Preparation and characterization of anti-fouling β-cyclodextrin/polyester thin film nanofiltration composite membrane

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ABSTRACT

Novel β-cyclodextrin ([β-CD])/polyester thin film nanofiltration composite membranes were prepared via in situ interfacial polymerization of trimesoyl chloride (TMC) and triethanolamine (TEOA) in the presence of β-CD. The effects of the concentration and pendant group of β-CD on the separation, morphology and anti-fouling performance of NF composite membrane were investigated. The results show that introducing an appropriate amount of β-CD into membrane effectively improves the membrane performance. When the concentration of β-CD is 1.8% (w/v) in the aqueous phase, the water flux of NF composite membrane reaches a value which is almost two times that of the bare polyester membrane, while maintaining the rejection to Na₂SO₄ at a relative high level. The NF composite membrane exhibits a remarkable increase in the negative charge density and salt rejection by the incorporation of sulfated β-CD ([β]-CD) which possesses sulfonic acid groups as pendant groups instead of hydroxyls. Furthermore, the β-CD/polyester NF composite membrane also presents a significant enhancement in the anti-fouling performance. Therefore, β-CD can be considered as a potential additive to improve the property of nanofiltration composite membrane.

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1. Introduction

Nanofiltration (NF) membrane is a kind of pressure driven membrane with separation characteristics between reverse osmosis (RO) and ultrafiltration (UF) membrane. Thanks to the advantages of high permeation flux, high retention of multivalent ion salts, low operation pressure and low maintenance cost, NF membranes have been used in various industrial fields, such as water treatment, pharmaceuticals, and biochemical industries, etc [1,2]. Most of NF membranes are thin-film composite (TFC) membranes prepared by interfacial polymerization. The TFC membrane is obtained by forming an ultrathin separation selective layer on a porous substrate wherein the benefits of two separate polymeric layers could be combined for the desired performance property. For long term practical operation, antifouling property of membrane is a major issue, because fouling usually causes various negative effects on membrane performance such as flux decline, increment of operation and maintenance costs, and membrane degradation [3,4]. Therefore, a great deal of research efforts have been devoted to the development of anti-fouling TFC membrane. Generally, several strategies are employed to improve antifouling properties of TFC membrane, including hydrophilic modification and incorporation of hydrophilic components. Membrane surface modification by grafting hydrophilic ingredient on membrane top layer has been reported to have a positive effect on fouling resistance, but it costs extra operation step or may change the membrane pore structure leading to a decline performance [5–7]. Incorporation of hydrophilic component into membrane thin film layer is considered to be a convenient and effective approach. Inorganic particles/polymer TFC membranes have been focused on developing antifouling membrane with improved comprehensive performance due to amounts of hydrophilic groups on inorganic particles [8–12]. However the interaction and compatibility between inorganic particles and polymer phases are still a challenge for excellent membrane performance. Hydrophilic organic molecules or macromolecules can also be used as anti-fouling component in the TFC membrane. For instance, An et al. [13] incorporated polyvinyl alcohol (PVA) into composite nanofiltration membranes in situ by adding different amounts of PVA into poly(piperazine) (PPI) aqueous solution during interfacial polymerization with trimesoyl chloride (TMC) and found introducing a small amount of PVA into composite membrane could improve its NF performance enormously.

Cyclodextrins (CDs) are cyclic oligosaccharides composed of several glucose units (6 units in α-CD, 7 units in β-CD or 8 units in γ-CD) linked by α-(1→4) bonds, with a torus-shaped structure characterized by a hydrophilic external surface and a relative hydrophobic cavity. Among them, β-CD is the most readily...
available, lowest-priced and generally the most useful CDs. Due to its special structure and surface properties, a plenty of applications about molecular discrimination of β-CD have been exploited, such as for pervaporation membrane and molecular filter [14–20]. The multi-hydroxyl of β-CD can also be replaced by other functional groups for better performance or other applications [21–23]. Furthermore, it has been found that toroid structure of β-CD with an inner cavity of several Angstroms in diameter has the tendency of allowing water to pass through it, so it has the potential to improve NF membrane permeability [24]. Besides, functional groups of β-CD or its derivatives can also contribute to the membrane hydrophilicity and permeability. However, to the best of our knowledge, there is rare research with a focus on the application of β-CD in TFC membrane and the corresponding membrane performance.

In this paper, a novel β-cyclodextrin (β-CD)/polyester thin film nanofiltration composite membrane was prepared via interfacial polymerization with trimesoyl chloride (TMC) and triethanolamine (TEOA) in the presence of β-CD. Because the hydroxyls of β-CD can react with the acid chloride group of TMC, β-CD molecules can be chemically introduced into the NF composite membrane in situ and thus a stable structure is formed to avoid the leaching of β-CD during long time operation. The effect of β-CD on the separation, morphology and anti-fouling performance of NF composite membrane was investigated. The samples were characterized in terms of pure water flux, rejection, water contact angle, streaming potential, SEM, AFM, and XPS.

2. Experimental

2.1. Materials

The microporous polysulphone supporting film was supplied by the Development Center of Water Treatment Technology (Hangzhou, China). Triethanolamine (TEOA), polyvinyl alcohol (PVA, 1750 ± 50) and bovine serum albumin (BSA) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Trimesoyl chloride (TMC) was purchased from Qindao Sanli Chemical Engineering Technology Co., Ltd (China). n-hexane was supplied by Shanghai Feida Industry & Trade Co., Ltd (China). Sodium dodecyl sulphate (SDS) was achieved from Wenmin Biochemistry Science and Technology Co., Ltd (Shanghai, China). β-cyclodextrin (β-CD) was purchased from Aladdin Co., Ltd. Sulfated β-cyclodextrin (sβ-CD) was obtained from Sigma-Aldrich Co., Ltd. Na₂CO₃, NaOH, NaCl, Na₂SO₄ and PEG 1000 were analytical grade and used without further purification.

2.2. Membrane preparation

The β-CD/polyester thin film nanofiltration composite membranes were prepared through an improved process of interfacial polymerization as our previous work reported [12]. First, an aqueous phase solution was prepared: TEOA (6%, w/v), SDS (0.3%, w/v) and a certain concentration of β-CD were placed in deionized water with the pH adjusted by a mixture of NaOH and Na₂CO₃, blended in 1:2 proportion; whereas the organic phase solution was prepared by dissolving TMC (0.6%, w/v) in n-hexane. The membrane preparation procedure and reaction formula is illustrated in Fig. 1. The microporous PSf supporting membrane was immersed into the organic phase for 30 min. Then, the TMC-saturated support membrane was immersed into the aqueous phase for 35 min. Afterwards, the membrane was put into the organic phase again for 35 min. The post-treatment process was carried out as follows. The membrane was subjected to a heat treatment at 60 °C for 30 min to stabilize the structure. And then the membrane was soaked in an aqueous solution of SDS (0.1%, w/v) with pH 11 for 24 h, and then washed with deionized water repeatedly and stored in deionized water. The above-mentioned operation proceeded in a 35 °C water bath.

2.3. Membrane characterization

The measurements of pure water flux and salt rejection were performed using a cross-flow membrane module at an operation pressure of 0.6 MPa. The water flux was calculated in Eq. (1):

\[
F = \frac{V}{At}
\]

where \( V \) is the total volume of permeated pure water, \( A \) is the membrane area, and \( t \) is the operation time. Deionized water was used for this measurement. The rejection was measured with 5 mmol/L Na₂SO₄ solution at an operation pressure of 0.6 MPa. The concentrations of the permeation and feed solutions were...
determined by electrical conductivity HANA-EC215 (Italy). The rejection was calculated in Eq. (2):

\[
R = 1 - \frac{C_p}{C_f}
\]  

(2)

where \( C_p \) and \( C_f \) are the concentrations of the permeant and feed solutions, respectively.

Water was used as the probe liquid for determination of the hydrophilicity at the membrane surface. The static contact angle of water on the surface of a polymer membrane was measured by using OCA15 (Dataphysics Co., Germany). The average value of the contact angle on each polymer membrane was calculated using at least five different locations on each membrane.

Reversible Ag/AgCl electrodes, placed on both sides of the membrane, were used to measure the resulting electrical potential difference (\( \Delta E \)) as the pressure difference across the membrane (\( \Delta P \)) changed through a digital electrometer (VC 890D, Shenzhen Victor Hi-tech Co. Ltd.). Then the streaming potential was calculated in Eq. (3):

\[
SP = \frac{\Delta E}{\Delta P}
\]  

(3)

the pressure difference ranged from 0 to 4 \( \times 10^5 \) Pa.

The morphologies of the surface of membranes were observed with a scanning electron microscope (TESCAN 5136MM) after being coated with gold. Quantitative surface roughness analysis of the nanocomposite membranes was measured using AFM imaging and analysis (Nanoscope IV). The surface roughness was reported in terms of the average plane roughness (Ra) and root mean square roughness (Rms).

XPS analysis was performed using a RBD upgraded PHI-5000CESCA system (PerkinElmer) with Mg \( K_a \) radiation (\( h\nu = 1253.6 \) eV).

3. Results and discussion

3.1. Effect of \( \beta \)-CD concentration on the membrane performance and morphologies

To gain an insight into the influence of \( \beta \)-CD concentration on the membrane performance, \( \beta \)-CD with concentrations of 0.6, 1.2, 1.8, 2.4 and 3.0% (w/v) was, respectively added into aqueous phase to prepare NF composite membrane. The bare polyester NF membrane without \( \beta \)-CD was also prepared for comparison.

Fig. 2 is a plot of pure water flux and rejection to \( \text{Na}_2\text{SO}_4 \) vs. \( \beta \)-CD concentration in the aqueous phase. It is found that the water flux increases dramatically with the increasing concentration of \( \beta \)-CD in the aqueous phase. The rejection of \( \text{Na}_2\text{SO}_4 \) decreases slightly when the \( \beta \)-CD concentration is lower than 1.8% (w/v), but it drops sharply at higher concentration of \( \beta \)-CD.

The hydrophilicity of membrane surface was firstly investigated by measuring the water contact angles of NF composite membranes. As the amount of \( \beta \)-CD in aqueous phase increases, the hydrophilicity of membrane increases theoretically. From Fig. 3, the contact angle of membrane decreases obviously with the increasing \( \beta \)-CD concentrations. But at high concentration of \( \beta \)-CD (3.0%, w/v), the contact angle increases, possibly relating to the severe agglomeration of \( \beta \)-CD. Therefore, the increase in membrane permeability with \( \beta \)-CD concentration could be explained taking into account a combination of several factors [12,13,18,21,24]. First, the hydrophilicity of the NF composite membrane increases with the increasing \( \beta \)-CD content in the aqueous solution due to the existence of multi-hydroxyl of \( \beta \)-CD. The hydrogen bond interaction between water molecules and membrane surface is therefore enhanced in the presence of \( \beta \)-CD, and thus the water transport through the composite membrane is facilitated. Secondly, the additional channels at the polymer/\( \beta \)-CD interface are introduced into the membrane by the immobilization of \( \beta \)-CD. The molecular-scale mixing between \( \beta \)-CD and polymer chains as well as the relative rigid structure of \( \beta \)-CD disrupts the regular packing of polyester, leading to an increased chain–chain space. Because of the densely populated hydroxyl groups at the exterior of \( \beta \)-CD, the newly created spaces are more

| Table 1 Relative surface atomic concentration of membranes of bare polyester and \( \beta \)-CD/polyester NF composite membrane. |
|-----------------|-----------------|-----------------|-----------------|
| Membrane samples | \( C \) (%)   | \( O \) (%)   | \( N \) (%)   | \( O/N \)   |
| Polyester NF composite membrane | 67.1  | 27.84  | 5.06  | 5.50   |
| \( \beta \)-CD/polyester NF composite membrane (1.8 w/v% \( \beta \)-CD) | 68.47 | 27.38  | 4.15  | 6.59   |
hydrophilic compared with those of bare polyester and are favorable to the free and direct pass through of water. Thirdly, the reactivity of β-CD is lower than that of TEOA, giving rise to a lower cross-linking structure of membrane surface layer. This loose and hydrophilic surface layer contributes to the enhancement of water flux. Furthermore, β-CD inner cavity with diameter of ~6 to 6.4 Å may probably provide the fast passages for water molecules. Herein, PVA/polyester NF composite membrane was

Fig. 4. SEM images of the surfaces of NF composite membranes prepared with different concentrations of β-CD (w/v): (a) 0%; (b) 0.6%; (c) 1.8%; (d) 3.0%.

Fig. 5. AFM images of the surfaces of NF composite membranes prepared with different concentrations of β-CD (w/v): (a) 0%; (b) 0.6%; (c) 1.8%; (d) 3.0%.
prepared using the same preparation condition (1.8% (w/v) of PVA in aqueous phase) to illustrate the role of inner cavity of β-CD. PVA is chosen because the fraction of hydrophilic groups (–OH) on its structure is quite similar to that of β-CD and it presents a linear structure without inner cavity. Compared with PVA/polyester membrane (about 18 L/m² h), β-CD/polyester NF composite membrane presents a higher water flux and a similar salt rejection. Thus the result may serve as an evidence that the inner cavity of torus-shaped β-CD is favorable for the water permeability without sacrificing Na₂SO₄ selectivity, because the diameter of β-CD inner cavity is larger than water molecule diameter (2.7 Å) but smaller than the hydrated sodium and sulfate ion diameters (9 and 10 Å).

However, when β-CD concentration exceeds a threshold value (> 1.8%, w/v), the agglomeration of β-CD even phase separation happens, due to hydrogen bonding among the β-CD molecules themselves. The non-uniform dispersion or agglomeration of β-CD may bring about defects and cracks of membrane thin layer, resulting in a severe deterioration of salt rejection. In a conclusion, β-CD/polyester thin film nanofiltration composite membrane with significantly improved water flux and well-maintained salt rejection can be obtained when an appropriate amount of β-CD (1.8%, w/v) is added into aqueous phase during the membrane preparation.

The chemical compositions of skin layer of bare polyester and β-CD/polyester NF composite membrane were analyzed through XPS analysis and the results are summarized in Table 1. The value of O/N increases evidently from 5.50 to 6.59 when β-CD is introduced into the membrane. On the one hand, the large number of hydroxyl groups in β-CD could result in an increase in O/N value. On the other hand, the lower cross-linking structure caused by the introduction of β-CD may also contribute to the increased O/N value. Thus, it indicates that β-CD has been immobilized into membrane surface by in situ interfacial polymerization successfully, producing a surface thin layer with lower cross-linking structure and higher hydrophilicity [13].

Table 2

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ra (nm)</th>
<th>Rms (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>109.4</td>
<td>90.8</td>
</tr>
<tr>
<td>0.6% β-CD</td>
<td>101.8</td>
<td>84.5</td>
</tr>
<tr>
<td>1.8% β-CD</td>
<td>96.1</td>
<td>80.4</td>
</tr>
<tr>
<td>3% β-CD</td>
<td>60.6</td>
<td>48.4</td>
</tr>
</tbody>
</table>

3.2. Effect of pendant group of β-CD on the membrane performance

Thanks to the multi-hydroxyl at the exterior of β-CD, high hydrophilicity of β-CD plays an important role in the improvement of membrane performance. Since hydroxyl of β-CD can be easily modified by other groups, it is deserved to investigate the influence of pendant group of β-CD on the membrane performance. Sulfated β-cyclodextrin (sβ-CD) whose exterior decorated with sulfonic acid
groups instead of hydroxyl groups, is a common derivative of β-CD and is often used for direct methanol fuel cells [22,23]. Herein, sβ-CD is employed for the preparation of sβ-CD/polyester NF composite membrane to investigate the effect of pendant group of β-CD on the membrane performance. The properties of sβ-CD/polyester membrane, β-CD/polyester membrane and bare polyester membrane are demonstrated in Fig. 6. For better comparison, the concentration of β-CD and sβ-CD is fixed at 1.8% (w/v) using the same preparation technique.

Compared with bare polyester membrane and β-CD/polyester membrane, sβ-CD/polyester membrane possesses moderate water permeability. The water flux of sβ-CD/polyester membrane is probably related with the property of sβ-CD which can not react with TMC, leading to a smaller sβ-CD loading in thin layer and less effect on the density of membrane structure. So the water flux of membrane with sβ-CD is lower than that of membrane with β-CD. However, the flux of sβ-CD/polyester membrane is still higher than that of bare polyester membrane due to the hydrophilic character of sβ-CD. As a neutral solute, PEG 1000 is used to characterize the molecular weight cut off of membranes. Seen from Fig. 6, β-CD/polyester and sβ-CD/polyester membranes have a similar rejection to PEG1000, which is slightly lower compared with bare polyester membrane. It suggests that the incorporation of β-CD and sβ-CD may result in a lower cross-linking structure of membrane surface layer. As far as retention property, the rejection to salt for a charged NF membrane is not only related with the pore size of the membrane, but also largely depends on the electrostatic action between the membrane and the ions in solution [26,27]. Thus, the surface charge character of the membrane in terms of streaming potential was examined and it can be found that sβ-CD/polyester membrane possesses the most negative value and thus the most negative charge density of membrane surface. The negative charge on the membrane surface will attract cation and repulse anion, contributing to a high rejection of multi-valent anion salt. So the sβ-CD/polyester membrane exhibits the highest Na2SO4 rejection. However, for the rejection to NaCl, the bare polyester membrane possesses the highest one. The diameters of hydrated sodium and chloride ion are close to that of β-CD inner cavity, so NaCl may permeate through the β-CD inner cavity. With a high negative charge on the membrane surface, sβ-CD/polyester membrane obtain a higher NaCl rejection than β-CD/polyester membrane. Therefore, the introduction of sβ-CD into the NF composite membrane can also improve the permeability with an enhanced separation performance, especially applied in separating multi-valent anion.

3.3. Effect of β-CD on the membrane anti-fouling performance

Membrane fouling is usually examined with a separate solution of salt and organic pollutants, or a mixed solution of salt and organic pollutants [28]. In order to simulate real operating environment, both Na2SO4 and Na2SO4/bovine serum albumin (BSA) mixtures are used. Fig. 7 illustrates the changes in flux and rejection of NF composite membranes with different concentration and pendant group of β-CD within an operation time of 25 h. In Fig. 7a, the flux of all membranes declines notably within the first 8 h, and then decreases slightly, reaching a relative stable state. It is reported that the rate and the extent of fouling are most significantly influenced by the roughness of the membrane surface [29]. The large number of hydroxyls of β-CD retards the cross-linking reaction and form strong intermolecular hydrogen bonding, leading to a smoother membrane surface as mentioned above. Thus β-CD/polyester NF composite membrane exhibits an outstanding improved anti-fouling ability, which is ascribed to its smoother surface and higher hydrophilicity. The NF composite membrane containing sβ-CD still has the highest rejection, while it does not present obvious difference on the antifouling performance compared with bare polyester membrane, probably as a result of its rough morphology (Figs. 8 and 9). In Fig. 7b, the salt

![Fig. 8. SEM images of the surfaces of NF composite membranes with different concentration and pendant group of β-CD: original membrane (a) 0%, (b) 1.8% β-CD, (c) 1.8% sβ-CD; fouled membrane (d) 0%, (e) 1.8% β-CD, (f) 1.8% sβ-CD.](image-url)
rejection increases at the initial running period because the membranes become more compact at the operation pressure. Furthermore, it is found that all rejection to salt is higher when a mixture of 5 mmol/L Na₂SO₄ and 50 mg/L BSA is applied as feed solution, and this probably because the adsorption of BSA on the membrane surface performs as blockage of the transport of salt.

Fig. 8 represents SEM images of the original and fouled membranes with different concentration and pendant group of β-CD. It is observed that the surfaces of fouled membranes are smoother compared with original membranes, as a result of valleys on original membranes covered by BSA. The roughness of the membrane surface can be quantified from the AFM results as presented in Fig. 9 and Table 3. Clearly, the RMS value of original β-CD/polyester NF composite membrane is the smallest, which is consistent with its best anti-fouling performance. Therefore, SEM and AFM results further demonstrate that the introduction of β-CD into NF composite membrane can effectively enhance the anti-fouling performance of membrane.

3.4. Comparison with commercial NF membrane

The performances of three kinds of polyester membranes prepared in this article are compared with some commercial NF membranes [2] and the results are summarized in Table 4. Herein

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Surface roughness values of the NF composite membranes with different concentrations and pendant groups of β-CD by AFM.</th>
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<tbody>
<tr>
<td>State</td>
<td>Membrane</td>
</tr>
<tr>
<td>Original</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>1.8% β-CD</td>
</tr>
<tr>
<td></td>
<td>1.8% sβ-CD</td>
</tr>
<tr>
<td>Fouled</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>1.8% β-CD</td>
</tr>
<tr>
<td></td>
<td>1.8% sβ-CD</td>
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<table>
<thead>
<tr>
<th>Table 4</th>
<th>Comparison of some commercial NF membranes with polyester NF membrane.</th>
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</thead>
<tbody>
<tr>
<td>Membrane type</td>
<td>Pressure (MPa)</td>
</tr>
<tr>
<td>NF-40 (Polyperazine-amide)</td>
<td>2.0</td>
</tr>
<tr>
<td>NF-40HF (Polypiperazine-amide)</td>
<td>0.9</td>
</tr>
<tr>
<td>HSS205A (Polyaromatic-amide)</td>
<td>0.5</td>
</tr>
<tr>
<td>NTR-7250 (Polyvinyl alcohol)</td>
<td>1.4</td>
</tr>
<tr>
<td>Polyester (Prepared in this paper)</td>
<td>0.6</td>
</tr>
<tr>
<td>β-CD/polyester (Prepared in this paper)</td>
<td>0.6</td>
</tr>
<tr>
<td>sβ-CD/polyester (Prepared in this paper)</td>
<td>0.6</td>
</tr>
</tbody>
</table>
triethanolamine (TEOA) is used as an active monomer to prepare polyester NF membrane, because it is environment-friendly, economical and easy to be obtained [30]. Polyester NF membranes, especially β-CD/polyester membrane, have a considerable overall performance including water flux and rejection compared with commercial NF membranes.

4. Conclusions

Novel β-cyclodextrin (β-CD)/polyester thin film nanofiltration composite membrane was prepared via in situ interfacial polymerization of trimesoyl chloride (TMC) and triethanolamine (TEOA) in the presence of β-CD. The effects of β-CD on the structure, morphology and separation performance of NF composite membrane were investigated by the measurements of pure water flux, rejection, water contact angle, SEM, AFM, and XPS. The β-CD/polyester NF composite membrane exhibits improved water permeability and membrane hydrophilicity. When the concentration of β-CD is 1.8% (w/v), the water flux of NF membrane reaches a value which is almost two times that of the bare polyester membrane, without sacrificing a severe degree of rejection. The addition of sulfated β-CD (s-β-CD) can cause a remarkable increase in the negative charge density and salt rejection of membrane. Furthermore, NF composite membrane incorporated with β-CD displays a significant improvement on anti-fouling performance. Compared with some commercial NF membranes, polyester NF membranes we prepared, especially β-CD/polyester membranes, have a considerable overall performance including water flux and rejection.

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