High flux membrane based on in-situ formation of zirconia layer coated the polyethersulfone substrate for ions separation

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ABSTRACT

A flawless, extremely loose, membrane, efficient for multivalent ions separation, has been successfully synthesized by the in-situ formation approach. The as-synthesized nanofiltration (NF) membrane, NF_PES-Zr, proceeded from a thin film layer of nanoparticles (NPs) zirconium that coated the platform of the polyethersulfone (PES) ultrafiltration (UF) membrane through a bio-glue made from dopamine hydrochloric and sodium bicarbonate buffer. The estimation of the average pore size of the novel organic-inorganic NF membrane NF_PES-Zr using the filtration velocity approach of Guerout-Elford-Ferry was close to 0.9 nm. NF_PES-Zr membrane holds a record in permeate water flux release of about 62.5 L.m⁻².h⁻¹ and was revealed to be effective for multivalent ions separation. A 5 days-test performed on NF_PES-Zr demonstrated its long-term stability and showed a rejection rate of 93.4% and 37.8% respectively for Ca²⁺ and Na⁺.

Key words | ions rejection, nanofiltration, nanoparticle, organic-inorganic membrane, polyethersulfone, zirconium

HIGHLIGHTS

- Nanoparticle zirconium deposition by in-situ formation method.
- Modification of an ultrafiltration membrane to a nanofiltration membrane.
- Energy dispersive spectrometry (EDS) associated with field emission scanning electron microscopy (FESEM) for membrane surface structures characterization.
- High flux membrane for ions separation.
INTRODUCTION

Nanofiltration (NF) membranes possess properties between reverse osmosis (RO) and ultrafiltration (UF) with a pore size close to 1 nm, which corresponds to a molecular weight cut-off (MWCO) between 300 and 500 Da and can nowadays reach 300 kDa. Nanofiltration membranes (NFMs) in contact with aqueous solution are lightly charged because of the adsorption of charged solute on its surface and mainly due to surface functional groups dissociation that occurred (Mohammad et al. 2015). In the case of polymeric NFMs, which possess ionizable groups such as sulfonic acid groups, carboxylic groups, etc., that result in the charged surface in contact with feed solutions. NFMs exhibited high performance in the rejection of inorganic salts even of small molecular organics in the same way as RO membranes (Worou et al. 2021a, 2021b). Distinguishing features of NFMs are best performance rejection towards multivalent ions, higher flux permeation in comparison with RO membranes, and low monovalent ions removal (Elcik et al. 2016; Lv et al. 2016; Nicomel et al. 2016). These tremendous properties have promoted NFMs to be used in niche applications in several areas particularly in drinking water production, wastewater treatment, food engineering, biotechnology, and pharmaceutical (Donnan 1995; Mohammad et al. 2015; Siddique et al. 2020).

The NF process is reported to be extremely complex and dependent on both interfacial and micro-hydrodynamic events that occur at its surface, even within its nanopores. Donnan, steric, transport, and dielectric effects combined determine the NF membranes removal performance (Worou et al. 2021a, 2021b). The famous Donnan effect makes clear not only the equilibria but also the potential interactions between the membrane surface and the charged species inside the feed solution (Worou et al. 2021a, 2021b). Neutral solutes transport is performed via the steric mechanism, which is a size-based exclusion, and was already well settled through various studies on ultrafiltration (UF) membranes (Deen 1987). NF membranes’ charge originates from their surface functional groups that ionize and also from the structure of their pores (Hagmeyer & Gimbel 1998; Ernst et al. 2000). These functional groups could be basic in nature, acidic, or indeed both, depending on the nanoparticles (NPs) materials utilized during the preparation process. It was demonstrated that the pH of the solution strongly influenced the dissociation of such surface groups, since the membrane, at a specific pH value, may display an isoelectric point (Childress & Elimelech 1996). In addition, Afonso et al., have established that Nanofiltration membranes show a weak ion-exchange ability, and even on some occasions, ions from feed solution can adsorb to the NFM surface generating a modification of membrane charge (Afonso et al. 2001). The fixed membrane charge and ion valence in solution in contact with membrane determine the electrostatic attraction or repulsion force that appears on the localized ionic surroundings as a direct consequence of the aforementioned dielectric phenomena. The dielectric exclusion phenomena are not well understood yet since there are two competing hypotheses that try obscurely to explain the exact nature of interaction that takes place. The first hypothesis is called the ‘image forces’ phenomenon (Yaroshchuk 1998; Nicomel et al. 2016) while the second is called the ‘solvation energy barrier’ mechanism (Bowen & Welfoot 2002). These two exclusion phenomena
were investigated in detail (Oatley et al. 2012), and it was shown that they are a fruit of both nano-length scales and extreme spatial confinement that occur during NFMs separations mechanism. It was also reported that solutes moving freely in feed solution were disrupted by dragging forces exerted by the solvent passing by the confined pores’ structure. The transport of this solute across the nanopores structure is highly affected by the local environment and is credibly considered as hindered. Since it’s understood that the dimensions of the NFMs layers are close to atomic length scale, the limitations in available measurement technologies, the knowledge of NFMs surface properties and structural characterization has been delayed and resulted in a significant debate (Schafer 2005), and the dielectric exclusion phenomenon is especially contested (Wong et al. 2016).

Currently, there are satisfactory results available to conclude the existence of a porous active film in most NFMs. To achieve the characterization of these pores, four main methodologies are used, (i) the gas adsorption/desorption method or Brunauer-Emmett-Teller (BET) technique (Wang et al. 2013; Fang et al. 2014), (ii) indirect measurement of pore size that consists of the use of neutral solute removal investigation and models (Oatley et al. 2013; García-Martín et al. 2014), (iii) reverse surface impregnation (RSI) combined with transmission electron microscopy (TEM) (Mohammad et al. 2015), and (iv) atomic force microscopy (AFM) for direct measurement of pore size, surface roughness, topography, etc. (Misdan et al. 2015).

Zirconium dioxide (ZrO2) was adopted as the inorganic selective layer because it has been widely used for high-performance filtration membranes as an inorganic component with superior physical, chemical, and thermal stability and good hydrophilicity (Lv et al. 2016; Worou et al. 2021a, 2021b). The thin ZrO2-layer was then obtained from the controlled hydrolysis process of zirconium sulfate tetrahydrate (Zr(SO4)2) under equilibrium reactions (Equations (1)–(3)) developed later. In this article, AFM associated with scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) were used to characterize the as-synthesized membrane structure after the growth of zirconia (ZrO2) on polyethersulfone (PES) ultrafiltration platform by the in-situ formation approach. Water contact angles (WCA) and zeta potential were also measured with the aim of determining the novel membrane properties.

**EXPERIMENTAL SESSION**

**Materials and agents**

Polyethersulfone (PES) ultrafiltration (UF) membrane (MWCO = 100 kDa; L = 1 m; l = 1 m) was a commercial product of Shanghai Corun Membrane Technology Co. Ltd (China); PES represented the substrate. Various salts including CaCl2 and NaCl were supplied by Aladdin (China) for membrane separation tests. Deionized (DI) water, dopamine hydrochloride (98%, (HO)2C6H3CH2 CH2NH2.HCl), and sodium bicarbonate buffer (pH 8.0, NaHCO3) solution were purchased from Aladdin (China) for substrate preparation and to conduct interfacial polymerization. Zirconium sulfate tetrahydrate (Zr (SO4)2.4(H2O)), hydrochloric acid solution (12 mol/L), butanol, and sodium hydroxide (NaOH) were all obtained from Sino Pharm Chemical Reagent Co.

**The fabrication process for the novel membrane NF_PES-Zr**

Small pieces of about 2,922 mm² of polyethersulfone ultrafiltration membrane were introduced in sodium hydroxide solution (2.0 mol/L) for 2 h at 50 °C. A fresh solution was prepared for deposition by dissolving 4 g of dopamine hydrochloride in 1 L of sodium bicarbonate buffer solution (pH = 8.0, 40 mmol/L). The deposition time was set at 2 h. Both dopamine and sodium bicarbonate buffer acted like ‘bio-glue’ to prepare the top surface of PES. The resulting membrane pieces were pre-wetted in butanol for 25 min and then immersed into the fresh solution (‘bio-glue’) and stirred at 25 °C for 2 h. The resulting membranes at this last step were called G-PES. Dopamine/sodium bicarbonate buffer coated PES was G-PES. The as-synthesized mussel-inspired platform (G-PES or dopamine HCl/sodium bicarbonate buffer coated PES) was washed in deionized (DI) water several times and dried in the ambient environment. 1 g of zirconium sulfate tetrahydrate (Zr (SO4)2.4(H2O)) was dissolved in 250 mL of hydrochloric solution (40 mmol/L). Then, pieces of G-PES were introduced into the solution for 2 days at room temperature of 25 °C. The resulting membrane was called NF_PES-Zr. This organic-inorganic membrane was washed in DI water several
times and dried in an oven for 5 h to evaluate its performance. The reactions and steps for the fabrication process for the novel membrane NF_PES-Zr are shown in Equations (1)–(3) and Figure 1.

**Hydrolysis process of zirconium sulfate tetrahydrate to zirconia (ZrO$_2$)**

\[ 2[Zr(SO$_4$)$_2$] + 3H$_2$O \rightarrow [Zr$_2$(OH)$_3$(SO$_4$)$_4$]$^{3-}$ + 3H$^+$ \] (1)

\[ [Zr$_2$(OH)$_3$(SO$_4$)$_4$]$^{3-}$ + 3OH$^-$ \rightarrow Zr$_2$(OH)$_6$SO$_4$ + 3SO$_4^{2-}$ \] (2)

\[ Zr$_2$(OH)$_6$SO$_4$ + 2OH$^-$ \rightarrow 2ZrO$_2$ + SO$_4^{2-}$ + 4H$_2$O \] (3)

**Performance of the novel synthesized membrane NF_PES-Zr**

The membrane performance of NF_PES-Zr was evaluated by using a laboratory scale cross-flow flat membrane module under 6 bars at 25°C. The effective area was 2,922 mm$^2$ for each sample. Two different salts CaCl$_2$ and NaCl have been dissolved in DI water with a concentration of 1,000 mg/L and used as feed solutions with a fixed cross-flow rate of 30 L/h. The water flux ($F_w$, L.m$^{-2}$.h$^{-1}$) and rejection ($R, \%$) were calculated by the following equations, Equations (4) and (5):

\[ F_w = \frac{Q}{A \cdot t} \] (4)

\[ R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \% \] (5)

where $C_p$ and $C_f$ are respectively the solute concentrations in permeate and feed sides, which were measured by a conductivity meter (Metrohm AG) and inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7300 DV, PerkinElmer).

The next equation was used to evaluate the overall porosity ($\varepsilon$) (Xu et al. 2018; Worou et al. 2021a, 2021b):

\[ \varepsilon(\%) = \left(\frac{W_w - W_d}{\rho_f V_m}\right) \times 100 \] (6)

where $W_w, W_d$, are the weight and dry weight of the membrane (g), $\rho_f$ is water density (g/cm$^3$) and $V_m$ is membrane small size volume in cm$^3$.

For the estimation of pore size, the filtration velocity approach was used, and for that the Guerout-Elford-Ferry equation have been used (Wan Ikhsan et al. 2021; Worou et al. 2021a, 2021b):

\[ r_m = \left(\frac{2.9 - 1.75e}{\eta \cdot Q \cdot A \cdot \Delta P}\right)^{\frac{1}{2}} \] (7)

where $\eta$ is water viscosity (8.9×10$^{-4}$ Pa.s), $Q$ is permeate flux (m$^3$.s$^{-1}$), $\Delta P$ is operating pressure 6 bars, $I$ is membrane thickness (m), and $A$ is the surface area of the membrane sample (m$^2$).

The measuring was performed at least five times and the average was chosen. The NF_PES-Zr membrane was also continuously tested on the cross-flow flat membrane module for 5 days with a report of salt removal rate and water flux every 12 h.

Figure 1 | Deposition of zirconium nanoparticles on a layer of polydopamine/sodium bicarbonate buffer.
MEMBRANE CHARACTERIZATION

Surface properties characterization

Water contact angle (WCA)

Water contact angle measurements have been done with a Drop Meter A-200 contact angle system purchased from MAIST Vision Inspection & Measurement Co. Ltd, China. Measurements have been performed on PES, G-PES, and NF_PES-Zr membranes. These membranes were immersed in ethanol for 25 min and dried in an oven before the contact angles were measured (Figure 5(a)).

Zeta potential

An electrokinetic analyzer, purchased from SurPASS Anton Paar, GmbH, Austria, was used to evaluate the charging property of each membrane’s surface. Three (03) samples had their zeta potential measured, PES, G-PES, and NF_PES-Zr membranes, as made explicit in Figure 5(b).

Stability test in various solvents

An immersion test has been performed on NF_PES-Zr to determine its long-stability in solvents for a five-day test at room temperature. Water flux and rejection were measured at each 12 h. Membranes withdrawn after this period were carefully rinsed with deionized (DI) water and dried in atmospheric conditions. The results are reported in Figure 7(b).

Surface structures characterization

Figure 2 shows the diagram of the main tools used in this study to characterize the surface structure of the NF_PES-Zr membrane. Field emission scanning electron microscopy (FESEM), with a ZEISS Sigma 500 purchased from Pittsburgh, PA, USA, has been used in this study to analyze the surface morphology of the synthesized organic-inorganic membrane NF_PES-Zr.

Atomic force microscopy (AFM), Multi-Mode Vecco, from Denton, TX, USA, has been very useful for the novel organic-inorganic NF_PES-Zr membrane morphology and roughness measurement.
An energy dispersive spectrometer (EDS) was combined in this study with field emission scanning electron microscopy for more insights on the membrane surface elements’ charge, their arrangement, and especially about the phase state of the zirconium film. The three elements especially observed on the membrane’s surface were zirconium (Zr), carbon (C), and oxygen (O).

**RESULTS AND DISCUSSION**

**Surface structures of novel synthesized NF_PES-Zr membrane**

Figure 3(a) shows the surface morphology observed through FESEM of the novel organic-inorganic membrane NF_PES-Zr and its roughness is immediately depicted in Figure 3(b). Figure 3(b) confirms what has been observed in Figure 4(a), especially since the maximum roughness is evaluated at 8.02 nm. This membrane is very smooth, and this is understandable, given that NF_PES-Zr stayed for two days in a solution of zirconium sulfate tetrahydrate (Zr (SO4)2.4 (H2O)). The dopamine hydrochloric and sodium bicarbonate buffer solutions mixture plays its role of bio-glue well since it promotes the deposition of the upper layer of zirconium nanoparticles. The hydrolysis process of zirconium sulfate tetrahydrate to the zirconium dioxide (ZrO2) is explained by Equations (1)–(3).

An energy-dispersive spectrometer (EDS) has been combined with scanning electron microscopy (SEM) to gain accurate insights into the arrangement and eventual function of nanoparticles (NPs) ZrO2. NF_PES-Zr samples...
have been tested and the results are reported as graphs in Figures 4 and 3(c)–3(f). EDS’ measures focused on three (03) elements, carbon (C) in Figure 3(d), oxygen (O) in Figure 3(f), and zirconium (Zr) in Figure 3(e) due to their unique X-ray emissions. Thus, each atomic position has been located by its unambiguous chemical signal. The emission light of each atom of C, O, and Zr was distinct from their neighbors due to their high contrast. With this information, it is henceforth possible to characterize and modify the materials at the atomic scale. The chemical elements carbon (C), oxygen (O), and zirconium (Zr) were well arranged on the NF_PES-Zr membrane surface, Figure 3(d)–3(f), respectively. This view was once again sustained by the SEM image in Figure 3(a).

The chemical structure of the NF_PES-Zr membrane surface was then investigated by FT-IR/ATR. Figure 5 shows that the novel synthesized organic-inorganic nanofiltration membrane has characteristic peaks at around 2,200, 1,100, and 900 cm⁻¹ in the FT-IR/ATR spectrum, which are assigned to the O-H, C-C (double covalent bond), and Zr-O stretching vibrations in the pyrocatechol groups. Furthermore, this analysis revealed that zirconia (ZrO₂) exists in two distinct geometric forms: (i) monoclinic zirconia (m) and (ii) tetragonal zirconia (t). The sharpest peaks reaching 1700 are attributable to the solid double covalent bond of carbon atoms. The softest peaks are characteristic of the single covalent bond between the oxygen atom and the hydrogen atom, which must undergo deprotonation.

**Surface properties of NF_PES-Zr membrane**

Each of the above-mentioned tools provided useful information on membrane surface structures. Nevertheless, because of the length-scales involved and the different imperfections that may be associated with each technique, it is recommended to use a combination of tools. Another key variable recommended for a better NFMs process understanding is the characterization of the membrane surface properties. For that purpose, the water contact angle (WCA), depending on the nature of the contact solution and zeta potential (which is affected by pH and concentration), were evaluated.

Figure 6(a) depicts the evaluation of the wettability of PES, G-PES, and NF_PES-Zr membranes, with a
DropMeter A-200 contact angle system purchased from MAIST Vision Inspection & Measurement Co. Ltd, China. The PES membrane displayed the best hydrophilicity due to its ether groups combining with the porous structure. Mohammad et al. demonstrated that PES exhibits good hydrophilicity due to its molecular structure, which facilitates hydrogen bonding with water molecules. Therefore, a higher volume of permeate could be attained using PES membrane (Mohammad et al. 2015). The same trend has been earlier observed by two of the world’s leading manufacturers of filter solutions such as polyethersulfone (PES), GVS Group and Pall, which described PES as ‘an inherently hydrophilic membrane that wets out quickly and completely resulting in fast filtration with superior flow rates and high throughputs’.

The water contact angles of both G-PES and NF_PES-Zr were quite similar from 80 s. The WCA increased with the deposition of zirconium nanoparticles (NPs). The as-synthesized NF_PES-Zr membrane is the least hydrophilic of the three membranes tested. The novel organic-inorganic membrane NF_PES-Zr exhibits excellent hydrophilicity (30°–70°) and could be fast spread out by the water, which is required for a good performance for NF membranes.

A pseudo-measurement of the Donnan potential was then used to investigate the membrane surface zeta potential (ζ) and the results are shown in Figure 6(b) (Cheng et al. 2011; Déon et al. 2012; Bauman et al. 2013). The state of PES, G-PES, and NF_PES-Zr membranes’ surface charge was measured in the pH range 3–10. G-PES membrane (dopamine hydrochloric/sodium bicarbonate buffer coated PES) exhibited a negatively charged surface in contact with a basic solution (pH > 6), because of the deprotonation of its pyrocatechol groups (C₆H₄(OH)₂ → C₆H₄(O⁻)₂) on its top layer surface. NF_PES-Zr membrane surface is less negatively charged than G-PES membrane surface since the NPs zirconium in solution generates positive ions Zr⁴⁺. The three membranes possessed a negative charge above pH 9.5. The negative ions could be easily and efficiently removed for pH > 9.5 according to the Donnan effect.

The average pore size evaluated with Equations (7) is now expressed in graphs for more understanding. Figure 7(a) shows the evolution of pore size with the deposition of the different layers of ‘bio-glue’ for G-PES membrane and NPs zirconium layer with the novel organic-inorganic thin-film composite NF_PES-Zr membrane. The pore size decreases with the formation of layers on the PES platform. The pore size of NF_PES-Zr is around 0.9 nm, which is in tune with the NFMs’ class. The porosity of PES, G-PES, and NF_PES-Zr are respectively 68.5, 64, and 53% (Figure 7(b)). This variation in porosity is understandable, the nanoparticles, because of their very small size (the order of a
nanometer), succeeded in filling the voids of the platform without changing its volume. It was also reported early in this study that the PES membrane exhibited the most excellent hydrophilicity due to its porous structure Figure 6(a). Moreover, it is well known that NPs, especially if they are hydrophilic, tend to migrate and stay on the membrane top layer surface, leading to a reduction of the pore size (Daneshvar et al. 2005).

Nanofiltration membranes (NFMs) are nowadays applied to separate and remove ions with different valences from drinking water production and wastewater treatment. The water flux of PES, G-PES, and NF_PES-Zr membranes are respectively 87, 85.7, and 62.5 L.m⁻².h⁻¹ (Figure 8(a)). The water flux from the PES membrane to the G-PES membrane decreases very slightly while the PES platform was coated by ‘bio-glue’ dopamine hydrochloric/sodium bicarbonate buffer solutions. Both membranes are very loose. From G-PES membrane to NF_PES-Zr membrane the water flux decreases dramatically because of the change that occurs in the membrane nature from UF membrane to NF membrane at the time of in-situ formation of the zirconium layer.

The novel NF_PES-Zr membrane exhibits excellent Ca²⁺ rejection of about 94%. But this membrane is not competent to remove monovalent ions such as Na⁺ (Figure 8(b)). A five-day test has been performed on the NF_PES-Zr membrane to verify its performance stability (Figure 8(b)). NF_PES-Zr membrane, during 120 h, was tested continuously and both rejection and water flux were reported each 12 h. The rejection decreased very slightly during the 120 h of the long test and stabilized around 93.4%. The water flux also was almost constant throughout the five-day test.

Figure 9 depicts a comparative rejection of divalent cation Ca²⁺ of PES, G-PES, and NF_PES-Zr. The rejection performance of the three membranes was respectively about 26, 32, and 94%. This result is hardly surprising since only the NF membranes have proven their competence in effectively rejecting multivalent ions. On the other hand, PES and G-PES membranes are extremely porous with flow rates reaching 87 L.m⁻².h⁻¹. The flow rate of the NF_PES-Zr membrane is reduced due to the deposition on its surface of a layer of fine elements, known under the name of nanoparticles (NPs), contributing to reducing the size of the pores in the active layer of the membrane. Thus, the water flux of NF_PES-Zr decreases dramatically to stabilize around 62.5 L.m⁻².h⁻¹.

Table 1 is about the water flux and rejection performance of some earlier synthesized membranes and of this study.

**CONCLUSION**

A new membrane was fabricated, and in comparison with other membranes manufactured before it using the same platform (Vatanpour et al. 2012; Vatanpour et al. 2014) and the same coating layer (Lv et al. 2016), was found to be
extremely loose (Table 1). A flawless and efficient multi-valent ions separation membrane has been successfully synthesized by the in-situ formation approach. The as-synthesized nanofiltration (NF) membrane, NF_PES-Zr, proceeded from a thin film layer of nanoparticles (NPs) zirconium coating the platform of polyethersulfone (PES) ultrafiltration (UF) membrane through a bio-glue made from dopamine hydrochloric and sodium bicarbonate buffer. The estimation of the average pore size of the novel organic-inorganic NF membrane NF_PES-Zr using the filtration velocity approach of Guerout-Elford-Ferry was close to 0.9 nm. NF_PES-Zr membrane holds a record in

### Table 1 | Synthesized membranes water flux and rejection performance in this study and some earlier reported ones

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Water flux ($L m^{-2} h^{-1}$)</th>
<th>Rejection (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES/ZrO$_2$</td>
<td>62.5</td>
<td>93.4</td>
<td>This study</td>
</tr>
<tr>
<td>HPAN/ ZrO$_2$</td>
<td>60</td>
<td>&gt;90</td>
<td>Lv et al. (2016)</td>
</tr>
<tr>
<td>Modified membrane (0.5-Ach)</td>
<td>30</td>
<td>95</td>
<td>Bagheripour et al. (2018)</td>
</tr>
<tr>
<td>PES/TiO$_2$-co-MWCNTs</td>
<td>5.6</td>
<td>75.8</td>
<td>Vatanpour et al. (2012)</td>
</tr>
<tr>
<td>PES/TiO$_2$</td>
<td>4.2</td>
<td>81.9</td>
<td>Vatanpour et al. (2012)</td>
</tr>
<tr>
<td>PES/functionlized MWCNTs</td>
<td>24</td>
<td>80</td>
<td>Vatanpour et al. (2014)</td>
</tr>
<tr>
<td>PES/Graphene Oxide</td>
<td>20.4</td>
<td>96</td>
<td>Zinadini et al. (2014)</td>
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<tr>
<td>Graphene oxide polyamide</td>
<td>42</td>
<td>90</td>
<td>Zhang et al. (2017)</td>
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<tr>
<td>Carboxyl-functionalized graphene oxide polyamide</td>
<td>49</td>
<td>90</td>
<td>Zhang et al. (2017)</td>
</tr>
<tr>
<td>TFC nanofiltration/functionlized chitosan</td>
<td>22.9</td>
<td>90.8</td>
<td>Miao et al. (2015)</td>
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<tr>
<td>NF_PAN_Ti</td>
<td>56</td>
<td>89.3</td>
<td>Worou et al. (2021a)</td>
</tr>
<tr>
<td>NF-PANZr</td>
<td>58</td>
<td>99.3</td>
<td>Worou et al. (2021b)</td>
</tr>
</tbody>
</table>

**Figure 9** | Long-term stability test on PES, G-PES, and NF_PES-Zr membranes. Test conditions: 0.6 MPa; cross-flow rate – 30 L/h; pH – 6.0; $[Ca^{2+}]$ – 1,500 mg/L.
permeate water flux release of about 62.5 L.m⁻².h⁻¹ and was revealed to be effective for multivalent ions separation. A five-day test performed on NF_PES-Zr demonstrated its long-term stability and showed a rejection rate of 93.4% and 37.8% respectively for Ca²⁺ and Na⁺. We hope that this simple technique to implement will inspire the fabrication of a new generation of membranes.

ACKNOWLEDGEMENTS

The authors would like to thank our group members for their kind help and suggestions.

CONFLICT OF INTEREST

The authors declare no competing financial interest

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 16 November 2020; accepted in revised form 20 March 2021. Available online 30 March 2021.