High salt permeation nanofiltration membranes based on NMG-assisted polydopamine coating for dye/salt fractionation

Yongliang Chen, Chunju He*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials

College of Materials Science and Engineering

Donghua University

Shanghai, 201620, P.R. China

Abstract: Non-polyamide composite nanofiltration (NF) membranes based on N-methyl-D-glucamine (NMG)-assisted polydopamine (PDA) coating were prepared by a simple deposition process followed by glutaraldehyde crosslinking, which showed excellent structural stability so as to solve the problem as encountered by commercial NF membrane. The addition of NMG promoted the deposition and polymerization of dopamine to form a dense and homogeneous selective layer with improved hydrophilicity in a time-saving mode. The composite membranes under optimal conditions exhibited high pure water flux of $10.29 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, high organic dye rejection of over 99.0% and high Na_2SO_4 rejection of 81.2%. Particularly, as compared with the previously reported commercial NF membranes, one big advantage for high NaCl permeation was presented, due to low NaCl rejection with narrow range under the filtering process of different salt concentrations. Furthermore, 24 h continuous filtration experiment using mixtures of acid red 18 and NaCl showed low salt rejection ($< 14.0\%$) and high dye rejection ($> 99.0\%$), indicating that the composite membranes have potential for dye/salt fractionation. Apart from providing a new candidate membrane for dye/salt fractionation, the successful development of structure-stable polydopamine-based NF membrane is expect to speed up the paces toward practical applications of non-polyamide membranes in the near future.

Keywords: NMG-assisted dopamine deposition; Michael addition; NaCl permeation; dye rejection, dye/salt fractionation

1. Introduction

Nanofiltration (NF) has been widely used in wastewater treatment, water softening, separation and purification process due to the advantages of low operation pressure, low energy consumption, high flux, high retention of multivalent ions and organic molecular (200 – 1000 Da) [1-4]. Until now, NF membranes are dominated by the composite membranes prepared through interfacial polymerization, which usually comprise a thin active layer on a porous support [5-8]. However, the big difference in swelling degree and the weak interaction between the support and the active layer result in the peeling of active layer from support in harsh environments containing organic solvents [9-11], which inevitably shortens the lifetime of the membranes and increases the operation cost. To overcome this drawback, great efforts have been made, i.e. creating covalent or ionic linkage through plasma treatment or grafting method so as to construct adhesive layer between the active layer and the support [11-15]. Despite the fact that the above-mentioned methods can be effective in improving the adhesive property, they also suffer from some drawbacks regarding their multiple or complex operations, which limits their wide use.

Inspired by mussel adhesion, dopamine can form a self-polymerized coating with the strong and universal adhesion ability on various substrates in aqueous environments, where most adhesives function poorly [16-18]. In light of the above property, polydopamine (PDA) coating can be used as a separate layer to prepare the composite membrane with strong adhesion strength between the active layer and the substrate surface [19-24]. Li et al. fabricated a novel hydrophilic NF membrane by simply dipping polysulfone substrates in dopamine solution, but this approach needed 20 h and could not obtain layer dense enough for excellent rejection i.e. the CaCl_2 rejection of 68.7% [24]. Zhao et al. further modified the membrane through trimesoyl chloride (TMC) interfacial polymerization after dopamine deposition, but this approach still could not get good rejection to the dyes (< 1000 Da) i.e. approximately 90% rejection to Congo red [10]. Therefore, the reported pure PDA coating does not have excellent separation performance since the resultant PDA particles are deposited on the substrate in a loose and heterogeneous mode. Moreover, the deposition process

is generally time-consuming, which further precludes the practical application of PDA coating on NF membrane.

The dye industry in China possesses 70% world production and domestic consumption accounts for 83% of the production, which produces a large amount of dyeing wastewater containing a large number of inorganic salts, mainly NaCl, leading to the loss of valuable organic products and serious environmental pollution [25]. Therefore, the treatment of the dyeing wastewater is an urgent problem due to inefficiency of conventional treatment systems, especially the effective separation of NaCl and dye for the recovery and purification of dyes. NF membrane with a molecular weight cutoff of 200-1000 Da and pore size of 0.5-2.0 nm has been considered as a competitive method due to high retaining to dye molecules as well as partial permeation for NaCl [25-32]. However, various NF membranes including commercial NF membranes typically tend to exhibit high NaCl rejection as well as high rejection to small organic molecules (150-500 Da), which can't separate NaCl from the dye effectively. Moreover, most commercial NF membranes belong to polyamide NF membranes, which can be easily contaminated by most textile dyes through chemical bonds and this fouling is irreversible [33-35]. Therefore, advanced non-polyamide NF membranes with high dye rejection as well as low NaCl rejection are required for the treatment of dye/salt wastewater.

In this work, continuous high-quality PDA layer supported on a porous PES substrate is presented through N-methyl-D-glucamine (NMG)-assisted dopamine deposition followed by GA crosslinking. NMG, an amino-containing molecule, was employed to adjust the self-polymerization process of dopamine through Michael addition reaction so as to obtain a dense, uniform layer in a short time [7, 16]. The resulting membranes exhibited high dye rejection and multivalent ion rejection, low NaCl rejection, good permeability and excellent structural stability. As such, unique high NaCl permeation characteristics together with good structure stability strongly encourage us to use PDA coating as a next-generation membrane for dye/salt fractionation.

2. Experiments

2.1 Materials

Polyethersulfone (PES) ultrafiltration membranes (MWCO = 10 KDa) were purchased from Risingsun Membrane Technology Co. Ltd (Beijing, China). Dopamine hydrochloride (DA) and N-methyl-D-glucamine (NMG) were obtained from Energy Chemical (Shanghai, China). Piperazine (PIP) and 1,3,5-benzenetricarboxylic acid chloride (TMC, 98%) were from Sigma-Aldrich and used as received. Tris(hydroxymethyl)aminomethane was purchased from TCI (Shanghai, China). Glutaraldehyde (GA) solution (25%), hexane, inorganic salts, methylene blue ($C_{37}H_{27}N_3Na_2O_9S_3$, $M_w=799$), congo red ($C_{32}H_{22}N_6Na_2O_6S_2$, $M_w=696$) and acid red 18 ($C_{18}H_{13}N_3Na_2O_8S_2$, $M_w=509$) were procured from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All the chemical agents were used without further purification.

2.2 Membrane preparation

PES ultrafiltration membrane was fully wetted in ethanol and deionized water, which was immersed in the fresh prepared DA-NMG solutions at 30°C for 2 h to ensure full soaking and appropriate polymerization, washed by deionized water for several times and immersed in 3wt% GA alcohol solution for 20 min at 50°C to ensure appropriate interfacial polymerization. The as-prepared membrane was treated at 50°C for 20 min in vacuum at last. The preparation process and mechanism for DA-NMG/GA composite membrane is illustrated in Schematic 1a in detail. To find the most appropriate NMG concentration for a denser and defect-free layer based on NMG-assisted PDA coating, a series of DA-NMG/GA composite membranes are prepared on the PES substrate with different NMG concentration. The resultant membranes, designated as DA-NMG/GA composite membranes, were fully washed and then stored in deionized water for further characterization.

A conventional polyamide (PA) nanofiltration composite membrane, named PA/PES composite membrane was prepared through interfacial polymerization.

Briefly, the dense skin side of substrate was soaked in 2wt% PIP aqueous solution for 5 min. Then PIP impregnated membrane was taken out from PIP solution and the excess water was drained off in the air, then transferred into 0.1wt% TMC hexane for 1 min. The resultant membranes were heatcured at 50°C for 10 min and then stored in water until it was tested.

During the experiment, DA and NMG were respectively dissolved in Tris-HCl buffer solution (pH=7.0, 20mM) with designed mass ratio. The dopamine concentration was fixed to 2 g·L⁻¹, varying the concentration of NMG. The DA/GA composite membrane was named M0 and the DA-NMG/GA composite membranes were named from M1 to M8, corresponding to the NMG concentration from 1 g·L⁻¹ to 8 g·L⁻¹. And the membranes without GA crosslinking were named DA-NMG composite membranes.

2.3 Membrane characterization

The chemical structure of the investigated membranes were measured by Fourier transform infrared spectrometer (ATR-FTIR, Nicolet 8700, USA) with the range of 4000-400 cm⁻¹.

The X-ray photoelectron spectroscopy (XPS, Shimadzu AXIS Ultra DLD, Japan) with a monochromated Al K X-ray source (1486.6 eV photons) was used to test the more details in chemical components. All the high-resolution spectra were collected at 90° take-off angle.

The surface morphology of the membranes was observed with a field emission scanning electron microscope (FESEM, Hitachi, S-4800, Japan) operating at an acceleration voltage of 10.0 kV and 100kV. The investigated membranes needed to be dried by vacuum freeze-drying and sputtered with gold for producing electric conductivity before observation.

The surface zeta potentials of the membranes in medium with different pH were tested using the nanoparticle size analyzer (DelsaNano, Beckman Coulter, USA) by switching to the test mode of zeta potential.

To observe the change of surface hydrophilicity of the composite membranes, the static and dynamic water contact angles (WCAs) were measured by an OCA40Micro

contact angle system (Germany) at room temperature. The contact angles for all samples were the average values for at least five contact angles at different locations on one surface.

2.4 NF performance of the prepared DA-NMG/GA composite membranes

The separation performances of the DA-NMG/GA composite membranes were evaluated using a dead-end filtration system with an effective area of 12 cm² under 0.35 MPa at 25 ± 2 °C. The membranes were initially prepressured at 0.4 MPa with deionized water for 30 min. The water flux (J_w , L·m⁻²·h⁻¹) and rejection (R , %) were calculated by the following equations:

$$J_w = \frac{V}{A \times t} \quad (1)$$

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

where V (L) is the volume of permeate water, A (m²) is the membrane area, t (h) is the operation time, C_p and C_f are the solute concentrations in permeate and feed respectively. The concentration of salt solution and dye solution in initial feed solutions was 1 g·L⁻¹ and 0.1 g·L⁻¹ respectively. The salt concentration in permeate solution was detected with electrical conductivity (DDS-11A, Shanghai Leichi Instrument Co, Shanghai, China) and the dye concentration in permeate solution was measured by a UV-vis spectrophotometer (UV-1800, Shimadzu).

2.5 Structural stability of the composite membranes

The DA-NMG/GA composite membranes were immersed in ethanol, a pH 1 HCl solution and a pH 14 NaOH solution to evaluate the structural stability according to the deterioration extent of performance.[9, 10] The pure water flux and rejection were measured every 3 days to observe the change of the separate performance and the composite membranes were calculated for 12 days continuously. Moreover, the long-term operation stability of the composite membranes was evaluated through 12 days continuous filtration and the pure water flux and rejection were measured every one day to observe the change of the separate performance.

3. Results and discussion

3.1 Formation of homogeneous NMG-assisted PDA coating

Schematic 1. Schematic diagram of the preparation process of DA-NMG/GA composite membrane (a), proposed reaction mechanism of DA self-polymerization process and NMG-assisted DA self-polymerization process (b), crosslinking reaction

mechanism (b).

It is known that PDA coating with strong adhesive capacity can be formed on various substrates through self-polymerization of dopamine [7, 16]. However, this PDA coating based layer is not developed fully to provide satisfactory separation performance even through some techniques such as DA double-coating [24] or TMC cross-linking [10] due to the heterogeneity of pure PDA coating. It is believed that the development of the homogeneous coating is the key to form a uniform and dense layer on the substrate. Although the mechanism of dopamine-inspired thin-film deposition is not well understood, the Michael-addition reaction is the generally accepted PDA coating formation mechanism [18]. As shown in Schematic 1b, the amine group in NMG can react with dopamine through Michael addition reaction, therefore, NMG can be employed to assist the self-polymerization process of dopamine. As shown in Schematic 1a, NMG-assisted dopamine deposition helps to the successful formation of homogeneous coating developed on the surface of PES substrate, in stark contrast to the formation of heterogeneous coating via pure dopamine deposition, which is also seen by SEM (Figure 2). Figure 1 presents that the colors of the freshly prepared mixed dopamine solution (Figure 1a) and the as-prepared membrane surface (Figure 1b) deepen with the addition of NMG, which indicates NMG promotes polymerization of dopamine, thus leading to the homogeneous deposition of dopamine. We consider that the development of uniform NMG-assisted PDA coating on the PES substrate may be due to the interaction between dopamine and NMG during the deposition process, which is further proved by SEM, ATR-FTIR and XPS.

Figure 1. (a) The photograph of the freshly prepared mixed dopamine solution with different NMG content ($0\text{--}3\text{ g}\cdot\text{L}^{-1}$), corresponding to M0-M3. (b) The photograph of the substrate, M0, M1, M2 and M3. And the molecular structures of (c) dopamine and (d) NMG.

3.2 Characterization of the DA-NMG/GA composite membranes

Figure 2. Surface and cross-section SEM images of the substrate, M0, M1, M3 and M7.

Surface and cross-section morphologies of the membranes are investigated by SEM as shown in Figure 2. It is seen that heterogeneous PDA layer with some large agglomerates is formed in M0 by dopamine self-polymerization, which is not sufficient enough to cover all the surface pores of the substrate. Thus the defects on the membrane will greatly weaken the separation efficiency of membrane. In contrast,

homogeneous PDA coating is developed via NMG-assisted dopamine deposition (M1-M7), due to the existence of NMG undergoing strong interaction with dopamine through Michael addition during the deposition process [18, 23, 36], which renders the substrate surface with less visible pores (M1 and M7) or even no visible pores (M3). Meanwhile, as can be seen by the cross-section SEM of M0-M7, the thickness of the active layers are all calculated to be about less than 10 nm and have no significant change with the increasing NMG content. Moreover, it can be seen the surface of M3 is rougher than M1 and M7 from the SEM. As shown in Figure 1a and 1b, when the NMG concentration is increased from 1 g/L to 3 g/L, the polymerization process of dopamine is increased, leading to more nodular structure, so the surface of M3 is rougher than M1. However, when the NMG concentration is increased from 3 g/L to 7 g/L, some visible pores appear on the surface of M7, indicating the formation of a uncontinuous layer and it is reasonable to deduce that the excessive NMG may hinder homogeneous deposition of dopamine, leading to less nodular structure on the surface, so the surface of M3 is also rougher than M7. Thus, an optimal NMG concentration is required to develop a continuous and dense layer on the substrate, which plays a significance role in exhibiting excellent NF performance.

Figure 3. ATR-FTIR spectra (a) and XPS spectra (b) of PES substrate, M0 and M3.

With the development of uniform coating on the PES substrate, NMG-assisted PDA coating is fully cross-linked by GA to prepare the DA-NMG/GA composite membranes (Scheme 1c), which is investigated by ATR-FTIR (Figure 3a). As can be seen by SEM (Figure 2), M3 has a continuous and denser layer, so the ATR-FTIR of

M3 is chosen to characterize the chemical structure of the DA-NMG/GA composite membranes. Absorption band at 1643 cm^{-1} is attributed to the N-H vibration in PDA, which indicates that PDA has been successfully coated on PES substrate by dopamine self-polymerization in accordance with the work of Li et al. [24]. Meanwhile, the adsorption band appeared at 1515 cm^{-1} is attributed to C=N bonds produced by crosslinking reaction between unreacted amine group in PDA and GA, rendering PDA coating to be a denser layer [7]. Moreover, the O-H adsorption band at 3400 cm^{-1} in M3 is enhanced as compared with M0 (Figure 3a), resulting from the introduction of NMG with multi-hydroxy group inside the PDA coating, which also proves that the development of homogeneous coating on the substrate is due to the interaction between dopamine and NMG during the deposition process and it is believed that NMG, as an amino-containing molecule, reacts with dopamine through Michael addition reaction [7, 16].

Furthermore, the surface elemental compositions are characterized by XPS as shown in Figure 3 (b). Compared with the PES substrate, the nitrogen peak for M0 and M3 is ascribed to nitrogen element in dopamine or NMG, which proves that the PDA coating or NMG-assisted PDA coating is successfully developed. But in the XPS spectrum of M0, the sulfur peak still exists, which indicates the existence of pure PDA coating defects on the substrate in accordance with the SEM (Figure 2, M0) due to the heterogeneous deposition. In addition, the sulfur peak in the XPS spectrum of M3 is eliminated as compared with the XPS spectrum of M1, which indicates the NMG-assisted PDA coating is well-covered on the substrate without any defects in accordance with the SEM (Figure 2, M3) due to the formation of an uniform layer based on homogeneous coating.

Figure 4. (a) Dynamic water contact angle of the substrate, M0 and M3, (b) Zeta potential of the DA-NMG composite membrane and the DA-NMG/GA composite membrane (M3) at various pH value.

The water contact angle (WCA) is employed to evaluate the surface hydrophilicity or wettability of the membranes as shown in Figure 4a. As compared with the substrate, the WCAs of M0 and M3 are significantly reduced, indicating the surface hydrophilicity of M0 and M3 are both improved, due to the development of PDA coating or NMG-assisted PDA coating on the substrate. In addition, M3 based on NMG-assisted PDA coating exhibits a WCA declining from 58° to 47° in 120 s as compared with that of M0 from 66° to 63° , indicating M3 shows better wetting ability due to the capability of the hydrophilic molecular (NMG) to imbibe water via the multi-hydroxy group. And it is believed that the improved hydrophilicity of the composite membranes will play an important role in achieving good separation performance.

Membrane surface charge plays an important role for separating charged solutes in a NF process. Figure 4b shows the zeta potentials of the DA-NMG composite membrane and the DA-NMG/GA composite membrane (M3) under various pH conditions. It can be seen that zeta potential of the DA-NMG/GA membrane decreases slightly compared to the DA-NMG membrane, because some of the amino groups in PDA reacted with the aldehyde groups in GA. Isoelectric point of M3 is at $\text{pH}=5.2\pm0.5$. In general, the NF process is conducted at around $\text{pH}=6.0$, therefore, M3 is slightly negative charged during NF operation, which would be higher rejection

for multi-valence anionic according to the Donnan and dielectric effects [24, 37].

3.3 Separation performance of the DA-NMG/GA composite membranes

Figure 5. Effect of NMG concentration (a) and deposition time (b) in water phase on the separation performance of the DA-NMG/GA composite membranes.

The DA-NMG/GA composite membranes are further characterized with a traditional NF process. Though SEM (Figure 2), some visible pores on the membrane surface are both observed under the preparation condition of low NMG concentration (M1) and high NMG concentration (M7), which will lead to degeneration of the membrane separation performance. As shown in Figure 5a, as the NMG concentration is increased from 0 to 3 g·L⁻¹, the water flux is gradually decreased and the rejections to Na₂SO₄ and the Acid Red 18 are increased, indicating a denser and defect-free layer is developed with the increasing NMG concentration. However, further increasing NMG concentration from 3 to 8 g·L⁻¹, the rejection is decreased and the pure water flux is increased gradually. Therefore, 3 g·L⁻¹ is taken as the optimal concentration for NMG-assisted dopamine in this study.

Similarly, the deposition time of dopamine is used to control the thickness of the PDA coating, which plays an important role in the membrane separation performance. Specially, if the deposition time is too short, the layer based on NMG-assisted coating will not be sufficiently thick to cover all the surface pores of the substrate, leading to membrane leakage. To obtain the most appropriate deposition time and thickness for the layer based on NMG-assisted PDA coating, a series of DA-NMG/GA composite

membranes were prepared on the PES substrate with different deposition time at the fixed NMG concentration of $3\text{g}\cdot\text{L}^{-1}$. The separation performances of the membranes are tested to obtain an optimized deposition time. As shown in Figure 5 b, when the deposition time is less than 2 h, the water flux is decreased dramatically while the rejection to Acid Red 18 is increased from 83.4% to 99.2% and the rejection to Na_2SO_4 is increased from 46.9% to 81.2%, indicating the formation of a denser and thicker layer with longer deposition time. However, as the deposition time goes beyond 2 h, the salt and dye rejections remain constant and the flux is decreased. Thus, a deposition time of 2 h is chosen for the preparation of the DA-NMG/GA composite membranes with high flux and high rejection in this work.

Figure 6. The separation performance of DA-NMG/GA composite membranes (M3) for different organic dyes (a) and different inorganic salts (b), effect of feed concentration on the separation performance at different dye concentrations (c) and different NaCl concentrations(d).

As shown in the Figure 6a, under the optimal preparation conditions M3 exhibits high permeate flux ($9.15\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) and high rejection ($> 99.0\%$) for methylene

blue (799 Da), Congo red (696 Da) and acid red 18 (509 Da), which indicates the composite membranes possess excellent separation performance for organic dyes (500 Da - 1000 Da). Then, various salt solutions are filtrated to investigate the effect of ions on the separation performance of the composite membranes as shown in Figure 6b. The rejection to Na_2SO_4 is as high as 81.2% and the rejection to NaCl is only 13.8%. Meanwhile, the salts rejection obeys the following order: $\text{Na}_2\text{SO}_4 > \text{MgSO}_4 > \text{NaCl} > \text{MgCl}_2$, indicating the surface of M3 is negatively charged during the NF operation, corresponding to the sequence of negatively charged NF membrane [37]. In addition, the characteristic of high organic dye rejection (> 99.0%) and low NaCl rejection (13.8%) suggests that M3 suits well for organic dye/NaCl mixture separation.

Table 1. The separation performance of typical commercial NF membranes in the literature and this study.

Membrane	Manufacturer	Pure water flux, $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$	Operating condition	Salt rejection, %
SeproNF 2A	Ultura[25]	10.50 ^a	0.1-40.0 g/L NaCl at 5 bar and 25 °C	6.9-33.3 ^a
CK	Osmonics[38]	2.42 ^a	0.059-5.85 g/L NaCl, flux of 4 $\mu\text{m/s}$ at 25 °C	45.5-77.7 ^a
DK	Osmonics[38]	3.05 ^a	0.059-5.85 g/L NaCl, flux of 4 $\mu\text{m/s}$ at 25 °C	22.0-75.6 ^a
NF20	Sepro[39]	9.83 ^a	0.59-51.48 g/L NaCl, flux of 10 $\mu\text{m/s}$ at 40 °C	10.7-34.8 ^a
NF	Sepro[39]	9.43 ^a	0.59-51.48 g/L NaCl, flux of 10 $\mu\text{m/s}$ at 40 °C	18.2-75.2 ^a
NF 270	Dow[40]	-	5.0-25.0 g/L NaCl at 5 bar and 25 °C	7.2-21.8 ^a
M3	This work	10.29	1.0-40.0 g/L NaCl at 3.5 bar and 25 °C	5.2-13.8 ^a

^a Data redrawn from references.

The effect of feed concentration on the separation performance of M3 is presented to further study the application of M3 in dye recovery. As shown in Figure 6c, the dye concentration has no pronounced impact on the dye rejection for M3 and the dye rejection is just slightly decreased with the increasing dye concentration. As shown in Figure 6d, the NaCl rejection of M3 is decreased from 13.8% to 5.2% as the

NaCl concentration is increased, which may be ascribed to the weakening Debye length of the electrostatic interaction between the charged ions and negatively charged membrane surface [41]. In addition, the separation performance of typical commercial nanofiltration membranes for salt retention is summarized as illustrated in Table 1. Compared with the commercial nanofiltration membranes, M3 has a rather low NaCl rejection, with a narrow range from 5.2% to 13.8%, and higher pure water ($10.29 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), indicating M3 has a salt high permeation, due to higher diffusion coefficient for NaCl [3]. These results reveal that M3 has potential to be applied for organic dye/salt mixture separation.

Figure 7. Variations of separation performance with operation time for M3 using dye/salt mixture ($0.1 \text{ g}\cdot\text{L}^{-1}$ acid red 18 + $1 \text{ g}\cdot\text{L}^{-1}$ NaCl) model.

To evaluate the feasibility of DA-NMG/GA composite membranes on dye/salt fractionation, 24 h continuous filtration experiment using mixtures of acid red 18 and

NaCl is presented in the Figure 7. The flux of M3 is slightly decreased from 31.56 to 27.67 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ with the operation time. This may be primarily ascribed to the increasing dye concentration in feed solution, resulting in the evolution of dye cake layer on the membrane surface [27]. Moreover, M3 always maintains low salt rejection and high dye rejection, indicating that the DA-NMG/GA composite membranes is a promising alternative to fractionate the salt from dye/salt mixtures.

3.4 Structural stability of the DA-NMG/GA composite membranes

Figure 8. Variations of separation performance with different immersion time in ethanol for M3 (a) and for PA/PES composite membrane (b), pH 1 HCl solution for M3 (c) and pH 14 NaOH solution for M3 (d).

Furthermore, the structural stability of the composite membrane based on NMG-assisted PDA coating is tested. As shown in Figure 8(a-b), the water flux and

Na₂SO₄ rejection for M3 do not change significantly with the increasing immersion time in ethanol. Meanwhile, the Na₂SO₄ rejection for the PA/PES composite membrane decreases from 81.3% to 36.6% while the pure water flux increases from 20.32 to 58.68 L·m⁻²·h⁻¹ after 12 day ethanol treatment, which is ascribed to the weak interaction between the active layer and the support, leading to the detachment of the active layer from the swelling support so as to cause the deterioration of the separation performance of the composite membranes. These results indicate M3 has great durability under alcohol treatment compared with a conventional PA composite membrane due to strong interaction between DA skin layer and support. As shown in Figure 8a, the water flux and Na₂SO₄ rejection for M3 do not change significantly with the increasing immersion time in ethanol. As shown in Figure 8a, the Na₂SO₄ rejection for the PA/PES composite membrane decreases from 81.3% to 36.6%, while the pure water flux increases from 20.32 to 58.68 L·m⁻²·h⁻¹ after 12 day ethanol treatment, which is ascribed to the weak interaction between the active layer and the support, leading to the detachment of the active layer from the support so as to cause the deterioration of the separation performance of the composite membranes. These results indicate M3 has great durability under alcohol treatment compared with a conventional PA composite membrane due to strong interaction between DA skin layer and support. Figure 8(c-d) shows the separation performance of M3 has no significant change after immersing in a pH 1 HCl solution and a pH 14 NaOH solution for 12 days, which indicates M3 can be applied for the treatment of dyeing wastewater with different pH mode, due to the chemical stability of crosslinking polydopamine. In addition, the water flux of M3 has no significant change during 12 days continuous filtration along with the Na₂SO₄ rejection of approximately 80% as shown in Figure 9. These results suggest that M3 exhibits good structural stability and excellent durability in long-term operation process, which is closely related to good adhesion ability between the separation layer and the PES substrate via strong and multiple binding forces including covalent bond and noncovalent bond [9, 10, 42]. The favourable structural stability renders the composite membrane a longer lifespan and a wider range of use, which is crucial for the practical applications of the

composite NF membrane.

Figure 9. Variations of separation performance for M3 with the operation time

In practice, pH variations have great effect on the permeability and selectivity of the membranes during the dye separation process, which can affect the zeta potential on the membrane surface and the electrostatic interactions in the feed [33, 43]. As shown in Table 2, the permeate flux and rejection are both slightly increased when pH is increased from 3 to 9. Below the isoelectric point (5.2 ± 0.5), the active layer on M3 has a positive charge and can react with anionic dyes ($\text{HO-PDA-NH}_3^+ + \text{dyeSO}_3^- \rightarrow \text{dyeSO}_3^- \text{NH}_3^+ \text{-PDA-OH}$), which will contribute to the evolution of cake-enhanced concentration polarization and dye cake layer formation, so a rapid flux decline is observed under pH 3 condition. Above the isoelectric point, the active layer has a negative charge so M3 under pH 9 condition has a highest rejection to negatively-charged acid red 18 according to Donnan exclusion theory. In conclusion, the separation performances under different pH condition have no significant change, maintaining permeate flux of approximately $9.00 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ and rejection of 99.90%, which indicates M3 can be applied for the treatment of dyeing wastewater with different pH mode.

Table 2. Variations of separation performance for M3 under different pH conditions using 0.1 g·L⁻¹ acid red 18 dye solution mode.

	The separation performance of M3 after 1 h		The separation performance of M3 after 24 h	
	Permeate flux, L·m ⁻² ·h ⁻¹ ·bar ⁻¹	Rejection, %	Permeate flux, L·m ⁻² ·h ⁻¹ ·bar ⁻¹	Rejection, %
pH 3	9.14	99.88	8.98	99.89
pH 6	9.42	99.90	9.25	99.90
pH 9	9.57	99.91	9.31	99.92

4. Conclusions

A continuous and dense layer with good structural stability was successfully developed on the PES substrate by employing a facile NMG-assisted dopamine deposition process. NMG played two important roles: (1) the amine group in NMG can react with dopamine through Michael addition reaction, which will adjust the self-polymerization process of dopamine, resulting in the formation of a homogeneous PDA coating; (2) the multi-hydroxy group in NMG can improve the surface hydrophilicity or wettability of the composite membranes. The DA-NMG/GA composite membrane (M3) under optimal conditions exhibited high pure water flux, high dye and Na₂SO₄ rejection. Meanwhile, M3 showed low NaCl rejection, with narrow range, compared with the commercial nanofiltration membranes. Particularly, high salt permeation and high dye rejection were maintained during the 24 h continuous filtration experiment, indicating that the DA-NMG/GA composite membrane is a new candidate for dye/salt fractionation. Furthermore, after immersing in ethanol, pH 1 HCl solution and pH 14 NaOH solution for 12 days, the composite membranes shows good structural stability without significant separation performance change. In addition, the separation performances under different pH condition do not change significantly, which indicates M3 shows membrane stability with the pH variations during the treatment of dyeing wastewater. The successful development of

high salt permeation NF membranes based on homogeneous NMG-assisted PDA coating not only provides a candidate for dye/salt fractionation but also suggests great potential for practical applications of non-polyamide membranes in the near future.

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