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Enhancing antifouling property of commercial polyamide reverse osmosis membrane by surface coating using a brush-like polymer containing poly (ethylene glycol) chains

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ABSTRACT

To enhance fouling resistance, the commercial polyamide reverse osmosis (RO) membrane was coated using a brush-like polymer containing poly (ethylene glycol) chains. The membrane properties, including hydrophilicity, charge and roughness, were improved after surface modification. The coated and uncoated RO membranes were characterized by attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM), static contact angle (CA) and streaming potential. The pure water flux and salt rejection of RO membranes before and after surface coating were measured. Moreover, the fouling experiments were performed using simulated foulants including protein, cationic surfactant and colloidal solution. The results indicated that the coated RO membrane exhibited better resistance compared to that of uncoated membrane.

Keywords: Reverse osmosis membrane; Surface coating; Poly (ethylene glycol); Antifouling; Hydrophilicity; Charge property; Surface roughness

1. Introduction

The growth of world population and the development of global economy will result in an increasing demand for water. Faced with a growing water crisis, the world is turning more and more to desalination as a solution [1]. In fact, many reverse osmosis (RO) plants have been built in the Middle East region and other countries in recent few years. At present, most commercially available RO membranes for desalination of brackish water and seawater are of thin film composite type [2,3]. These membranes exhibit excellent performance and superior economics, but fouling remains a serious problem that limits their more widespread use [4,5]. Therefore, the research and development of antifouling RO membranes are of great significance. So far, a number of studies have been conducted about the surface modification of commercial RO membranes, which is considered as a potential way to improve antifouling resistance. The reported surface modification methods of RO membranes range from physical adsorption [6] and coating [7–9] to in-situ redox initiated grafting [10,11], plasma polymerization [12] and chemical coupling [13,14].

Among these methods, surface coating is a simple and easily operated way for industrial application, and it has been paid much attention to by many researchers and RO membrane manufacturers [7–9,15,16]. For example, Hachisuka et al. coated electric neutral polyvinyl alcohol onto polyamide RO membrane for improving the antifouling properties in industrial wastewater and cationic surfactant feeding solutions [7]. Louie et al. applied polyether-polyamide block copolymer

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(PEBAX® 1657) to three types of commercial polyamide RO membranes as a fouling-resistant coating layer [8]. In addition, Tang et al. systematically investigated the physiochemical properties of eight commercial RO membranes by XPS, TEM, ATR-FTIR and streaming potential analysis, including two high-pressure seawater RO membranes (SWC4 and SW30HR) and six brackish water RO membranes (LFC1, LFC3, ESPA3, LE, XLE and BW30) developed by different manufacturers. The results confirmed the presence of a neutral aliphatic coating layer rich in hydroxyl groups for some of the membranes [16].

It can be seen that the coating materials for surface modification of RO membranes are commonly hydrophilic or/and electric neutral. As a kind of uncharged and highly hydrophilic polymer, poly(ethylene glycol) (PEG) and its derivates are very appropriate for membrane surface modification due to their extraordinary antifouling abilities. Meanwhile, they have flexible long chains, large exclusion volume and unique coordination with surrounding water molecules in an aqueous medium [17,18]. It has been proved that the surface-bounded PEG chains can be very effective in preventing adsorption of hydrophobic or large molecules from membrane surface, following the steric repulsion mechanism. The steric repulsion effect is due to the loss of configurational entropy resulting from volume restriction and osmotic repulsion of PEG chains [14]. In recent years, PEG materials have been comprehensively used for surface modification of ultrafiltration (UF), nanofiltration (NF) and RO membranes in recent years [19–24].

However, PEG is a water soluble polymer and can not be directly used in surface modification or coating of membranes. Therefore, many studies have been performed to introduce PEG onto membrane surface by various methods. For example, we modified RO membrane surface using PEG derivates by chemical grafting in our previous studies, and some promising results were obtained [14,24]. Mickols introduced PEG diepoxide into polyamide RO surface by crosslinking and the subject membrane provided improved resistance to fouling [13]. Similarly, Sagle et al. modified GE AG RO membranes using a series of crosslinked PEG-based hydrogels based on poly (ethylene glycol) diacrylate as the crosslinker and poly (ethylene glycol) acrylate as comonomer. The fouling results indicated that the modified membranes exhibited improved fouling resistance and an improved ability to be cleaned after fouling compared to unmodified membranes [15].

Based on the discussion above, we synthesized a brush-like polymer containing PEG chains and applied it to surface modification of commercial RO membrane in this study. The polymer was water-insoluble but could be dissolved in methanol, which provided the feasibility for surface coating to develop antifouling membranes. The surface morphology and property of membrane before and after modification were investigated using attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle (CA) and streaming potential measurement. The pure water flux, salt rejection and fouling resistance of coated and uncoated RO membranes were also compared.

2. Experimental

2.1. Membranes and reagents

The RO membranes used in this work were kindly supplied by Hangzhou Beidouxing Membrane Co., Ltd., China, which were fabricated by interfacial polymerization using trimesoyl chloride (TMC) and m-phenylene diamine (MPD) on polysulfone support. Poly (ethylene glycol) methyl ether methacrylate (PEGMEMA, ~475 g/mol) and 4-methoxyphenol were obtained from Aldrich. Methyl methacrylate (MMA) was purchase from Tianjin Damao Chemical Reagents Co., Ltd. Azo(bis)-isobutyronitrile (AIBN) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. Other common solvents and reagents were purchased commercially. The water used in this study was deionized water.

2.2. Synthesis of polymer for surface coating

The brush-like polymer containing PEG chains was synthesized according to Reference [21,25]. 90 g of MMA, 60 g of PEGMEMA, and 1.5 g of AIBN were added to 250 ml of THF in a 1000 ml round-bottom flask equipped with a condenser. The solution was degassed by bubbling nitrogen for 20 min, followed by refluxing at 70°C for 18 h. The reaction was terminated by the addition of 4-methoxyphenol. After cooling, the solution was precipitated in petroleum ether. The resulting copolymer was purified by several precipitations in petroleum ether and dried under vacuum at 25°C for 24 h. The synthesis of brush-like polymer containing PEG chains for surface coating was shown in Fig. 1.

2.3. Surface coating of RO membrane

Coating solutions were prepared by dissolving the synthesized brush-like polymer in methanol (0.2, 0.5, 1.0 and 2.0 wt.%). The common dip-coating method was applied in this study [8]. After coating, the membranes were immediately dried in an oven at 50°C for 10 min, followed by immersing the coated membranes in deionized water at room temperature. The coated membranes were washed with deionized water for several times and then stored in deionized water for use.

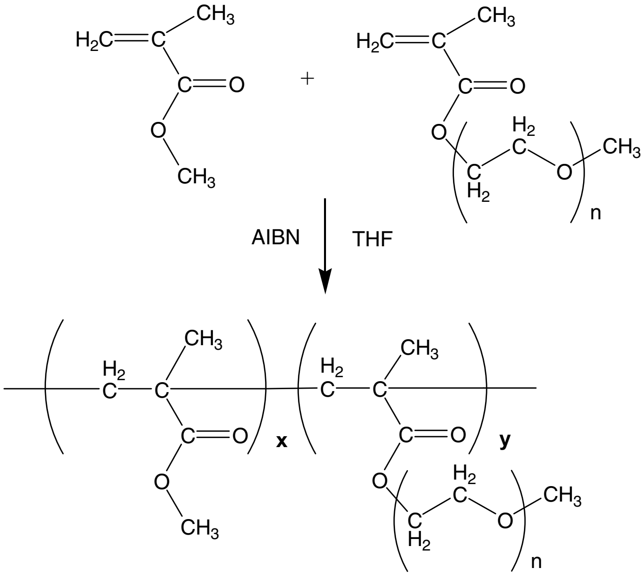


Fig. 1. Synthesis of brush-like polymer containing PEG chains.

2.4. Surface characterization

The change of chemical composition between membranes before and after coating was investigated using Fourier transform infrared spectroscopy (Equinox 55) with an ATR unit (ZnSe crystal, 45°). The surface morphology of uncoated and coated RO membranes was observed by SEM (Philips XL30E) and AFM (Digital Instruments Inc., Santa Barbara) using a Nanoscope III equipped with 1553D scanner. The AFM images were acquired by scanning the sample in air under tapping mode [11]. The hydrophilcity of membrane surface was evaluated by measuring the static contact angle using a contact angle goniometer (JC2000C Contact Angle Meter, Powereach Co., Shanghai, China) with sessile drop method [26]. In addition, the streaming potential of RO membranes was also investigated according to Reference [27].

2.5. Performance measurement and fouling experiments

The performance measurement and fouling experiments of uncoated and coated RO membranes were tested with a laboratory-scale crossflow test unit (see in Fig. 2). The salt rejection (R) and pure water flux (F) of the membrane were calculated as Eqs. (1) and (2):

$$R = \left(1 - C_p/C_f\right) \times 100\% \quad (1)$$

$$F = V/At \quad (2)$$

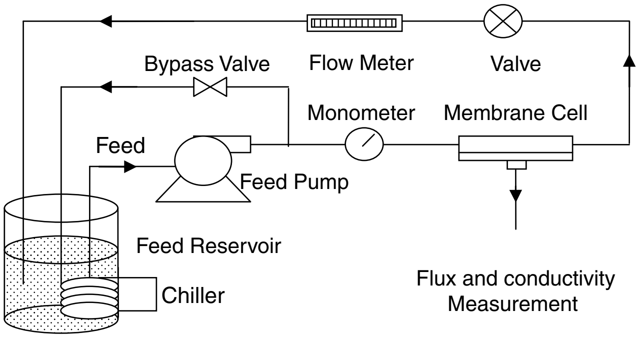


Fig. 2. Schematic diagram of RO membrane test unit.

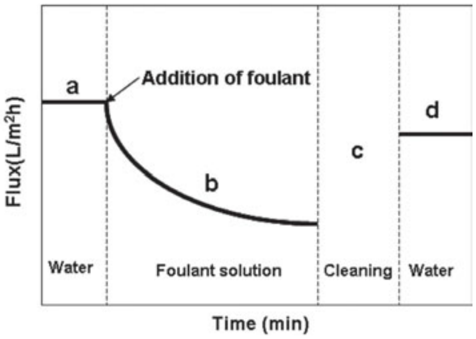


Fig. 3. Experimental protocol for RO membrane fouling and cleaning.

where, C_p and C_f were the salt concentration of permeate solution and feed solution, V was the volume of permeate water during the test time, A was the effective membrane area, and t was the test time, respectively.

In fouling experiments, each membrane was compacted with deionized water until the permeate flux was constant. The pure water flux was recorded. Then, the reservoir was emptied and the simulated contaminant solution was poured. The time-varying permeate flux was measured. After 160 min, the membrane was rinsed with deionized water and the recovered flux was measured. The experimental protocol for RO membrane fouling and cleaning was shown in Fig. 3. The data in fouling experiments were normalized. The value of relative flux (%) was calculated by comparing the water flux before and after fouling or cleaning.

3. Results and discussion

3.1. ATR-FTIR spectroscopy

ATR-FTIR spectroscopy is a convenient and effective way to determine the chemical composition of outmost part in a thin film composite RO membrane. The ATR-FTIR spectra of uncoated and coated RO membranes were shown in Fig. 4. According to Reference [28], the penetration depth of ATR-FTIR was about 0.5–1.0 μm,

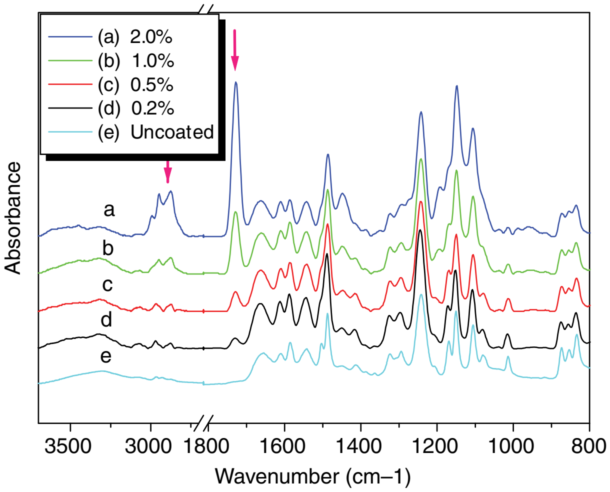


Fig. 4. ATR-FTIR spectra of uncoated and coated RO membranes.

which was relatively greater than the thickness of polyamide barrier layer of about 0.2–0.3 µm [2]. Consequently, the characteristic peaks of both polyamide layer (such as 1660 cm^{-1} and 1544 cm^{-1}) and polysulfone support membrane (such as 1584 cm^{-1} and 1243 cm^{-1}) could be observed. Compared to the uncoated membrane, some new peaks appeared in ATR-FTIR spectra of coated membrane at about 1734 cm^{-1} and 2876 cm^{-1}, which could be ascribed to C=O vibration and –CH$_2$– symmetric stretch of PEG in coated polymer, respectively [10,11]. As the polymer concentration increased in the applied coating solution, the intensity of both peaks above increased. Meanwhile, the spectral intensity at 1080 cm^{-1} for C–O and C–C stretch of PEG also increased and gradually merged with other peaks [14].

Similar to Reference [8], the coated membrane with relatively high concentration polymer solution (2.0 wt.% in this study) was used for the following investigations.

3.2. Membrane surface morphology

In order to examine the morphological changes of RO membranes before and after surface coating, the SEM images were firstly performed with a magnification of 2,500 (see in Fig. 5). It could be seen that the uncoated membrane exhibited a unique and characteristic ridge-and-valley structure [2]. After coating, the brush-like polymer was filled in the valleys of polyamide RO membrane, resulting in a smoother surface. However, the deposited polymer was a continuous film, and parts of original polyimide peaks remained exposed at the surface. The three-dimensional AFM images of 10.0 µm scans in Fig. 6 more clearly indicated that the brush-like polymer applied on RO membrane produced a coating that caused the decrease of membrane surface roughness, which was consistent with the researches reported by Louie et al. [8].

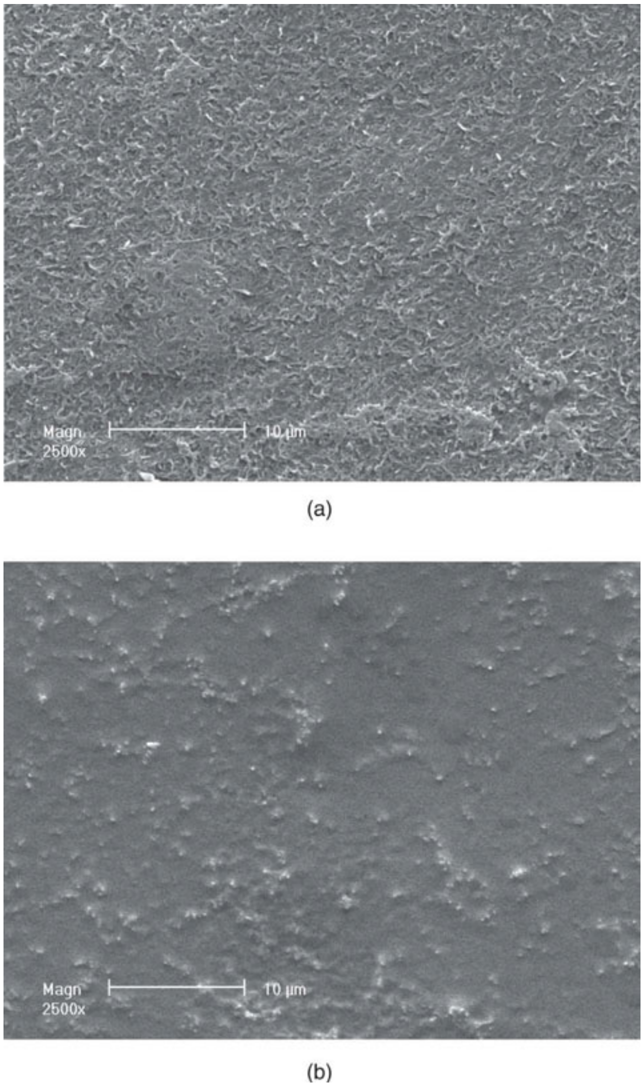
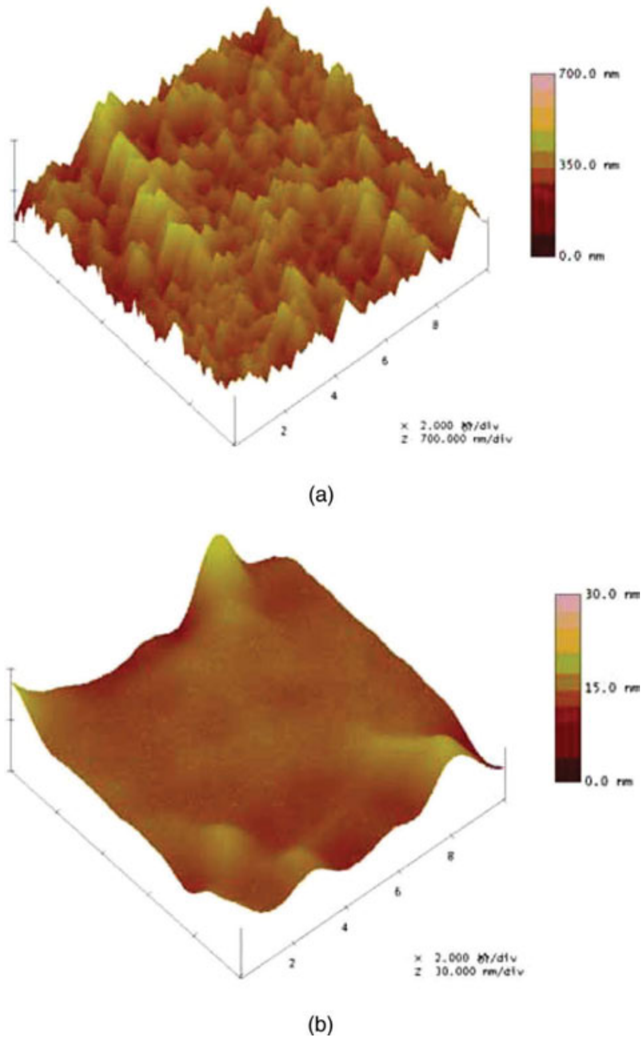


Fig. 5. SEM micrographs of membranes before and after surface coating with a magnification of 2500: (a) uncoated; (b) coated.

3.3. Hydrophilicity

The relative hydrophilicity or hydrophobicity of membrane surface could be characterized on the basis of static contact angle [26]. In general, lower static contact angle indicated better hydrophilicity. For hydrophobic foulants such as proteins, the enhancement of membrane surface hydrophilicity could decrease the extent of hydrophobic interactions, consequently, reducing membrane fouling. The static contact angle of RO membrane



(a)

(b)

Fig. 6. Three-dimensional AFM images of uncoated and coated RO membranes: (a) uncoated; (b) coated. The size of images is 10 µm × 10 µm.

decreased from 52.7° to 46.2° after coating (see in Table 1), implying the improvement of surface hydrophilicity. This was because that the coated polymer contained abundant hydrophilic groups. Moreover, the flexible hydrophilic PEG chains would spread towards water phase in aqueous surrounding, creating a hydrophilic PEG layer on top surface of coated RO membrane. The measured results were in good agreement with the reports by other researchers who introduced PEG materials into membrane surface [18–20, 29].

3.4. Pure water flux and salt rejection measurement

The pure water flux uncoated and coated RO membranes were measured and listed in Table 1. It could be seen that the surface coating in this study caused decreases in water flux. The similar results were also obtained when RO membranes were coated using different polymers [7–9,15]. The decrease in water flux could be mainly attributed to both of following reasons: (1) the coated layer increased permeation resistance; (2) the characteristic ridge-and-valley structure of uncoated membrane made it have greater micro permeation area [30], which was reduced after coating due to the filling of valleys. On the other hand, the salt rejection for a 1500 ppm NaCl feeding solution of uncoated and coated were also measured and listed in Table 1. Unlike the pure water flux, the coating process showed no significant change in salt rejection, which was also consistent with the results obtained by some other researchers [8,15].

3.5. Fouling experiments

The milk solution, dodecyltrimethylammonium bromide solution (DTAB, a cationic surfactant) and colloid solution were used for simulating the protein fouling, charged foulant and colloid fouling, respectively. These foulants were commonly used in the fouling experiments of RO membranes [13,15,24]. The concentrations of foulants were all 100 ppm in this study. The time-varying results of uncoated and coated membranes were shown in Figs. 7, 8 and 9. It could be clearly seen that the RO membrane after coating using brush-like polymer containing PEG chains exhibited better antifouling properties than those of uncoated one. The coated membrane showed relatively smaller flux decrease after fouling and higher recovered flux after cleaning.

Table 1
Pure water flux, salt rejection, static contact angle and streaming potential of RO membranes before and after coating

Sample	Pure water flux[a] (l/m^{2}h)	Salt rejection[b] (%)	Contact angle (°)	Zeta potential[c] (mv)
Uncoated membrane	50.5	96.7	52.7	–15.4
Coated membrane	17.1	96.8	46.2	–3.8

[a] Operating conditions: deionized water, 1.05 MPa, 25°C.
[b] Operating conditions: 1500 ppm NaCl solution, 1.05 MPa, 25°C.
[c] Operating conditions: 0.01 mol/l KCl, pH=7, 25°C.

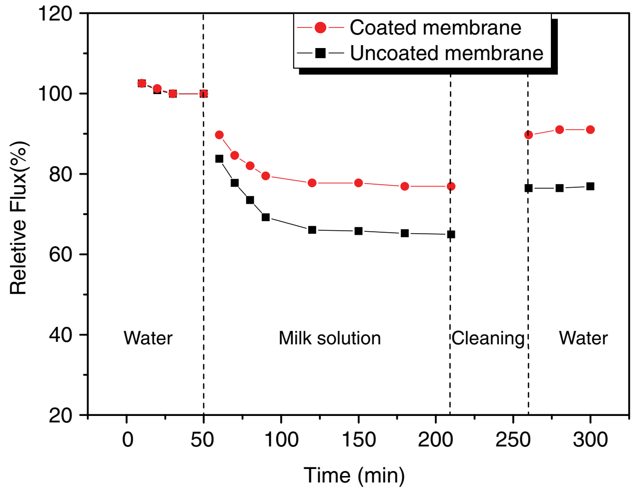


Fig. 7. Fouling experiments of RO membranes before and after coating using milk solution as simulated foulant.

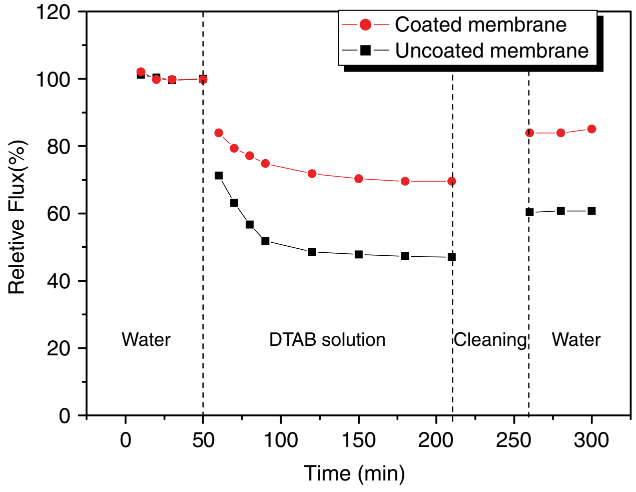


Fig. 8. Fouling experiments of RO membranes before and after coating using DTAB solution as simulated foulant.

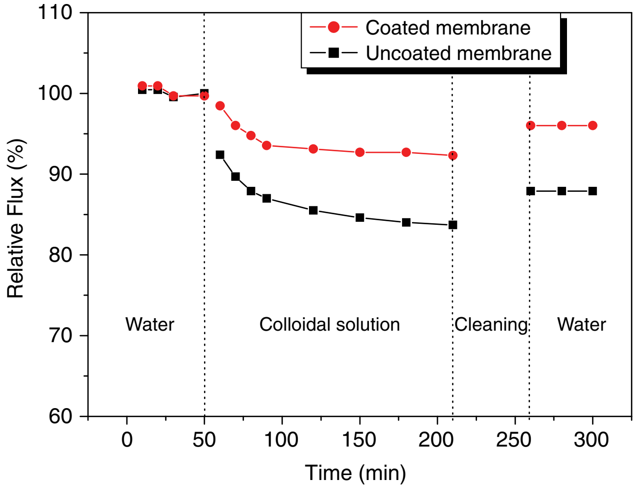


Fig. 9. Fouling experiments of RO membranes before and after coating using colloidal solution as simulated foulant.

It was generally acknowledged the physicochemical property of membrane surface, mainly including hydrophilicity, charge and roughness, was the important factor to influence membrane fouling. The increase of hydrophilicity and decrease of charge and roughness was reported to reduce fouling of proteins, particles with negative charge and colloid, respectively [23]. In this study, the surface property of RO membrane was changed by introducing PEG-containing polymer. Firstly, the membrane surface hydrophilicity was relatively improved according to the measurement of static contact angle. Moreover, the coating created a smoother membrane surface, i.e., decreasing the roughness. These results were both advantageous to the improvement of membrane antifouling performance. In addition, the streaming potential of RO membrane changed from –15.4 mV to –3.8 mV at pH 7.0 after coating (see in Table 1), which could reduce the adsorption of DTAB onto membrane surface. In fact, using neutral compounds to shield the negative charges of the underlying polyamide membrane and, hence, reduce interaction between charged foulants and the membrane surface, has been considered as an alternative antifouling approach [8]. For example, Hachisuka et al. coated electric neutral polyvinyl alcohol onto polyamide RO membrane for improving the antifouling properties in cationic surfactant feeding solution [7].

4. Conclusions

A brush-like polymer containing PEG chains was applied to the surface modification of commercial polyamide RO membrane by coating. The immobilization of PEG-containing polymer layer on membrane improved the physicochemical property of coated membrane surface, i.e., increase of hydrophilicity and decrease of charge and roughness, which was advantageous to enhancing membrane antifouling properties. The coating caused a decrease in pure water flux, but had no significant influence on salt rejection. Compared to uncoated membrane, the coated membranes were more resistant to fouling in protein, cationic surfactant and colloid feeding solutions. However, it should be noted that the coating conditions should be further studied to obtained better results, for example, remaining higher pure water flux and so on.

Acknowledgement

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