and formed a cross-linked area on the membrane surface. In the Fig. 3b-3d, the cross-linked area on 8-GO-TFC membrane surface was more significant and larger than 16-GO-TFC membrane. Thus, 8-GO-TFC membrane exhibited a higher hydrophilicity than 16-GO-TFC membrane, which was consistent with the data of water contact angles and flux reported in Table 2. As shown in Fig. 3e and 3f, the ridge heights of the TFC membrane appeared to be slightly higher than those of the 16-GO-TFC membrane, which likely corresponds to the higher surface roughness of the TFC. In addition, the average thickness of the PA layer also decreased with the incorporation of GO content (Fig. 3e and 3f). The denser surface and the decrease of the roughness and thickness of the GO-modified TFC membranes were
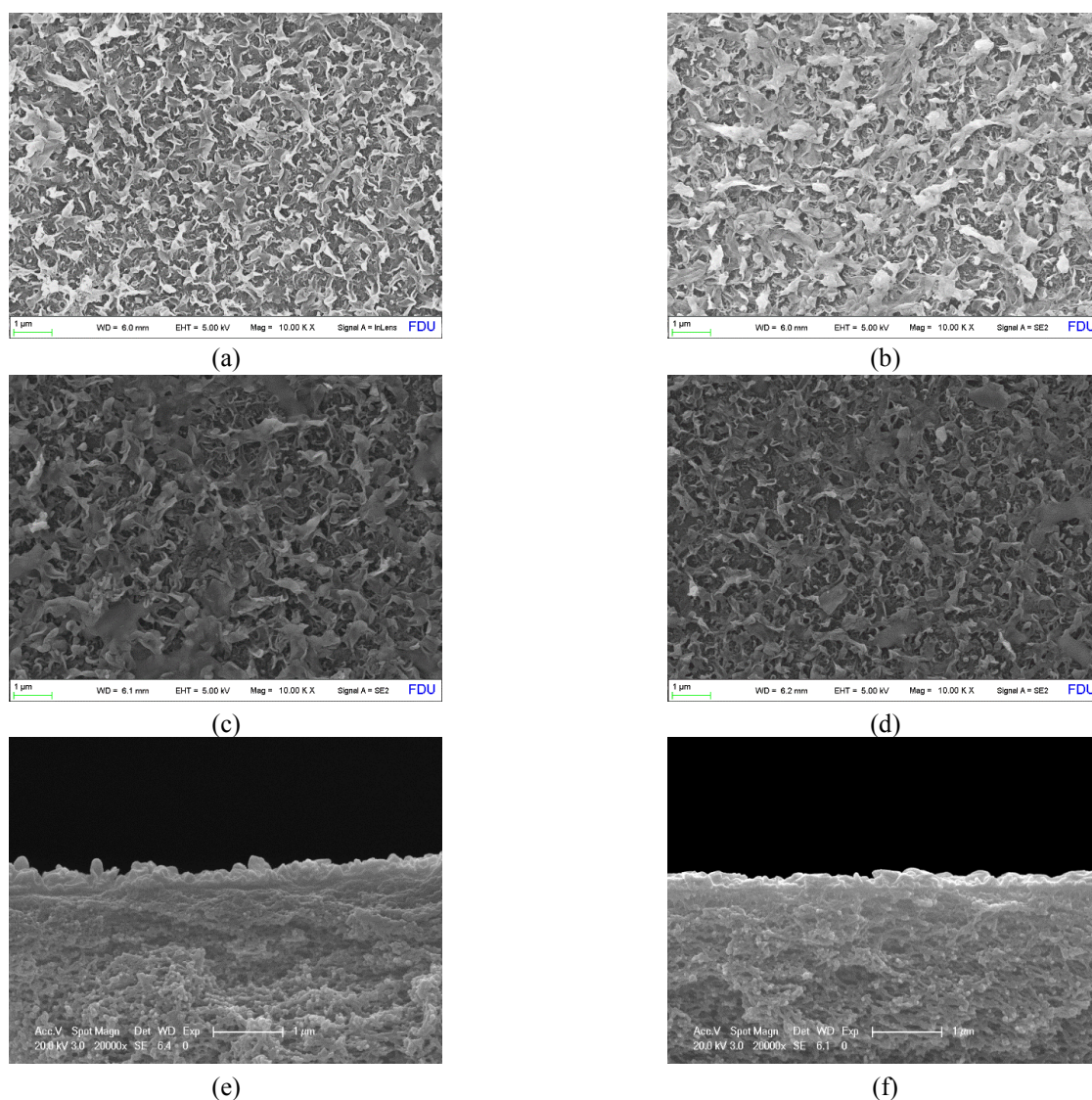
Fig. 3 SEM images of the top surfaces of: (a) TFC, (b) 4-GO-TFC, (c) 8-GO-TFC, (d) 16-GO-TFC and the cross-sections of: (e) TFC and (f) 16-GO-TFC

attributed to the retardation of MPD diffusion into the organic solvent by the GO nanosheets. The leaf-like surface resulted from a slow reaction between the TMC and the GO-carboxyl groups. In contrast, a nodular structure formed because of the fast reaction between the MPD and TMC during the interfacial polymerization process. Furthermore, the hydrogen bonds formed with the presence of hydroxyl groups on GO, leading to a more compact chain structure on the membrane surface (Bano *et al*. 2015). Accordingly, the formation of the PA layer was affected the incorporation of GO, which in turn led to a different surface morphology between the pure PA TFC membrane and the GO-modified TFC membranes.

The three-dimensional AFM images of the pure PA TFC and GO-modified TFC membranes (Figs. 4a and 4b; the average roughness (R_a) and the root mean square roughness (R_q)) exhibited the characteristic ridge-and-valley structure of the polyamide. The surface roughness of the GO-modified TFC membrane was apparently lower than that of the TFC membranes. This observation agrees with the SEM images, wherein the PA layer of the GO-modified TFC membranes was smoother, thinner and denser.

3.2 Rejection of target compounds

3.2.1 Effect of GO on foulant rejection

The effect of the GO content on the rejection efficiency of the target PPCPs compounds of the pure PA TFC and GO-modified TFC membranes was shown in Fig. 5. Generally, 4-GO-TFC experienced the best rejection values of these three PPCPs compounds among 4 membranes. For reserpine and tetracycline hydrochloride, the rejection rate appeared to be very stable, indicating better anti-fouling properties for this membrane.

Combined with the flux characteristics described in section 3.1, the appropriate amounts of incorporated GO led to a higher flux without sacrificing the foulant rejection properties. The reasons that the 4-GO-TFC membrane obtained better rejection rates might be that: (i) the GO
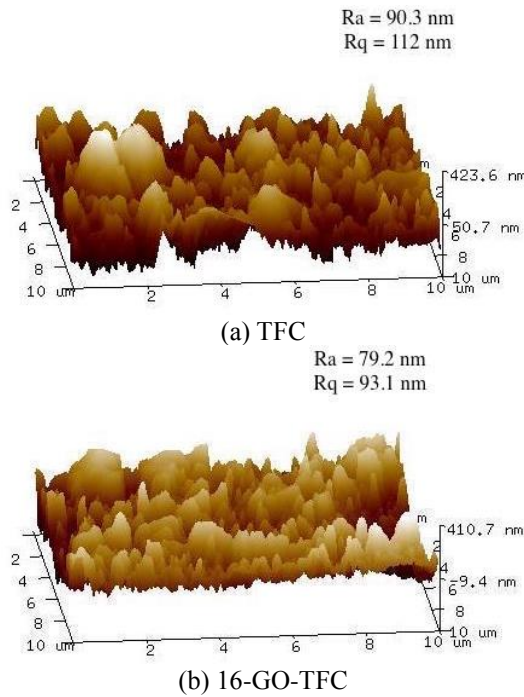
Ra = 90.3 nm
Rq = 112 nm

(a) TFC

Ra = 79.2 nm
Rq = 93.1 nm

(b) 16-GO-TFC

Fig. 4 Three-dimensional AFM images of the surfaces of:
(a) TFC and (b) 16-GO-TFC

(a)

(b)

(c)

Fig. 5 The rejection of (a) reserpine, (b) norfloxacin (c)
tetracycline hydrochloride for TFC, 4-GO-TFC, 8-GO-
TFC and 16-GO-TFC (pH=3)

enhanced the hydrophilicity of the TFC membrane effectively preventing hydrophobic foulants, which can be attributed to strongly bounded water molecules on the surface (Ulbricht 2006, Yoon *et al*. 2007). In particular, improved hydrophilicity of the membranes can enhance the ability of rejecting hydrophobic foulants by excluding the foulant molecules outside the membrane matrix and forbidding them to pass through the membrane. (ii) The incorporation of GO included the effect of charge repulsion impacting the separation performance of the GO-modified TFC membrane due to the improved electrostatic interaction between the foulants and membranes (Hu and Mi 2013, Van der Bruggen *et al*. 2008, Verliefde *et al*. 2008). And (iii) the denser surface of the GO-modified TFC membrane in comparison with the pure PA TFC membrane (SEM images in Fig. 3) contributed to a much higher foulant rejection efficiency corresponding to the size exclusion principle. However, membranes 8-GO-TFC and 16-GO-TFC were more hydrophilic than membrane 4-GO-TFC (Table 2) while exhibited lower PPCPs rejection. In the filtering process, the PPCPs rejection was not controlled only by membrane hydrophilicity and charge repulsion, many other factors may also affect the rejection. performance of membranes. The improved water flux of GO-TFC and 16-GO-TFC membranes will subsequently affect the PPCPs rejection, which may be the reason for this phenomenon.

In addition, the foulant molecules size also affected the rejection by the membranes. Among the three PPCPs, reserpine showed the highest rejection (reserpine: 96.61%, norfloxacin: 93.26% and tetracycline hydrochloride: 93.61% by TFC at 120min), which can be attributed to its highest molar weight (reserpine:608.68, norfloxacin:319.33 and tetracycline hydrochloride:480.90).
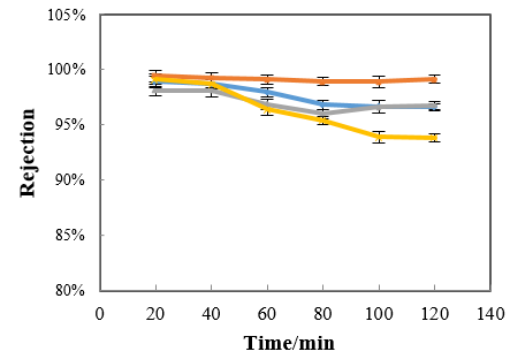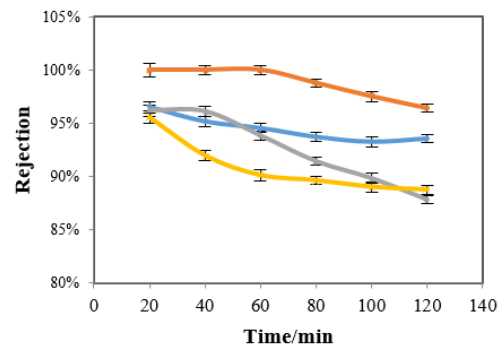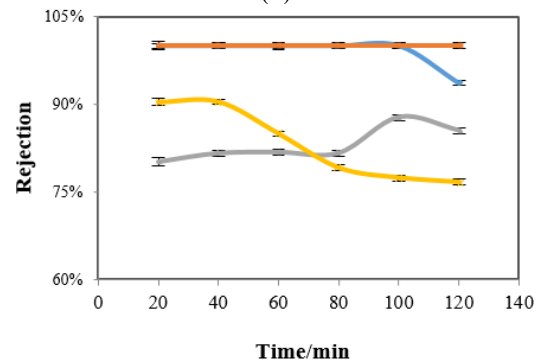
3.2.2 Effect of pH on foulant rejection

To investigate the effect of pH on the rejection efficiency of the membranes, experiments were carried out with feed solutions for the TFC and 4-GO-TFC membranes at different pH values (3, 7 and 11) and the results were shown in Fig. 6. For reserpine, the rejection appeared to follow the trend in the change of pH by both the TFC and 4-GO-TFC membranes. For norfloxacin, the rejections decreased as the pH increased from 3 to 11, which was due to the strong solute-membrane affinity (Xu *et al*. 2010). It was worth mentioning that the rejection of the 4-GO-TFC membrane appeared to be less sensitive to changes in the pH than that of the TFC membrane. A similar trend was observed in the rejection of tetracycline hydrochloride, which had a gentler downward trend in the rejection for the 4-GO-TFC membranes.
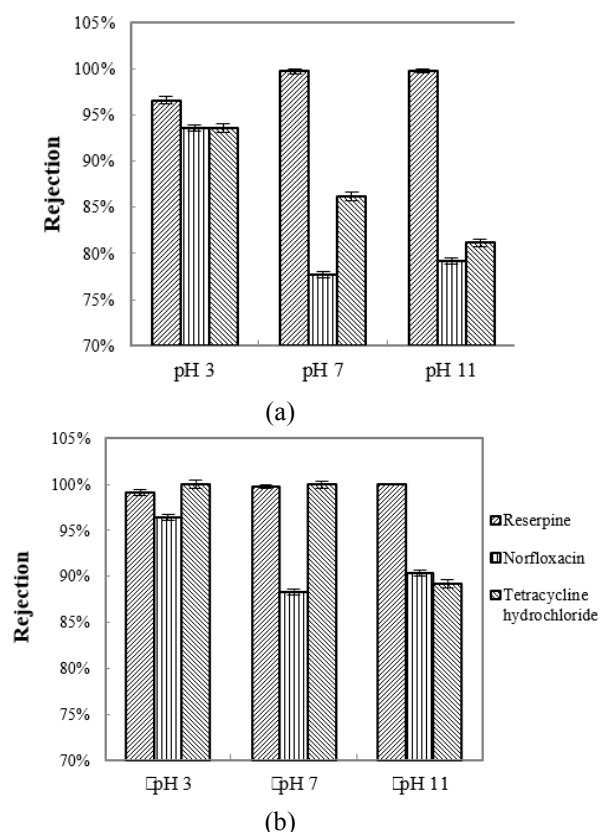
(a)

(b)

Fig. 6 The rejection of reserpine, norfloxacin and tetracycline hydrochloride as a function of pH (3, 7 and 11) for (a) TFC and (b) 4-GO-TFC

3.2.3 Effect of fouling on foulant rejection

The effects of organic fouling were investigated by introducing alginate (SA) at a concentration of 25 mg/L into the feed solution. It is widely accepted that both the surface morphology and surface charge affects the fouling behavior of a membrane. Fig. 7 shows the rejection trend of the three target compounds in 2h, in which the 4-GO-TFC exhibited a higher rejection as well. Compared with the data of Fig. 5, the presence of alginate in the feed solution reduced the norfloxacin and tetracycline hydrochloride rejection to a certain extent (from 97.23%±1.92% to 70.06%±4.60% and 99.52%±0.53% to 65.24%±4.80%) and a slight reduction was observed for reserpine (from 98.03%±1.22% to 96.12%±1.32%). In this study, the GO-modified membranes maintained a higher flux and at the same time, a higher rejection of foulant under organic fouling conditions, which means that the performance of the membrane significantly improved with the addition of GO. This suggests that the higher hydrophilicity, negative charge and smoothness that resulted from the hydrophilic groups of the GO contributed to the anti-fouling ability of the membrane, which was determined to be a positive change with the incorporation of GO (Wang *et al*. 2012). The surface adsorption properties of the membrane depend on the hydrophilicity; thus, for better resistance against fouling, improving the hydrophilicity of a membrane can be a good approach to some extent. The adhesion of hydrophobic fouling materials to the membrane surface might be mitigated by improving the hydrophilicity (Kim *et al*. 2005).
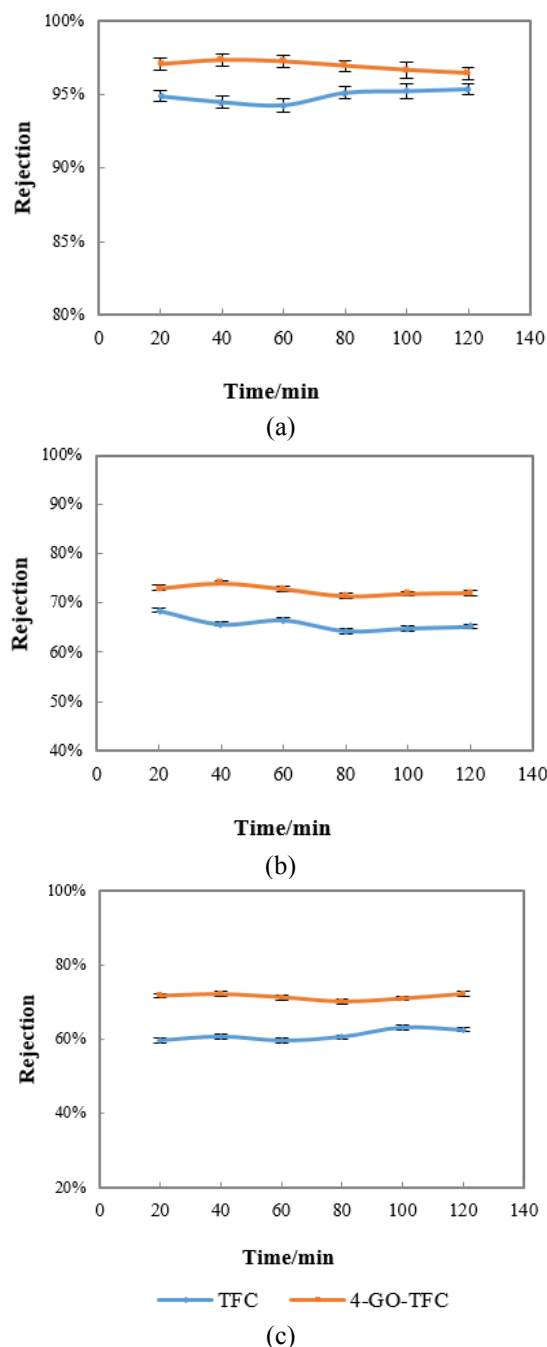

(a)

(b)

(c)

Fig. 7 The rejection of (a) reserpine (b) norfloxacin (c) tetracycline hydrochloride as a function of foulant for TFC and 4-GO-TFC

3.2.4 Effect of ionic strength on foulant rejection

To study the effect of the ionic strength on the rejection efficiency of three target compounds, the salt content of the feed solution was adjusted with NaCl (10 and 20 mM). In addition, the effect of the addition of alginate (SA) was also investigated. Fig. 8 shows the rejection from the membranes under 4 conditions: 10 mMNaCl, 20 mMNaCl, 10 mMNaCl + 25 mg/L SA and 20 mMNaCl + 25 mg/L SA. For both membranes, the increase in the ionic strength of the feed solution showed no effect on the rejection of reserpine (96.61% at origin solution, 96.17% at 10mMNaCl and 96.80% at 20 mMNaCl for TFC); meanwhile, better

(a)

(b)

☐ 10mM NaCl　　　　　☒ 20mM NaCl
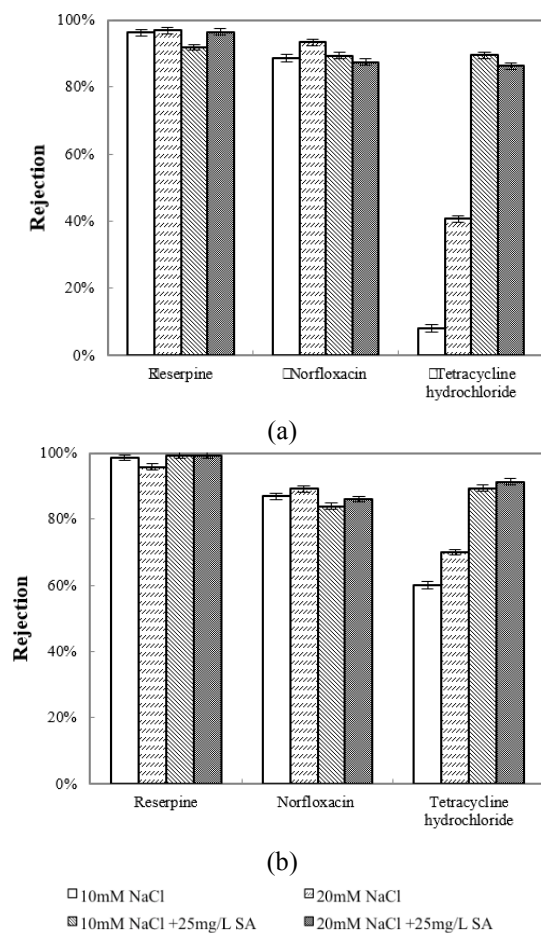☒ 10mM NaCl +25mg/L SA　☒ 20mM NaCl +25mg/L SA

Fig. 8 The rejection of reserpine, norfloxacin and tetracycline hydrochloride as a function of ionic strength for (a) TFC and (b) 4-GO-TFC

rejection efficiencies were achieved by the 4-GO-TFC membrane with the introduction of alginate (99.33% at 10 mMNaCl + 25 mg/L SA and 99.28% at 20 mMNaCl + 25 mg/L SA) in comparison with TFC membrane (91.83% at 10 mMNaCl + 25 mg/L SA and 96.45% at 20 mMNaCl + 25 mg/L SA). For norfloxacin, the rejection increased as the ionic strength increased for 4-GO-TFC, while for TFC it was true in absence of SA. Similarly, increasing the ionic strength of the feed solution increased the rejection of tetracycline hydrochloride and the presence of alginate in the feed solution also improved the rejection at both higher and lower ionic strengths. It was obvious that the GO-modified membrane was less sensitive to the effects of ionic strength and alginate fouling for the rejection of tetracycline hydrochloride.

4. Conclusions

In this study, GO-modified TFC membranes were prepared via an IP reaction on commercial PSf UF membranes. A variety of techniques were applied to characterize pure PA TFC and GO-modified TFC membranes. The FE-SEM images of the surfaces and cross-sections of the membranes indicated that the active layer became denser, smoother and thinner with the incorporation

of GO, which might contribute to the higher pure water flux observed in the water permeation tests compared to that of the pure PA TFC membranes. In addition, according to the rejection efficiency in the nano-filtration experiments for the three target compounds, it can be concluded that the appropriate amount of incorporated GO led to a higher flux in the membranes without sacrificing the foulant rejection capabilities. As to the effect of pH, the GO-modified TFC membrane appeared to be less sensitive to changes in the pH than the TFC membrane. Furthermore, it was observed that the GO-modified TFC membrane was less sensitive to the effects of ionic strength and alginate fouling for the rejection efficiency of three target compounds, demonstrating that GO-modified TFC membranes had a superior anti-fouling ability than the TFC membrane.

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