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A novel positively charged composite nanofiltration membrane prepared by bio-inspired adhesion of polydopamine and surface grafting of poly(ethylene imine)

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ABSTRACT

Novel positively charged composite nanofiltration membranes were facilely prepared by polydopamine (PDA) deposition followed by poly(ethylene imine) (PEI) grafting on polyethersulfone (PES) substrates. Scanning election microscope (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM), zeta potential measurement and water contact angle measurement were employed to characterize the surface chemical composition and morphology of the resultant membranes. The rejection of salts was increased but the pure water flux was decreased with the increase of PDA deposition time, PEI concentration, PEI reaction temperature and time. The salts rejection followed the sequence: $MgCl_2 > CaCl_2 > MgSO_4 > Na_2SO_4$, confirming that the membranes were positively charged. The rejection of $MgCl_2$ could reach 73.7%, whereas the rejection of $CaCl_2$ was 57.1%. Moreover, the membranes exhibited a superior rejection of up to 96.5% for cationic dyes.

1. Introduction

Nanofiltration (NF), a pressure-driven membrane separation process between ultrafiltration (UF) and reverse osmosis (RO), has been gaining increasing attention and wide applications in water softening, recovery of pharmaceuticals and retention and concentration of dyes, because of its relatively low operation pressure, high permeation flux, as well as low initial investment and operation costs [1–8]. At present, most of commercial NF membranes are negatively charged or neutral [1,9], which are prepared primarily by interfacial polymerization [10,11] and their applications are primarily oriented to the retention of low-molecular-weight molecules and multivalent anions [12]. Theoretically, positively charged NF membranes are more efficient for removal of multi-valent cations, such as Ca^{2+}, Mg^{2+} (water softening) and heavy metal ions, purification of cationic dyes, recovery of cathode electrophoresis lacquer and separation of amino acids below their isoelectric points [12,13].

In recent years, several approaches has been developed to prepare positively charged NF membranes, including phase inversion [14–16], surface crosslinking [1,17–21], layer-by-layer assembly [22,23] and surface grafting [24,25]. Among these approaches, surface grafting in particular UV-initiated grafting has drawn great interest due to its easy operation and low cost. Moreover, the chemical bond between the substrate membrane (support layer) and the active layer may increase the stability of the NF membranes [24]. Deng et al. [24] prepared a series of positively charged NF membranes by UV-initiated grafting polymerization of methacrylatoethyl trimethyl ammonium chloride (DMC) onto polysulfone (PSf) ultrafiltration membrane substrates. The resultant membranes exhibited good rejection of $MgCl^2$ with a high flux and the filtration performance of the resultant NF membranes can be controlled by adjusting the monomer concentration, irradiation time and irradiation distance. Zhong et al. [25] fabricated novel positively charged NF membranes using sponge-like sulfonated polyphenylenesulfone (sPPSU) membrane substrates via UV grafting technique. The resultant NF membranes showed superior rejections for both $MgCl_2$ (up to 95.20%) and Safranin O dye (up to 99.98%). Nevertheless, only photosensitive polymers can be used as the substrate materials for UV-initiated grafting, which may severely limit the applicability of this approach. Moreover, ultra violet may lead to the damage of membrane substrates because of its high energy at low wavelengths. Therefore, it is of great significance to develop a universally applicable surface grafting method to prepare positively charged NF membranes.

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Dopamine has attracted much attention recently due to its potent adhesion property. Lee et al. [26] reported that dopamine polymerized in weak alkaline aqueous media to form highly adherent polymer coatings on most organic and inorganic materials. Based on the strong adhesion behavior and the intrinsic capacity for facile secondary treatments, a great deal of approaches have been put forward for surface modification of solid materials [27–30]. McCloskey et al. [31,32] successfully modified a variety of membranes by polydopamine (PDA) deposition and poly(ethylene glycol) (PEG) grafting to improve the anti-fouling properties of the membranes. Zhu et al. [33] previously fabricated a novel NF membrane by coating a PDA layer onto the polysulfone (PSf) substrate. However, in order to achieve the desirable performance, the modification of the membranes by PDA deposition always takes at least 20 h, which is rather time-consuming.

Herein, we introduce a novel method to fabricate a positively charged composite NF membrane with polydopamine (PDA) as a transition layer. Poly(ethylene imine) (PEI) molecules were covalently grafted onto the surface via Michael addition reaction and/or Schiff base reaction with the quinone functional groups of the PDA layer. Recently, a similar approach was developed by Li et al. to fabricate a positively charged NF membrane consisting of a dense active layer from PEI crosslinking on a porous polysulphone (PS) substrate which was modified by PDA [34]. The big difference between this approach and our approach was the inclusion of a crosslinking step in the former. Moreover, Li's work mainly focused on the effects of the PEI existence, the thermal treatment and the types of cross-linkers on the NF performance. However, our work mainly focused on the PDA deposition and the PEI grafting process. The effects of PDA deposition and PEI grafting conditions on surface chemical composition, morphology, permeability and rejection performance of the resultant membranes were investigated in detail.

2. Experimental

2.1. Materials

Dopamine hydrochloride was purchased from Yuancheng Technology Development Co. Ltd. (Wuhan, China). Poly(ethylene imine) (PEI, 50 wt% in water, *Mw*=70,000) was purchased from Kaiyang Biotechnology Co. Ltd. (Shanghai, China). The molecular structures of dopamine and PEI are shown in Fig. 1. Polyethersulfone (PES, Ultrason 6020 P, *Mw*=29,000) purchased from BASF Co. (Germany) was dried at 110 °C for 12 h before use. *N*, *N*-dimethylformamide (DMF), polyethylene glycol 2000 (PEG2000), alcohol, Methylene blue trihydrate, Orange GII and other inorganic salts were purchased from Kewei Chemicals Co. (Tianjin, China). Tris (hydroxymethyl) aminomethane was purchased from Sigma-Aldrich Co. (Shanghai, China). Water used in all experiments was prepared by Reverse Osmosis with the pH value of 6.0 ± 0.2.

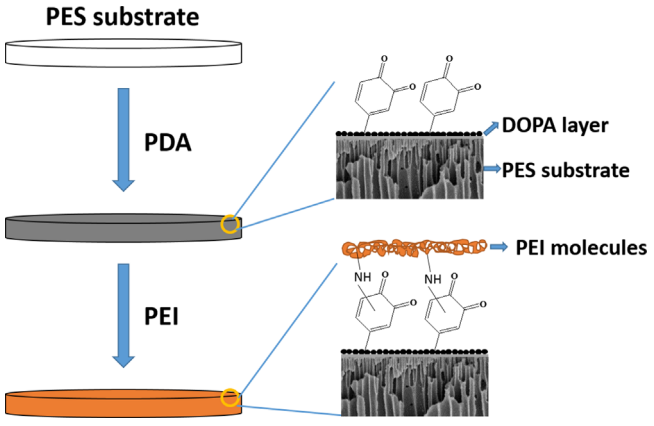

Fig. 1. Scheme of the preparation of PEI-PDA/PES composite membrane via PDA deposition followed by PEI grafting.

2.2. Membrane preparation

PES UF membranes were fabricated with DMF as the solvent and PEG2000 as the pore-forming agent via non-solvent induced phase separation (NIPS) and surface segregation which had been described in our previous studies [35,36]. The casting solution was stirred for 4 h at 60 °C and then left for 4 h to release the bubbles completely. Then the solution was cooled to room temperature and cast on glass with a steel knife and immersed in a water coagulation bath. The fabricated PES UF membranes were used as the porous substrates after washed thoroughly with deionized water over 24 h to remove residual DMF solvent. An aqueous dopamine solution was prepared by dissolving dopamine hydrochloride (2.0 g/L) in Tris buffer solution (pH=8.5 ± 0.2, 50.0 mM). After dried in the air, the clean PES UF membranes were immersed in the above-mentioned dopamine solution and shaken at room temperature for a certain time (0.5 – 4.0 h). The oxidation of dopamine to form polydopamine required the involvement of oxygen [26,32], so the solution was left open to the air. Then the membranes were taken out from the solution and rinsed thoroughly with deionized water. The resultant membranes, designated as PDA/PES composite membranes, were used for characterization and further surface modification.

Aqueous PEI solutions were prepared by dissolving PEI in pure water without further pH adjustment. The above PDA/PES composite membranes were immersed into the PEI aqueous solutions at a certain temperature (27.0 – 80.0 °C) for a certain time (1.0 – 5.0 h). The concentration of PEI ranged from 0 to 4.0 g/L. Then the resultant membranes, designated as PEI-PDA/PES composite membranes, were taken out and rinsed thoroughly with deionized water and stored in deionized water for further characterization and evaluation.

The membranes prepared with different PDA deposition time and different PEI concentrations were numbered respectively, which are listed in Table 1.

2.3. Membrane characterization

The surface morphologies of the membranes were observed by a field emission scanning electron microscope (FESEM, Nanosem 430). The membrane samples frozen in liquid nitrogen were

Table 1
Zeta potentials of the composite membranes prepared with different PDA deposition time and different PEI concentrations.

Composite membrane[a]	PDA deposition time (h)	PEI concentration (g/L)	Zeta potential (mV)[b]
0#	0	0	−41.0 ± 0.5
1#	2.0	0	−15.3 ± 0.3
2#	0.5	2	4.6 ± 0.1
3#	1.0	2	9.1 ± 0.2
4#	2.0	2	12.2 ± 0.3
5#	3.0	2	14.6 ± 0.3
6#	4.0	2	16.5 ± 0.3
7#	2.0	1	9.7 ± 0.2
8#	2.0	3	10.6 ± 0.3
9#	2.0	4	12.1 ± 0.3

[a] The PEI-PDA/PES composite membranes were prepared under the condition of PEI reaction temperature of 60.0 °C and PEI reaction time of 4.0 h.

[b] The streaming potential measurement was carried out in a background electrolyte solution containing 1 mM KCl (pH=6.0 ± 0.2) at 25.0 °C.