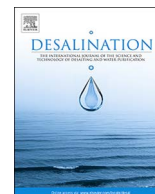




Contents lists available at ScienceDirect

Desalination

journal homepage: [www.elsevier.com/locate/desal](http://www.elsevier.com/locate/desal)

# Layered double hydroxide nanoparticle modified forward osmosis membranes via polydopamine immobilization with significantly enhanced chlorine and fouling resistance

Peng Lu, Shuai Liang, Tuantuan Zhou, Tianshan Xue, Xueyi Mei, Qiang Wang\*

College of Environmental Science and Engineering, Beijing Forestry University, 35 Qinghua East Road, Haidian District, Beijing 100083, PR China

## ARTICLE INFO

### Keywords:

Polyamide thin-film composite membrane  
Chlorine resistance  
Anti-fouling  
Layered double hydroxide

## ABSTRACT

Currently, the degradation of polyamide (PA) layers in thin-film composite (TFC) membranes due to chlorine-based chemical cleaning is still the major obstacles to the development of reverse and forward osmosis (FO) technologies. In this study, layered double hydroxide (LDH) nanoparticles were bound on the TFC membranes by virtue of a polydopamine (PDA)-induced immobilization process to enhance its chlorine and fouling resistance. Two modification strategies as deposition and dip-coating were compared. The accelerated chlorination experiments using 1000 ppm NaOCl indicated the excellent chlorine-resistant performance of the deposition-modified TFC membrane, the chlorine-resistant time was improved about 96 times than the control membrane. The LDH layer served as a barrier to protect the PA layer from chlorination. Moreover, the LDH-modified membrane exhibited a better resistance to organic fouling. Also, the bound LDH layer succeeded to reduce the attachment of bacteria, indicating a promising anti-fouling capability. In general, the modification using the LDH nanoparticles effectively improved the chlorine and fouling resistance of the TFC membranes, suggesting promising applications in various areas.

## 1. Introduction

Membrane processes are now an important separation technology used in waste water reclamation and desalination [1,2]. Forward osmosis (FO) is an emerging membrane separation technology that utilizes the difference of osmotic pressure between a feed solution (FS) and a concentrated draw solution (DS) to drive water across a semi-permeable membranes. Compared with reverse osmosis (RO) processes, the FO processes have shown advantages such as low or no hydraulic pressures during operation, high rejection to a wide range of contaminants, and lower membrane fouling [3,4]. The development of appropriate FO membranes, however, remains as one of the major challenges for their practical applications [5]. Currently two types of membranes have been studied for FO applications, which are asymmetric cellulose triacetate (CTA) membranes and thin film composite (TFC) membranes consist of an ultra-thin polyamide (PA) rejection layer and a porous support layer [6]. Recently, PA TFC membranes have been receiving much attention due to their high mechanical strength, superior water flux, high selectivity, and hydrolytic stabilities [7–10].

Although PA TFC membranes provide better performance in terms

of salt rejection and water permeability, its resistance to fouling and oxidizing agents such as chlorine has to be further improved for its wide practical applications [11]. For FO process, the loose fouling layer near the membrane surface can be readily removed by hydrodynamic shear forces [12,13]. The biological fouling is the major cause and is pervasive membrane fouling that decreases membrane performance [14–16]. Added as a disinfectant to control biofouling or as a membrane cleaning agent, the oxidizing agents can result in conformational changes of the polymer chains, and consequently cause the failure of the membrane separation in terms of a sharp decline in salt rejection [17,18]. Based on the above two issues, PA TFC membranes with improved chlorine resistance and anti-fouling are highly demanded [10,19–21].

Surface modification has been considered as a convenient method for improving the chlorine resistance and anti-biofouling properties of membranes. Zhao et al. [22] prepared TFC membranes incorporated with modified multi-walled carbon nanotubes (MWNTs) and resulted in better antioxidant properties than unmodified PA TFC membrane. Xu et al. [19] improved the anti-biofouling and chlorine resistant properties of a commercial PA TFC membrane by carbodiimide-induced grafting with imidazolidinyl urea. Kwon et al. [23] demonstrated that

\* Corresponding author.

E-mail address: [qiangwang@bjfu.edu.cn](mailto:qiangwang@bjfu.edu.cn) (Q. Wang).

<http://dx.doi.org/10.1016/j.desal.2017.04.030>

Received 20 December 2016; Received in revised form 30 April 2017; Accepted 30 April 2017  
0011-9164/ © 2017 Elsevier B.V. All rights reserved.

the modification of membranes using sorbitol polyglycidyl ether ring-opening polymerization can improve chlorine resistance and increase salt rejection. Recently, polydopamine (PDA) has drawn much attention because its polymerization on the surface of nanoparticles (e.g.  $\text{TiO}_2$ ) can strengthen the firm adherence of the nanoparticles to the membrane surface [24,25]. This binding method can overcome the limitations caused by the traditional self-assembly, entrapment, and chemical binding methods [25].

Layered double hydroxides (LDHs) are a class of ionic lamellar compounds made up of positively charged brucite-like layers with an interlayer region containing charge compensating anions and water molecules [26–28]. LDHs also have basic properties, memory effect, hydrophilicity, and high anion-exchange capacities, etc. For example, thanks for its higher layer charge density and consequent stronger driving force for uptake of  $\text{Cl}^-$  in the interlayer galleries, LDHs have been utilized as additives for inhibiting the autocatalytic degradation of polyvinylchloride (PVC) and thus enhancing its thermal stability [29–31]. In addition, the hydrophilic LDH nanoparticles on membrane surface can improve the anti-fouling performance of the resultant membranes [32,33]. Hence, we started to be interested in whether the LDH nanoparticles can be used as a promising modifying materials for improving the chlorine resistance and anti-fouling of PA TFC membranes.

The incorporation of LDHs into the porous support layer of TFC membranes has been investigated in our previous work [34,35]. Thus, the purpose of the present study is to develop a modified membrane for chlorine resistance and anti-fouling by integrating LDHs nanoparticles onto the surface of PA via PDA. The influence of the LDHs nanoparticle modification on the contact angle, zeta potential, surface morphology, roughness, chlorine resistant and anti-fouling performance of the PA TFC membranes was systematically investigated. The FO performance of the unmodified and modified membranes was compared. To the best of our knowledge, this is the first report on the preparation of LDH nanoparticles modified PA thin-film composite FO membranes via PDA self-polymerization with significant improved chlorine resistance and anti-fouling.

## 2. Experimental

### 2.1. Materials

Polysulfone (PSf, *Mn*: 22,000 Da) and polydopamine (PDA, 98.5%) were provided by Sigma-Aldrich. Polyester non-woven fabric (PET, grade 3249) was provided by Ahlstrom (Helsinki, Finland) was used as a backing layer for PSf supports. 1-methyl-2-pyrrolidinone (NMP, ~99.5%), *N,N*-dimethylformamide (DMF, ~99.8%), 1,3-phenylenediamine (MPD, > 99%), 1,3,5-benzenetricarbonyl trichloride (TMC, ~98%),  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , NaOH, and  $\text{Na}_2\text{CO}_3$  were provided by Sinopharm Chemical Reagent Co., Ltd. TMC was dispersed in Isopar-G, a proprietary nonpolar organic solvent (Univar, Redmond, WA). For membrane performance tests, NaCl (ACS reagent, Sinopharm Chemical Reagent Co., Ltd) and NaClO (available chlorine 8–12%, Sinopharm Chemical Reagent Co., Ltd) were dissolved in deionized (DI) water obtained from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA).

### 2.2. Preparation of LDH nanoparticles suspension

$\text{Mg}_3\text{Al-CO}_3$  LDH nanoparticles was synthesized by a traditional coprecipitation method as described in our previous work [27,34]. Briefly, 50 mL aqueous solution A containing 0.0375 M  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.0125 M  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and 50 mL aqueous solution B containing 0.025 M  $\text{Na}_2\text{CO}_3$  were first prepared. Next, solution A was added drop-wise to solution B with the pH of mixture solution was strictly controlled (pH meter, METTLER TOLEDO) at 12 using 4 M NaOH solution. The suspension solution was aged under

continuous stirring at room temperature for 12 h. All the obtained LDHs were washed with  $\text{H}_2\text{O}$  till pH was 7. The samples were further washed intensively with acetone in order to prevent LDHs agglomeration [36]. The FT-IR profile indicated that the acetone washing process did not change the functional groups of LDH nanoparticles (see Fig. S-1). The obtained LDH nanoparticles were immediately dispersed in the Tris buffer solution (pH = 8.5, 10 mM) and sonicated for 30 min. The  $\text{Mg}_3\text{Al-CO}_3$  LDH nanoparticles suspension was thus obtained.

### 2.3. Preparation of TFC membranes

PSf substrates were fabricated using phase inversion method as described in our previous work [34,35]. The casting solution was prepared by dissolving 12 g PSf in 88 g NMP/DMF mixture solvent (mass ratio was 3:1), followed by stirring at room temperature for 8 h and then stored in a desiccator for at least 15 h. A 150  $\mu\text{m}$  casting knife (Elcometer 3530) was used to spread the PSf solution onto the wetted PET fabric. NMP was applied to wet the fabric and the excess NMP was removed using a clean paper. The whole substrate was immediately immersed in a coagulation bath containing 3 wt% NMP solution for 10 min at room temperature to initiate the phase inversion. The obtained PSf substrate was then stored in a DI water bath for the following interfacial polymerization.

The PA rejection layer was prepared via interfacial polymerization process between MPD and TMC on the surface of the as-prepared PSf substrates. First, the PSf substrate was immersed in a 3.4 wt% MPD aqueous solution for 120 s. An air knife was then used to remove excess MPD solution off the PSf surface. Next, the MPD-saturated substrate was immersed into a 0.15 wt% TMC solution for 60 s, resulting in the formation of an ultrathin PA layer film. The composite membranes were cured in DI water at 95 °C for 120 s, then rinsed with 200 ppm NaOCl and 1000 ppm  $\text{NaHSO}_3$  aqueous solution for 120 and 30 s, respectively. The NaOCl solution rinsing step was used to extract the unreacted aromatic polyamine from the ultrathin polyamide and stabilize the polyamide against further oxidation [37]. At last heat-curing step at 95 °C for 120 s. The fabricated TFC membrane was rinsed thoroughly and stored in DI water at 4 °C.

### 2.4. Preparation of LDHs modified TFC membranes

First, the membrane was coated via PDA self-polymerization. The TFC membrane was fixed on a glass plate and then dried by compressed air for 5 min. Dopamine solution ( $2 \text{ mg mL}^{-1}$ ) was made by dissolving dopamine hydrochloride in Tris buffer solution (pH = 8.5 and 10 mM). The TFC membrane was immersed in the dopamine aqueous solution and kept for 120 min at 30 °C. Then the PDA coated TFC membrane (as PDA-TFC) was carefully taken out from the PDA aqueous solution and rinsed for 10 s with DI water in order to remove the residual unbound PDA.

Next, the PDA-TFC membrane was immersed in the LDHs suspension for 1 h (as  $\text{LDH}_{\text{ab}}$ -TFC) or the PDA-TFC membrane was immersed in the suspension of LDHs until desiccation (as  $\text{LDH}_{\text{de}}$ -TFC) at 30 °C. Finally, the LDHs modified membranes were rinsed with DI water for 10 s. Fig. 1 shows the schematic diagram for the preparation of LDH nanoparticles modified PA TFC membrane via dip-coating and deposition methods. Table 1 shows the key parameters for the preparation of LDH nanoparticles modified PA TFC membrane via dip-coating and deposition methods. The PDA bonding method has been proven to be capable of providing an efficient, strong and irreversible binding effect for LDH nanoparticles [24,25].

### 2.5. Evaluation of FO performance

The schematic diagram of the lab-scale FO testing system and experimental setup has been described in our previous work [34]. The effective membrane area is 11.87  $\text{cm}^2$ . Fig. S-2 shows the water flux and

Download English Version:

<https://daneshyari.com/en/article/4987572>

Download Persian Version:

<https://daneshyari.com/article/4987572>

[Daneshyari.com](https://daneshyari.com)