Fabrication of novel poly(m-phenylene isophthalamide) hollow fiber nanofiltration membrane for effective removal of trace amount perfluorooctane sulfonate from water

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\textbf{A B S T R A C T}

This study investigated the separation performance of a hollow fiber nanofiltration membrane, which was fabricated from poly(m-phenylene isophthalamide) (PMIA) using a dry-jet wet spinning technology, for sustainable water recovery from water containing trace amount of perfluorooctane sulfonate (PFOS) that was a persistent organic pollutant commonly existed in water. SEM spectra indicated that the cross section of the hollow fiber membrane had an asymmetrical structure that consisted of a dense outer surface acting as a selectively layer, a spongy-like transition layer, and finger-like microporosids close to the inner surface. The average pore size and molecular weight cut-off, which were estimated using the solute rejection method, were 0.404 nm and 904 Da, respectively. The PFOS rejection experiments were carried out at the trans-membrane pressures ranging from 4 x 10\textsuperscript{5} Pa to 1.0 x 10\textsuperscript{5} Pa and PFOS concentrations from 50 \textmu g/L to 500 \textmu g/L. In all cases, the PFOS rejections were found to be increased as the PFOS concentration increased. The impact of the pH value and Ca\textsuperscript{2+} concentration of the feed solution on the PFOS rejections was studied in detail. The PFOS rejections improved from 97.10\% to 99.40\% at a trans-membrane pressure of 1.0 x 10\textsuperscript{5} Pa. The sorption/desorption experiments indicated that the amount of PFOS adsorbed on the membrane surface was five times higher in the presence of Ca\textsuperscript{2+} (2 mM). AFM experiments also demonstrated that the membrane surface was rough with the addition of Ca\textsuperscript{2+}. Hence, the presence of Ca\textsuperscript{2+} enhanced the PFOS adsorption in the membrane surface and caused more pore blockage of the membrane. As such, the decline in the water flux and augmentation in the PFOS rejection were observed.

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1. Introduction

Perfluorooctane sulfonate (PFOS), a typical perfluorinated compound, is a fully fluorinated eight-carbon alkane with a sulfonate group at one end [1]. PFOS is widely used in the textile and chemical industries, coating materials, fire retardants, drug packaging materials, and surfactants owing to its excellent thermal and chemical stability, and non-hydrophilic and non-lipophilic properties [2–5]. Although PFOS plays an important role in the developing industry, its environmental persistence and bioaccumulation may be potentially hazardous [6]. PFOS and its derivatives have attracted global concerns owing to their harmful effects on the environment and humans. In 2009, PFOS was categorized as one of the persistent organic pollutants (POPs) [7]. To date, PFOS has been detected in various water supplies, especially surface water, ground water, and tap water for drinking purposes worldwide. Evidently, the PFOS contamination has posed a threat to the security of drinking water for humans in some areas [8,9]. Although United States and some European countries have proposed regulations to limit the use of PFOS, it is still being used in many industrial applications due to the lack of available immediate alternatives. Therefore, development of cost-effective water treatment technologies to remove PFOS has drawn increasing attentions.

PFOS is difficult to decompose under traditional conditions including oxidation, reduction, and biological degradation [10,11]. Recent studies show that some methods, such as sonochemical decomposition [12], adsorption using activated carbon or anion-exchange resins [13,14], and UV-mediated photodegradation [15], can remove PFOS from aqueous solution. However, these technologies are mostly for
wastewater treatment, and require long reaction time, high energy consumption, as well as complex and specific operating conditions. In contrast, membrane technologies, especially reverse osmosis (RO) and nanofiltration (NF), are recognized as an effective method to remove organic pollutants from water. Commercial RO and flat sheet NF membranes have shown great potential to remove PFOS from wastewater and drinking water. Tang et al. demonstrated the feasibility of using commercial RO membranes to remove PFOS from semiconduc- tor wastewater. The experimental result showed that the RO membranes rejected 99% or more of the PFOS over a wide range of PFOS concentrations (0.5–1500 mg/L) in the feed solutions [16]. They also studied the separation performance of a water solutions containing 10 ppm PFOS using three commercial NF flat-sheet membranes (DK, NF90 and NF270). The result showed that the rejection efficiencies for NF membranes ranged from 90% to 99%). [5] Zhao et al. studied the effect of calcium ions on PFOS rejections using a commercial flat- sheet NF270 membrane and reported that the PFOS rejection could be enhanced from 94.0% to 99.3% with an increase of the calcium ion concentration from 0 to 2 mmol/L [17]. However, to our best knowl- edge, all the researches on PFOS removal are based on either commercial flat-sheet RO membranes or commercial flat-sheet NF membranes. Hollow fiber NF membranes have not been explored in this application to date. It is worth stressing that most of commercial NF membranes are thin-film composite (TFC) membranes [18], such as NF series made by Filitnec Corporation, ESNA series by Hydronau- tics Company, Desal series by GE Osmotics Company, NTR series by Nitto Denko Company, ATF series by Advanced membrane Technology Inc., UTC series by Toray Industries, etc., and the current dominant commercial NF membranes are generally fabricated by interfacial polymerization (IP), chemical modification or coating. Although these techniques have been widely applied in industry, their fabrication processes are sophisticated and need a long production cycle. In addition, most above-mentioned NF membrane modules are still constructed into flat-sheet, spiral-wound or tubular configurations. The resulted hollow fiber modules have some intrinsic advantages including: (1) the better packing density; (2) the lager membrane surface area per unit module volume; (3) the self-mechanical support capability; (4) no demand of feed and permeate spacers; and (5) cost-effective large-scale production and operation [21,22]. Hence, developing hollow fiber NF membranes gives an alternative (maybe more suitable) solution for PFOS water treatment. To our best knowledge, materials for fabricating NF hollow fiber membrane are mainly limited to CA, PESK, PES, etc. [21,23–29]. The development of poly(m-phenylene isophthalamide) (PMIA) NF hollow fiber membrane has not been reported before. PMIA has outstanding thermal resistivity (Tg= 270 °C) and great chemical stability that makes it an ideal membrane material [30,31]. In addition, there is an urgent need to develop solute- selective, efficient, chemical-stable and low-priced NF membranes in hollow fiber form using adopting new outstanding materials and simple spinning technologies. Thus this work explored the feasibility of using PMIA to fabricate hollow fiber NF membrane for treating PFOS wastewater.

Above all, there is an urgent need to develop solute-selective, more efficient, chemical-stable and low-priced NF membranes in hollow fiber form through adopting new outstanding materials and simple spinning technologies. In this study, poly(m-phenylene isophthalamide) (PMIA) NF hollow fiber membranes have been prepared by a dry-jet wet spinning technology. And the resulted hollow fiber membranes were investigated for the removal of PFOS from aqueous solution. The separation performance and morphologies of the PMIA membranes are characterized, and the effects of PFOS concentration, solution pH, and ionic strength on the water flux and PFOS rejection are investigated.

2. Materials and methods

2.1. Materials

Potassium perfluorooctane sulfonate (PFOS, ≥ 99%, molecular weight= 538 Da, molecule size= 1.088 nm) was purchased from AccuStandard, Inc. (New Haven, USA) and its chemical and molecular structures are shown in Fig. 1. Poly(m-phenylene isophthalamide) (PMIA, molecular weight= 140,000 Da) was obtained from DuPont (USA) and its chemical structure is shown in Fig. 2. HPLC-grade acetonitrile and methanol were acquired from Fisher Scientific (China). Sodium chloride (NaCl), sodium sulfate (Na2SO4), magnesium chloride (MgCl2), magnesium sulfate (MgSO4), and calcium chloride (CaCl2) (analytical grade, > 99%) were bought from Sigma-Aldrich (USA). NN-dimethylacetamide (DMAC, > 98%) was employed as PMIA solvent and purchased from Shanghai Jingwei Chemical Co., Ltd. (China). Calcium chloride, humic acid sodium salt, sodium hydroxide, and hydrochloric acid (analytical grade, > 99%) were supplied by Sigma-Aldrich (USA). N,N-dimethylacetamide (DMAC, > 98%) was employed as PMIA solvent and purchased from Shanghai Jingwei Chemical Co., Ltd. (China). PVP K15 (Average MW= 10,000 Da) was obtained from Tokyo Chemical Industry Co., Ltd (Japan). Lithium chloride (LiCl, > 95%) and acetone (> 99.5%) were supplied by Tianjin Guangfu Research Institute of Fine Chemical Engineering (China). Glucose, saccharose, raffinose, and α-cyclodextrin were purchased from Sigma-Aldrich (USA). Molecular weights, diffusivity properties, and Stokes radii of the neutral solutes are listed in Table 1 [32]. High-purity Mill-Q water with an electrical resistivity of 18.2 MΩ cm was used in all experiments.

2.2. Preparation of PMIA NF hollow fiber membrane and membrane module

A polymer dope solution of PMIA/DMAC/LiCl/acetone/PVP K15 (20/66/4.5/8/1.5 wt%) was prepared in a reaction vessel. The mixture was continuously stirred until a homogeneous polymer solution was obtained. After that, the dope was degassed for 12 h. A dry-jet wet spinning method was used to prepare the PMIA hollow fiber NF membrane. The dope solution and bore fluid were

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Fig. 1. The chemical structure and molecular structure of PFOS.

Fig. 2. The chemical structure of PMIA.
co-extruded through a spinneret to form a hollow fiber. The detailed spinning parameters are listed in Table 2. The hollow fibers were soaked in a circulating water bath for 72 h to leach out the residual solvent. After that, the hollow fiber membrane was transferred to a 50 wt% glycerol aqueous solution for 48 h and then air-dried at room temperature.

Eight filament modules with an effective membrane length of 22 cm were fabricated. Specifically, 8 PMIA hollow fiber membranes were assembled into a nylon tube. Each module was sealed by epoxy and then immersed in deionized water for one day to remove glycerol before use.

2.3. Characterization of the membrane morphology

The structure and morphology of the NF hollow fiber membrane were monitored on a HITACHI S-3000N scanning electron microscope (SEM, Hitachi Ltd., Japan). Before observation, the membrane samples (surface and cross-section) that were randomly selected were frozen in liquid nitrogen, fractured, and sputtered with platinum using a HITACHI E-1010 ion sputtering coater.

2.4. Membrane performance tests

Filtration experiments were conducted using a cross-flow in-house laboratory-scale membrane test unit (shown in Fig. 3). The hollow fiber membrane modules were outside-in modes. The flow rate of the feed solutions was fixed to be 1.50 L min\(^{-1}\) to minimize the effect of concentration polarization. Before permeation test, each hollow fiber module was pre-pressurized under a pressure of \(10 \times 10^5\) Pa in order to ensure a stable flux. Subsequently, the membranes were subjected to the solute separation experiments whereby different solutions, containing inorganic salts, neutral organic solutes, and PFOS were passed through the membrane shell side. The water flux, \(F\) (L/m\(^2\) h), is determined as follows:

\[
F = \frac{J}{S_t}
\]  

where \(J\) (L) is the water permeation volume; \(S\) (m\(^2\)) is the membrane effective filtration area; and \(t\) (h) is the operation time.

The solute rejection, \(R\), is calculated as follows:

\[
R = \left(1 - \frac{C_p}{C_o}\right) \times 100\%
\]  

where \(C_p\) (g/L) and \(C_o\) (g/L) are the solute concentrations in the permeate and feed solutions, respectively.

The experimental design and separation procedure are described below:

1. Determination of the salt rejections: Different inorganic salt solutions were prepared by dissolving NaCl, Na\(_2\)SO\(_4\), MgCl\(_2\), and MgSO\(_4\) in deionized water at a concentration of ~3.4 mM. The temperature and flow rate of the feed solution were maintained at 25 ± 1°C and 0.32 m/s, respectively. The feed solution was circulated for 1 h until the entire system reached steady state. Then, the feed and permeate solutions at different pressures were sampled to measure the salt concentrations. The salt concentrations were determined using an electrical conductivity meter (DDSJ-308A, Shanghai Leici Instrument Works, China).

2. Determination of the neutral solute rejections: The feed solutions were prepared by dissolving four neutral solutes in deionized water at a concentration of 100 mg/L. The feed temperature and cross-flow rate were the same as those introduced in step (1). The trans-membrane pressure was maintained at \(7 \times 10^5\) Pa. The neutral solute separation data were used to calculate the molecular weight cut-off (MWCO), mean pore size, and pore size distribution of the membrane. The concentration of the neutral solutes in the feed and permeate solutions was determined by measuring the total organic carbon (TOC) content using a TOC analyzer (Liquid TOC, Elementar, Germany).

3. Determination of the PFOS rejections: The PFOS solutions were prepared by dissolving PFOS in deionized water. The experimental procedure was the same as steps (1) and (2). HCl

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**Table 2**

| Solute              | MW (g/mol) | \(D_s\) (\(\times 10^{-9}\) m\(^2\) s\(^{-1}\)) | \(r_s\) (nm) |
|---------------------|------------|---------------------------------|--------------|
| Glucose             | 180        | 0.67                            | 0.365        |
| Saccharose          | 342        | 0.52                            | 0.471        |
| Raffinose           | 504        | 0.42                            | 0.584        |
| \(\alpha\)-Cyclodextrin | 972      | 0.35                            | 0.701        |

**Table 1**

| Spinning parameters | Value               |
|---------------------|---------------------|
| Dope solution temperature (°C) | 50                  |
| Spinneret dimension OD/ID (mm) | 1.40/0.70           |
| Bore fluid/external coagulant | Tap water 25 ± 1°C  |
| Dope flow rate (mL/min) | 6.0                 |
| Bore fluid flow rate (mL/min) | 3.0                 |
| Air gap (cm) | 25                  |
| Take-up speed | Free fall            |
| Room relative humidity (%) | 25 ± 3              |

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**Fig. 3.** Schematic diagram of the filtration unit.
(0.1 M) and NaOH (0.1 M) were used to adjust the pH of the feed solution. The concentration of PFOS in the feed and permeate solutions was determined using an ultra-performance liquid chromatography–tandem mass spectrometer (LC–MS/MS, Waters ACQUITY UPLC/Quattro Premier XE MS/MS) (Waters Corporation, USA). A C18 column (2.1 × 150 mm²) obtained from Waters Corporation (USA) was used and a mixture of acetonitrile/ammonium acetate (70/30, v/v) was used as the mobile phase at a flow rate of 0.2 mL/min. The sample injection volume was 10 μL. The selected-ion monitoring (SIM) model was used to quantify the analytes (m/z = 499.05). A prominent peak was observed at 1.8 min, and the detection limit for PFOS was 0.1 μg/L. The PFOS rejection was estimated using Eq. (2) with the PFOS concentrations in the feed and permeate sides.

2.8. Membrane surface analysis

All AFM measurements were performed using a Multimode SPM equipped with a J-type piezoelectric scanner and a Nanoscope III a controller (Digital Instruments, USA). The membrane surface images were obtained with a scan size of 5 μm × 5 μm. Roughness values were estimated from topography scans using the Nanoscope control software (Version 7.30).

3. Results and discussion

3.1. Morphology of PMIA NF hollow fiber membrane

Fig. 4 illustrates the structure of the NF hollow fiber membrane that features a typical asymmetric structure comprising an outer-selective skin, finger-like macrovoids, a spongy-like transition layer, and cellular-like macrovoids. During the dry-jet wet spinning process, acetone, as one volatile non-solvent additive, rapidly vaporizes to the air before the nascent hollow fiber enters the coagulant bath. It results in a more concentrated polymer solution in the outer surface than in the inner surface and bulk part of the hollow fiber. And this instigates the formation of a denser outer surface of the hollow fiber membrane that acts as the selective layer. The finger-like and cellular-like macrovoids are observed close to both the outer and inner surfaces of the hollow fiber because of the rapid liquid–liquid demixing process [36], whereas the spongy-like structure forms in the middle of the hollow fiber membrane because of the delayed phase separation. Rapid liquid–liquid demixing happens when the membrane is formed immediately after immersion into the non-solvent bath (water). Generally, when liquid–liquid demixing occurs rapidly, membranes with a relatively porous top layer, finger like cavities and cellular-like macrovoids narrow to the outer and inner surfaces are obtained [37]. However, in this study, the as-spun fiber firstly goes through the air gap, the volatile acetone evaporates rapidly from the outer film interface. Thus the liquid–liquid demixing process takes place after a finite period of time. Membranes with a relatively dense top layer are obtained, and the finger-like structure close to the outer surface becomes smaller and narrower [38,39]. On the contrary, the liquid–liquid demixing process that occurred at the inner surface is relatively faster than that happened near to the outer surface. That is due to that the dope solution and bore fluid (water) are co-extruded through the spinneret, and the diffusion exchange between the solvent and non-solvent is instantaneous that results in a highly unstable dope solution so that a rapid demixing process occurs. Such condition favors the formation of cellular-like macrovoid structures [40]. In the transition layer, located in the middle of the membrane, spongy-like structure is formed due to the delayed phase transition process. Two factors may lead to this result: first, the diffusion front in the transition layer moves far away from the dope solution–coagulant interface; and second, the diffusion barrier formed by the rapid liquid–liquid demixing near the outer and inner surface hinders the mutual diffusion speed between the solvent and non-solvent gel in the middle of the membrane. In this situation, it takes more induction time for non-solvent diffusing into the dope solution to form nuclei; thus the growth of the macrovoids is impossible and only a spong-like structure forms [41]. In addition, this type of structure affords high stability and good separation performance of the hollow fiber membrane under high pressure operation. Moreover, the uniform, dense, and smooth outer surface is responsible for the excellent anti-fouling property.
3.2. Water flux and charge characterization of PMIA NF hollow fiber membrane

Fig. 5(A) shows the permeation performance of the PMIA hollow fiber membrane under different trans-membrane pressures. It can be seen that pressure has a significant influence on the separation performance. The pure water flux (F) increases almost linearly as the pressure increases from 4 × 10^5 Pa to 10 × 10^5 Pa. The one week filtration test under a pressure of 10 × 10^5 Pa was carried out to verify the long term stability of the PMIA hollow fiber membrane. According to Fig. 5(B), the pure water flux decreases rapidly at the first 10 h, and then becomes stable at the following 150 h. The flux reduction in the first few hours is due to the compaction of the membrane surface under the high pressure and/or the pore plugging impact by fouling [42]. The SEM pictures indicate no significant deformation or shrinkage of the pores of the hollow fiber membranes before and after one week filtration test under 10 × 10^5 Pa. This proves that the membrane has a very good mechanical stability that is attributed to the rigid aramid groups and the three-dimensional hydrogen bonding networks of the PMIA polymer.

The PMIA NF hollow fiber membranes exhibit different rejections to cations and anions owing to the negatively charged surface properties of the NF membrane. Fig. 5(C) shows the rejections to four types of electrolytes at a concentration of 3.4 mM, pH = 7, and different pressures. The salt rejection (R) decreases in an order of R(Na2SO4) > R(MgSO4) > R(NaCl) > R(MgCl2). The PMIA NF membrane displays higher rejections to salts containing divalent anions with a higher co-ion charge, and lower rejections to salts containing divalent cations with a higher counter-ion charge. This observation is consistent with the exclusion mechanism, as reported by Donnan [43]. That is, the sulfonic acid groups on the membrane surface exert a stronger electrostatic repulsion effect on SO4^2− than on Cl−. According to the Donnan exclusion mechanism, the extent of rejection of these 1:1 type electrolytes (MgSO4 and NaCl) shall be equal; however, a lower rejection level of NaCl relative to that of MgSO4 is observed in this study. This phenomenon is attributed to the higher diffusivities of the smaller-sized hydrated Na+ and Cl− when compared with those of the larger hydrated Mg2+ and SO4^2− [44,45] (Na+ is bigger than Mg2+). Additionally, it can be observed that the rejection of NaCl is higher than that of MgCl2. This can be explained by the charge shielding effect: Mg2+ has a higher positive charge density than Na+, which enhances the shielding effect of the NF membrane negative charge, leading to a reduced rejection degree of Mg2+. The solute rejections of all four studied electrolytes increase with increasing applied trans-membrane pressures. This is due to the fact that the water flux increases relatively higher than the solute flux, which causes a decrease in solute permeate concentration and an increase in solute rejection.

3.3. Characterization of membrane molecular weight cut-off, mean effective pore size, and pore size distribution

The PMIA NF hollow fiber membranes are characterized by the solute transport method to determine the molecular weight cut-off (MWCO, molecular weight of solute with a retention level of 90%), mean effective pore size, and pore size distribution of the membrane. The relationship between the neutral solute Stokes radius and solute rejection is illustrated in Fig. 6(A). The MWCO of PMIA NF hollow fiber membrane is 904 Da, as calculated from Eq. (5). The cumulative pore size distribution curve and probability density function curve of PMIA NF hollow fiber membrane, as determined by Eqs. (3) and (4), respectively, are illustrated in Fig. 6 (B) and (C), respectively. The PMIA membranes exhibit a narrow pore size distribution with a mean effective pore radius of 0.404 nm. These results indicate that the PMIA NF membrane has the potential to effectively remove PFOS molecule that has a molecular size of 1.088 nm.

3.4. Effect of PFOS concentration on PFOS rejection

The effect of PFOS concentration (i.e., 50, 100, 200, and 500 µg/L) on the rejection of PFOS using the PMIA NF hollow fiber membrane is studied, and the experimental results are shown in Fig. 7(A) and (B). As observed, (1) PFOS rejection increases with increasing PFOS
concentrations at all trans-membrane pressures; (2) the water fluxes gradually decrease at the first 700 min then become stable; and (3) the water fluxes increase with the decrease in the PFOS concentration. Similar results were also observed by Tang et al. [16] who attributed these to the increased amount of PFOS molecules entrapped in the pores and accumulating on the membrane surface that caused the lower water flux and higher PFOS rejection. The separation mechanisms of the NF membranes follow (1) size exclusion and (2) electrostatic effect. Typically, the size exclusion mechanism dominates the overall separation performance. Thus, as the concentration of the PFOS and the operation time increase, the amount of PFOS molecules entrapped in the PMIA polyamide skin and accumulating on the membrane surface shall also increase. This leads to the reduction in water flux and augment in PFOS rejection.

Interestingly, the rejection level of PFOS decreases with increasing pressures from $4 \times 10^5$ to $10 \times 10^5$ Pa at a given PFOS concentration. The MW of PFOS is 538 Da, which is lower than MWCO of PMIA membrane. Therefore, the rejection of PFOS is likely to vary according to the solution pH. Fig. 8(A) shows the effect of solution pH on the removal of PFOS. As observed, the solution pH has a significant influence on the PFOS rejection. The rejection to PFOS improves from 91.17% to 97.49% as solution pH increases from 3.2 to 9.5 at $4 \times 10^5$ Pa. PFOS has a pKa of about $-4$ [47], hence under the studied pH, PFOS exists as anions in solution; the removal of PFOS at different pHs is affected by the properties of the membrane surface [48]. Fig. 8(B) shows the zeta potentials of the PMIA NF hollow fiber membrane at different pHs. The membrane displays increasing surface charge with increasing pH. This is due to that the polyamide membrane skin layer possesses dissociable carboxylic group. Thus, the membrane surface can exhibit either a negative or a positive surface charge depending on the solution pH [49]. The zeta potential measurements support this conclusion since the NF membrane has much stronger negative charge at alkaline conditions than positive charge at acid conditions [50]. Because the point of zero charge of the PMIA membrane is $\sim 3.54$, the membrane surface is negative when pH is greater than 3.54. Accordingly, rejection of PFOS is lower at pH $= 3.2$ and higher as pH $> 3.2$. The higher rejection is attributed to the stronger electrostatic repulsion between the PFOS and PMIA membrane surface with increasing pH.

### 3.5. Effect of solution pH on PFOS rejection

The separation performance of the PMIA NF hollow fiber membrane mainly depends on the membrane surface charge, which can be influenced by the solution pH. The PMIA membrane is believed to be positively charged at low pHs and negatively charged at high pHs. Therefore, the rejection of PFOS is likely to vary according to the solution pH. Fig. 8(A) shows the effect of solution pH on the removal of PFOS. As observed, the solution pH has a significant influence on the PFOS rejection. The rejection to PFOS improves from 91.17% to 97.49% as solution pH increases from 3.2 to 9.5 at $4 \times 10^5$ Pa. PFOS has a pKa of about $-4$ [47], hence under the studied pH, PFOS exists as anions in solution; the removal of PFOS at different pHs is affected by the properties of the membrane surface [48]. Fig. 8(B) shows the zeta potentials of the PMIA NF hollow fiber membrane at different pHs. The membrane displays increasing surface charge with increasing pH. This is due to that the polyamide membrane skin layer possesses dissociable carboxylic group. Thus, the membrane surface can exhibit either a negative or a positive surface charge depending on the solution pH [49]. The zeta potential measurements support this conclusion since the NF membrane has much stronger negative charge at alkaline conditions than positive charge at acid conditions [50]. Because the point of zero charge of the PMIA membrane is $\sim 3.54$, the membrane surface is negative when pH is greater than 3.54. Accordingly, rejection of PFOS is lower at pH $= 3.2$ and higher as pH $> 3.2$. The higher rejection is attributed to the stronger electrostatic repulsion between the PFOS and PMIA membrane surface with increasing pH.
3.6. Effect of ionic strength on PFOS rejection

To study the effect of ionic strength on PFOS rejection, calcium chloride (CaCl$_2$) which is typically present in water is used as the background electrolyte calcium ions. Calcium ions at a concentration of ~2 mM have been detected in natural water sources [51]. Therefore, in this study, calcium ions at concentrations from 0.1 mM to 2 mM are added to the feed solution containing 100 μg/L PFOS at pH = 7 to investigate the effect of ionic strength on PFOS rejection. As shown in Fig. 9(A), the rejections of PFOS increase with increasing Ca$^{2+}$ concentrations at a given trans-membrane pressure. An increase in PFOS rejection from 97.10% to 99.40% at 4 x 10$^5$ Pa is observed when the Ca$^{2+}$ concentrations increase from 0.1 mM to 2 mM. The improvement can be attributed to pore blockage effects as exerted by the ions [52,53]. Accordingly, the effective pore size on the membrane surface is expected to decrease, and consequently leads to increased
rejection of PFOS. Membrane pore blockage by Ca\(^{2+}\) will lower the number of available pores for filtration. This will hinder the passage of PFOS and water molecules through the membrane. As illustrated in Fig. 9(B), the presence of Ca\(^{2+}\) in the feed solution leads to a reduction in permeate flux compared with that in the absence of Ca\(^{2+}\), with slightly higher flux decay rates with increasing Ca\(^{2+}\) concentrations. Thus, the comparison of the flux decay rate suggests that a higher Ca\(^{2+}\) concentrations results in the increased Ca\(^{2+}\) precipitation on the membrane and pore blockage, consequently leading to increased PFOS rejection and flux decline [54–56].

Moreover, some researchers attribute this beneficial effect to the onset of specific bridging interactions between Ca\(^{2+}\) and the sulfonate group of PFOS [57–59]. Zhao et al. further demonstrate the formation of CF\(_3\)(CF\(_2\))\(_7\)SO\(_3\)Ca\(^{2+}\) cation and neutral CF\(_3\)(CF\(_2\))\(_7\)SO\(_3\)CaO\(_3\)-(S(CF\(_2\))CF\(_3\))

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**Fig. 8.** (A) Effect of solution pH on the removal of PFOS. (B) Zeta potentials of the PMIA NF membrane at different solution pHs.

**Fig. 9.** (A) Effect of Ca\(^{2+}\) concentration on the removal of PFOS. (B) Flux decay rate \(F/F_0\) in the presence of different Ca\(^{2+}\) concentrations: \(F\) is flux at one certain time; \(F_0\) is the pure water flux.

**Fig. 10.** The schematic diagram for different PFOS systems.

**Fig. 11.** Adsorption amount of PFOS in different feed solutions.
in this circumstance using density functional theory calculations [17]. As shown in Fig. 10, not only this bridging interaction improves molecular polarity, but also increases the molecule size of PFOS. Ca$^{2+}$ as a cation enhances the adsorption of negatively charged PFOS, and further creates a dense layer on the membrane surface. Accordingly, the membrane sieve effect is expected to be more effective.

Fig. 12. AFM images of the PMIA membranes before and after filtration of different PFOS feed systems. (A1, B1) virgin PMIA membrane; (A2, B2) 100 ppb PFOS; (A3, B3) 100 ppb PFOS + 0.1 mM Ca$^{2+}$; (A4, B4) 100 ppb PFOS + 1 mM Ca$^{2+}$; and (A5, B5) 100 ppb PFOS + 2 mM Ca$^{2+}$. 
under these conditions. It can thus be concluded that the PFOS rejection can be improved in the presence of Ca$^{2+}$ ions, owing to interactions with the membrane and PFOS molecules.

3.7. Desorption of PFOS

Perfluorooctanesulfonic acid (PFOS) filtration tests using the home-made PMIA hollow fiber nanofiltration membranes were carried out and the rejection to PFOS was higher than 94%. In addition, the rejection of PFOS could be further improved by adjusting the pH value or adding Ca$^{2+}$ cation into the PFOS solutions. However, a decrease in the water flux with the operation time was observed that was attributed to the accumulation of PFOS on the membrane surface. To investigate this phenomenon, the PFOS adsorption on the PMIA hollow fiber membrane was determined using a method similar to Ref. [60]. Furthermore, atomic force microscopy (AFM) was also adopted to characterize the three-dimensional image and roughness of the surface of the virgin and fouled membrane [61–65]. Flux reduction as observed from Figs. 7B and 9B suggests that there is certain amount of PFOS adsorbing to the PMIA NF membrane. Fig. 11 presents the adsorption amount of PFOS in different feed solutions. The sorption amount of PFOS increases from 0.464 × 10$^{-1}$ to 6.456 × 10$^{-1}$ μg/cm² when the PFOS concentration increases from 50 to 500 μg/L. The higher sorption amounts of PFOS at the higher PFOS concentrations indicate a higher number of PFOS molecules accumulating on the membrane surface or entrapped in the membrane pores. The addition of Ca$^{2+}$ ions also enhances the sorption capacities. The PFOS adsorbing on the membrane surface is 5.474 × 10$^{-1}$ μg/cm² at a concentration of 2 mM Ca$^{2+}$, which is approximately five times higher than without Ca$^{2+}$. AFM images shown in Fig. 12 also prove these results. The PFOS adhesion has a strong influence on surface roughness. As shown in Table 3, the virgin PMIA membrane has an average roughness of 3.67 nm, and the average roughness increases from 3.83 nm to 9.79 nm with increasing Ca$^{2+}$ concentration. Clearly, more Ca$^{2+}$ facilitates PFOS adsorption on the membrane surface and increases surface roughness. The significant improvement in the sorption capacity can be attributed to the neutralization of the negatively charged PFOS and PMIA NF membrane surface by Ca$^{2+}$. The sorption and entrainment of PFOS on the membrane greatly inhibit the passage of water molecules. Therefore, the water flux decreases and the PFOS rejection is improved by adding Ca$^{2+}$.

4. Conclusion

A novel negatively charged PMIA nanofiltration hollow fiber membrane with high-pressure resistant has been fabricated by a dry–wet phase inversion technique. The membrane possesses a typical asymmetric structure. The MWCO and mean effective pore size of the membrane are 904 Da and 0.404 nm, respectively. The PMIA NF membrane rejects different salts in the order of Na$_2$SO$_4$ > MgSO$_4$ > NaCl > MgCl$_2$ at pH 7.0. The rejection level of salts containing divalent anions is higher than that of salts containing divalent cations, in accordance with the Donnan effect. The PMIA NF hollow fiber membrane efficiently rejects PFOS owing to a combined steric hindrance and Donnan exclusion effect. Filtration experiments indicate that the rejection of PFOS increases with increasing PFOS concentration and solution pH. Rejection of PFOS increases from 91.17% to 97.49% as pH increases from 3.2 to 9.5 at a pressure of 4 × 10$^5$ Pa. Moreover, a higher Ca$^{2+}$ concentration improves the PFOS rejection owing to pore blockage and specific bridging interactions between Ca$^{2+}$ and the sulfonate group of PFOS. These factors not only improve molecular polarity, but also increase the molecule size of PFOS. Desorption experiments show that the sorption amount of PFOS increases with increasing PFOS concentration or ionic strength. AFM images also demonstrate that the membrane surface roughness increases with the increasing Ca$^{2+}$ concentration. Overall, these results suggest that the newly fabricated PMIA NF hollow fiber membranes have potential for application in PFOS removal.

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Nomenclature

PMIA poly(m-phenylene isophthalimide)  
PFOS perfluorooctane sulfonate  
POPs persistent organic pollutants  
NaCl sodium chloride  
Na$_2$SO$_4$ sodium sulfate  
MgCl$_2$ magnesium chloride  
MgSO$_4$ magnesium sulfate  
CaCl$_2$ calcium chloride  
DMACP$_2$Ndimethylacetamide  
PVP K15 polyvinylpyrrolidone K15  
LiCl lithium chloride  
F$^-$ water flux (L/m² h)  
J water permeation volume (L)  
S membrane effective filtration area (m$^2$)  
t operation time (h)  
R rejection (%)  
C$_p$ permeate concentrations (g/L)  
C$_r$ feed concentrations (g/L)  
MWCO molecular weight cut-off (Da)  
R$_f$ solute rejection (%)  
r$_s$ Solute radius (nm)  
μ$_g$ geometric mean radius (nm)  
σ$_g$ geometric standard deviation  
μ$_n$ mean effective pore radius (nm)  
σ$_n$ geometric standard deviation  
d$_p$ effective pore radius (nm)  
MW molecular weight (g/mol)

References

[1] E. Kiss, Fluorinated Surfactants: Synthesis, Properties, and Applications, Marcel Dekker, New York, 1994.
[2] S. Fujii, C. Polprasert, S. Tanaka, N.P.H. Lien, Y. Qiu, New POPs in the water environment: distribution, bioaccumulation and treatment of perfluorinated
[59] F. Wang, K.M. Shih, Adsorption of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on alumina: influence of solution pH and cations, Water Res. 45 (2011) 2925–2930.
[60] Y.N. Kwon, K. Shih, C.Y. Tang, J.O. Leckie, Adsorption of perfluorinated compounds on thin-film composite polyamide membranes, J. Appl. Polym. Sci. 124 (2012) 1042–1049.
[61] C.Y. Tang, Y.N. Kwon, J.O. Leckie, The role of foulant–foulant electrostatic interaction on limiting flux for RO and NF membranes during humic acid fouling—theoretical basis, experimental evidence, and AFM interaction force measurement, J. Membr. Sci. 326 (2009) 526–532.
[62] A.R. Costa, M.N. de Pinho, M. Elimelech, Mechanisms of colloidal natural organic matter fouling in ultrafiltration, J. Membr. Sci. 281 (2006) 716–725.
[63] E.M. Vrijenhoek, S. Hong, M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, J. Membr. Sci. 188 (2001) 115–128.
[64] L.D. Tijing, Y.C. Woo, J.-S. Choi, S. Lee, S.H. Kim, H.K. Shon, Fouling and its control in membrane distillation—a review, J. Membr. Sci. 475 (2015) 215–244.
[65] W.R. Bowen, N. Hilal, R.W. Lovitt, C.J. Wright, Characterisation of membrane surfaces: direct measurement of biological adhesion using an atomic force microscope, J. Membr. Sci. 154 (1999) 205–212.