Green fabrication of a positively charged nanofiltration membrane by grafting poly(ethylene imine) onto a poly (arylene ether sulfone) membrane containing tertiary amine groups

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Abstract

A green method to prepare asymmetric positively charged poly(arylene ether sulfone) nanofiltration (NF) membranes was explored by grafting water-soluble poly(ethylene imine) (PEI) onto a poly (arylene ether sulfone) membrane containing tertiary amine groups (PES-TA) and cross-linking with poly(ethylene glycol) diglycidyl ether (PEGDGE). The modifications were shown to increase the positive charge and decrease the pore size of the PES-TA substrate. The optimized NF membrane displayed a pure water flux of 15.5 L m⁻² h⁻¹. Membrane rejection NaCl, MgCl₂, and methyl violet (MV) (at a constant pressure of 4 bar) were measured to be 46.2%, 94.9%, and 99.8%, respectively. Moreover, the membrane maintained excellent chlorine resistance during 100 h of exposure to chlorine. Thus, the membrane shows potential for water desalination and purification applications.

Keywords: Poly (arylene ether sulfone); Phase inversion; Surface grafting; Nanofiltration membrane; Chlorine tolerance

1. Introduction

Membrane technologies have been implemented successfully in water purification for decades. There is a pressing need to purify water at lower cost and by

using less energy [1]. Nanofiltration (NF) is a low-energy purification process used for water treatment. In addition to saving energy, the unique traits of NF include low environmental impact, high retention of multivalent ions, and a pore size range of 0.5–2 nm [2]. The separation mechanism of NF includes both size exclusion and the Donnan effect [3]. In the last decade, the field of NF has expanded rapidly, leading to significant applications such as desalination of brine and pharmaceutical preparations [4, 5].

Methods to prepare NF membranes include interfacial polymerization (IP), coating technologies, and immersed coagulation phase inversion [6-9]. Polyamide membranes prepared by IP technology have an unrivalled flux and high retention of salt, which allows water purification operations at lower pressures and with low-energy consumption rates. However, polyamide membrane may not be appropriate for many water sources, because of their poor resistance to acids, bases and chlorine [8]. Coating technologies, including spin coating, dip coating, and spray coating, have been utilized to add a thin layer of polymer on a porous support membrane to enhance the functional performance of NF membranes [10]. These coating technologies address many of the shortfalls of polyamide membranes and provide the membrane with good resistance to the aforementioned conditions [11]. Unfortunately, the thinly coated layer has been shown to readily detach from the membrane, because of the different tolerance of the coating polymer and the support layer polymer during water purification under high pressure. Another shortcoming of the coating method is that the solvent used to coat the polymer must wet the membranes and must not dissolve or swell the ultrafiltration support [12]. Although membranes prepared via IP and coating techniques have been well received by industry, the ability to make integrally skinned asymmetric membranes via a single-step fabrication process [12-14] is of broad interest. Asymmetric membranes generated by phase inversion have been applied in the desalination process [6] and organic solvent nanofiltration (OSN) [9, 15]. High charge density and hydrophilicity are required to improve water permeability. However, NF membranes fabricated with charged polymers are susceptible to water swelling, which results in reduced salt

rejection and degradation of the favorable mechanical properties [16, 17].

Various post-modification methods have been investigated to improve the performance of asymmetric NF membranes without sacrificing mechanical properties. UV-photografting [18, 19], ATRP grafting [20], and covalent bond grafting [21] have been widely used to obtain the desired high surface charge density to enhance the rejection of dyes and salts. Covalent bond grafting has also been shown to increase the antifouling properties of NF membranes [22]. In the grafting process, reducing the use of organic solvents is necessary to decrease manufacturing costs and to produce enable greener membrane-preparation processes [21].

Previous work in our laboratory has demonstrated that poly(arylene ether sulfone) with tertiary amine groups (PES-TA) is a promising candidate for achieving asymmetric NF membranes with reasonable rejection for multivalent salts and dyes [23]. In this work, a green surface-modification process for PES-TA was developed to achieve an asymmetric positively charged NF membrane. The tertiary amine groups of PES-TA at the membrane surface were quaternized by reaction with water-soluble poly(ethylene glycol) diglycidyl ether (PEGDGE). The residual epoxy groups were then end-capped with poly(ethylene imine) (PEI). The morphology, pore size, and performance of these membranes are characterized in this study.

2. Experimental

2.1 Chemicals

Cardo poly(arylene ether sulfone) with pendant tertiary amine groups (PES-TA) was prepared as previously described [23]. The chemical structure is shown in Fig. 1. Poly (ethylene glycol) diglycidyl ether (PEGDGE) (MW: 218 g mol⁻¹) and poly (ethylene imine) (PEI) (average MW = 1,200 g mol⁻¹, 50 wt.% in H₂O) were purchased from Sigma-Aldrich. Methyl violet (MV), NaCl, and MgCl₂ were purchased from Sinopharm Chemical Reagent Co., Ltd. All other chemicals were of analytical grade and purchased commercially.

Fig. 1 The chemical structure of PES-TA

2.2 Asymmetric membrane preparation

An asymmetric PES-TA NF membrane was prepared using a classical non-solvent induced phase inversion method [24]. The polymer PES-TA was dissolved in N, N-dimethylformamide (DMF) and tetrahydrofuran (THF) co-solvent to form a homogenous 22 wt.% polymer solution at 60 °C. The ratio of solvent and co-solvent was 3–2 and the membrane preparation conditions were as referenced reported previously [23]. The polymer solution was cast onto a nonwoven polyester fabric with a 150-micron blade at 30 °C, and 30% relative humidity. A 5 s evaporation period was allowed before immersion into a deionized (DI) water coagulation bath. THF is a volatile solvent and its partial evaporation before immersion into the coagulation bath is necessary for the formation of a tight top layer with elevated PES-TA concentration. After the evaporation period, the cast film was immersed into a 30 °C DI coagulation bath. The phase-separated films were taken out of the coagulation bath and rinsed with 50 °C DI water for 30 min to remove residual solvent. Samples were stored in DI water.

2.3 Membrane surface grafting

2.3.1 Preparation of PEGDGE-modified PES-TA NF membranes

The PES-TA membrane was modified by immersion into an aqueous solution containing PEGDGE, to enable reaction between the PES-TA NF membrane's intrinsic tertiary amine groups and the epoxy groups of PEGDGE. The PEGDGE solutions were made up as 1, 2, 4, 8, and 10 g PEGDGE dissolved in 100 mL DI water to produce concentrations of 1, 2, 4, 8, and 10 wt.%, respectively. PES-TA membranes were immersed in PEGDGE aqueous solutions with different concentrations and heated at 60 °C for 10 h. The membrane was then removed from the reaction solution and washed thoroughly with DI water. The membrane is designated as PES-TA-PEGDGE.

2.3.2 Preparation of PES-TA-PEGDGE-PEI NF membranes

Residual epoxy groups in the chain terminal of PES-TA-PEGDGE NF membrane were end-capped with polyethylene imine (PEI) solution at 60 °C for 2 h, in order to enhance the density of the surface's positive charge, by protonation of the PEI molecules. The concentration of the PEI solution was determined to be in the range of 0–6 wt. %. Finally, the resultant membrane, designated as PES-TA-PEGDGE-PEI was washed and stored in DI water for further characterization.

2.4 Membrane characterizations

X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 290 system) was used to analyze the surface composition of the membranes. Al/K α (h ν =1486.6 eV) was used as the X-ray source. Quantification was based on peak areas. The surface morphology of the unmodified and modified PES-TA membrane samples was observed by atomic force microscopy (AFM, Bruker Dimension ICON SPM). Nanoscope analysis software version 1.40 was used for image acquisition and the AFM images were captured as a 3D model. Static contact angles were recorded by the sessile drop method using Drop Shape Analysis DSA10 (Krüss GmbH, Germany) at ambient temperature. Water droplets (5 μ L) were dropped carefully on to the membrane surface with a micro-syringe. The reported data were determined from the average of at least 10 measurements in different positions for each sample. The

streaming potential measurement was determined using an electrokinetic analyzer (SurPASS, Anton Paar GmbH, Austria). The streaming potential was detected by Ag/AgCl electrodes. A 10 mM KCl background electrolyte solution was used and the pH was adjusted with 0.1M HCl and 0.1M NaOH.

2. 5 Separation and permeation properties

Both the unmodified and modified PES-TA NF membranes were tested using flat-sheet cross-flow test cells with an effective area of 23.75 cm² at 4 bar and 25 °C. The membrane samples were pressurized with DI water at 4 bar for 4 h before data collection. The membrane flux was measured by collecting the pure water permeate for a given period. The permeation flux (F) was calculated according to the following equation:

$$F = \frac{V}{At} \quad (1)$$

where F is the permeate water flux (L m⁻² h⁻¹), V is the volume of permeate (L) collected over a period of time t (h), and A is the effective area of the membrane (m²).

Electrolyte solutions of NaCl and MgCl₂, each with a concentration of 500 mg L⁻¹, and methyl violet, with a concentration of 100 mg L⁻¹, were used for NF tests. The membrane rejection was measured by collecting the salt solution for a given period. The rejection (R) for each solute was calculated according to the following equation:

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

where C_p and C_f (mg mL⁻¹) are the concentrations of the permeate and the feed, respectively. The salt concentration was measured using a conductance meter (Elmeiron Conductivity Meter CC-501, Poland) and the dye concentration was measured using UV Spectrophotometer-1800 (SHIMADZU).

When the pH of the solution was controlled with HCl and NaOH aqueous solutions, salt concentrations of both the feed and the permeated solutions were measured by atomic adsorption spectrometry. Each test was conducted three times.

The salt rejection was calculated from Equation 2.

2.6 Membrane molecular weight cut off

The membrane molecular weight cut off (MWCO) was determined by filtration of polyethylene glycol (PEG) with molecular weights ranging from 200 to 4000 Da in a 100 mg L⁻¹ aqueous solution at an operating pressure of 4 bar. The molecular weight of PEG that was 90% rejected was defined as the MWCO. The concentrations of PEG in the feed and permeate were measured using a total organic carbon analyzer (TOC-VCPH SHIMADZU). All the measurements were based on the average value of three samples.

2.7 Chlorine tolerance test

The membranes were immersed in a 1 g L⁻¹ NaOCl solution for 100 h. Following chlorine exposure, the membranes were washed with DI water for 5 min before testing. The chlorine tolerance of the membranes was evaluated by measuring the flux and salt rejection.

3. Results and discussion

3.1 Membrane preparation and characterization

The preparation procedure of the positively charged PES-TA-PEGDGE-PEI NF membrane is illustrated in Scheme 1. Firstly, PES-TA asymmetric membranes were prepared using the classical non-solvent induced phase separation (NIPS) method. In the NIPS process, the interaction between hydrophilic tertiary amine side chains and water drives tertiary amine chains to migrate toward the membrane surface [25]. The tertiary amine groups on the membrane surface are beneficial to further grafting reactions. Then, water-soluble PEGDGE containing epoxy groups can easily react with the tertiary amine groups by ring opening. PEGDGE was grafted onto the PES-TA substrate and ultimately formed an epoxy layer. The intermediate membrane, consisting of some remaining PEGDGE with free epoxy groups, was further reacted by covalent bonding, to form a separation layer. This finally functionalization of the epoxy-bearing PES-TA-PEGDGE membrane was achieved by immersion into a PEI aqueous solution, to allow the residual epoxy groups of the PES-TA-PEGDGE membrane to react with amine groups of PEI. The concentrations of PEGDGE and

PEI were determined to be 10 wt.% and 4 wt.%, respectively, by the characterization methods discussed below. The selection of these concentrations will be further discussed in section 3.2 and 3.3.

Scheme 1 Fabrication process of PES-TA-PEGDGE-PEI NF membrane by grafting PEI onto PES-TA membrane surface and cross-linking with PEGDGE.

High-resolution N1s XPS spectra were recorded to determine the semi-quantitative ratio of quaternary amines and tertiary amines on the pristine and modified PES-TA NF membrane surface. The XPS data of the elemental composition of the membrane surfaces are given in Table 1. As shown in Fig. 2, the N1s spectra can be resolved into C–N and C–N⁺ components with binding energies of ca. 399.5 and 402.0 eV, respectively. After PEGDGE grafting (Fig. 2b), a new peak in the N1s spectrum at 402.0 eV is observed. The appearance of this peak suggests PEGDGE reacts with the tertiary amine groups, and was thus successfully grafted on the surface of the PES-TA membrane. Table 1 shows the atom percentage of oxygen, which increased from 12.24% in the unmodified PES-TA to 21.43% in PES-TA-PEGDGE, confirming that PEGDGE was grafted onto the PES-TA membrane surface. The XPS spectrum of the PES-TA-PEGDGE-PEI membrane is presented in Fig. 2c. Compared with PES-TA-PEGDGE, the proportion of quaternary amine and tertiary amine for PES-TA-PEGDGE-PEI NF membrane (23%) was greater than for the

PES-TA-PEGDGE NF membrane (18%). In addition, Table 1 shows the atom percentage of nitrogen increased after PEI modification. These results indicate the amount of surface quaternary amine groups present in the NF membranes further increased following the second (PEI) modifying process.

Fig. 2 The XPS N1s high resolution scans of (a) PES-TA, (b) PES-TA-PEGDGE (10 %), and (c) PES-TA-PEGDGE (10%)-PEI (4%) NF membranes.

Table 1. XPS analysis of the membranes surface composition and C-N⁺/C-N ratio.

Membrane	PES-TA (%)	PES-TA-PEGDGE (10%) (%)	PES-TA-PEGDGE (10%)-PEI (4%) (%)
C1s	84.15	74.17	75.60
N1s	3.61	4.40	5.59
O1s	12.24	21.43	18.81
C-N ⁺ /C-N	—	18	23

Atomic force microscopy (AFM) was utilized to investigate the surface roughness of the membranes. The AFM images and the average roughness of the unmodified and modified PES-TA membrane surfaces are presented in Fig. 3. The average roughness of PEGDGE-modified PES-TA membrane was higher than for the unmodified PES-TA membrane. In the 3D images of PEGDGE-modified PES-TA membranes (Fig. 3b), the formation of cuspidal outshoots perhaps indicates the conformation of PEGDGE to the PES-TA membrane ridge-and-valley surface structure during grafting [26]. Furthermore, the average roughness of the PES-TA-PEGDGE-PEI NF membrane was 11.50 nm (Fig. 3c), which is higher than that of PES-TA-PEGDGE membrane. This increased roughness may contribute to the coverage of macromolecular PEI on the membrane surface and the observed “peak and valley” formation.

Fig. 3 AFM surface morphology of (a) PES-TA, (b) PES-TA-PEGDGE (10%), and (c) PES-TA-PEGDGE (10%)-PEI (4%) NF membranes.

Hydrophilic surfaces have been proven to improve the permeation of membranes by water, because of the interaction of hydrophilic groups and water molecules, via hydrogen bonds or electrostatic attraction. The hydrophilicity of the unmodified PES-TA and modified PES-TA membrane surfaces was characterized by measuring

the water contact angle values of membrane surface (Fig. 4). It was clear that the pristine PES-TA membrane had the highest contact angle value of $74.8 \pm 2.7^\circ$. In comparison, the water contact angle of PES-TA-PEGDGE decreased to $61.6 \pm 1.7^\circ$ from $74.8 \pm 2.7^\circ$, suggesting that PEGDGE grafting made the membrane surface more hydrophilic. Moreover, after reacting PEI with residual epoxy groups, the hydrophilicity of the membrane surface further increased, shown by a further decrease in the water contact angle of the membrane surface to $57.6 \pm 1.7^\circ$. The observed improvement in the membrane surface hydrophilicity potentially endows the PES-TA-PEGDGE-PEI membranes with antifouling properties.

Fig. 4 Water contact angles of PES-TA, PES-TA-PEGDGE (10%), and PES-TA-PEGDGE (10%)-PEI (4%) NF membranes

Neutral solute rejection experiments were employed to estimate the membrane molecular weight cut-offs (MWCOs). Single-solutions of PEG between 200 and 4000 g mol⁻¹ (listed in Table 2) with concentrations of 100 mg L⁻¹ served as the feed solution at 4 bar. As can be seen from Fig. 5, the rejection of solute increased with increasing PEG molecular weight for all membranes. The MWCOs of PES-TA,

PES-TA-PEGDGE, and PES-TA-PEGDGE-PEI membranes are ~3074, 925, and 594 g mol⁻¹, respectively. From the relationship between the molecular weight of PEG and their Stokes radius shown in Table 2 [27], the mean pore size of PES-TA, PES-TA-PEGDGE, and PES-TA-PEGDGE-PEI membranes are determined as ~1.46, 0.75, and 0.59 nm, respectively. These results illustrate that the modification process narrowed the pores, effectively changing the membrane from an “open pore” to a “tight pore” NF membrane.

Table 2. Stokes radius and molecular weight of neutral solutes in aqueous solutions.

Solute	Molecular weight (g mol ⁻¹)	r _s (nm)
PEG-200	200	0.32
PEG-400	400	0.47
PEG-600	600	0.59
PEG-1000	1000	0.78
PEG-2000	2000	1.15
PEG-3000	3000	1.44
PEG-4000	4000	1.69

Fig. 5 The MWCOs of the original PES-TA, PES-TA-PEGDGE (10%) and PES-TA-PEGDGE (10%)-PEI (4%) membranes

3.2 PEGDGE concentration effect on membrane performance

To investigate the effects of PEGDGE concentration on membrane performance, six PEGDGE concentrations were used for grafting to the PES-TA membrane surface (0, 1, 2, 4, 8, and 10 wt.%). Fig. 6 shows the effect of PEGDGE concentration on the permeation flux and salt rejection. The unmodified PES-TA NF membrane has a low rejection of MgCl_2 and NaCl and a high pure water flux. The MgCl_2 and NaCl rejections sharply increase with PEGDGE modification. MgCl_2 rejection increases slowly after the PEGDGE concentration exceeds 1 wt.% and changes slightly after 8 wt.%. The trend of NaCl rejection was similar to that of MgCl_2 rejection. The flux decreases with a 1 wt.% PEGDGE concentration. When the PEGDGE concentration exceeds 1 wt.%, the flux increases with PEGDGE concentration. It has been shown previously that the PEGDGE graft monomer can cover the pore openings and narrow the pore radius on the membrane surface [21]. Thus, the membrane flux decreases and salt rejection increases initially (with 1 wt.% PEGDGE). The increased MgCl_2 and NaCl rejection is also attributed to the formation of quaternary amines on the PEGDGE-modified PES-TA NF membrane surface. The flux increases after the PEGDGE concentration exceeds 1 wt.%, characterized by the improvement in membrane hydrophilicity as the PEGDGE concentration increases. As a result, 10 wt.% was fixed as the concentration of PEGDGE that needs to be further investigated.

Fig. 6 Performance changes of PES-TA-PEGDGE NF membranes as a function of PEGDGE concentration in aqueous solution

3.3 PEI concentration effect on membrane performance

The effect of PEI concentration on the performance of PES-TA-PEGDGE-PEI membranes was investigated using the conditions determined above (PEGDGE (10 wt.%), 60.0 °C for 2.0 h). As shown in Fig. 7, increasing the PEI concentration from 0 to 6 wt.% caused the pure water flux to decrease slightly from 20.0 to 15.5 L m⁻² h⁻¹, while the rejection of MgCl₂ and NaCl increased, as expected. We suggest that, after PEI grafting, the flux decreased perhaps because the flexible chains of PEI block the pores of the epoxy-bearing PES-TA-PEGDGE membrane [28]. The rejection of salt increased because the highly positively charged PEI on the membrane surface generated an electrostatic repulsion to cations. Another reason may be that the decreased pore size of membrane surface caused the rejection to increase. Consequently, we selected the membrane containing approximately 4 wt.% PEI as the optimal case because of high salt rejection and available flux.

Fig. 7 Effect of PEI concentration on the pure water flux and salt rejections of PES-TA-PEGDGE-PEI membrane.

3.4 Zeta potential of membrane surfaces

The surface potential of NF membranes determines the isoelectric pH for the separation of different charged salts, dyes, and organic matter [3]. In a given electrolyte solution (10 mmol KCl) at any pH, the change in the zeta potential values of the three NF membranes directly reflects the difference in charge density on membrane surface. The pH-dependent zeta potentials of the prepared NF membranes are illustrated in Fig. 8. As the pH values were gradually increased, the negative zeta potential values of the PES-TA and PES-TA-PEGDGE membranes increased, and the positive zeta potential of PEI-grafted membrane decreased. At high pH, the positively charged quaternary amine groups presented in the PES-TA-PEGDGE-PEI membrane surface are neutralized by electrostatic interaction with anions [29, 30]. The unmodified PES-TA membrane had the lowest zeta potential at all pH values. The PES-TA-PEGDGE-PEI membrane had the highest positive zeta potential values and therefore possessed the most positive surface potential. These results are supported by the chemical composition of the surface, described in Sec. 3.1, and the predicted

presence of a large amount of positively charged quaternary amines on the surface, arising from the protonation of PEI in the PES-TA-PEGDGE-PEI membrane.

Fig. 8 Zeta potentials of the original PES-TA, PES-TA-PEGDGE (10%) and PES-TA-PEGDGE(10%)-PEI (4%) membranes at different pH values

3.5 Performance of the original and modified NF membranes

Nanofiltration performance of the unmodified and modified PES-TA NF membranes was investigated (Fig. 9). Aqueous solutions of NaCl and MgCl₂ (500 mg L⁻¹) and methyl violet (MV) dye (100 mg L⁻¹) were employed to measure the separation performance of the membranes at constant pressure (4 bar). The pure water permeation of PES-PEGDGE-PEI was less than that of PES-TA because of the narrowed mean pore size (described in Sec. 3.3). In addition, the rejection of NaCl and MgCl₂ was greater for PES-PEDGE-PEI, owing to the decrease in the membrane pore size and increase in the positive charge density. Donnan exclusion and steric hindrance also explain the above results.

Table 3 summarizes the separation properties of literature-reported and commercially available NF membranes. The PES-TA-PEGDGE-PEI membranes

reported here exhibited higher MgCl_2 rejection compared to that shown by SPEEK/PEI-PI and PCNFM3 NF membranes, without significantly sacrificing the flux. This may be attributed to both the strongly cationic and more hydrophilic surface of the PES-TA-PEGDGE-PEI membrane. Most of the commercial nanofiltration membranes are negatively charged polyamide membranes. Therefore, to allow comparison with the PES-TA-PEGDGE-PEI membrane, one positively charged polyamide membrane, Toray UTC20, was used as a control. Because of the difference in their preparation method, polyamide membranes have superior performance, compared with that shown by asymmetric nanofiltration membranes.

Fig. 9 Separation properties of different inorganic salts and dyes for the original PES-TA, PES-TA-PEGDGE (10%), and PES-TA-PEGDGE (10%)-PEI (4%) membranes

Table 3. Comparisons of the separation properties of PES-TA-PEGDGE (10%)-PEI (4%) membrane with that of literature reported and commercial NF membranes

Membrane	PWF (L m ⁻² h ⁻¹)	Salt rejection (%)		Operating pressure (bar)	Salt concentration (mg L ⁻¹)	Ref.
		MgCl ₂	NaCl			
PES-TA-PEGDGE (10%)-PEI (4%)	15.5	94.9	46.2	4	500	This work
SPEEK/PEI-PI NF	40.6	86	60	13.8	500	[3]
PCNFM3	19.8	94.3	60.7	6	1000	[31]
UTC20	132.0	98	55	10.0	1500	[32]

3.6 Effect of pH on membrane separation performance

PEI, which is rich in amine groups, increased the surface charge of the PES-TA-PEGDGE-PEI membrane. Amines are weak bases, and their protonation leads to pH-dependent surface charges on the membrane. Therefore, we determined the effect of solution pH on the PES-TA-PEGDGE-PEI membrane performance. When the pH of the MgCl₂ solution was 10, sediments were observed during tests. Thus, a maximum pH value of 10 was chosen. Fig. 10 shows that rejection of both NaCl and MgCl₂ decreased with increased solution pH. As the pH increases, the PES-TA-PEGDGE-PEI membrane surface becomes neutralized by the free hydroxide ions in the basic aqueous solution. This causes the Donnan exclusion effect, and consequently MgCl₂ rejection, to decrease. This decrease confirms the influence of amine groups' protonation/deprotonation on the membrane's separation performance.

Fig. 10 Salt rejection of PES-TA-PEGDGE (10%)-PEI (4%) membrane as a function of pH

3.7 Chlorine tolerance of PES-TA-PEGDGE-PEI membrane

Chlorine tolerance was investigated by immersing the PES-TA-PEGDGE-PEI membrane in a solution of NaOCl (1000 mg L⁻¹). As shown in Fig. 11, no obvious change in the pure water flux was observed. When the PES-TA-PEGDGE-PEI membrane was immersed in an aqueous NaOCl solution for 10 h, the rejection of both NaCl and MgCl₂ decreased. Salt rejection remained constant with further increase in exposure time. The alkaline NaOCl solution caused neutralization of the positive charges on the PES-TA-PEGDGE-PEI membrane surface by hydroxide ions, affecting the salt rejection of the membrane. Polyamide membranes typically degrade because chlorine attacks amide bonds (–CO–NH–) [33, 34]. The PES-TA-PEGDGE-PEI membrane has no amide bonds and is therefore predicted to show minimally sensitivity to chlorine exposure. From the chlorine

exposure tests, we conclude that the PES-TA-PEGDGE-PEI membrane exhibits excellent chlorine tolerance during extended durations of chlorine exposure.

Fig. 11 Chlorine tolerance property of the resultant PES-TA-PEGDGE (10%)-PEI (4%) NF membrane

4. Conclusions

Novel integrally skinned asymmetric NF membranes were successfully prepared using a green process, via grafting PEI onto the PES-TA substrate and cross-linking with PEGDGE. By adjusting the concentrations of PEGDGE and PEI, optimal grafting conditions of 10 wt.% PEGDGE and 4 wt.% PEI were determined. After surface modification, the membrane's pore sizes narrowed from 1.46 nm to 0.59 nm and the membrane surface became more positively charged, as shown by zeta potential measurements. The PES-TA-PEGDGE(10%)-PEI(4%) membrane showed optimal performance, with a pure water flux of $15.5 \text{ L m}^{-2} \text{h}^{-1}$, and NaCl, MgCl_2 , and MV rejections of 46.2%, 94.9%, and 99.8%, respectively. Furthermore, the resulting

membrane exhibited excellent chlorine tolerance, as shown by exposure to a solution of NaOCl solution, with a concentration of 1000 mg L^{-1} , for 100 h. The membrane's chlorine tolerance is proposed to be caused by its lack of amide bonds. These results demonstrate that this membrane can be used in water treatment, dye purification, and desalination.

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Abbreviations

AFM	atomic force microscopy
A	effective membrane area (m^2)
C_p	concentration of the permeation (mg mL^{-1})
C_f	concentration of the feed (mg mL^{-1})
DMF	N,N-Dimethylformamide
F	pure water flux ($\text{L m}^{-2} \text{ h}^{-1}$)
h	hour
IP	interfacial polymerization
L	liter

MW	molecular weight
MV	methyl violet
MWCO	molecular weight cut off
NF	nanofiltration
PEGDGE	poly (ethylene glycol) diglycidyl ether
PEI	polyethyleneimine
PEG	polyethylene glycol
RO	reverse osmosis
r_s	stokes radius
s	second
t	testing time (h)
PES-TA	cardo poly (arylene ether sulfone) with pendant tertiary amine groups
THF	tetrahydrofuran
V	volume of permeate water (L)
XPS	X-ray photoelectron spectroscopy

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