Positively charged loose nanofiltration membrane grafted by diallyl dimethyl ammonium chloride (DADMAC) via UV for salt and dye removal postprint

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Abstract

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Preamble

Positively Charged Loose Nanofiltration Membrane Grafted by Diallyl Dimethyl Ammonium Chloride (DADMAC) via UV for Salt and Dye Removal

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Abstract: A novel positively charged loose nanofiltration (NF) membrane was feasibly fabricated by UV-induced photografting polymerization of diallyl dimethyl ammonium chloride (DADMAC) on a polysulfone ultrafiltration membrane. A possible reaction mechanism was proposed wherein a linear chain structure and/or pyrrole-like five-membered nitrogen heterocyclic structures on the side chain were grafted to form the active barrier layer. The resulting NF membrane demonstrated a relatively loose average pore size of 8.6 nm and a positively charged surface. Owing to the nanoscale ultrathin barrier layer and the combination of Donnan exclusion and steric hindrance, the NF membrane exhibited good hydrophilicity, a high pure water flux of 60 L/m^{2}h (at 0.5 MPa), excellent salt rejection for Mg^2 (90.8%), Al^3 (94.0%), and Ca^2 (91.5%), and high dye rejection for methylene blue (99.4%) and congo red (100.0%). The salt rejection performance for different salts followed the order: AlCl > CaCl > MgCl > NaCl > LiCl > MgSO > Na SO . The membrane also demonstrated favorable fouling resistance to seawater and BSA solution. The grafting polymerization kinetics were comprehensively investigated with respect to irradiation time, monomer concentration, and irradiation intensity. X-ray Photoelectron Spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), and contact angle measurements were employed to investigate membrane chemistry, morphology, and hydrophilicity.

1. Introduction

Nanofiltration (NF) membranes have established technical superiority over reverse osmosis and ultrafiltration, particularly in applications such as low-energy seawater desalination, drinking water softening, food chemistry, petrochemistry, catalysis, and pharmaceutical manufacturing. This advantage stems from their unique characteristics: a molecular weight cut-off for dissolved organic solutes between 200 and 2000 Da, relatively lower operating pressure compared to reverse osmosis, and the ability to achieve separation of different valence ions due to selective permeation of mono- and multi-valent ions. For instance, the rejection of divalent and multivalent ions typically exceeds 90%, while monovalent ion rejection remains below 80%. It is universally acknowledged that the separation mechanism of NF membranes combines both steric hindrance and Donnan exclusion.

To date, NF membranes have been fabricated primarily through two methods: one-step phase separation [1–3] and multi-step modification on a base ultrafiltration membrane [4–7]. The direct phase separation method can prepare integrally skinned asymmetric nanofiltration membranes from polyetherimide, polyacrylonitrile, and polyethersulfone, among others. The latter approach typically involves two steps: first preparing the base ultrafiltration membrane via phase inversion [8–11], then constructing the functional active layer for nanoscale selective permeation using diverse techniques including dip-coating [12,13], interfacial polymerization [4,7,14,15], surface cross-linking [16–18], and UV-induced grafting polymerization [6,19,20]. For example, a soluble poly(ether ether sulfone) (PEEK) ionomer with pendant quaternary ammonium groups (QAPEEK) was dip-coated onto a polysulfone ultrafiltration membrane to form a positively charged nanofiltration membrane [12,13]; however, the van der Waals forces between the coating and base membrane cannot guarantee long-term stability of nanofiltration performance during operation. In interfacial polymerization and cross-linking approaches, trimesoyl chloride (TMC) and aliphatic amines or triethanolamine are typically used to form the thin barrier film, where reaction kinetics, monomer type and concentration, polymerization time, and temperature are the main factors determining membrane performance. UV-induced grafting polymerization offers advantages of feasible operation and controllable reaction; UV irradiation initiates free radical formation on polysulfone ultrafiltration membranes and enables covalent bonding of vinyl monomers to form a firm selective barrier layer. Various monomers with positive charges, negative charges, or hydrophilic properties can endow the nanofiltration membrane with desired characteristics. Table 1 summarizes the performance of NF membranes from previous studies. Most NF membranes are either neutral or negatively charged in aqueous environments due to the natural properties of the materials; however, positively charged membranes are highly demanded for current applications such as removal of multivalent cations from water, recovery of valuable cationic macromolecules in bioprocess and pharmaceutical industries, and removal of heavy metals or dyes from effluents. To alleviate fouling by ions or organic matter, it is necessary to endow membranes with certain hydrophilicity.

In this paper, a novel positively charged loose nanofiltration membrane with relatively low operating pressure and high water flux was feasibly prepared via UV-induced grafting polymerization. To the best of our knowledge, comprehensive studies on the photopolymerization of diallyl dimethyl ammonium chloride (DADMAC) on polysulfone membranes via UV have not been reported previously. DADMAC is a positively charged and hydrophilic monomer that facilitates feasible polymerization and crosslinking on the nanofiltration membrane. It can self-crosslink and form the barrier layer under UV irradiation. The UV-induced grafting polymerization kinetics, including reaction time, monomer concentration, and irradiation intensity, were investigated. The surface chemical composition, morphology, roughness, surface hydrophilicity, water flux, and rejection of different ions and dyes (e.g., methylene blue and congo red) were analyzed and discussed.

2.1. Materials

Diallyl dimethyl ammonium chloride (DADMAC, 65 wt.% in water) was purchased from Shangdong Luyue Chemical Co., Ltd, China. Lithium chloride (LiCl), sodium chloride (NaCl), sodium sulfate (Na SO), magnesium sulfate (MgSO), magnesium chloride (MgCl), calcium chloride (CaCl), and aluminum chloride (AlCl) were purchased from Aladdin Chemistry Co., Ltd, China for measuring NF membrane rejection properties. Bovine serum albumin (BSA) was purchased from Aladdin Chemistry Co., Ltd, China. Seawater was collected from the East China Sea. The polysulfone ultrafiltration (UF) membrane used as the basic support was prepared in our laboratory by the traditional phase inversion method as described in our previous work [21]; the base membrane had a molecular weight cut-off (MWCO) of 25-30 kDa and a pure water flux (F) of [value missing in original text].

2.2. Fabrication of Nanofiltration Membrane

The polysulfone ultrafiltration membrane was immersed in 300 ml of DADMAC aqueous solution at various concentrations (10, 30, 40, 45, 50, 55, and 65 wt.%). UV-induced grafting polymerization was initiated using a 400 W UV lamp with a wavelength of 365 nm. The polymerization was carried out directly at room temperature under air atmosphere. The reaction time was varied from 1, 3, 5, 7, 9, 10 to 15 min, and the irradiation intensity was tuned by adjusting the vertical distance from the lamp to the sample (10, 18, 22, 26, and 30 cm). Detailed preparation conditions are summarized in Table 2 . After grafting polymerization, the NF membranes were washed sequentially with ethanol and deionized water three times to remove residual monomers.

2.3. Characterization of Nanofiltration Membrane

The surface chemistry of the nanofiltration membrane was characterized using X-ray Photoelectron Spectroscopy (XPS, AXIS ULTRADLD, Japan). The take-off angle of the photoelectron was set at 90°. The morphology of the cross-section and top surface of membranes was characterized using scanning electron microscopy (SEM, S-4800, Hitachi, Japan); cross-section samples were fractured in liquid nitrogen, and all samples were sputter-coated with gold for 2 min. AFM images of the top surfaces were obtained using a Dimension 3100V SPM from Veeco, US, operated in tapping mode with a scan size of 2 m × 2 m to observe roughness and morphology at the molecular level.

Contact angle (CA) was measured to determine NF membrane hydrophilicity using a contact angle system (OCA20, Dataphysics, Germany). The contact angle change with drop age was recorded. The average pore size and pore size distribution were determined by a liquid-liquid porometer (LLP-1200A, Porous Materials Inc., US) [21,22].

The filtration performance of the membrane was measured using a cross-flow filtration system (Saifei Company, China) with an effective membrane area of 24 cm^2. Pure water flux (F), seawater flux, and BSA (1 g/L) permeation flux were measured at 0.5 MPa after pre-compaction for 40 min at 0.6 MPa. Each sample was measured three times and the average value reported. F was defined by formula (1):

$$F = \frac{V}{A \cdot t}$$

where V is the permeate volume (L), A is the membrane effective area (m^2), and t is the operation time (h).

The dye rejection of the NF membrane was characterized using methylene blue (Mn = 319.9 Da) and congo red (Mn = 696.7 Da) aqueous solutions. The absorbance of feed and permeate solutions for methylene blue (max = 660 nm) and congo red (max = 510 nm) were examined using a UV-VIS-NIR spectrometer (Lambda 950, Perkin Elmer, US). The rejection (R) was calculated using formula (2):

$$R = \left(1 - \frac{A_1}{A_0}\right) \times 100\%$$

where A and A are the absorbance of permeate and feed solutions, respectively.

The salt rejection ratio (Rs) of the membrane was characterized using 1 g/L salt solutions (including Na SO , MgSO , LiCl, NaCl, MgCl , CaCl , and AlCl). The conductivity of feed and permeate solutions was measured using a conductivity meter (DDS-11A, Shanghai Leici Instrument, China). Rs was calculated using formula (3):

$$R_s = \left(1 - \frac{C_1}{C_0}\right) \times 100\%$$

where C and C are the conductivity of permeate and feed solutions, respectively.

3.1. Proposed Mechanism of UV-Induced Grafting Polymerization

The possible mechanism of nanofiltration membrane fabrication is proposed in Fig. 1 [Figure 1: see original paper], which shows the molecular structures of monomer DADMAC with two double bonds (a) and polysulfone (b). Fig. 1(c) illustrates that UV-sensitive polysulfone generates sulfone and benzene ring-based radicals due to cleavage of the S–C bond, which subsequently initiates DADMAC polymerization to form either a linear chain structure or pyrrole-like five-membered nitrogen heterocyclic structures on the side chain. Therefore, the grafted chains bearing positive charges form the active barrier layer on the nanofiltration membrane as shown in Fig. 1(d), which will be further discussed in the following sections on chemistry and morphology.

3.2. Reaction Kinetics of UV-Induced Grafting Polymerization

To optimize the reaction conditions for NF membrane synthesis, the reaction kinetics of UV-induced grafting polymerization were investigated to examine the effects of reaction time, monomer concentration, and irradiation intensity on both pure water flux and MgCl rejection. As shown in Fig. 2 [Figure 2: see original paper], salt rejection increased significantly from 5.1% to 82.6% while pure water flux decreased from 520 L/m²h to 105 L/m²h when irradiation time was prolonged from 1 to 5 min. Further extending the irradiation time from 7 to 15 min resulted in a gradual increase in salt rejection from 90.8% to 99.1% and a steady decrease in pure water flux from 60 L/m²h to 25 L/m²h.

As shown in Fig. 3 [Figure 3: see original paper], salt rejection increased markedly from 2.0% to 84.8% while pure water flux decreased significantly from 900 L/m²h to 115 L/m²h as monomer concentration increased from 10% to 45%. Further increasing monomer concentration from 50% to 65% led to a gradual increase in salt rejection to 97.6% and a steady decrease in pure water flux from 60 L/m²h to 23 L/m²h.

As shown in Fig. 4 [Figure 4: see original paper], salt rejection increased noticeably from 58.9% to 90.8% while pure water flux decreased from 105.7 L/m²h to 50.1 L/m²h as irradiation distance decreased from 30 to 22 cm. Further decreasing the irradiation distance to 10 cm resulted in a gradual increase in salt rejection to 95.3% and a steady decrease in pure water flux to 30.7 L/m²h.

Since the surface UV-initiated reaction is a free radical polymerization, the grafting degree is closely related to reaction time, monomer concentration, and irradiation distance. The analysis above demonstrates that increasing reaction time, increasing monomer concentration, and decreasing irradiation distance generally lead to decreased flux and increased rejection due to higher grafting degrees. Meanwhile, an inevitable trade-off phenomenon exists between flux and rejection, where higher grafting degree results in denser membranes with lower flux and higher rejection. Considering the balance between relatively high salt rejection and pure water flux, NF-4, NF-6, and NF-7 were selected for further investigation of properties and nanofiltration performance after optimization of reaction kinetics.

3.3. Surface Chemistry of NF Membranes

XPS was performed to analyze the surface chemical composition of NF membranes and confirm successful grafting of DADMAC onto the polysulfone UF membrane. As shown in Fig. 5 [Figure 5: see original paper], three new peaks appeared for NF-4, NF-6, and NF-7 membranes compared to the UF membrane. A peak at 399.5 eV was assigned to N1s, while peaks at 267.1 eV and 194.2 eV were assigned to Cl2s and Cl2p, respectively. Meanwhile, the peak intensities at S2s (231.9 eV) and S2p (164.8 eV) from the polysulfone UF membrane decreased after grafting polymerization, indicating that DADMAC was successfully grafted onto the polysulfone UF membrane. All new XPS peaks ascribed to DADMAC on NF membranes were also well supported by previous work from Professor Chung [23]. Furthermore, Table 3 shows that the mass concentration of N and Cl related to DADMAC gradually increased from NF-4 to NF-6 to NF-7, indicating that more monomers were covalently grafted onto the UF membrane with increasing irradiation time, which is in good agreement with Ref. [6] showing that the degree of grafting increased with irradiation time.

To further confirm successful immobilization of DADMAC on the polysulfone membrane, FTIR analysis was conducted as shown in Fig. 6 [Figure 6: see original paper]. The NF-4 membrane exhibited unique absorbance at 950 cm ^{1} and 3000-3500 cm ^{1} ascribed to C-N and N R , respectively, related to DADMAC. Absorbance at 2969-3000 cm ^{1} (C-H), 1450-1600 cm ^{1} (benzene ring), 1300-1350 cm ^{1} and 1160-1120 cm ^{1} (S=O), and 1000-1250 cm ^{1} (C-O-C) confirmed that the polysulfone structure remained essentially unchanged. Therefore, combining both XPS and FTIR results, it can be inferred that DADMAC has been successfully grafted onto the polysulfone membrane.

3.4. Morphology of NF Membranes

SEM images were used to analyze the microstructure of NF membrane surfaces and cross-sections. Figs. 7 and 8 [FIGURE:7, FIGURE:8] show SEM images of the cross-section and top surface of UF and NF membranes. No obvious differences were observed in the overall cross-section between UF and NF membranes at 5,000× magnification in Fig. 7 (left), and the finger-like structure in the cross-section was not influenced by grafting polymerization. However, the thickness of the denser active layer of NF membranes increased to 57, 157, and 214 nm for NF-4, NF-6, and NF-7, respectively, as shown in Fig. 7 (right) at 60,000× magnification, providing nanoscale water channels and selective rejection capability. The top surfaces of NF-4, NF-6, and NF-7 became denser and smoother due to covalent immobilization and coverage by the active polymer layer, as shown in Fig. 8 at 70,000× magnification.

To further investigate the influence of active layer immobilization on membrane surface morphology, AFM was conducted to monitor morphological changes and roughness of NF membranes. As illustrated in Fig. 9 [Figure 9: see original paper], the UF membrane exhibited a typical nodule-like microstructure surface, which was mutually verified by SEM in Fig. 8. For NF-4 and NF-6, sharper peaks appeared with the disappearance of the nodule-like microstructure, indicating immobilization and coverage of the active barrier layer by grafting polymerization. However, with increasing reaction time and resultant higher grafting degree, more grafted polymer chains covered the original membrane surface, showing a complete poly(DADMAC) layer with a thickness of 214 nm as mentioned above. Consequently, the new surface displayed a characteristic microstructure combining roundish peaks and valleys. The average surface roughness (Ra) reflected nanoscale morphological variation: Ra of NF-4 and NF-6 decreased to 2.43 nm and 1.81 nm from 3.8 nm of the initial UF membrane, while Ra of NF-7 with higher grafting degree increased to 4.14 nm.

3.5. Surface Wettability

Generally, hydrophilic membranes exhibit low fouling tendency, especially when treating water containing organic matter and dyes. The immobilization of a poly(DADMAC) layer endows the membrane with certain hydrophilicity. Fig.

10 [Figure 10: see original paper] depicts the time dependence of contact angle for UF and NF membranes. The contact angle of NF membranes was lower than that of the UF membrane, and the initial contact angle of NF-7 decreased to 41.8° with prolonging reaction time to 15 min. The initial contact angle of NF-7 decreased sharply in the first 20 s and then declined to 15° within 120 s, suggesting good hydrophilicity and wettability after grafting polymerization. Both the hydrophilic polymer layer and morphological roughness contributed to rapid wetting on the NF membrane surface, which is beneficial for improving antifouling performance against organic matter and salts.

3.6. Filtration Performances of NF Membranes

Due to its relatively high pure water flux and MgCl rejection, NF-4 was selected for further rejection testing. The pore size distribution of NF-4 was measured using liquid-liquid porometry as depicted in Fig. 11 [Figure 11: see original paper], showing an average pore size of 8.6 nm—larger than most nanofiltration membranes. Therefore, NF-4 can be considered a positively charged loose nanofiltration membrane.

Fig. 12 [Figure 12: see original paper] shows the rejection of NF-4 membrane for seven common inorganic salts. Rejection of different valence salts followed the order: AlCl > CaCl > MgCl > NaCl > LiCl > MgSO > Na SO , which is consistent with previous studies [6,17]. This rejection order can be interpreted by Donnan exclusion effects [24]. Rejection of divalent and multivalent cations was all higher than 90% (e.g., AlCl : 94.0%, CaCl : 91.5%, MgCl : 90.8%) due to strong electrostatic repulsion between higher valence cations and the positively charged ammonium N of the NF membrane, while rejection of monovalent ions was lower (e.g., NaCl: 47.6%, LiCl: 46.1%). However, electrostatic repulsion between positive ions was compromised by divalent anions (SO ^{2}) in this case, resulting in lower rejection of Na SO and MgSO .

To evaluate fouling resistance of NF-4 membrane to salts and organic matter, both seawater and BSA solution permeation tests were conducted at 0.5 MPa as depicted in Fig. 13 [Figure 13: see original paper]. NF-4 membrane showed a stable pure water flux of 60 L/m^2h, seawater flux decreased slightly to 55 L/m^2h, while BSA permeation flux remained at 25 L/m^2h even after 60 min. This excellent fouling resistance behavior can be attributed to the positively charged and hydrophilic surface.

Fig. 14 [Figure 14: see original paper] shows the decolorization and rejection rate of NF-4 membrane for methylene blue (Mn = 319.9 Da) and congo red (Mn = 696.7 Da). The feed solutions of methylene blue and congo red were dark red and dark blue, respectively, while both filtrates were clear and transparent. The rejection rates for methylene blue and congo red were 99.4% and 100.0%, respectively. The high rejection was mainly attributed to the smaller pore size (8.6 nm) and positively charged ammonium N of DADMAC; the positive surface efficiently repelled the dyes in aqueous media through electrostatic repulsion.

Therefore, NF-4 membrane achieved excellent dye rejection for methylene blue and congo red.

4. Conclusions

A positively charged loose NF membrane was fabricated by UV-induced grafting polymerization of DADMAC onto a polysulfone UF membrane. Reaction time, monomer concentration, and irradiation intensity were key kinetic parameters controlling membrane water flux and salt rejection. The optimized NF membrane was achieved by grafting 50 wt.% DADMAC solution for 7 min at an irradiation distance of 22 cm. Surface chemistry evidence (presence of N and Cl), increasing thickness of the dense barrier layer, and roughness variation all verified immobilization of the poly(DADMAC) layer on the membrane surface. The optimized NF membrane exhibited good hydrophilicity and a loose pore size of 8.6 nm. Rejection of different valence salts followed the order: AlCl > CaCl > MgCl > NaCl > LiCl > MgSO > Na SO , with rejection of divalent and multivalent cations all exceeding 90%. Pure water and seawater fluxes reached 60 L/m^2h and 55 L/m^2h, respectively, implying good fouling resistance to salts. Dye rejection for methylene blue and congo red was 99.4% and 100.0%, respectively.

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