Nanocomposite Substrate-Supported Nanofiltration Membrane for the Efficient Treatment of Rare Earth Wastewater

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Graphical abstract:

Abstract: Rare earth wastewater is an emerging wastewater featuring high salinity, strong acidity and a complex background with multiple contaminants. A nanofiltration (NF) membrane with a high water flux, high salt rejection and good stability is desired to tackle the challenge of rare earth wastewater to reduce its negative impact on the environment. Herein, a novel nanocomposite substrate-supported thin film composite (TFC) NF membrane with good stability and superior separation performance was reported. The inorganic two-dimensional O-MoS\textsubscript{2} nanosheets were embedded into the polysulfone (PSf) substrate via a nonsolvent-induced phase inversion method. The PSf/O-MoS\textsubscript{2} nanocomposite was used as the support for the interfacial polymerization between piperazine and vinyl chloride. The
hydrophilicity of the substrate layer was improved significantly with increasing O-MoS\(_2\) content. In addition, the pore structure of the substrate shifted from a larger irregular bubble pore structure into a finger-like porous structure when the content of O-MoS\(_2\) was 0.06 wt%. The alteration of the pore structure of the substrate affected the interfacial reaction. As a result, the nanocomposite substrate-supported TFC membrane had a 1.7 times higher water flux and improved salt rejections compared to that of the control membrane. The obtained NF membrane showed excellent separation performance with a high salinity removal efficiency of 95% in treating real rare earth wastewater (diluted 50 times, pH: 2.46). Moreover, the membrane had good stability during 24 h filtration, demonstrating its great potential in industrial applications. This work also highlights that the modification of the substrate by functional nanomaterials could provide versatile ways to improve the separation performance and stability of TFC membranes.

**Key word:** O-MoS\(_2\), nanocomposite substrate, nanofiltration, efficient treatment, rare earth wastewater

1. Introduction

As an important strategic resource of China, rare earths are widely used in many fields, such as the military, metallurgy, and petrochemical industries [1,2]. In recent years, the rare earth industry has been monotonous, and technology has dispersed [3]. In the rare earth smelting and separation process, due to processes such as saponification of the extractant, a large amount of ammonia nitrogen wastewater would be produced, which contains high concentrations of calcium and sodium ions, accompanied by a small amount of radioactive elements and heavy metals. The composition of rare earth sewage is complicated and difficult to treat [4,5]. If discharged directly without treatment, it would cause great harm to the environment.

Nanofiltration (NF) is a cost-effective and sustainable membrane separation technology that can remove organic molecules with a molecular weight between 200-1500 Da and has high desalination efficiency for multivalent ions [6–10]. NF could be a potential technique for deep pretreatment of rare earth wastewater and reduce the environmental burden by removing inorganic salts, toxic heavy metals and organic matter. Nevertheless, because of their strong acidity and high salinity, conventional
membranes have difficulty achieving good stability and superior separation capacity. Few studies have investigated the treatment of rare earth wastewater by membrane separation. As an example, Zhang et al. applied reverse osmosis membranes to treat rare earth wastewater [6]. To prevent the membrane from being damaged by the strong acids in wastewater, the pH of the wastewater needed to be adjusted before filtration. However, the membrane still had very low permeate flux, and a high energy input was required. It is desirable to design a high-performance NF membrane with good stability in harsh conditions to pretreat rare earth wastewater.

With the advances of nanotechnology, functional nanomaterials have been widely used to adjust the properties of thin-film composite (TFC) membranes by incorporating them into the polyamide (PA) layer. Typically, nanomaterials are added into the aqueous phase or organic phase, followed by interfacial polymerization (IP). The hydrophilicity, fouling resistance and separation performance of TFC membranes could be effectively improved [11–15]. However, these methods usually suffer the partial loss of nanomaterials, as reported by Li et al., which is not conducive to maintaining the superior performance of the membrane for long-term filtration [16]. These membranes are not favorable in harsh conditions, such as in rare earth wastewater, which generally has a high acidity.

Alternatively, the influence of the support layer on the IP reaction is often underestimated. Current studies show that the modification of the membrane support layer would affect the IP reaction. The PA layer of the TFC NF membranes could have different crosslinking degrees, thicknesses, surface roughness and pore sizes when the pore size and hydrophilicity of the base membrane are changed [17–22]. For example, aqueous monomers were more easily adsorbed onto a support layer with a higher hydrophilicity, making the reaction more complete and forming a denser PA layer with fewer defects. However, few of the studies have applied this strategy to tailor TFC membranes. Lai et al. improved the physicochemical properties of the PSf substrate and the PA selective layer by adding graphene oxide (GO) particles to the membrane matrix, taking advantage of the strong hydrophilicity and electronegativity of GO and enhancing the water flux and salt rejection performance of the membrane [23]. Molybdenum disulfide oxide (O-MoS$_2$) is an emerging nanomaterial, which has
a similar structure to GO. In our previous work, a Hummers method combined with high-energy ultrasonication was proposed to prepare O-MoS\(_2\). It shows high hydrophilicity and high electronegativity. In addition, it also has stable chemical properties and good nonswelling properties [24]. Yang et al. fabricated a TFC NF membrane by incorporating hydrophilic O-MoS\(_2\) into the PA layer [25]. The resultant membrane had improved water flux and salt rejection. Regarding the hollow fiber membrane, using the O-MoS\(_2\) with stronger mechanical and chemical stability of can also obtain a membrane with more resistance to fouling, stronger stability and better performance [26]. By taking advantage of these properties of O-MoS\(_2\), it is promising to improve the separation performance and stability of the TFC NF membrane by embedding O-MoS\(_2\) into the substrate layer.

Herein, a novel polysulfone (PSf)/O-MoS\(_2\) nanocomposite-supported thin film composite (TFC) NF membrane was developed. The self-synthesized O-MoS\(_2\) nanosheets were embedded into the PSf substrate layer to tailor the pore structure of the sublayer and to improve the stability and resistance of the TFC NF membrane in a strong acid solution. The effects of the nanosheet content on the hydrophilicity, pore size, surface topology and cross-sectional pore structure of the substrate were investigated. The TFC membrane was synthesized via IP between piperazine and vinyl chloride. The surface morphology, hydrophilicity and charge were characterized to understand the effect of the nanocomposite substrate on the IP reaction. Furthermore, the desalination performance, molecular weight cut-off (MWCO) and stability of the PSf/O-MoS\(_2\) membrane and the control membrane were compared. The potential application of the prepared NF membrane was demonstrated by separating real rare earth wastewater. The salinity removal efficiency and stability were evaluated. This work provides a new approach to fabricate NF membranes with high separation performances and good stability in harsh conditions by modification of the substrate through incorporating nanomaterials. The facile fabrication procedures and the reproducible results have great advantages over surface modifications of TFC membranes.

2. Experiment

2.1. Materials
The fabrication of polysulfone (PSf) ultrafiltration (UF) membrane via the phase
inversion process was used as the support of the subsequent NF membrane. O-MoS$_2$
was prepared from bulk MoS$_2$ (99.5%, Aladdin) according to Hummers’ method as
reported elsewhere [27]. An IP reaction was carried out on the membrane surface to
prepare the required NF membrane. The aqueous phase monomer was piperazine
(PIP, 99%), and 1,3,5-benzenetricarbonyl trichloride (TMC, 98%) was used as the
monomer in organic phase. Triethylamine (TEA, 99%) and (±)-camphor-10-sulfonic
acid (CSA, 99%) was added to the aqueous solution to adjust the s acidity and
alkalinity of the solution. N-hexane (≥97.0%, Sinopharm Chemical Reagent Co.) was
used as the solvent of the organic phase. The inorganic salts Na$_2$SO$_4$ (99%), MgSO$_4$
(AR), MgCl$_2$ (99.9%) and NaCl (99.5%) were purchased from Aladdin. Polyethylene
glycols (PEGs, Acros Organics) with molecular weights of 200, 400, 600, 1000, 2000,
10000, 20000 and 70000 Da were used as neutral solutes to evaluate the molecular
weight cutoff (MWCO).

2.2. Preparation of PSf/O–MoS$_2$ UF membrane

UF membranes were prepared by solution casting, followed by a nonsolvent-
induced phase inversion method. Five different casting solution formulations were
configured by doping different weight percentages of O-MoS$_2$ in the PSf polymer
solution, as listed in Table 1. First, appropriate amounts of PEG400 and O-MoS$_2$ were
mixed in N,N-dimethylacetamide (DMAc) solvent, followed by 2 h of ultrasonication
to disperse the O-MoS$_2$ and reduce agglomeration. PSf powder was added to the
solution and kept at 70 °C with continuous stirring. The resultant casting solution was
left to stand still at room temperature for 24 h to remove the air bubbles. The UF
membrane was prepared by casting a film with a thickness of 100 μm on an polyester
nonwoven fabric using a casting knife at a speed of 4 m/s. After a 5 s air bath at
ambient temperature, the casted membrane was placed into DI water and kept for at
least 12 hours. The precipitated PSf membranes were further thoroughly washed with
DI water. To prevent bacterial contamination, Use 0.5% sodium bisulfite solution
(NaHSO$_3$) as a reserve to store PSf UF membranes. These substrates were denoted as
PSf, PSf/O-MoS$_2$-x, where x represents the weight percentage of the O-MoS$_2$ in the
doping solution.

Table 1 Properties of the doping solutions for the preparation of PSf/O-MoS$_2$ UF membranes.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>PSf (wt%)</th>
<th>PEG400 (wt%)</th>
<th>O-MoS$_2$ (wt%)</th>
<th>DMAc (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf-0</td>
<td>18.00</td>
<td>1.00</td>
<td>–</td>
<td>81.00</td>
</tr>
<tr>
<td>PSf/O-MoS$_2$-3wt%</td>
<td>18.00</td>
<td>1.00</td>
<td>0.03</td>
<td>80.97</td>
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<tr>
<td>PSf/O-MoS$_2$-6wt%</td>
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<td>1.00</td>
<td>0.06</td>
<td>80.94</td>
</tr>
<tr>
<td>PSf/O-MoS$_2$-9wt%</td>
<td>18.00</td>
<td>1.00</td>
<td>0.09</td>
<td>80.91</td>
</tr>
<tr>
<td>PSf/O-MoS$_2$-12wt%</td>
<td>18.00</td>
<td>1.00</td>
<td>0.12</td>
<td>80.88</td>
</tr>
</tbody>
</table>

2.3 Preparation of PA selective layer

The separation layer of the TFC and thin film nanocomposite (TFN) membranes was prepared via in situ IP between PIP and TMC on the UF support membrane. First, clean the NaHCO$_3$ on the UF membrane, followed by drying at ambient temperature. Then, the PSf UF membrane pieces were impregnated in aqueous solution containing 1.50 wt% CSA, 1.50 wt% TEA and 1.60 wt% PIP for 30 s. Subsequently, the aqueous solution was drained, and the residual PIP aqueous solution was absorbed using tissue papers for a duration of 3 min. The membrane was then immersed in n-hexane containing 0.35 wt/v% TMC for 20 s. Finally, the membrane was dried in a 60°C oven for 2 min. The as-prepared NF membranes with the incorporation of nanoparticles at concentrations of 0.00, 0.03, 0.06, 0.09 and 0.12 wt/v% were denoted as the F0, F3, F6, F9 and F12 membranes, respectively. The preparation flow chart of the membrane is shown in Fig. 1.

2.4 Membrane and O-MoS$_2$ characterization

The prepared membranes were dried in an oven at 60 °C for over 48 h before characterization. The hydrophilicity of the UF support membrane and the NF
membrane was evaluated using a contact angle analyzer (OCA15EC, Dataphysics, Germany) by dropping 2 μl DI water onto the membrane surface. In order to observe the surface morphology and cross-sectional morphology of the UF base membrane and NF membrane, the field emission scanning electron microscope (SEM, EVO 18, Carl Zeiss, USA) was used to test them. Transmission electron microscopy (TEM, Talos-S, FEI, USA) was used to characterize the lamellar structure of O-MoS₂ and examine the distribution of the incorporated O-MoS₂ in the NF membrane matrix. X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi, USA) tested on nanoparticles and PSf-0 and PSf-MoS₂-6wt% UF membranes revealed the binding energy of O-MoS₂ and the atomic composition of the membrane. The atomic compositions of NF membranes F0 and F6 were determined by X-ray diffraction (XRD, X’Pert Pro, PANalytical, Netherlands). Noncontact atomic force microscopy (AFM, Bruker Dimension ICON, USA) was used to characterize the surface roughness of the prepared nanofiltration membranes and the thickness and morphology of the O–MoS₂ nanosheets. The zeta potential (Anton Paar Surpass 3, Austra) was using to measure surface charge of the membrane by a 1 mM KCl electrolyte solution at a clearance height of around 100 μm. The MWCO of the NF membrane was characterized by a total organic carbon/total nitrogen (TOC/TN) analyzer (Multi N/C 3100, Germany).

2.5. Membrane performance

2.5.1 Performance of O–MoS₂ UF membrane

A lab-scale cross-flow device with an effective filtration area of 12.6 cm² was used to evaluate the membrane filtration performance. The membrane was stabilized at a pressure of 2 bar for 30 min prior to the filtration test. The UF test was carried out at 25°C, 1 bar and the pure water flux of the membrane was calculated by equation (1):

\[ J_w = \frac{Q}{A t} \]  

where \( J_w \) is the water flux (L m⁻² h⁻¹), \( Q \) is the total volume (L) of the osmotic solution at a duration of \( t \) (h), and \( A \) is the effective membrane area (m²). Meanwhile, the rejection rate of bovine serum albumin (BSA) of the UF membrane was tested at a
concentration of 1 g/L.

2.5.2 Performance of the PA/O–MoS$_2$ NF membranes

Four inorganic salts, namely, Na$_2$SO$_4$, MgSO$_4$, MgCl$_2$ and NaCl, were selected as the solutes. A single salt solution with a salt concentration of 2000 ppm was used as the feed. Each membrane was compacted at a pressure of 2 bar for 30 min. The produced water was collected under 4 bar. The conductivity of the original solution and the permeate is measured by a conductivity meter (DDS-307A, Shanghai Lei Magnetic Instrument Factory, China). The approximate rejection rate calculation method is according to equation (2):

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right)$$  \hspace{1cm} (2)

where $C_p$ and $C_f$ respectively stand of the salt concentrations (mg/L) of original solution and effluent.

In the long-term stability test, the rejection of ions was also assessed by measuring the change in electrical conductivity in the feed and the permeate.

2.6. Pore size and pore size distribution of the PA/O-MoS$_2$ NF membrane

The pore size and pore size distribution were obtained by measuring the rejection of PEG with different molecular weights at a concentration of 1000 ppm at a pressure of 4 bar, 25°C. The 90% rejection rate corresponds to the MWCO, and the 50% rejection rate corresponds to the mean effective membrane pore size ($\mu_p$). The calculation of membrane pore size and pore size distribution is based on the following formula (3)-(5), as reported previously [28,29]:

$$a = 16.73 \times 10^{-10} \times M_{PEG}^{0.557}$$  \hspace{1cm} (3)

$$d_s = 2 \times a \times 10^7$$  \hspace{1cm} (4)

$$\frac{dR(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp \left[ -\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right]$$  \hspace{1cm} (5)

Where $a$ (cm) and $d_s$ (nm) are respectively described as the PEG’s Stoke radius and diameter. In general, when the PEG rejection rate reaches 50%, the $d_s$ value obtained ($\mu_s$) is approximately expressed as the average effective pore size ($\mu_p$) of the membrane.
3. Results and Discussion

3.1 Preparation and characterization of the O-MoS$_2$ nanomaterials

O-MoS$_2$ was prepared by the typical Hummers method. Because of the strong external force and oxidation effect during ultrasonication, the bulk O-MoS$_2$ crystals were exfoliated into few layered structures, as observed by transmission electron microscopy (TEM) (Fig. 2a-b). The planar hexagonal crystal structure of O-MoS$_2$ was characterized by high-resolution TEM, as shown in Fig. 2c-d. No defect was observed, indicating that the oxidation process had no damage to the surface of the crystal structure of O-MoS$_2$. The thickness of the prepared O-MoS$_2$ was measured by AFM. The results show that the prepared O-MoS$_2$ nanosheets have a size of several hundred nanometers and a thickness of approximately 5.6 nm. As reported by Yang et al. [25], the diffraction angle of O-MoS$_2$ is $2\theta=14.2^\circ$, which is characterized by XRD. The single layer thickness of O-MoS$_2$ was approximately 0.62 nm based on Bragg’s law. Therefore, the exfoliated O-MoS$_2$ had a thickness within 9 layers.

Fig. 2 TEM (a-b) and surface characteristics of O-MoS$_2$ nanosheets, (c) 2D AFM image and (d)
3.2 Effect of the addition of O-MoS$_2$ on the UF membrane

To investigate the effect of O-MoS$_2$ on the nonsolvent-induced phase inversion process, the top view and the cross-sectional structure of the prepared PSf UF support were characterized by SEM. The results are shown in Fig. 4. It can be clearly seen that the pores of the PSf/O-MoS$_2$-6wt% substrate become elongated during the phase inversion process, forming long finger-like cavities extending from top to bottom running through the membrane. This is mainly because the addition of hydrophilic O-MoS$_2$ leads to an increase in the exchange rate between the solvent and the nonsolvent during the phase inversion process [9,30]. This kind of pore is more conducive to water transport and salt rejection. This kind of long finger-like holes are close together to provide the membrane with stronger mechanical strength [11]. However, the increasing content of the 2D materials also leads to an increase in the viscosity of the casting solution (Table 2). As reported by Kim et al. [31], the increase in the viscosity of the casting liquid would slow down the mass transfer rate during the phase inversion process. This results in a secondary phase separation in which the closely arranged long finger-like pores will merge before solidification and
agglomerate to form larger and thicker bubble-like pores [32]. As a consequence, the skin layer consists of smaller irregular cavities, as observed in the PSf/O-MoS$_2$-9wt% and PSf/O-MoS$_2$-12wt% membranes compared with that of other membranes. The higher rejection of bovine serum albumin (BSA) of the PSf/O-MoS$_2$-6wt% membrane (92.3% vs 87.1%) also confirms that the O-MoS$_2$-embedded PSf substrate membrane had a denser surface structure than the control membrane.

<table>
<thead>
<tr>
<th>Rotating speed(r/min)</th>
<th>F0</th>
<th>F3</th>
<th>F6</th>
<th>F9</th>
<th>F12</th>
</tr>
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<tbody>
<tr>
<td>300</td>
<td>295</td>
<td>298</td>
<td>303</td>
<td>305</td>
<td>325</td>
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<td>278</td>
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<tr>
<td>900</td>
<td>256.7</td>
<td>258.9</td>
<td>265.8</td>
<td>274.2</td>
<td>285.8</td>
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</table>

Electronic copy available at: https://ssrn.com/abstract=4010370
Fig. 4 SEM images of the surface (a₁-a₅) and the cross-sectional (b₁-b₅) morphologies of the UF membranes (a₁, b₁-PSf/O-0, a₂, b₂-PSf/O-MoS₂-3wt%, a₃, b₃-PSf/O-MoS₂-6wt%, a₄, b₄-PSf/O-
The successful incorporation of the 2D O-MoS$_2$ materials in the PSf matrix was determined from XPS. As shown in Fig. 5, compared to the control PSf membrane, two new peaks were observed in the PSf/O-MoS$_2$-6wt% membrane at binding energies of 230 eV and 168 eV, ascribed to Mo3d and S2p. These two peaks are the characteristic peaks of MoS$_2$, as inferred from the XPS of O-MoS$_2$ (Fig. S1). The results demonstrated the existence of O-MoS$_2$ nanomaterials in the PSf UF membrane.

![XPS core level spectra for UF membranes](https://ssrn.com/abstract=4010370)
The pure water flux of the modified UF membranes was evaluated, as shown in Fig. 6b. The addition of the hydrophilic 2D material significantly enhanced the pure water flux of the UF membrane. This could be attributed to the improved hydrophilicity of the membrane surface as well as the more porous sublayer structure of the PSf/O-MoS$_2$ hybrid matrix. The PSf/O-MoS$_2$-6wt% membrane exhibited the highest water flux of 356.5 L m$^{-2}$ h$^{-1}$, which is about 2.3 times higher than that of the original membrane (156.6 L m$^{-2}$ h$^{-1}$). However, the enhanced permeability did not sacrifice the selectivity of the hybrid UF membrane. This was confirmed by the separation of neutral polyethylene glycol molecules. The PSf/O-MoS$_2$-6wt% membrane had a MWCO of 73,276 Da, which was much lower than that of the control PSf UF membrane with an MWCO of 113,541 Da, as shown in Fig. 6c. The corresponding average effective pore size decreased from 14.7 nm to 6.4 nm, implying that the top active layer of the UF membrane became relatively denser for the content of nanomaterials O-MoS$_2$ increased to 0.06wt% (Fig. 6d).
of the PSF-0 and PSF/O-MoS$_2$-6wt% UF membranes.

3.2 Characterization of PA/O-MoS$_2$ NF membranes

Fig. 7 shows the SEM images of the surface and cross section of the PA/O-MoS$_2$ NF membranes. The SEM image of the membrane surface clearly shows that a bubble structure with circular protrusion appears on the blank membrane surface, which is a typical structure of the PIP-based thin film PA surface. The results are consistent with the AFM observations.

Fig. 7 SEM surface morphologies of NF membranes (a$_1$-F0, a$_2$-F3, a$_3$-F6, a$_4$-F9 and a$_5$-F12).

The cross sections of the F0 and F6 membranes were observed by TEM shown in Fig. 8 (a-c). PA layer is successfully covered on the membrane. In Fig. 8b and 8c, it can be observed that O-MoS$_2$ nanoparticles are embedded in the PSf supporting layer.
Moreover, because the size of the nanoparticles in the substrate is much larger than the thickness of the PA layer, some O-MoS\textsubscript{2} on the surface of the base substrate will be exposed on the film surface, as shown in Fig. 8c, causing the film surface to bulge. To a certain extent, the surface roughness of the film is increased. The AFM data in the supporting information Fig. S2 and Table. S1 proves this inference. Another important reason for the increase in membrane surface roughness may be the increased surface hydrophilicity of the PSf/O-MoS\textsubscript{2} substrate, promoting the IP reaction by adsorbing more aqueous monomers, thereby producing a rougher surface.

![Fig. 8 TEM cross-sectional morphologies of the F0 (a) and F6 (b-d) membranes.](image)

To further determine the composition of the NF membrane, XRD tests were performed on typical F0, F6, and F12 samples. As shown in Fig. 9, the peak representing O-MoS\textsubscript{2} can be seen clearly in F6 and F12 [25]. Within the depth limit of XRD scanning, the PA layer generated by IP cannot completely cover O-MoS\textsubscript{2} in the membrane matrix. It is further proven that 2D material in the NF membrane matrix is effective.
The water contact angle and zeta potential of NF membranes were tested to determine the influence of the nanomaterials added to the base substrate. The results are shown in Fig. 10a and 10b. The water contact angle fluctuates between $45^\circ$ and $47^\circ$. Compared with the UF base membrane, since the PA layer formed improves the membrane surface hydrophilicity as a whole, the water contact angle measured mainly shows the hydrophilicity of the PA layer and has little relationship with the concentration of O-MoS$_2$ loaded in the membrane matrix. The zeta potential of the membrane surface is shown in Fig. 10b. When the pH is 8, the charge on the membrane surface decreases from -70.0 mV of F0 to -79.4 mV of F12. In the process of IP, the deprotons of the amine functional groups and the dissociation of the carboxyl groups on the membrane surface are the main reasons for the high negative charge of the membrane. On the other hand, the surface electronegativity of the modified NF membrane increases with the increase in the addition of 2D nanomaterials. A previous report noted that when nanofillers were incorporated into the matrix layer, the surface of TFN membranes tended to have a greater negative charge [23]. The membrane surface charge has a great influence on the salt rejection capacity of the membrane because sieving effect and Donnan effect are the main mechanisms of NF separation [35]. The greater the electronegativity of the membrane, the more negatively charged the membrane's repulsion, and the higher the separation efficiency [36,37].
3.3. Filtration performances of PA/O-MoS$_2$ NF membranes

Neutral PEG molecules of different molecular weights are used as markers to evaluate the MWCO of the prepared NF membranes. The results are shown in Fig. 11 (a-b). The F6 membrane has the smallest MWCO of about 937 Da. Theoretically, the addition of O-MoS$_2$ to the substrate membrane can effectively improve the support membrane structure in the phase inversion process, making the NF membrane pores narrower. Correspondingly, the MWCO should also be reduced. However, the MWCO is larger for the F12 membrane, which is about 1401 Da. F0 is slightly smaller than F12, reaching 1260 Da. This is probably because when the 2D material concentration in the membrane reaches 0.12 wt%, the pores (121,220 Da) are larger than those of the original membrane F0 (Fig. S3 and Table S2). Furthermore, as the concentration of nanoparticles increases, more O-MoS$_2$ is exposed on the surface of the film. These factors will cause defects in the PA layer formed on the surface [33]. On this basis, the mean effective pore size ($\mu_P$) of membranes F0 and F6 with the maximum molecular rejection for 50% rejection were calculated as 0.56 nm and 0.44 nm, respectively. Since one of the main principles of NF membranes to intercept particles in water is the screening effect, the reduction of membrane molecular rejection and the average effective pore size can directly enhance the membrane's ability to intercept smaller particles.

The pure water flux of the membrane was measured. the results are shown in Fig. 11c. The water flux is increased from 18.4 L m$^{-2}$ h$^{-1}$ for F0 to 30.8 L m$^{-2}$ h$^{-1}$ for F6,
with an increment of 67.4%. The thickness of the PA layer increases as the hydrophilicity of the membrane increases. However, as the pore structure, distribution and properties of the substrate membrane have been greatly enhanced, the water flux of the TFN membrane has still been improved. At the same time, the characteristics of the 2D material increase the membrane water flux [38]. The enhanced surface roughness may also contribute to the increased water flux of the TFN membrane compared to that of the control membrane [39,40]. However, as the content of O-MoS$_2$ in the base membrane increases, the water fluxes of membranes F9 and F12 start to decrease instead. It is also due to the strong hydrophilicity of membranes F9 and F12 that during the IP process, that is, the hydrophilic carrier forms more PA in the pores of the supporting membrane. The formed PA composite membrane is hydrophilic but may narrow the pores of the supporting membrane [41].

With the addition of 2D nanomaterials of different concentrations, the salt rejection ability of the membrane varies greatly. As shown in Fig. 11d, the F6 membrane with the best performance improved its ability to reject various salts to varying degrees, especially for divalent salts. The ability to retain Na$_2$SO$_4$ and MgSO$_4$ reached 96.7% and 91.5%, respectively. The rejection rate of monovalent salt is relatively low, less than 25%. This may be because the base membrane of F6 has a smaller pore size. This kind of base membrane has better salt rejection capacity, which is similar to a previous report [32]. A membrane with a larger pore size such as F0 and F3 is likely to form a thinner PA layer, which leads to a higher degree of defects and a lower salt rejection rate [42]. In the process of IP, PIP in the water phase would penetrate into the membrane pores with a larger pore size, causing PA to be produced inside the membrane pores. As a result, the PA layer on the top layer is thinner and may also cause larger defects, and thus the salt rejection rate is lower [44]. For the more hydrophilic membranes F9 and F12, due to the increase in the degree of hydrophilicity of the membrane surface, the PIP in the water phase would penetrate into the membrane pores faster, and the IP reaction may proceed in the pores. This leads to deterioration of membrane performance [45]. On the other hand, the
macropores of the base membrane and the looseness of the PA layer would cause the membrane to reduce salt retention [46].

The radii of the hydrated ions used in the experiment are shown in Table S3. The pore size of the membrane was much larger than the radii of the hydrated salt ions. For instance, the pore size of the F6 membrane had an effective pore size of 0.44 nm, which was higher than that of the divalent ions (rSO₄²⁻: 0.38 nm, rMg²⁺: 0.43 nm) and the monovalent ions (rNa⁺: 0.36 nm, rCl⁻: 0.33 nm). This indicates that the size sieving effect may be not the dominant separation mechanism for the NF membrane in this case. This phenomenon has also been widely reported [20]. It was believed that the Donnan exclusion effect may dominate ion separation in the NF process [47]. This also explained the rejection order of the 4 different salts by the membrane. According to research, for the salt retention of NF membranes, which one of size exclusion or electrostatic repulsion is dominant will affect the repulsion order of NaCl and MgCl₂ [46]. Due to the PA/PSf membrane, its MWCO is relatively large (about 937-1401 Da), electrostatic repulsion is dominant in the desalination process. In this case, the attraction of the negatively charged hybrid membrane to Mg²⁺ is greater than that of Na⁺, so the rejection rate of NaCl is higher than that of MgCl₂.
3.4. Stability test of PA/O-MoS$_2$ NF membranes

To investigate the stability of the composite membrane under long-term filtration in a high salt solution, a 2 g/L Na$_2$SO$_4$ salt solution was configured. The membrane was tested over 48 h at 4 bar. As shown in Fig. 12, the water flux decreases gradually with the operation time. Hybrid membrane F6 had a loss in water flux of 9.2%, dropping from 39.3 L m$^{-2}$ h$^{-1}$ to 35.7 L m$^{-2}$ h$^{-1}$, which was much outstanding than the performance of the control membrane F0 (15.1%). This can be ascribed that less compaction effect of the PSf substrate with the addition of the 2D material than the control, providing the TFC membrane with a higher pressure resistance. Despite the compaction of the membrane, both membranes had very stable salt rejection. The modified F6 membrane had a Na$_2$SO$_4$ rejection of 96.8%, which is higher than that of the control F0 membrane (92.7%). The results indicate that the nanocomposite PSf/O-MoS$_2$ NF membrane is promising in the treatment of high-concentration saline water.
Fig. 12 Stability test of the F0 and F6 membranes. A 2 g/L Na$_2$SO$_4$ aqueous solution was used as the solute.

3.5 Nanofiltration of the rare earth wastewater

The mining and smelting process of rare earth elements generally produces a large amount of wastewater containing low concentrations of rare earth elements. NF could be a potential advanced pretreatment of rare earth wastewater to remove most of the inorganic salts and toxic heavy metals as well as reduce the content of organic matter. Therefore, real wastewater from the precipitation and extraction stage of rare earth smelting calcium soap was used as the feed to evaluate the potential application of the newly designed NF membrane for the treatment of rare earth wastewater. The F0 and F6 membranes were tested, and their separation performances were compared in a cross-flow filtration system for a duration of 24 h at 4 bar. The water quality and the elemental compositions of the rare earth wastewater used in this work were measured and are summarized in Table 5. Rare earth wastewater has an extremely complex background containing more than 14 species and has a strong acidic pH of 0.87. Moreover, the wastewater has a high salinity with sodium ion concentrations up to 20,070 mg L$^{-1}$. It should be noted here that rare earth wastewater generally needs to be mixed with domestic sewage or rainwater to dilute its harsh conditions in municipal wastewater treatment plants. Thus, the raw wastewater was diluted 50 times before the test to ensure that the membrane was not damaged by the strong acid.
liquid and to mimic the real situation. After dilution, the pH of the solution rose to 2.36. Permeate was collected every hour. The salt removal efficiency is determined by measuring the conductivity of the produced water.

Table 5. Compositions of the original precipitation extraction wastewater from rare earth smelting calcium soap.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>0.87</td>
</tr>
<tr>
<td>NH₄⁺-N (mg/L)</td>
<td>≤15</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>154</td>
</tr>
<tr>
<td>Conductivity (ms/cm)</td>
<td>113.3</td>
</tr>
<tr>
<td>Salinity (%)</td>
<td>12.3</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>20070</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>5.1</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>-</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>36.9</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>107.7</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>24.2</td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>0.6</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>1935</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>198.5</td>
</tr>
<tr>
<td>TDS (g/L)</td>
<td>56.8</td>
</tr>
<tr>
<td>Co (mg/L)</td>
<td>0.1</td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>-</td>
</tr>
<tr>
<td>Cr (mg/L)</td>
<td>-</td>
</tr>
</tbody>
</table>

As shown in Fig. 13 (a-b), the control membrane (F0) and the nanocomposite membrane (F6) had a decreasing water flux during long-term filtration. This is mainly caused by membrane compaction, as observed in the stability test mentioned above (Fig. 10). In addition, the high content of TOC in the feed (representing high organic solutes) tends to foul the membrane surface by forming a cake layer. The flux of the O-MoS₂ nanocomposite membrane declined by 12.8% after running for 24 h, which is lower than that of the control membrane with a reduction of 19.2%. Initially, both membranes had very low salt retention but stabilized after 4-8 h due to physical compaction as well as the formation of a cake layer [48]. The F6 membrane was more easily stabilized than the F0 membrane. The salinity removal efficiency of the F6 membrane was maintained at 95%, which was much higher than that of the F0 membrane, with a removal efficiency of 90%. The conductivity of the permeate was
reduced significantly from 2610 μs/cm to 128.6 μs/cm. The results indicate that the hybrid nanocomposite membrane could effectively remove salt ions from rare earth wastewater at high salinity.

The stable rejection of the PSf/O-MoS$_2$-supported TFC membrane demonstrates that the O-MoS$_2$ hybrid membrane had excellent chemical resistance to harsh acidic conditions and high salinity (2610 μs/cm, pH=2.46). The newly developed membrane prepared via the facial addition of O-MoS$_2$ into the support layer of the TFC membrane is advantageous compared to the reported state-of-the-art techniques, such as coating, layer-by-layer assembly and incorporating 2D nanosheets into the PA selective layer. These membranes generally suffer from leaching or detaching issues during the initial operation stage [16]. Alternatively, embedding functional O-MoS$_2$ into the membrane sublayer is practical, reproducible and easy to fabricate.

### Fig. 13 Stability test of the F0 and F6 membranes. (a) The flux decline rate; (b) The salt rejection. Rare earth wastewater was used as the feed solution. Tested at: 4 bar and 25 ℃.

### 4. Conclusion

In this study, a novel nanocomposite PSf/O-MoS$_2$ membrane was prepared as the substrate of a TFC membrane. The substrate was fabricated via a phase inversion method by incorporating the synthesized O-MoS$_2$ 2D nanosheets into the doping solution. The asymmetric structure of the substrate varied with the content of the added O-MoS$_2$ nanoparticles. When the pore structure shifted from a bubble-like structure to a finger-like structure, the O-MoS$_2$ content in the membrane support layer reached 0.06wt%. In addition, the hydrophilicity of the substrate was improved
significantly as the contact angle was reduced from 79.0° to 62.3°. The pore size of
the top active layer was also reduced from 14.7 nm to 6.4 nm. The PSf/O-MoS$_2$-
supported TFC membrane showed 1.7 times higher water flux and higher salt
rejections than the pristine membrane. This is mainly because the support layer has a
better hydrophilicity and a denser pore size, giving rise to a less pore blocking effect
during the IP reaction and a less defective thin film. The potential application of the
PSf/O-MoS$_2$ substrate-supported TFC membrane was demonstrated by purifying real
rare earth wastewater under highly acidic conditions (diluted 50 times, pH: 2.46). The
PSf/O-MoS$_2$ nanocomposite TFC membrane showed excellent salinity removal
efficiency over 95%, which was higher than that of the control membrane (90%) and
good stability during a 24 h filtration. This work provides a new avenue to tailor the
separation performance of TFC membranes by incorporating nanomaterials into the
substrate layer. The work also validated that NF could be a promising technique to
address emerging challenging rare earth wastewater.

Declaration of competing interest

There are no conflicts to declare.

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References

Carvalho, J. Pinheiro-Torres, E. Pereira, Sustainable recovery of neodymium
and dysprosium from waters through seaweeds: Influence of operational
parameters, Chemosphere. 280 (2021) 130600.

[2] V. Balaram, Rare earth elements: A review of applications, occurrence,
exploration, analysis, recycling, and environmental impact, Geosci. Front. 10

preparation of single light rare earth carbonate by Mg(HCO$_3$)$_2$ precipitation

Electronic copy available at: https://ssrn.com/abstract=4010370


[29] Y. Li, E. Wong, A. Volodine, C. Van Haesendonck, K. Zhang, B. Van Der Bruggen, Nanofibrous hydrogel composite membranes with ultrafast transport...


