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Reduced graphene oxide-NH₂ modified low pressure nanofiltration composite hollow fiber membranes with improved water flux and antifouling capabilities

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ABSTRACT

Reduced graphene oxide-NH₂ (R-GO-NH₂), a kind of amino graphene oxide, was embedded into the polyamide (PA) layer of nanofiltration (NF) composite hollow fiber membranes via interfacial polymerization to enhance the permeate flux and antifouling properties of NF membranes under low pressure conditions. In addition, it could mitigate the poor compatibility issue between graphene oxide materials and PA layer. To evaluate the influence of R-GO-NH₂ on the performance of the NF composite hollow fiber membrane, SEM, AFM, FTIR, XPS and Zeta potentials were used to characterize the membranes. The results indicated that the compatibility and interactions between R-GO-NH₂ and PA layer were enhanced, which was mainly due to the polymerization reaction between amino groups of R-GO-NH₂ and acyl chloride groups of TMC. Therefore, salts rejection of the current membranes was improved significantly, and the modified membranes with 50 mg/L R-GO-NH₂ demonstrated highest performance in terms of the rejections, which were 26.9%, 98.5%, 98.1%, and 96.1%, for NaCl, Na₂SO₄, MgSO₄, and CaCl₂ respectively. It was found that with the R-GO-NH₂ contents rising from 0 to 50 mg/L, pure water flux increased from 30.44 ± 1.71 to 38.57 ± 2.01 L/(m²·h) at 2 bar. What's more, the membrane demonstrated improved antifouling properties.

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1. Introduction

Low pressure nanofiltration (NF) membranes which can be operated at low pressure (below 3 bar), have enormous potentials in water softening [1], food industry [2] and wastewater treatment [3]. Compared with most commercial NF, low pressure NF is more energy-saving. Previous results [4,5], indicated that the operating pressure of the membrane was strongly related to the membrane fouling phenomena. Under the high operating pressures, foulants easily attached on the membrane surface or entered its pores, thereby aggravating membrane fouling and decreasing the membrane lifetime. However, the fouling phenomenon of low pressure NF membranes could be evidently relieved at low operating pressure conditions. Currently, low pressure NF membranes were mainly fabricated by interfacial polymerization, through forming a dense polyamide (PA) thin layer on the surface of flat sheet or hol-

low fiber membranes [3,6]. The thin layer thickness of composite membranes was only 100–300 nm, which made the flux of composite membrane higher than others NF membranes at low operating pressure [7,8]. During the preparation process of NF composite membranes, many researchers applied hollow fiber membranes as the substrate due to their high-packing density, self-support, low demanding pre-treatment and high surface area to volume ratio [9–11]. Van der Meer et al. [12], found that the separate performance of an optimized NF hollow fiber module doubled compared to an optimized spiral-wound module. The inside-flow NF composite membranes, which were formed from a PA layer on the inner surface of the hollow fiber membrane exhibited better hydraulic flow conditions and lower concentration polarization as well as fouling tendency than the out-flow NF composite hollow fiber membranes [13]. Wang et al. [14], used piperazine (PIP), polyethylene imine (PEI) and mixed PIP/PEI as aqueous monomers, trimesoyl chloride (TMC) as organic monomer, to prepare a PA thin layer on the inner surface of NF composite hollow fiber membranes. The results showed that the pure water permeability of optimized NF membrane was 18.2 L/(m² H bar) at 2 bar. Wei et al.

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[15]. prepared inside NF composite membrane with PIP and TMC by interfacial polymerization, and the water flux of the membrane was approximately $30.0 \text{ L}/(\text{m}^2 \text{ H})$ at 2 bar.

Although the low pressure NF composite hollow fiber membranes have been widely reported, the issues of low flux, poor antifouling still exist [16–18]. In order to solve those problems, graphene based nanomaterials are widely used, due to their exceptionally high surface area, electron mobility, thermal conductivity, and mechanical strength [19,20]. Abundant researchers found that the introduction of graphene based nanomaterials in the membrane technology improved the water flux, antifouling property and antimicrobial properties of the membranes [21,22]. Especially, graphene oxide (GO), containing hydrophilic groups (such as hydroxyl and carboxyl groups), exhibited the ability to efficiently strengthen the water flux, chlorine tolerance and antifouling properties of the membranes [21,23]. Perreault et al. [22] found that PA composite membranes functionalized with GO possessed stronger antimicrobial property than pure PA composite membranes. Yin et al. [24]. modified PA composite membranes by embedding GO into PA layer, leading to the improvement of water flux from 39.0 ± 1.6 to $59.4 \pm 0.4 \text{ L}/(\text{m}^2 \cdot \text{h})$ and the antifouling performance of the membrane. However, the desalination performance of the NF membrane was decreased upon embedding of GO into the PA layer. Ali et al. [25]. also pointed out that the NaCl rejection of the membrane was decreased from 98% to 95% with increasing GO concentrations. This was mainly attributed to the poor compatibility between GO and PA layer, which produced defective pores in the PA layer.

Fortunately, introducing of different functional groups into the surface of the GO could be helpful to obtain better compatibility among the graphene material and polymer matrix [26,27]. Xu et al. [28]. found that carboxylated graphene oxide was more easily dispersed in the benzoxazine matrix than graphene oxide. The film modified by magnetic functional graphene oxide (MFGO) had more active sites for faradic reaction and larger specific capacitance than pure POAP [29]. Among the chemical groups, amine group has a high reactivity, a wealth of chemistry and can react with many chemicals such as polymers [30]. Many researchers [31,32] modified GO with amine groups and found that amine-functionalized graphene possessed excellent catalytic, electrochemical and adsorption performance. Meanwhile, amine-functionalized graphene is highly possible solve poor compatibility between graphene oxide materials and polyamide layer because the amino group of amino functional graphene oxide could react with the TMC during the interfacial polymerization process.

In this study, reduced graphene oxide- NH_2 (R-GO- NH_2), as an amino functional graphene oxide, was used to improve water flux and antifouling of NF composite hollow fiber membranes. The R-GO- NH_2 /PA layer was formed on the inner surface of PES hollow fiber ultrafiltration membranes via interfacial polymerization. Meanwhile, the NF membrane modified with GO was used as control. The influence of R-GO- NH_2 on the surface morphology, roughness, hydrophilic, permeate performance, antifouling properties of the membranes were investigated. SEM, AFM, FTIR, XRD and XPS were used to analyze the surface morphology, roughness and chemical structure, respectively. Zeta potential was applied to characterize the membrane surface charge. Finally, the influence of R-GO- NH_2 on the separation and antifouling properties of the membranes were studied.

2. Experimental section

2.1. Materials

Piperazine (PIP), trimesoyl chloride (TMC) and bovine serum albumin (BSA) were provided by Aladdin Industrial Co., Ltd

(Shanghai, China). Polyethersulfone hollow fiber ultrafiltration membranes (PES, Average pore diameter = $34.15 \pm 2.70 \text{ nm}$, Molecular weight cutoff = $100,000 \text{ Da}$) were supplied by SENUO Filtration Technology Co., Ltd (Tianjin, China). Reduced graphene oxide- NH_2 was purchased from NanoInnova Technologies SL (Spain). Graphene oxide (GO) was purchased from Nanjing XFNANO technology Co., Ltd (China). Polyethylene glycol (PEG), magnesium sulfate (MgSO_4), triethylamine (TEA), sodium sulfate anhydrous (Na_2SO_4), calcium chloride (CaCl_2), sodium chloride (NaCl), and n-heptane were all analytical reagents and used without further purification from Sinpharm Chemical Reagent Co., Ltd (China).

2.2. Fabrication of NF composite membranes modified with R-GO- NH_2 or GO

The NF composite membranes modified with and without R-GO- NH_2 were prepared by interfacial polymerization and the functional layer was formed on the inner surface of the PES hollow fiber membrane. The specific preparation procedure was as follows:

- (1) Firstly, R-GO- NH_2 powders were dispersed in 2% PIP solution with 1% TEA via ultrasonic dispersion method in the ice-water bath condition for 4 h. After that, the R-GO- NH_2 powders were uniformly dispersed in the aqueous solution (as seen in Fig.S3).
- (2) Secondly, the half-dozen of PES hollow fiber membranes with an effective length of 30 cm were fixed with epoxy resin in the glass tube. And the membrane modules were kept in deionized water at 25°C for 24 h.
- (3) Finally, an aqueous solution with 2% PIP, 1% TEA and different concentrations of R-GO- NH_2 were pumped into the inner side of the hollow fiber membrane module from the bottom side by a peristaltic pump, and circulated in the module for 15 mins at room temperature. And excess aqueous solution on the inner surface of hollow fiber membranes were eluted with n-hexane. After that, nitrogen gas was introduced through the inner side of membrane modules to dry the inner surface of hollow fiber membranes for 10 mins. Next, a 0.5% TMC-hexane organic solution was introduced into the inner side of the module from the bottom side by a peristaltic pump and contacted with the inner surface of the membranes for 2 mins to allow the interfacial polymerization reaction to take place. Finally, the organic solution was removed from the modules and the module was kept in deionized water.

The polyamide hollow fiber composite membrane was abbreviated as PA HFCM. The membranes with different concentration of R-GO- NH_2 was named as RGN-M, where M denoted the R-GO- NH_2 concentration of aqueous solution. For example, the NF composite hollow fiber membranes with 50 mg/L R-GO- NH_2 was named RGN-50.

The fabrication process of NF composite membranes modified with GO was the same as above.

2.3. Characterization methods

Chemical composition of the membranes and R-GO- NH_2 were obtained by ATR-FTIR (Nicolet 8700, Thermo Fisher Scientific, USA) technique via the attenuated total reflection (ATR) method. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface chemical structure of the membranes. The XPS result was obtained using X-ray photoelectron spectroscopy (Thermo Electron Corporation ESCALAB250) with an Al K α X-ray source (1486.6 eV) under $4.5 \times 10^{-12} \text{ bar}$. XPS were carried out by the hemisphere analyzer with a constant pass energy of 50 eV . This was corresponded to

Gaussian full width at half maximum (FWHM) of 1.2 eV [33]. Curve fitting of C 1s spectra was analyzed by using the XPS Peak 4.1 program. The XPS spectra were using Shirley-type background to subtract, and the Gaussian-Lorentzian peak shape were used after performing background and with a similar FWHM (full-width half-maximum) for all C1s peaks [34,35].

The membranes and R-GO-NH₂ were characterized by X-ray diffraction (Rigaku Dmax-2500, Japan) technique at 40 kV and 30 mA, with Cu K α radiation, $\lambda = 0.154$ nm. Diffraction patterns were run from 5°–80° at a scan speed of 5°/min, and the results were shown in Fig. 5S.

The morphologies (inner surface and cross section) of the membranes were characterized by scanning electron microscope (SEM, HITACHI S-3000N, Hitachi Ltd., Japan). Atom force microscope (AFM Digital Instruments, USA) was used to calculate the inner surface roughness of the membranes and investigate the change of membranes inner surface morphology with different concentration of R-GO-NH₂. The hollow fiber membrane was cutted open and spreaded on the stage. The membrane surface images were obtained with a scan area of 5 $\mu\text{m} \times 5 \mu\text{m}$. The work modes was tapping model and the scan rate was 0.5 Hz–1.0 Hz. Roughness values were estimated from topography scans using the Nanoscope control software (Version 7.30). The zeta potential of the membranes was determined by streaming potential measurements at room temperature. Streaming potential measurements were performed by using a SurPASS (Anton Paar, Graz, Austria) to measure zeta potentials of the membrane inner surface. Potassium chloride (1 mM) was used as electrolyte, whereas 0.1 N hydrochloric acid and 10 mM potassium hydroxide were used for pH titration. A contact-angle measurement apparatus (OCA 15EC, Germany Dataphysics company) was used to measure the water contact angles of the membrane inner surface, which were applied to analyze the hydrophilic of the membranes.

2.4. Separation performance tests of membranes

The water permeability, salts rejection and PEG neutral solute rejection of the membranes were carried out by an inner pressure cross-flow filtration set-up (Fig. 1) at room temperature. The feed solution was salt solution (1.0 g/L), PEG solution (0.2 g/L) or pure water. Before the test, all the membranes went through compaction with the feed solution for 2 h at 3 bar and were tested at 2 bar. The water flux of the membrane was obtained by Eq. (1):

$$F = \frac{V}{S \cdot t} \quad (1)$$

Where F is water flux of the membrane (L/(m² h)), V is permeation volume (L), S is the effective membrane area (m²) and t is the filtration time (h).

Salts or PEG rejection (R) was calculated by Eq. (2):

$$R = \left(1 - \frac{C_f}{C_0}\right) \times 100\% \quad (2)$$

Where, C_f and C_0 were the solute concentrations of permeate and the feed, respectively. The salt concentrations were examined via a conductivity meter (DDS-11A, Shanghai Leici Instrument Works, China). Concentrations of the PEG solutes in the feed and permeate solutions were measured by a total organic carbon analyzer (Liquic TOC, Elementar, Germany). All reported flux and rejection data were the average values of five measured data.

Fig. 1. Inner Pressure Cross flow operating apparatus: ① feed tank, ② valve, ③ security filters, ④ pump, ⑤ permeate, ⑥ concentrate, ⑦ pressure gauge ⑧ hollow fiber membrane cell.

3. Results and discussion

3.1. FTIR characteristics of the membranes

The influence of R-GO-NH₂ on the interfacial polymerization reaction as well as chemical composition of PA layer was analyzed by FTIR.

As shown in Fig. 2, all the membranes shown three particular peaks at 1578, 1484, 1239 cm⁻¹, which were associated with the benzene ring, C=C bond stretch and aromatic ether band, respectively, and the peaks at 1320, 1149 cm⁻¹ were due to asymmetric and symmetric stretches of sulfone group in PES molecule [36],[37]. Referring to Fig. 2 and Fig. S1, there was an obviously increase in transmittance at 1104 cm⁻¹ in the FTIR spectrum of RGN-50 compared with the PA CHFM, which was attributed to the additional intensity of C–O bond stretch (from R-GO-NH₂) and confirmed the presence of the R-GO-NH₂ in the RGN-50. The typical peak at 1730 cm⁻¹ could be ascribed to the stretching vibration of the C=O bonds in carboxyl groups, and generated by the hydration of unreacted acyl chloride groups of TMC [38]. Moreover, the presence

Fig. 2. FTIR spectra of PA CHFM and RGN-50.

Fig. 3. Schematic representation of chemical interactions between R-GO-NH₂, PIP and TMC.

of two peaks at 1653 and 1541 cm⁻¹ assigned to amides I (C=O) and II (N-H) in the spectra of RGN-50, respectively, suggesting the interfacial polymerization between the -NH₂ groups of R-GO-NH₂ and -COCl groups of TMC, and resulting in formation of the new acid chlorides groups (-CO-NH-). Compared with the spectra of PA CHFM, the spectra of RGN-50 shown a stronger and wider absorbance peak of -OH at 3000–3500 cm⁻¹. Since the R-GO-NH₂ was introduced to the PA layer, and leading to the increase of -OH content in the membrane surface. According to the above FTIR analysis, the reaction scheme and chemical structure of R-GO-NH₂/PA network were exhibited in Fig. 3.

3.2. XPS characteristics of the membranes

XPS has been widely used to characterize the chemical composite of the membrane surface [39,40]. Since the penetration depth of XPS is only 3.2 nm, it can directly reflect the chemical composite of the membranes surface [41]. Moreover, chemical environments of varied elements were also obtained by XPS spectra. In this study, XPS was performed to analyze the chemical state of PA CHFM and RGN-50.

The XPS spectra of PA CHFM and RGN-50 and the peaks for carbon, nitrogen and oxygen were observed in Fig. 4. As presented in Fig. 4(A) and (C), the oxygen element content of RGN-50 was slightly higher than that of PA CHFM. This could be caused by the surface located R-GO-NH₂. In order to characterize the chemical environment of carbon atoms, the XPS spectra of C(1s) was obtained and the results was exhibited in Fig. 4(B) and Table 1. For each membrane, the peaks were normalized with respect to the deconvoluted peaks were normalized with respect to the peak with the lowest binding energy (corrected to 283.9 eV). A positive shift indicates the element is bonded to electron withdrawing atoms (such as O, Cl, and F). [47] The C 1s peak of the PA HFCM shown that the lowest energy peak (N₁) was centred at 283.9 eV with a FWHM value of 1.2 eV. The other two peaks are centred at 285.7, 287.2 with corresponding FWHM values of 1.2, 1.4 eV. We call these three peaks C1, C2 and C3, respectively. A major peak at 283.9 eV was corresponded to carbon without adjacent electron withdrawing groups such as C-C or C-H bond. The secondary peak (3) with 1.8 shift was ascribed to C-N group [43]. Moreover, the minimum peak (C3) at 287.2 eV was corresponded to O=C-O and amide O=C-N group possibly due to the polymerization reaction between R-GO-NH₂

Fig. 4. Survey XPS spectra for PA HFCM and RGN-50: (A) Survey XPS spectra for PA HFCM, (B) C1 s spectrum of PA HFCM, (C) Survey XPS spectra for RGN-50, (D) C1 s spectrum of RGN-50.

Table 1

The energy shifts and FWHM of PA HFCM and RGN-50(C 1s spectra).

	Functional group	Binding energy (eV)	$\Delta\delta$ (eV)	FWHM(eV)	Reference
PA HFCM	C1:C–C/C–H	283.9	0.0	1.2	[42]
	C3:C–N	285.7	1.8	1.2	[43]
	C5:C=O	287.2	3.3	1.4	[44,45]
RGN-50	C1:C–C/C–H	283.9	0.0	1.3	[39]
	C2:C(graphite)	284.6	0.7	1.2	[43,46]
	C3:C–N	285.7	1.8	1.2	[43]
	C4:C–O–C	286.1	2.2	1.2	[43,49]
	C5:C=O	287.2	3.3	1.4	[44,45]

or PIP and TMC. Moreover, the minimum peak at 287.2 eV was corresponded to $\text{O}=\text{C}-\text{O}$ and amide $\text{O}=\text{C}-\text{N}$ group possibly due to the polymerization reaction between R-GO- NH_2 or PIP and TMC [41]. Unlike PA HFCM, the C1s spectrum of RGN-50 had two additional peaks (C2 and C4). The first peaks (C2) with a FWHM value of 1.2 eV, which might be assigned to carbon atoms in graphite, and was similar to the literature [43,48]. The others peak (C4) at 286.1 eV could be ascribed to C–O groups. [43,49], These observations indicated that R-GO- NH_2 was successfully introduced to the PA layer.

3.3. Surface morphology of the membranes

The thin layer structure of composite membrane (such as surface morphology, thin layer thickness and surface roughness) has

strongly related to the separation, water flux and antifouling property of the NF membrane, and could be characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM) [50,51].

The inner surface morphology of the composite hollow fiber membranes was shown in Fig. 5. Compared with the substrate (Fig. 5(A)), we could observe mass of nodules and firmly wrapped globules on the inner surface of the PA HFCM (Fig. 5 (B)), which was formed by the aggregation reaction of PIP and TMC [52]. However, the nodules and firmly wrapped globules on the substrate were decreased with the increase of the R-GO- NH_2 concentrations and the sheet structures were observed on the surface of the membranes modified with R-GO- NH_2 . According to FTIR and Fig. 3, R-GO- NH_2 nanosheets participated in the interfacial poly-

Fig. 5. SEM images of inner surface of (A) PES substrate, (B) PA CHFM, (C) RGN-25, (D) RGN-50, (E) RGN-75 and (F) RGN-100.

merization, leading to the formation of the network structure. This was quite different from the PA composite membranes modified by the other graphene based materials. Safarpour et al. [53] prepared PA composite membranes with R-GO/TiO₂, which demonstrated a denser and finely dispersed grainy structure due to the addition of R-GO/TiO₂. Bano et al. [54] found that GO slowed down the interfacial polymerization reaction rate, and the leaf-like structure on the substrate was formed.

When the concentration of R-GO-NH₂ was higher than 50 mg/L, the R-GO-NH₂ nanosheets were distinctly observed on membrane surface in Fig. 5(C–F) due to the aggregation effect of graphene materials. The similar phenomena was also found in PA composite membrane modified with GO [25].

The cross section structure of the membranes was shown in Fig. 6. The thin layer thicknesses of composite membranes were estimated by Image J processing software and the results was shown in Table 2. Compared with the substrate, both PA CHFM and PA CHFM modified with R-GO-NH₂ had a dense layer on the inner surface of the membrane and the thickness of the dense layer was in the range of 81.2 ± 9.1 and 113.4 ± 34.5 nm. As can be seen in Fig. 6(B), the functional layer thickness of the membrane modified with R-GO-NH₂ was thinner than that of the PA HFCM, and it was proportional to the concentration of R-GO-NH₂. This was attributed to the strong absorption of R-GO-NH₂ nanosheets. During the interface polymerization process, the substrate contacted with the aqueous, R-GO-NH₂ nanosheets would quickly absorb onto the substrate surface and prevent the PIP molecular from reacting with TMC, and forming a thinner layer. Meanwhile, when R-GO-NH₂ concentration was increased, excessive loading of R-GO-NH₂ would generate the aggregation effect, leading to the increase of thin layer thickness [25]. And the functional layer thickness of the RGN-50 was smaller than other membrane, which was achieved by the homogeneous distribution of R-GO-NH₂ on the membrane surface.

In order to further analyze the surface morphology of the film, AFM was used to characterize the three-dimensional morphology of the membrane surface, and which could provide a quantitative measurement method of surface roughness [55]. As we known, membrane surface roughness had great influence on the water permeation flux and membrane fouling phenomenon [51,56,57]. Thus the influence of R-GO-NH₂ on the membrane surface roughness was studied and the results was exhibited in Fig. 7 and Table 2.

Fig. 7 shown the three-dimensional AFM images of the membranes modified with and without R-GO-NH₂, the brightest point presented the highest section of the membrane surface and the darkest regions indicated the valley bottom of the membrane surface in the images. As exhibited in Fig. 7, the membrane surface morphology was greatly changed after adding R-GO-NH₂. Since the R-GO-NH₂ reacted with TMC, and forming a network structure on the substrate surface (as shown in Fig. 3). According to Table 2, the inner surface morphology of the membrane with low R-GO-NH₂ concentration ($c \leq 75$ mg/L) were smoother than that of PA CHFM. The surface of RGN-50 was smoother than that of other membranes. However, the roughness of RGN-100 was higher than other membrane due to the Langmuir-Blodgett film deposition effect, R-GO-NH₂ nanosheets were likely to be oriented horizontally arrangement along the substrate surface when excess aqueous solution was vertically removed from the substrate surface [21,58].

The water contact angle of the membranes modified with different concentrate of R-GO-NH₂ was characterized and the result was shown in Table 2. The water angle of the membranes was slightly decreased from 58.29 ± 1.58 to $53.03 \pm 2.15^\circ$ with increasing of R-GO-NH₂ content, suggesting the enhancement of membrane surface hydrophilicity. This could be caused by the introduction of R-GO-NH₂, which contained hydrophilic groups. Meanwhile, the enhancement of membrane surface hydrophilicity was helpful to inhibit the membrane fouling phenomenon, especially for organic fouling [59,60].

3.4. ZETA potential of the membranes

Membrane surface charge could greatly impact on the anti-fouling and separation properties [61,62]. The separation mechanism of NF was based on size-exclusion and Donan exclusion effect [63]. Therefore, the zeta potential was used to represent the surface charge distribution of the thin layer and characterized by streaming potential measurement method.

Zeta potential was used to analyze the inner surface charge strength of PA CHFM and RGN-50 at pH ranging from 3 to 11. According to Fig. 8, it could be observed that the isoelectric point of the membranes shifted from 4.3 to 5.2 after modifying by R-GO-NH₂. Below the isoelectric point, the positive charge membrane was attributed to the preferential adsorption of cation H⁺ from the electrolyte solution and the combination between unreacted amine

Fig. 6. SEM images of cross section of (A) PES substrate, (B) PA CHFM, (C) RGN-25, (D) RGN-50, (E) RGN-75 and (F) RGN-100.

Table 2

Roughness, contact angle, polyamide layer thickness and mean pore size of the membranes

Membranes code	Roughness/nm			Contact angle/°	Thickness /nm	Mean pore size/nm
	RMS	Ra	Rz			
PA CHFM	33.95	25.20	184.12	58.29 ± 1.58	113.4 ± 34.5	0.546
RGN-25	32.14	22.83	141.55	55.31 ± 0.97	94.1 ± 12.6	0.543
RGN-50	29.53	21.70	139.24	53.03 ± 2.15	81.2 ± 9.1	0.521
RGN-75	30.48	21.94	126.37	53.42 ± 1.16	87.3 ± 15.1	0.553
RGN-100	62.30	43.78	162.75	56.29 ± 1.89	103.6 ± 12.5	0.588

groups of R-GO-NH₂ and cation H⁺ (R-GO-NH₂ + H⁺ → R-GO-NH₃⁺) [9]. Above the isoelectric point, the negative membrane surface was caused by the preferential adsorption of anions OH⁻ or Cl⁻ from the electrolyte solution and the dissociation of carboxyl groups of the membrane surface. In addition, the absolute value of zeta potential of RGN-50 membrane was larger than that of PA CHFM with pH of 6.2 or higher, which was caused by dissociation of hydroxyl and carboxyl groups of R-GO-NH₂ [64]. It implied that RGN-50 had stronger electrostatic repulsion to salt ions than PA HCM.

3.5. Separation performance of the membrane

The mean pore size of the membranes was measured by PEG rejection method and the detailed calculation process was shown in supporting information (Fig. S3) [65]. As shown in Table 2, the mean pore size of RGN-50 was the smallest, since the R-GO-NH₂ could uniformly distributed in the substrate surface. When the R-GO-NH₂ concentration was higher than 50 mg/L, the mean pore size of membrane was increased due to the aggregation effect.

The Na₂SO₄ rejection (1000 ppm) and pure water flux of the membranes were checked at 2 bar and the results were shown in Fig. 9 and Fig. S4. The results (Fig. 9) showed that the pure water flux of the membranes was increased from 30.44 ± 1.71 to 59.39 ± 2.59 L/(m²·h) with increasing of R-GO-NH₂ concentrations in the range of 0–100 mg/L. Since the R-GO-NH₂ provided a passage-way of water molecules [24,25]. Based on the water contact angle (Table 2), the increase of membrane surface hydrophilicity was contributed to strengthen the water flux of the membranes. The SEM image shown that the functional layer of the membranes modified with R-GO-NH₂ was thinner than that of PA CHFM. Rao et al. [8] found that the water flux of the PA composite membrane was

negative correlating to the thin layer thickness of the membrane [66]. Thus the decrease of thin layer thickness was also beneficial to improve the water flux of composite membranes. By increasing the GO concentration (according to Fig. S4), the permeate water flux increased from 30.44 ± 1.71 L/(m²·h) to 98.5 ± 0.4 L/(m²·h), while the rejections of Na₂SO₄ quickly decreased from 97.6 ± 0.51% to 55 ± 3.1% because of the poor compatibility between GO and PA layer. Compared with the membrane modified with GO, the membranes modified with R-GO-NH₂ exhibited better separation property.

The obtained results (Fig. 9) indicated that the RGN-50 possessed superior Na₂SO₄ rejection property. However, the Na₂SO₄ rejection was deteriorated when the R-GO-NH₂ concentration above 50 mg/L. Many factors could explain this phenomenon. Firstly, the zeta potential of RGN membrane was greater than that of PA membrane. Thus, the electrostatic repulsion forces between salt ions and the surface charge of the membranes modified with R-GO-NH₂ was stronger than that between salt ions and surface charge of PA CHFM. Secondly, mass of R-GO-NH₂ would aggregate on the surface of support membrane at high concentration of R-GO-NH₂ (c > 50 mg/L), which would increase the volume void between R-GO-NH₂ and polymer, thus salt ions passed the membrane by the void more easily [24].

Fig. 10 presented pure water flux of PA CHFM and RGN-50 with feed pressure. According to Spiegler-Kedem models, the pure water flux of the membranes is positively proportional to the operating pressure: $F = Lp(\Delta p - \Delta\pi)$ (where F is the water flux, Lp is the solute permeability coefficients and Δp is transmembrane hydraulic pressure) [67]. Therefore, Lp of PA CHFM and RGN-50 were 8.83 L/(h·m²·bar) and 14.76 L/(h·m²·bar), respectively.

Fig. 7. AFM images of inner surface of the membranes modified with different R-GO-NH₂ concentration.

The separate performance of PA CHFM and RGN-50 for four kinds of salts solution were shown in Fig. 11. The obtained results indicated that the salts separation performance of RGN-50 was higher than that of PA CHFM. Since the electrostatic repulsion forces between salt ions and membrane surface of RGN-50 was stronger than that between salt and PA CHFM [68]. Meanwhile, the pore size of RGN-50 was smaller than that of PA CHFM. The salts rejection of the membrane to four kinds of salts follows the sequence

of R (Na₂SO₄) > R (MgSO₄) > R (CaCl₂) > R (NaCl). According to zeta potential datas, both PA CHFM and RGN-50 possessed negative charges at pH=7. As anionic membranes, the negative surface charges of the membranes possessed strong electrostatic repulsion forces to negative ions (such as SO₄²⁻ and Cl⁻), especially for SO₄²⁻. Compared with the Cl⁻, the SO₄²⁻ with larger hydrated radius, ion radius and lower diffusion coefficient (Table 3) faced stronger steric hindrance resistance. Therefore, the rejection of sulfate salts

Fig. 8. Zeta potential of PA CHFM and RGN-50 as function of pH value.

Fig. 9. Effect of R-GO-NH₂ concentration on the Na₂SO₄ rejection and pure water flux of the membranes at pH 7.0 and 25 °C.

Fig. 10. Pure water flux of PA CHFM and RGN-50 at pH 7.0 and 25 °C.

(such as Na₂SO₄, MgSO₄) was greater than that of chlorides (such as MgCl₂, NaCl). For the rejection of MgSO₄ and Na₂SO₄, Mg²⁺, as a divalent counter-ion, had greater effect on the negative electric field than Na⁺, so the Donnan exclusion effect between MgSO₄ and

Fig. 11. Permeation performance of PA CHFM and RGN-50 for different salts at 2 bar, pH = 7 and T = 25 °C (C salts = 1000 ppm).

Table 3

Ion radius, hydrated radius and diffusion coefficient of different ions.

	Ion radius [70] (nm)	Hydrated radius [70] (nm)	Diffusion coefficient [71] (10 ⁻⁹ m ² /s)
Na ⁺	0.10	0.36	1.33
Mg ²⁺	0.07	0.43	0.71
Ca ²⁺	0.10	0.41	0.79
Cl ⁻	0.18	0.33	2.03
SO ₄ ²⁻	0.29	0.38	1.07

the membranes got weaker [69]. Thus the MgSO₄ rejection was lower than that of Na₂SO₄. According to Table 3, the hydrated radius of Ca²⁺ was larger than that of Na⁺, so the steric hindrance effect of CaCl₂ was stronger than that of NaCl. Based on the above analysis, the salt ions rejection of the membranes was due to both Donnan effect and steric hindrance.

3.6. Antifouling performance of the membranes

During the process of water treatment, the foulants (such as salts, protein, organic matter) would attach on the membrane surface or enter the membrane pores which would decrease the separation performance of the membranes and ultimately reduce the membrane life [72].

The antifouling performance of PA CHFM and RGN-50 were evaluated with durable performance at long time. In the course of the test process, the membranes were washed by water backwashing dynamically for 2 h after 8 h operation per day. Normalized flux and Na₂SO₄ rejection were used to analyze the antifouling performance and the results was presented in Fig. 12. After the operation of 7 days, the Na₂SO₄ rejection of RGN-50 and PA CHFM were decreased from 98.9 to 97.6% and 98.1–96.1%, respectively, which was due to concentration polarization effect? Based on the above results, the normalized flux of RGN-50 was always higher than that of PA CHFM, which meant that RGN-50 had stronger antifouling performance than PA CHFM. Since R-GO-NH₂ improved the zeta potential and hydrophilic of the membranes, the RGN-50 possessed stronger electrostatic repulsion forces and anti-adsorption to BSA than PA CHFM. Moreover, the roughness of the membranes had great influence on the membrane fouling. Vrijenhoek et al. [5] found that foulants attached more easily on the rough membrane surface than on the smooth membrane surface. As shown in Table 2, the roughness of RGN-50 was smaller than that of PA CHFM. As a result, the foulants had lower tendency to attach on the membrane surface of RGN-50.

Fig. 12. Membrane performance in long term use and SEM images of inner surface of PA CHFM (before: A, after: B) and RGN-50 (before: C, after: D).

4. Conclusion

In summary, R-GO-NH₂ was successfully incorporated into the PA layers of NF hollow fiber composite membranes via interfacial polymerization. Based on the separation tests, the R-GO-NH₂ possessed good compatibility with PA layer. The FTIR and XPS results implied that R-GO-NH₂ could polymerize with TMC, resulting in a network structure on the inner surface of hollow fiber membrane. Moreover, SEM and AFM results demonstrated that both the thin layer thickness and surface roughness of the membranes were decreased, when the R-GO-NH₂ was added into the PA layer. Meanwhile, the hydrophilicity and electrostatic repulsion was enhanced due to containing of hydroxyl groups and carboxyl groups in the R-GO-NH₂. The optimum balance of flux and rejection could be achieved when the PA membrane was modified with 50 mg/L R-GO-NH₂, which possessed the highest Na₂SO₄ rejection of 98.21 ± 0.28% and the water flux of 38.57 ± 2.01 L/(m² h). Based on BSA fouling test, the membranes modified with R-GO-NH₂ exhibited stronger anti-fouling properties than the pristine PA membrane.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2017.04.080>.

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