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Increasing the performance of reverse osmosis membranes via the interfacial copolymerization of β-cyclodextrin with *m*-phenylenediamine/trimesoyl chloride

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ABSTRACT

A novel β-cyclodextrin (β-CD)/polyamide film reverse osmosis (RO) membrane was prepared by in situ interfacial polymerization via mixing β-CD with *m*-phenylenediamine in the aqueous phase prior to reaction with trimesoyl chloride. The effects of the β-CD concentration on the morphology and separation performance of the RO membrane were studied. β-CD was employed to improve the pure water flux of the membrane. When the concentration of β-CD in aqueous solution was 1.5% (w/v), both the rejection of NaCl and the pure water flux were maintained at a high level. In this case, water flux of the β-CD-modified RO membrane was nearly1.52 times that of the β-CD-free polyamide membrane. This increase might have been caused by the high concentration of β-CD hydrophilic hydroxyl groups, which appeared to directly improve the performance of the composite film. In addition, the unique properties of the resulting membrane, including the loosely cross-linked structure formed by β-CD and the polyamide film, the intramolecular cavity existed in β-CD and the affinity of β-CD to water molecules, was ascribed as the reasons for the improved performance of higher permeability.

Keywords: β-cyclodextrin; Polyamide; Reverse osmosis; Interfacial polymerization; Surfactants

1. Introduction

Reverse osmosis (RO) is the process of separating solvent and solute, and the driving force of this process is the differential pressure on both the sides of a semipermeable membrane. Thin-film composite (TFC) aromatic polyamide RO membranes were successfully developed in the 1980s, commercialized thereafter, and promoted vigorously. Although efforts toward the improvement of conventional TFC membranes are still ongoing, increasing membrane performance requires a significant breakthrough [1–4]. Aromatic polyamide RO membranes have persisted as the most prevalent RO membrane products to date. Due to their many advantages, including their high flux, high retention of multivalent ion salts, low operation pressure, and low maintenance costs, RO membranes have been used in various industrial fields, such as the water treatment, pharmaceutical, and biochemical industries, among others [5,6]. Meanwhile, RO plays important roles in the seawater and brackish water desalination and ultrapure water preparation. In long-term practical operation, fouling usually produced many negative effects on membrane performance, such as decreased flow, increased operating and maintenance costs, membrane degradation, and so on. Therefore, improving membrane antifouling performance is an important issue deserving of further study [7,8]. The incorporation of a hydrophilic

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component into a thin-film membrane layer is considered to be a convenient and effective approach to maintain membrane performance. For example, in a study by Choi et al. [9], different amounts of β-cyclodextrin (β-CD) were added to a triethanolamine aqueous solution for reaction with trimesoyl chloride (TMC) via interfacial polymerization (IP), demonstrating β-CD could be incorporated into a composite nanofiltration (NF) membrane in situ. Their results showed that introducing a small amount of β-CD into the composite membrane greatly improved its NF performance.

CDs are a class of cyclic oligosaccharides produced via the digestion of starch by CD glycosyl transferase, which is expressed during the culture of *Bacillus cereus*. The most notable feature of this enzyme is an aromatic ring outside its hydrophilic region. CDs exhibit a variety of the most common degrees of polymerization; the most common are 6-,7-, and 8-, which correspond to α, β-, and γ-CDs, respectively. Among them, the largest industrially produced CD is β-CD, due to its highly desirable properties, relatively low price, and number of potential applications. β-CD-based products are widely used in the food, pharmaceutical, agricultural, and cosmetics industries as well as in nanocoatings, molecular recognition, chemical analysis, catalytic reactions, and other fields. Due to its unique surface properties and structure, β-CD has been used in many applications that exploit its molecular discrimination properties, including uses in pervaporation and molecular filtration membranes [10–20]. Furthermore, the toroid structure of β-CD has an inner cavity several angstroms in diameter that permits the passage of water; thus, the use of β-CD as an additive has the potential to improve the permeability of NF membranes [9]. The multi-hydroxyl groups in β-CD are able to be replaced by other functional groups to increase membrane performance or for use in various other applications [9,15,21,22]. The use of CDs as additives in membranes has been demonstrated to have a significant impact on membrane separation performance [23–34].

In this work, a novel β-CD/polyamide RO membrane was prepared via the IP of *m*-phenylenediamine (MPD) and TMC in the presence of β-CD and characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). β-CD molecules were introduced into the RO membrane by in situ reaction, resulting in the formation of a stable structure that avoided the leaching of β-CD during long-term operation. Leaching was avoided because the hydroxyl groups of β-CD had reacted with the acyl chloride groups of TMC. The effects of β-CD on the separation, morphology, and antifouling performance of RO composite membranes were investigated. The rejection, pure water flux, and water contact angle of the membrane samples were used for characterization. The prepared membrane demonstrated increased water permeability over traditional RO membranes as well as potential for use in desalination and concentration applications.

2. Materials and methods

2.1. Materials

MPD and TMC were purchased from J&K Scientific Ltd. (Beijing, China). β-CD (98%) was purchased from Sigma–Aldrich (Shanghai, China). Sodium dodecyl sulfate (SDS), triethylamine (TEA), camphorsulfonic acid (CSA), and *n*-hexane were purchased from Aladdin (Shanghai, China). All reagents were used without further purification. Polysulfone (PSf) ultrafiltration membranes were supplied by Hangzhou Water Treatment Technology Development Center (Hangzhou, China).

2.2. Membrane preparation

β-CD/polyamide-modified RO membranes were prepared via IP reaction. First, an aqueous phase solution was prepared containing MPD (2%, w/v), SDS (0.1%, w/v), a certain concentration of β-CD, and deionized water. Then, the solution pH was adjusted using a 2:1 mixture of CSA and TEA. An organic phase solution was prepared by dissolving TMC (0.1%, w/v) in *n*-hexane. The reaction and membrane preparation procedure are illustrated in Fig. 1.

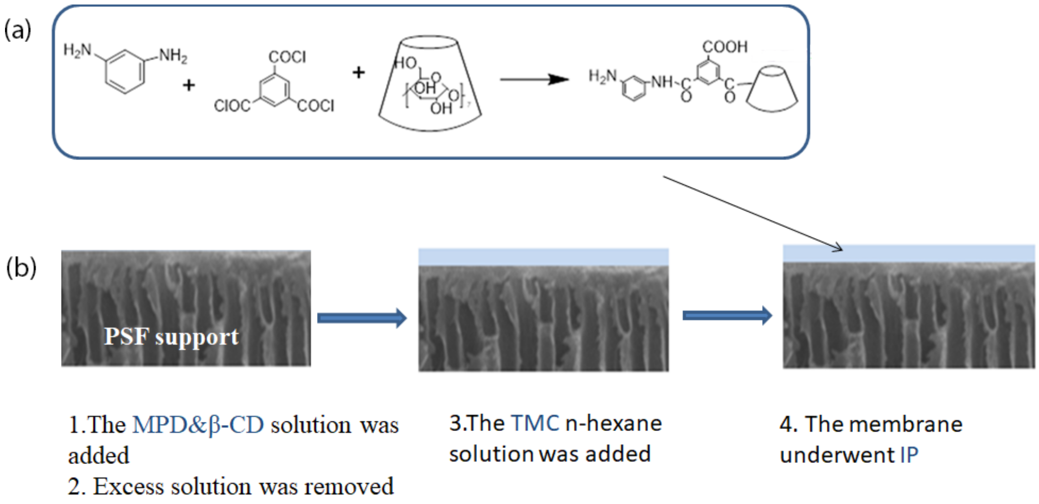

Fig. 1. (a) Schematic of the preparation procedure of a β-CD/polyamide RO composite membrane. (b) The IP reaction between TMC and MPD in the presence of β-CD.

The aqueous solution was poured onto the surface of the microporous PSf membrane; the membrane was covered completely for 2 min. The excess solution was then drained, and the film was hung vertically until no residual solution was visible on the surface of the film surface. Subsequently, the organic phase solution was poured onto the membrane, the membrane was covered completely for 30s, the excess solution was then drained, and the membrane was heat-treated at 60°C for 10 min to aid the formation of a stable structure. Finally, the membrane was soaked in pure water for 12 h for testing purposes. The above procedure was performed at room temperature.

2.3. Membrane characterization

Salt rejection and pure water flux were measured using a cross-flow membrane module at an operation pressure of 1.6 MPa and a temperature of 25°C. All membranes were compacted for 60 min to obtain a stable fluid, and performance was then tested under the same conditions. Rejection was measured using a 2,000 ppm of NaCl solution at an operation pressure of 1.6 MPa. The concentrations of the efflux and feed solutions were determined by an electrical conductivity meter (DDSJ-308A, Leizi, China). The rejection *R* was calculated by the following Eq. (1):

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

where C_p and C_f denoted the concentration of the efflux and influx solutions, respectively. The water flux *F* was calculated from Eq. (2):

$$F = \frac{V}{A \times t} \tag{2}$$

where *V* (L) represented the volume of the permeated pure water, *A* (m^2) represented the membrane area, and *t* (h) denoted the operation time. The Eq. (3) was used to calculate the diffusion coefficient (B_s) of NaCl during the rejection:

$$B_s = F \times \left(\frac{1}{R} - 1\right) \tag{3}$$

The hydrophilicity of the composite membrane was measured by a contact angle goniometer (OCA-20, Dataphysics, Germany). Deionized water was used as the probe liquid at room temperature. The value for each polyamide membrane was determined by measuring the contact angles of at least five different locations on each membrane. The morphologies of the composite membrane surfaces were visualized by SEM (S8010, HITACHI, Japan) after being dried under vacuum and sputter coated with gold. The quantitative surface roughness values of the wet polyamide membranes were determined using AFM (AFM, Dimension Icon, Bruker, Germany). The surface roughness values were reported as both the average plane roughness and root mean square roughness. XPS (Kratos AXIS Ultra DLD, Japan) was used to characterize the chemical composition and structure of the composite membranes. XPS was performed using an RBD upgraded PHI-5000CESCA system (PerkinElmer, USA).The zeta potentials of the membranes were measured with an electrochemical analyzer (Sur PASS 3, Anton Paar GmbH, Austria) using 1 × 10^{-3} mol/L of KCl solution as the background electrolyte solution. The pH of this aqueous solution was adjusted to 2–10 with 0.1 M HCl and 0.1 M NaOH at room temperature. For each measurement, two 20 mm × 10 mm membrane samples were fixed onto sample holders using adhesive tape. The sample holders were inserted into an adjustable-gap cell. A gap of 100 μm between the sample surfaces was used for measurements. The membrane surfaces were placed facing each other, and the samples were rinsed with the measuring electrolyte solution thoroughly before any measurements were performed.

3. Results and discussion

3.1. Effects of SDS concentration on membrane performance

To determine the effects of surfactants on film properties, the following experiments were performed. An aqueous phase solution containing MPD (2%, w/v) and varied SDS (0.0%, 0.05%, 0.1%, 0.15%, or 0.2% w/v) was prepared. The pH was adjusted using a 2:1 mixture of CSA and TEA. An organic phase solution was prepared by dissolving TMC (0.1%, w/v) in *n*-hexane. The results of pure water flux are shown in Fig. 2.

Fig. 2 shows that with the increase of SDS concentrations, the diffusion coefficient of NaCl through the membrane decrease firstly, and then tend to be constant. The results can be understood from a surfactant molecules facilitated IP. When the content of SDS is low, the surfactant molecules are arranged at the interface between the aqueous and oil phases as a monolayer, which reduce the surface tension and form MPD enrichment zone. The concentration of MPD at the interface is higher than that in the aqueous phase, which promotes the reaction between MPD and TMC. The decrease of the diffusion coefficient and water flux of the membrane is assigned to the increasing degree of cross-linking. When the concentration of surfactant increases to the critical micelle

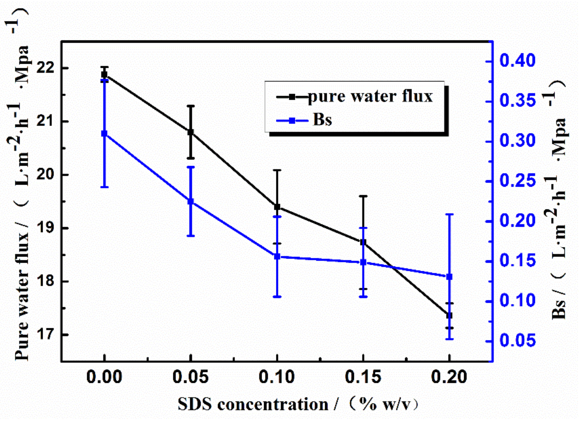

Fig. 2. Effects of SDS concentrations on pure water flux and diffusion coefficient.

concentration, the concentration of MPD at the interface reaches the maxima, and the cross-linking reaction reaches the maximum limit, which is responsible for the plateau of diffusion coefficient at higher SDS concentrations.

3.2. Effect of β-CD concentration on membrane performance

To gain insight into the effects of the β-CD concentration on membrane performance, β-CD concentrations of 0.5, 1, 1.5, and 2 (% w/v) were used to prepare RO composite membranes. RO membranes prepared without β-CD (β-CD-free) were served as the control sample.

Fig. 3 shows that water flux and the diffusion coefficient increased dramatically as the concentration of β-CD increased when the β-CD concentration was lower than 1.5% (w/v). The improvement of permeance was most likely due to the much smaller degree of cross-linking that is induced by β-CD, which resulted in a loose film membrane. The explanation is confirmed by the rejection results, which decreases from ~99% to 98.1% when concentration of β-CD increases from 0 to 1.5 wt%. When the concentration of β-CD exceeds 1.5% (w/v), the membrane performance deteriorate significantly, which might have resulted from the obviously decreased cross-linking. The result from compositional analysis has provided evidence for this explanation.

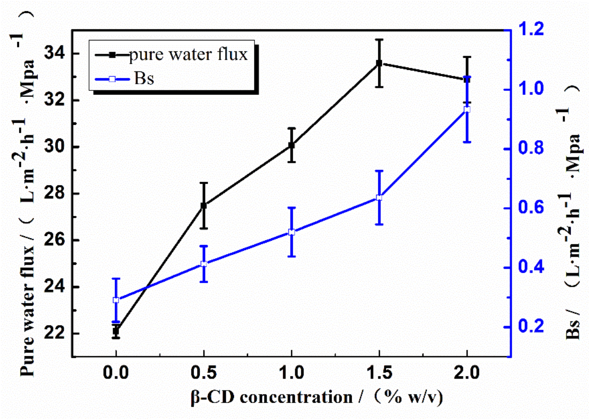

Fig. 3. Effects of β-CD concentration on the pure water flux and diffusion coefficient.

3.3. Effects of β-CD concentration on membrane morphology

The SEM images (Fig. 4) of membranes prepared from different concentrations of β-CD showed that roughness on surface decreased as the β-CD concentration increased. When the β-CD concentration exceeded 1.5%, the surface roughness increased, which was further confirmed by AFM results shown in Fig. 5. According to the findings showed in literature, the lower reaction rate of the IP reaction resulted in a smoother surface compared with that of β-CD-free membranes [15], and the β-CD in aqueous solution will decrease the cross-linking reaction rate because β-CD is less reactive than MPD. As a result, the retardation effect became increasingly prominent with an increase of the β-CD concentration in solution. This explanation consists with the flux as well as the diffusion coefficient shown in Fig. 3. Therefore, when appropriate amounts of β-CD (1.5%, w/v) was added to the aqueous phase, β-CD/polyamide TMC RO membranes with significantly improved water flux and well-maintained salt rejection were obtained.

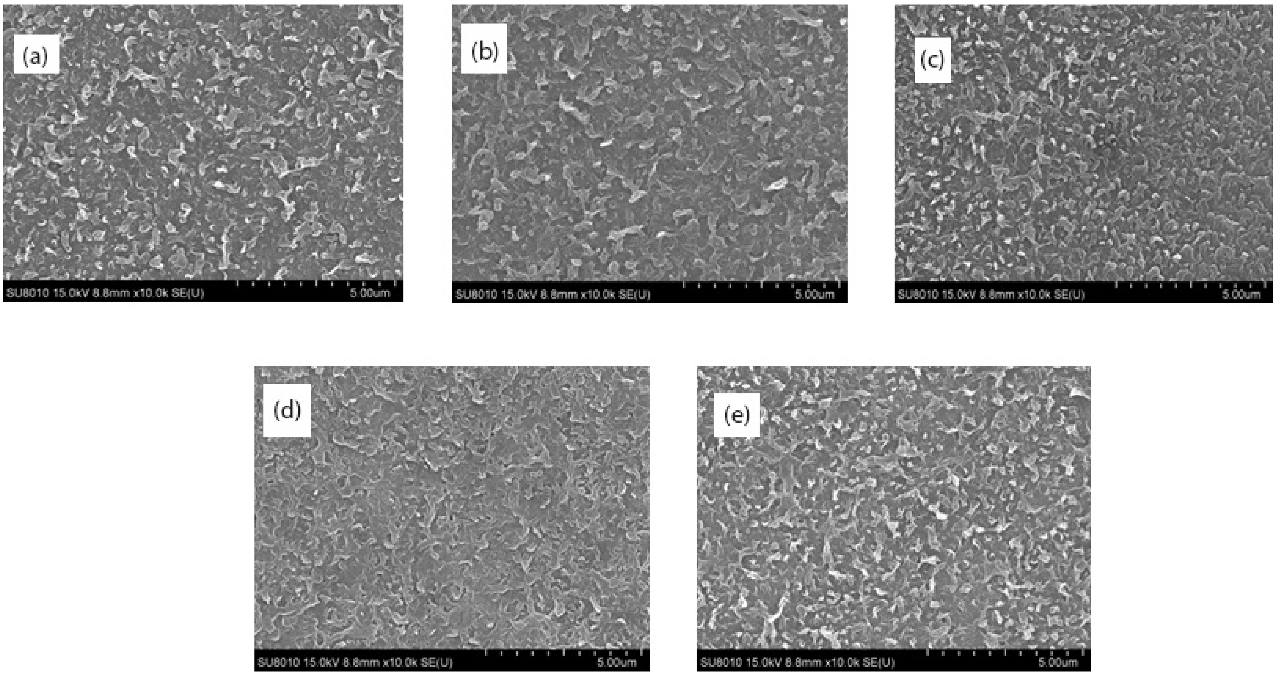

Fig. 4. Surface morphologies of membranes prepared from the following concentrations of β-CD: (a) 0%, (b) 0.5%, (c) 1.0%, (d) 1.5%, and (e) 2.0% (w/v).

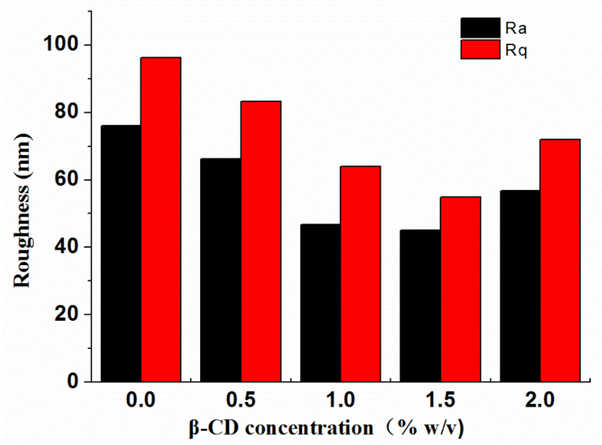

Fig. 5. Surface roughness (under the liquid) of membranes prepared from the following concentrations of β-CD: 0%, 0.5%, 1.0%, 1.5%, and 2.0% (w/v).

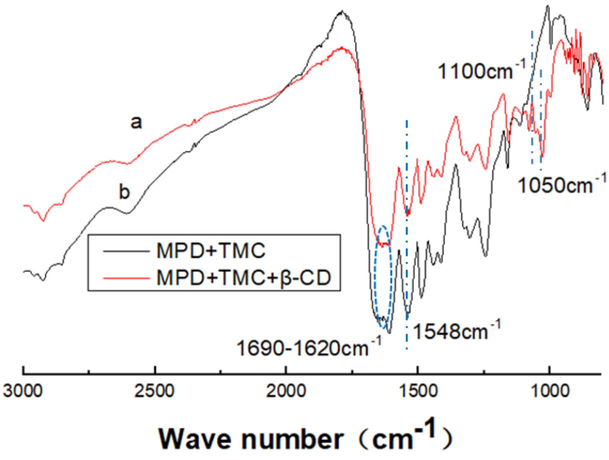

Fig. 6. ATR-FTIR spectra of RO membranes prepared with and without β-CD.

3.4. *Effects of β-CD concentration on surface composition and hydrophilicity*

The surface chemical compositions of the membranes fabricated from IP were analyzed by ATR-FTIR, and the results are shown in Fig. 6. The adsorption bands at 1,620–1,690 cm^{-1} and 1,548 cm^{-1} were assigned to the well-defined amide I band (C=O stretching-dominant contributor and C–N stretching as well as C–C–N deformation vibrations in a secondary amide group) and the amide II band (N–H in-plane bending and N–C stretching vibration of a –CO–NH– group), respectively [35]. The adsorption appeared at 1,050–1,100 cm^{-1} in membranes prepared with β-CD were attributed to the hydroxyl groups at the periphery of β-CD, demonstrating that β-CD reacted smoothly with TMC during the IP. The successful introduction of β-CD into polyamide layer was further confirmed by XPS analysis, the result of which is shown in Table 1.

The chemical compositions of the skin layers of the β-CD-free/polyamide and β-CD/polyamide RO membranes were further analyzed via XPS, and the results are summarized in Table 1. When β-CD was introduced to the membrane, the value of O/N increased from 1.76 to 2.53. On the one hand, the increase in the O/N value might have occurred because of the large number of hydroxyl groups in β-CD. On the other hand, the loosely cross-linked structure, which resulted from the addition of β-CD, might have caused the increased O/N value. Thus, the results from XPS proved that β-CD had been immobilized successfully onto the membrane surface by in situ IP. The large number of hydrophilic hydroxyl groups in β-CD effectively improved the hydrophilicity of prepared membranes, which is beneficial for the improvement of water flux as shown by Chen et al. [17].

Table 1
Relative surface atomic concentrations of the β-CD-free polyamide membrane and β-CD/polyamide RO composite membranes

Membranes	C (%)	O (%)	N (%)	O/N
0% β-CD	64.29	22.30	12.68	1.76
0.5% β-CD	64.65	23.30	11.34	2.05
1.0% β-CD	63.23	25.06	10.97	2.28
1.5% β-CD	63.65	25.34	10.01	2.53
2.0% β-CD	66.36	22.99	10.27	2.24

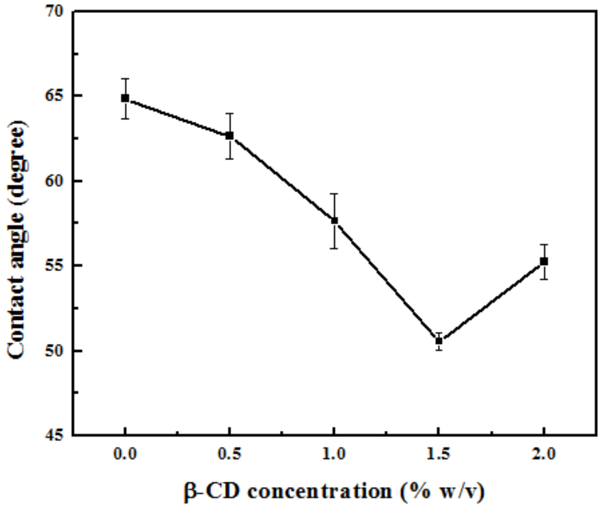

Fig. 7. Water contact angles of RO composite membranes as a function of β-CD concentrations.

As shown in Fig. 7, the membrane contact angle decreased significantly as the concentration of β-CD increased. However, when the concentration of β-CD reached 2% w/v, the contact angle began to increase. A possible reason for this observation can be ascribed to the increased surface roughness, which is proved by AFM results shown in Fig. 5. A variety of factors should be considered when discussing the effects of the β-CD concentration on membrane permeability [16,17,22]. First, due to the hydrophilicity introduced by the hydroxyl groups from β-CD, the hydrogen bond interaction between water molecules and membranes increased. As a result, the transportation of water through the composite membrane is improved. Second, the introduction of β-CD might have introduced additional water channels into the polyamide/β-CD interface, resulting in more hydrophilic voids than those present in β-CD-free polyamide membranes,

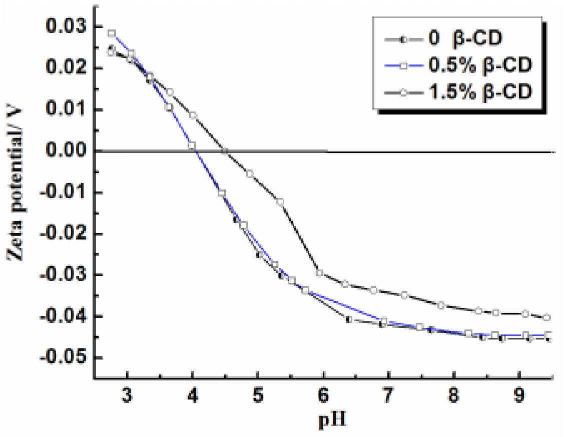

Fig. 8. Zeta potentials of RO membranes prepared from varied contents of β-CD.

which cause the water to flow freely and pass directly through the β-CD membrane [34]. Third, the molecular-level mixing between β-CD and the polymer chain and the relatively rigid structure of β-CD might have disrupted the regular packing of the polyester, resulting in an increased chain–chain space [34]. Fourth, the reactivity of β-CD is lower than that of MPD, which might have resulted in a lower cross-linked membrane surface layer structure. This loose and hydrophilic surface layer might lead to increased water flux. Finally, the lumen diameter of β-CD has been reported to range from 6.0 to 6.4 angstroms and facilitate the rapid passage of water molecules. All of these reasons will contribute to the increase of water flux when β-CD is adopted.

3.5. Zeta potential

Zeta potentials of the β-CD-free and β-CD-modified membranes were carefully studied (Fig. 8). The results showed that the zeta potential of the β-CD-free film changed from 25 to –45 mV when pH increased from 3.0 to 9.5. However, upon the addition of β-CD, the zeta potential increased and isoelectric point of the β-CD-modified membrane surfaces increased to pH = 4.6, which was much higher than that of β-CD-free membranes. In addition, the results showed that the pH range of the β-CD-modified membranes was significantly higher than that of other membranes and ranged from 5.5 to 9.5. Typically, membranes of lower zeta potentials usually exhibited better antifouling properties [36,37]. Generally, the membrane surface with zeta potential more near to neutral can decrease the electrostatic interactions with charged foulants, due to the decrease of the amounts of its surface charges. On the other hand, the β-CD modification caused higher potential should exhibit strong antifouling property to hydrophobic organic foulants, owing to the weak interactions between hydrophilic –OH groups and organic foulants.

4. Conclusion

Novel β-CD/polyamide TFC RO membranes were prepared by the in situ IP of β-CD/MPD and TMC. The effects of β-CD on the structure, morphology, and separation performance of the RO composite membranes were investigated by measuring the rejection, pure water flux, and water contact angles of the membranes as well as analyzing the membranes via SEM, AFM, and XPS. The β-CD/polyamide RO composite membranes exhibited improved water permeability and membrane hydrophilicity. When the concentration of β-CD was 1.5% (w/v), the water flux of the RO membranes achieved a value nearly 1.52 times larger than that of the β-CD-free polyamide membrane while maintaining a high rejection rate. Because of its unique properties, the β-CD/polyamide RO composite film might have stronger antifouling properties than unmodified polyamide films. The method described herein is a simple and effective way to improve the performance of composite membranes.

Acknowledgments

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