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An investigation on the antifouling ability of PVDF membranes by polyDOPA coating

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ABSTRACT

This work studied the surface modification of poly(vinylidene fluoride) (PVDF) membranes by coating poly(3,4-dihydroxyphenylalanine) (polyDOPA) for the purpose of an investigation on the antifouling ability. In mild alkaline environments, both oxidized and deoxidized 3,4-dihydroxy-L-phenylalanine were able to self-polymerize and form a polyDOPA coating attached firmly onto PVDF membrane surfaces. The membrane hydrophilicity was evaluated by water intake and water contact angle measurements. The oxidized and deoxidized polyDOPA-coated modified membranes displayed substantial resistance to bovine serum albumin fouling compared with pure PVDF. The chemical compositions of modified membrane surfaces were determined by fourier transform infrared spectrometer analysis and X-ray photoelectron spectroscopy. Morphological changes of membrane surfaces were detected by using scanning electron microscopy. The coating durability experience was carried out in acid and base solutions at pH 1.45, 4.75, 9.25, and 11.5, respectively. The antifouling effect of deoxidative polyDOPA-coated membranes keeping wet was better than that of oxidized PolyDOPA-coated membranes due to the presence of phenolic hydroxyl groups except in strong base solution and dry environment.

Keywords: Antifouling; Surface coating modification; Oxidized and deoxidized PolyDOPA; Polyvinylidene fluoride (PVDF)

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1. Introduction

Poly(vinylidene fluoride) (PVDF) membrane is widely used in microfiltration, nanofiltration, ultrafiltration, and ion-exchange membranes due to its excellent chemical resistance, well-controlled porosity, and good thermal property [1,2]. Despite these advantages, PVDF porous membranes still have some limitations, especially in biomedical application and membrane bioreactor process containing organic molecules or proteins. The hydrophobic nature and propensity for adsorptive fouling cause reduction in separation performance and shorten the membrane life [3–5]. An effective method to promote the application of ultrafiltration technology is to obtain the hydrophilic membranes with enhanced fouling resistance.

Several approaches generally including surface coating, surface modification, and blending with hydrophilic polymers are employed to improve the hydrophilic properties of hydrophobic membranes. Coating porous membranes with hydrophilic and

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functional polymer is a suitable and convenient method to overcome its shortcoming [6,7]. Liu et al. [8,9] have studied the permeable and antifouling properties of terylene membranes which are dip-coated by polyrotaxanes-TiO_2-polyvinyl alcohol (PRs-TiO_2-PVA) or the combination of activated carbon fiber (ACF) powder and Ce^{3+}-TiO_2. Boributh et al. [1] has investigated PVDF modified membranes by three different methods, i.e. immersion method, flow through method, and the combination of flow through and surface flow method using chitosan solution. Wang et al. [7,10] has fabricated a high flux and anti-fouling filtration membrane by coating chitosan and polyvinyl alcohol/4-vinylpyridine (PVA-g-4VP) graft polymer on surface of non-woven fabric (NWF). An adsorption-crosslinking process of PVA has also been introduced to modify the surface of polyethersulfone (PES) ultrafiltration membranes [11]. Several simple, lightly cross-linked quaternary phosphonium- and ammonium-based polymer coatings have been found to effectively resist the non-specific adsorption of proteins by Hatakeyama et al. [12]. Surface modification by physical adsorption of Tween 20 and anionic surfactant solution takes place, sodium dodecyl benzene sulfonate (SDBS) has been accomplished on different microporous membranes [13,14].

Recently, mussel adhesive proteins (MAPs) excreted by marine mussels have attracted much attention for their ability to form strong adhesive interaction with various substrates in wet environment [15]. Studies of these functionally unique proteins have revealed the presence of the unusual amino acid 3,4-dihydroxy-L-phenylalanine (DOPA), which is formed by posttranslational modification of tyrosine [16]. Using DOPA or its derivatives such as 3,4-dihydroxyphenethylamine (dopamine) to form the coating is becoming a versatile and attractive method for surface modification of solid materials. The fouling-resistant surfaces are made by covalently grafting amine- or thiol-terminated methoxy-poly(ethylene glycol) [(mPEG-NH_2 or mPEG-SH) in 10 mM tris, pH 8.5, 50℃] to the polydopamine-coated surface [16]. Xi et al. [17] has performed a surface hydrophilic modification for polyethylene, PVDF and polytetrafluoroethylene porous membranes using coating and polymerization of DOPA and dopamine. Subsequently, heparin is immobilized covalently onto the obtained PVDF/poly(DOPA) composite membranes by the coupling between heparin and poly(DOPA) coating [18]. The aim of the present studies was to investigate different DOPA states, such as oxidized and deoxidized poly(3,4-dihydroxyphenylalanine) (polyDOPA), modyfing the structures and antifouling properties of PVDF membrane and to determine if such modifications could form a stable coating on PVDF membrane surface.

2. Experimental

2.1. Materials

The PVDF powder was purchased from Shanghai 3F New Materials Co., Ltd. and dried at 70℃ for 12 h before use. The homemade hydrophobic PVDF membranes prepared by non-solvent induced phase separation were chosen as the samples for surface modification. 1-methyl-2-pyrrolidinone (NMP) was obtained from BASF Chemical Co., Ltd. (Tianjin, China). Poly(ethylene glycol) (PEG) with a molecular weight of 20,000 as additives and tris(hydroxymethyl) aminomethane (Tris) were purchased from Sinopharm Chemical Reagent Co., Ltd. DOPA (Afar) was used as received. Sodium bisulfite ($NaHSO_3$) was obtained from Tianjin Guangfu Fine Chemical Research Institute. Bovine serum albumin (BSA) was purchased from Shanghai Guoyao Chemical Co., Ltd. Other chemicals were all of commercial analytical grade.

2.2. Preparation of PVDF membranes

Casting solutions were prepared by dissolving PVDF (17 wt.%) and PEG20000 (3 wt.%) into NMP. The casting solutions were vigorously stirred for homogeneous mixing, and left for 4 h to allow complete release of bubbles. The solutions were cast on glass plates with a steel knife, and the glass plate was subsequently immersed in a coagulation bath of deionized (DI) water. The formed membranes were peeled off and washed thoroughly with DI water to remove residual solvent and pore-forming agents, and immersed in DI water before use.

2.3. Modification of oxidized and deoxidized polyDOPA on PVDF membranes

Oxidized DOPA solution was prepared by dissolving DOPA in Tris (10 mM), and adjusted to pH 8.5 using HCl. The deoxidized DOPA solution was prepared by dissolving DOPA in Tris (10 mM), and adjusted to pH 8.5 using $NaHSO_3$. PVDF membranes were soaked thoroughly with anhydrous ethanol before immersed into the DOPA solution (2.0 g/L). The reaction was carried out in a shaker bath at 30℃ for 20 h with a vibration velocity of 200r/min. Then the membranes were taken out and washed with DI water and anhydrous ethanol alternatively at 45℃ for 24 h with a vibration velocity of 200r/min. After dried to a constant weight in a vacuum oven, the modified membrane was used for characterization. In the durability experiment, the membrane samples were scoured thoroughly in a 200 ml of acid (HCl) or base (NaOH) solution (pH 1.45, 4.75, 9.25 and 11.5) at 50℃ with a vibration velocity of 220r/min.

2.4. Characterization of modified membranes

Water contact angles were measured with an angle-meter (Automatic Contact Angle Meter, Model DSA100, KRUSS, Germany) at 25℃. The DI water was dropped on the sample surface at 10 different sites. The average of the measured values from three independent membranes for each modified membrane was taken as its water contact angle. The relative humidity was less than 40%.

Pure water intake was measured by the liquid adsorption method. The equilibrium amount of liquid water adsorbed by a sample film was determined by immersing it in DI water for 30 h at 25℃, blotting it between two pieces of filter paper, and weighing. The PVDF coating membranes were dried in a vacuum oven for 24 h and then the dry membranes were measured again. In order to investigate the water intake content of dried coating membranes, membranes firstly were dried in a vacuum oven for 24 h, and measured. Then the dried membranes were again immersed in DI water for 30 h at 25℃, and blotted between two pieces of filter paper to get the weights. The percent water content was calculated by Eq. (1):

$$A = \frac{W_w - W_d}{W_w} \times 100\% \tag{1}$$

where A was the water content (%), W_w and W_d (mg) were the wet and dry weight of the measured membranes, respectively.

The chemical composition of PolyDOPA modified PVDF membranes was characterized using fourier-transform infrared spectroscopic (FT-IR) spectrophotometer (Bruker optics). Each spectrum was captured by averaged 32 scans at a resolution of 4 cm^{-1}. X-ray photoelectron spectroscopy (XPS) spectra for the top surfaces of these membranes were recorded on a PHI 5300 ESCA System (Perkin-Elmer Co., America) employing Al Ka excitation radiation (1,486.6 eV). The X-ray source works at a power of 250 W (12.5 kV). Binding energies were calibrated by using the containment carbon (C1s = 284.6 eV). Survey spectra were run in the binding energy range of 0–1,000 eV and high-resolution spectra of C1s were collected. The cross-section morphologies of modified membranes were observed by scanning electron microscopy (SEM) using a HITACHI S-4800 scanning microscope. The membranes frozen in liquid nitrogen were broken and sputtered with gold before SEM analysis.

2.5. Protein adsorption experiments

To evaluate the fouling resistance of the pristine membrane and the polyDOPA-coated membranes, BSA adsorption experiments were performed by the following procedure. A membrane with an area of 25 cm^2 was soaked thoroughly in anhydrous ethanol and phosphate buffer solution (PBS) for 30 min, respectively, and the membrane was immersed into a 1.0 g/L BSA solution prepared with PBS (pH = 7.4). Then the tubes with 7 ml of BSA solution and membranes were placed in a water bath of 37° C to incubate for 24 h. The concentration of BSA solution was determined using a UV spectrophotometer (UV-2450, Shimadzu) at 280 nm wavelength. The apparent amount of protein adsorbed by the membrane was calculated from the concentration difference of BSA solution before and after adsorption. The average of at least three measurements was reported.

2.6. Cross-flow membrane filtration and fouling reversibility experiments

A cross-flow membrane filtration (CMF) unit was constructed. The conformation dimensions of flow chamber with the cross-flow channel were of 80 mm height by 100 mm width and 100 mm length. The test membrane was placed between the top and bottom plate and was held tightly by o-rings. The filterable area of the membrane is 19.6 cm^2. After fixing, the membrane was pre-pressurized with DI water at 150 kPa for 30 min until the TMP was stable. The entire system was operated in a closed loop, so that the pressure on the feed side was extremely stable during the experiment. A gear pump (Kflow, 200 ml/min) was used to circulate the feed solution through the CMF unit. Then the pressure was reduced to 100 kPa of the operating pressure, The permeate flux was collected in a 10 ml of tube so that DI water flux (Jw_1) was calculated by determining the filtrate volume at fixed operation time. After the cell and solution reservoir were emptied, an appropriate amount of BSA (1.0 g/L) stock solution was then added into a 1,000 ml beaker, the fouling experiments were carried out. After performing for 30 min, the samples of 10 ml permeate was collected in order to calculate BSA retention. After BSA ultrafiltration, The fouled unit and membrane were cross-flow cleaned with DI water for 10 min, and the water flux of cleaned membrane was calculated (Jw_2) in the same way of Jw_1.The entire process was performed in three circles.

3. Results and discussion

The self-polymerization of polyDOPA and the formation of melanin were presented in Fig. 1. DOPA is the catalytic product of tyrosine in the presence of the enzyme tyrosinase, followed the autooxidation process into DOPA quinone and 5,6-quinone indole, that is, so-called melanin. Oxidation of the catechol side chain of DOPA occurs in the alkaline marine environment, giving rise to quinones that further react to cross-link adhesive proteins via aryl–aryl coupling (di-DOPA formation) or possibly via Michael-type addition reactions with amine-containing protein residues [15]. The role of DOPA in MAPs is not fully understood. For the oxidized polyDOPA-coated membrane, the quinone carbonyl groups are difficult to revert to phenol hydroxyl groups. However, it is available for the polyDOPA with unoxidized hydroxyl groups via adding the reducing agent such as sodium bisulfite in the initial reaction.

3.1. Characterization of surface morphology polyDOPA-coated membranes

The surface images of PVDF pristine membrane and polyDOPA-coated membrane were shown in Fig. 2. With the same concentration of 2 g/L DOPA solution, the color of oxidized polyDOPA-coated membrane surface becomes increasingly darker with reaction time (a < b < c) owing to the generation of more melanin. When pristine membranes were immersed in the used black solution for the secondary reaction, the melanin could still react with the membrane surface. It indicates that the effective adsorption site and reaction site germinate due to the existence of quinone group. Measurement of adhesive interactions between oxidized DOPA and surfaces is complicated by the highly reactive nature of semi-quinones and quinones [15]. Then the resultant membrane with oxidized coating was kept in DI water for 10 months, the membrane surface did not induce a color change as shown in image d. When pristine membranes were immersed in the DOPA solution with $NaHSO_3$, the color of membrane surface and solution after the reaction would not turn black (Fig. 2(e)). It indicates that the oxidation of phenolic hydroxyl groups will not occur in the presence of the reducing agent $NaHSO_3$.

As shown in Fig. 3(a–c), the membrane surfaces with oxidized and deoxidized polyDOPA coating are much smoother than that of the original PVDF membrane. The cross-sectional morphologies of original and coating membranes were shown in Fig. 3(d–f). All the membranes exhibit a similar asymmetric structure, which is the typical structure of ultrafiltration membranes with a top dense layer, a porous sublayer and fully developed macropores at the bottom. From the cross-sectional amplified images in Fig. 3(d–f), it can be seen that the cross-sectional structure of original

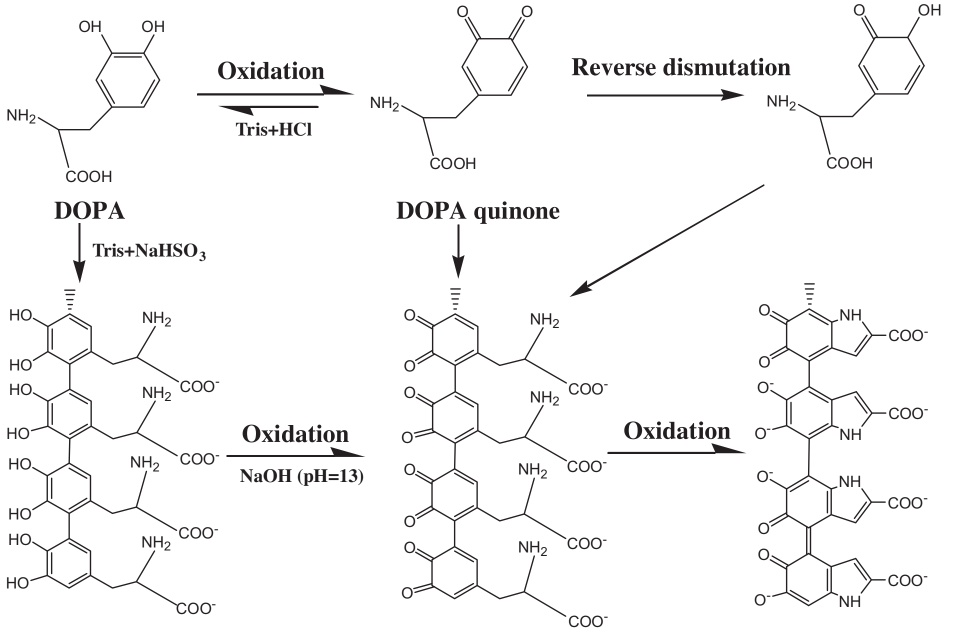

Fig. 1. Schematic illustration of self-polymerization of DOPA.

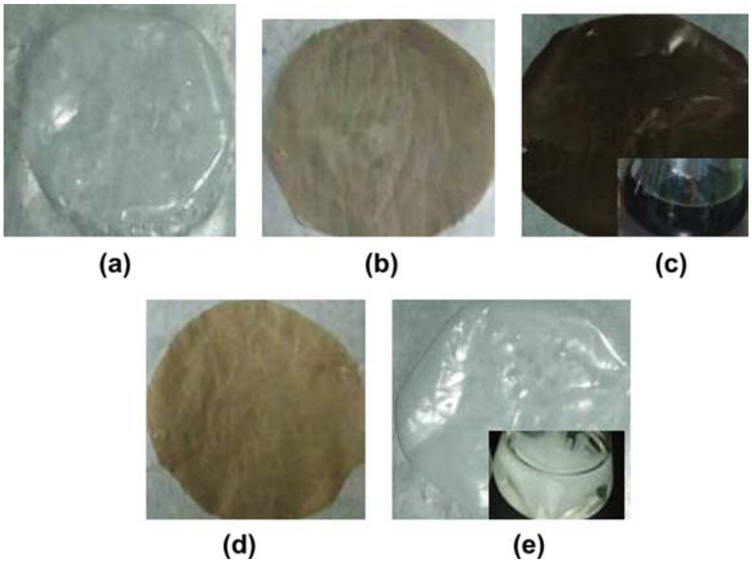

Fig. 2. Photo images of membranes (a) PVDF pristine membrane, (b) oxidized polyDOPA-coated membrane after 6 h reaction time, (c) Oxidized polyDOPA-coated membrane and reaction solution after 20 h reaction time, (d) polyDOPA-coated membrane immersed in the used oxidized solution for 20 h and then kept in DI water for 10 months, (e) deoxidized polyDOPA-coated membrane and reaction solution with the addition of reducing agent $NaHSO_3$ after 20 h of reaction time.

membrane is similar to the deoxidized polyDOPA-coated membrane, whereas oxidative polyDOPA-coated membrane displays a fresh coating, indicating that DOPA has been coated on the sub-layers. The hydroxyl groups on the deoxidized polyDOPA-coated membrane surface may be dehydrated and oxidized as the dry measurement environment. Thus there is no obvious change for the surface of deoxidized polyDOPA-coated membrane.

3.2. *Durability of polyDOPA-coated membranes in acid or base solution*

After coating with polyDOPA for 20 h, the stability test of membrane surface is shown in Figs. 4 and 5, which were examined in acid or base solution (pH = 1.45, 4.75, 9.25 and 11.5, respectively) at 50℃ with the vibration velocity of 220r/min. In the initial stage, the pH of the solution with coating membranes declines dramatically, conjectured that some coatings are desorbed from membrane surface due to their unstable multilayer adsorption. It is not precluded that the hydrogen ions dissociated from the carboxyl groups-containing coating and caused the decline of the solution pH value. However, the pH of the solution with deoxidized polyDOPA-coated membranes declined faster than that with oxidized polyDOPA-coated membranes. It maybe also due to the dissociation of hydrogen ions of unoxidized phenol hydroxyl groups from the deoxidized polyDOPA coating. Then, let the solution with oxidized coating membranes rest for 20d at room temperature, the solution pH still declines till it reaches a certain extent, especially in relatively strong base solution. Afterward, the pH values of the solution fluctuated within a small range despite strong vibration at 50℃. That is to say a dynamic equilibrium of adsorption and desorption exists between the solution and membrane surface or by achieving the acid-base equilibrium. The color of oxidized coating surface was prone to fade. However, there was almost no change for the pH value of the solution with deoxidized polyDOPA-coated membranes after a day or two of scouring. It can be concluded that polyDOPA adsorbed between PVDF skin-layer and coating interface remains relatively stable.

3.3. *Chemical compositions of polyDOPA-coated membranes*

The surface compositions of PVDF membranes coated with polyDOPA were analyzed by XPS. Fig. 6 shows curve fitting for original PVDF, deoxidized, and oxidized polyDOPA-coated membranes. Deconvolution of the C1s core-level spectrum of original PVDF can be curve-fitted with two peaks at 290 and 285 (Fig. 6(a)), which are assigned to CF_2 and C–H/C–C, respectively. The C1s spectrum of deoxidized polyDOPA-coated PVDF membranes can be mainly curved into three components with binding energies of about 285.5, 288.7, and 290 eV (Fig. 6(b)) attributing to the

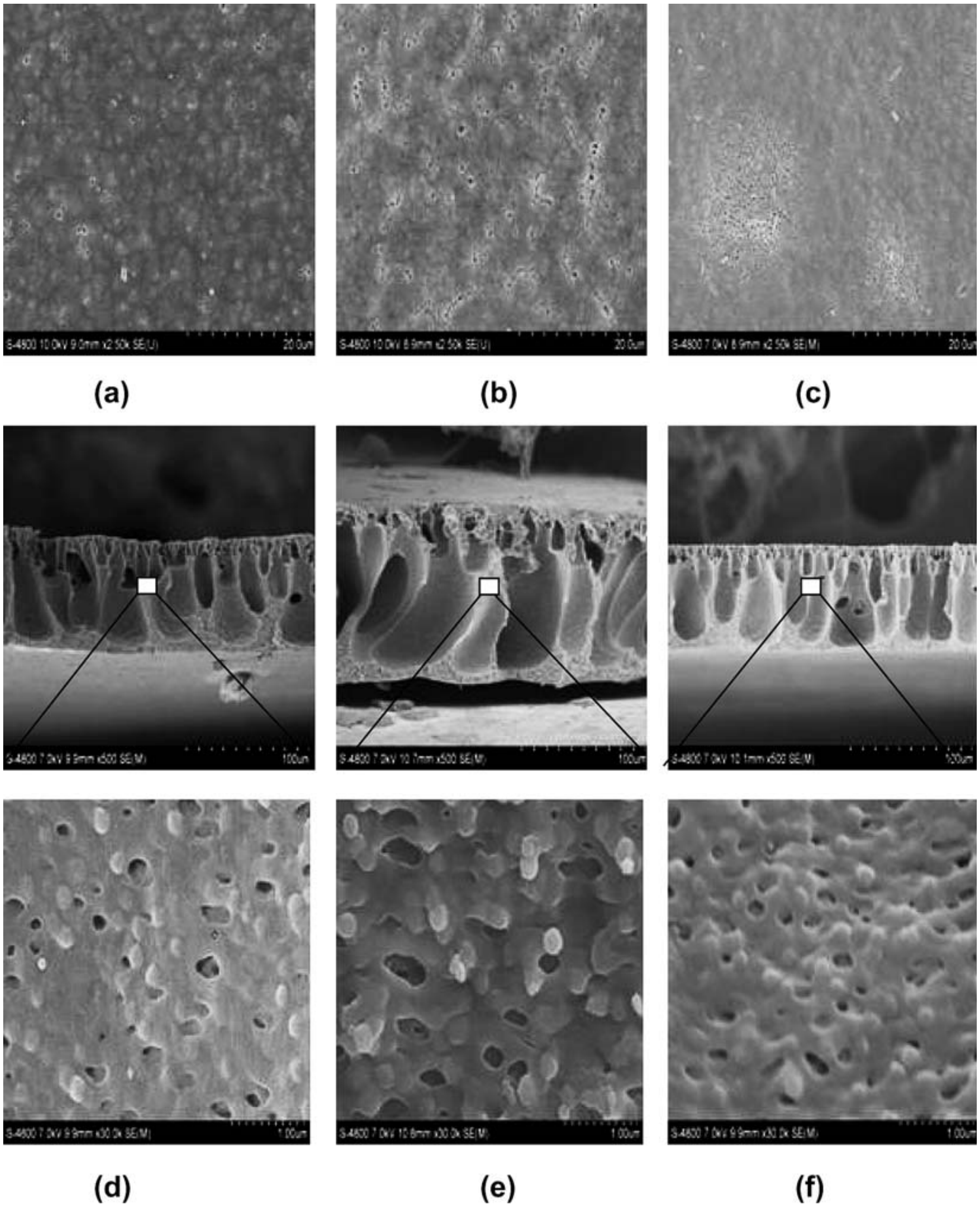

Fig. 3. SEM images of the morphology of the uncoated and coated PVDF membranes. Surface morphology (a) PVDF pristine membrane. (b) Oxidized polyDOPA-coated membrane. (c) Deoxidized polyDOPA-coated membrane. Cross-sectional morphology and amplified images. (d) PVDF pristine membrane. (e) Oxidized polyDOPA-coated membrane. (f) Deoxidized polyDOPA-coated membrane.

C–H (containing C–N), O–C=O, and CF_2 species while those of oxidized polyDOPA-coated membranes can be curved into four main peaks with binding energies of about 285, 286.5, 288.8, and 290.2 eV (Fig. 6(c)) which is attributed to the C–H (containing C–N), C–OH, O–C=O, and CF_2 species, respectively. The results of core-level C1s spectra prove the coverage of DOPA on the PVDF membrane surface. The appearance of hydroxyl peaks at 286.5 eV proves that hydroxyl groups can coexist with quinone groups on oxidized polyDOPA-coated membranes. However, the hydroxyl peaks on deoxidized polyDOPA-coated membranes disappear, which is ascribed to the oxidation of hydroxyl groups and dehydration reaction of hydroxyl groups with carboxyl groups during dry process. The O1s spectrum can be resolved into the

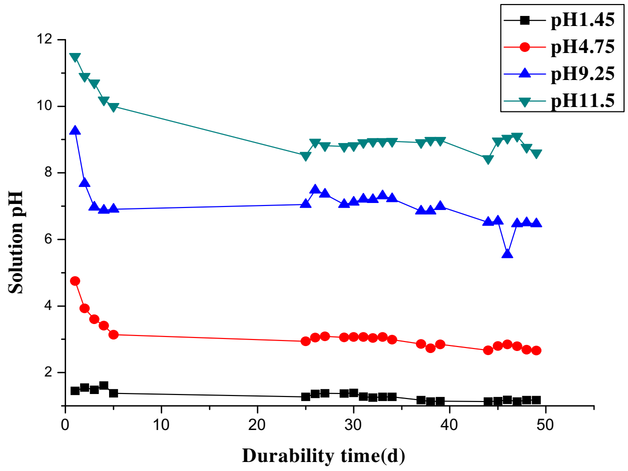

Fig. 4. Durability of oxidized polyDOPA-coated membranes in acid or base solution.

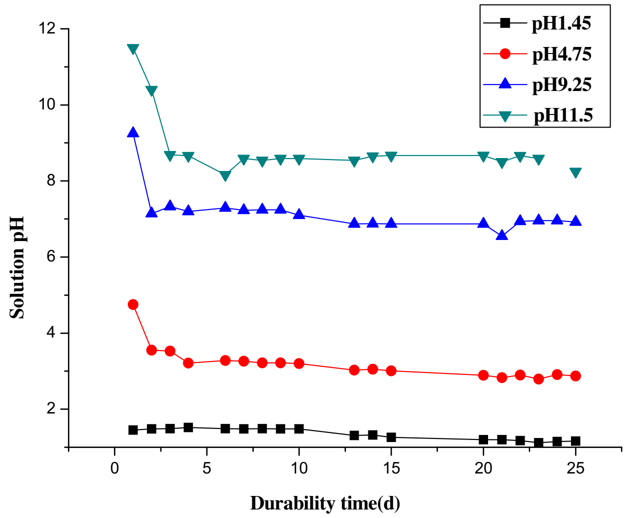

Fig. 5. Durability of deoxidized polyDOPA-coated membranes in acid or base solution.

typical peaks corresponding to C=O (532.2 eV) in Fig. 4(d) and (e), which is ascribed to the existence of carboxyl groups, which also proves the conclusion mentioned above. The hydroxyl peaks do not appear in the O1s spectrum of oxidized polyDOPA-coated membrane. It is possible the majority of the carbonyl groups cover up the minority of hydroxyl groups.

Table 1 shows the atomic percentage on the membrane surface measured by XPS, and the measuring depth is 1–5 nm. There is no obviously change for the thickness of coating membrane compared with PVDF pristine membrane using a desktop thickness micrometer. The appearance of nitrogen and oxygen element on the deoxidized and oxidized polyDOPA-coated PVDF membranes indicates that the polyDOPA coatings have covered the membrane. Furthermore, the nitrogen composition of oxidized polyDOPA-coated membranes is 2.57, which is higher than that of deoxidized polyDOPA-coated membrane (1.01). This is consistent with the unstable adsorption of outer layer of deoxidized polyDOPA coating on PVDF membranes.

The FT-IR measurement is used to characterize the chemical composition of the coating PVDF membranes. The typical spectrum of original PVDF membranes and polyDOPA-coated membranes was shown in Fig. 7. The absorption peaks of pristine PVDF membrane and polyDOPA-coated membranes at 2,977 and 2,853 cm^{-1} are contributed to C–H stretching of CH$_3$, and C–H stretching of CH$_2$ appears at 2,920 cm^{-1}. In the case of polyDOPA-coated membrane, the absorption peak at 3,024 cm^{-1} is assigned to =C–H resonance vibration in the aromatic ring. The phenolic hydroxyl group and amine group stretching vibrations exist at 3,460 cm^{-1}. The new absorption peaks at 1,641 cm^{-1} in the spectrum of the coating membrane are ascribed to the amine group. The appearance of amine, carbonyl, and hydroxyl peaks confirms the formation of polyDOPA coating on the PVDF membrane surface. Additionally, the absorbance at about 2,233 cm^{-1} attributed to C-N of polyDOPA chains further shows polyDOPA coating has indeed been introduced onto the PVDF membrane surface.

The FT-IR spectra of the deoxidized and oxidized polyDOPA-coated membranes after durability experiments at pH = 11.5 were displayed in Fig. 8. The N-H shearing vibration of the amine group is observed at 1,511 cm^{-1}. The presence of the carbonyl groups can be ascertained from the bands of C=O stretch at 1,736 cm^{-1}. In the case of D–COOH/D–COONa, the spectrum of lightly stir-mixed proportions revealed the broad bands attributable to (acid-salt) dimers at 1,735 and 1,645 cm^{-1} [19]. The absorption band in the range of 3,610 and 1,230 cm^{-1} was seen due to the –OH stretching vibration of phenolic hydroxyl groups on the oxidized polyDOPA-coated membranes after the durability experiment at pH = 11.5. It also indicates the coexistence of phenolic hydroxyl groups and quinone carbonyl groups on the oxidized polyDOPA-coated membranes. Although some typical peaks also appear on deoxidized polyDOPA-coated membranes, –OH stretching vibration is not present due to the oxidation of phenolic hydroxyl groups.

3.4. Hydrophilicity of polyDOPA-coated membranes

The water intake content of fabricated membrane samples was measured and shown in Fig. 9. It indicates that the water intake contents of oxidized

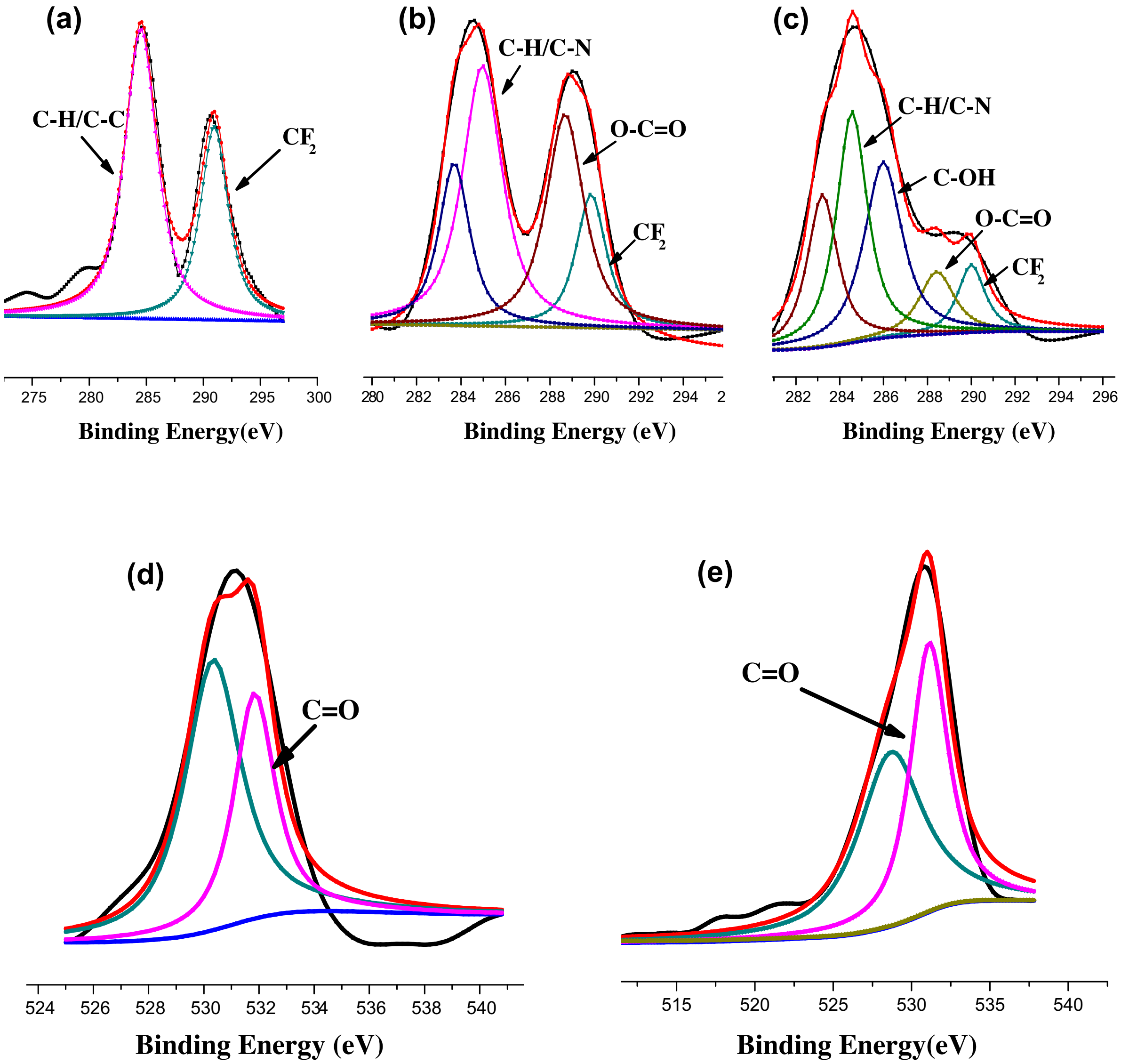

Fig. 6. XPS curve-fitted spectra of sample membranes: (a, b, c) C1s of pristine PVDF, deoxidized and oxidized polyDOPA-coated PVDF, (d, e) O1s of deoxidized, and oxidized polyDOPA-coated PVDF.

Table 1
Elements composition (at.%) on the membranes surface determined by XPS

Membrane	C1s	N1s	O1s	F1s
PVDF pristine membrane	51.05			48.96
Deoxidized polyDOPA-coated membrane	45.87	1.01	4.93	48.19
Oxidized polyDOPA-coated membrane	57.40	2.57	12.25	27.78

polyDOPA-coated membrane (b) are higher than that of PVDF pristine membrane (a), whether they undergo a transition of dry to wet process or that of wet to dry process. The water intake contents of deoxidized polyDOPA-coated membrane (c) are far higher than that of other sample membranes after a process of wet-to-dry state, and much lower after the process of dry-to-wet state. The color of deoxidized polyDOPA-coated membrane surface still remains white in the dry state. One possibility is vacuum drying, where an esterification reaction occurs between carboxyl groups and hydroxyl groups, which makes the membrane surface more hydrophobic. Maybe the hydrophobicity is enhanced from the oxidation of DOPA-hydroxyl into DOPA-carbonyl, although there are no typical pink colors emerging on the deoxidized polyDOPA-coated membrane.

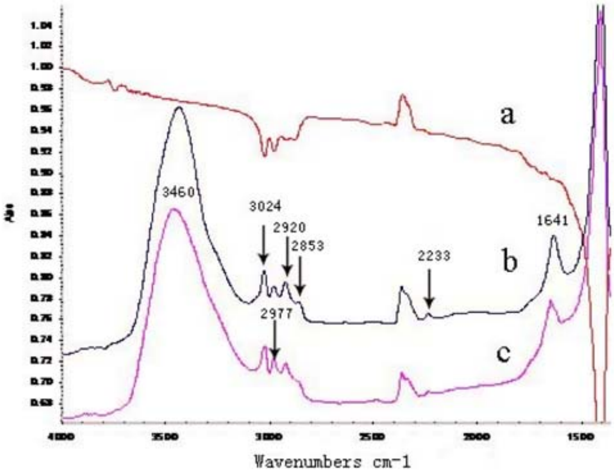

Fig. 7. FT-IR spectra of the pristine PVDF membrane (a), deoxidized (b) and oxidized (c) polyDOPA-coated membranes.

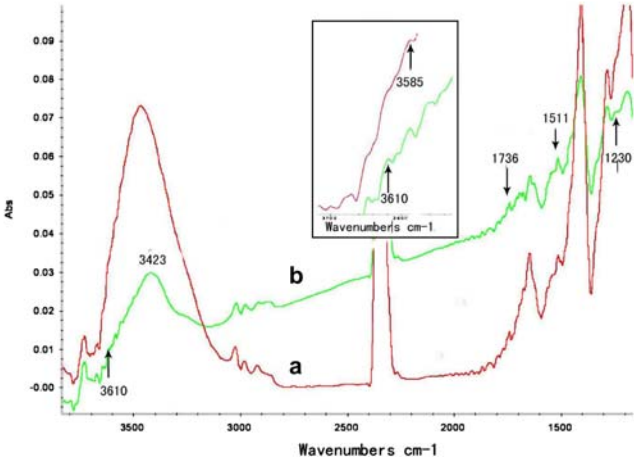

Fig. 8. FT-IR spectra of the deoxidized (a) and oxidized (b) polyDOPA-coated membranes after durability experience at pH = 11.5.

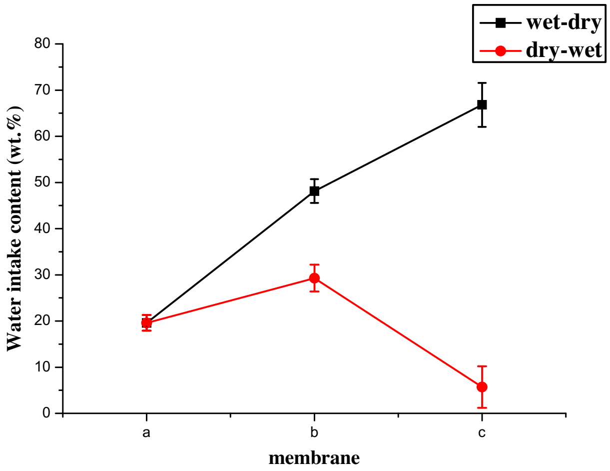

Fig. 9. Water intake content in the different membrane samples (a) PVDF pristine membrane, (b) oxidized polyDOPA-coated membrane, and (c) deoxidized polyDOPA-coated membrane.

Water contact angles were employed to evaluate the effect of the membrane surface hydrophilicity, and lower water contact angle represents higher hydrophilicity. In Fig. 10, the water contact angle of polyDOPA-coated PVDF membranes that reacted for 20 h is lower than 89.1° of original membrane without coatings. It suggests that the hydrophilicity of the membrane surface with polyDOPA coatings is enhanced, especially for the oxidized polyDOPA-coated membrane. After durability experience, the contact angles of oxidized polyDOPA-coated membranes are all lower than that before experience, reflecting that hydroxyl groups on the surface slightly increase after durability test. These maybe parts of the phenolic hydroxyl groups on the inner layer that are not fully oxidized, then they are covered by the outer coatings. That is, it does not reach a final equilibrium between DOPA-hydroxyl and DOPA-quinone. The contact angles of deoxidized polyDOPA-coated membrane after durability experience are even higher than those of the PVDF pristine membrane. It also means that the dehydration of

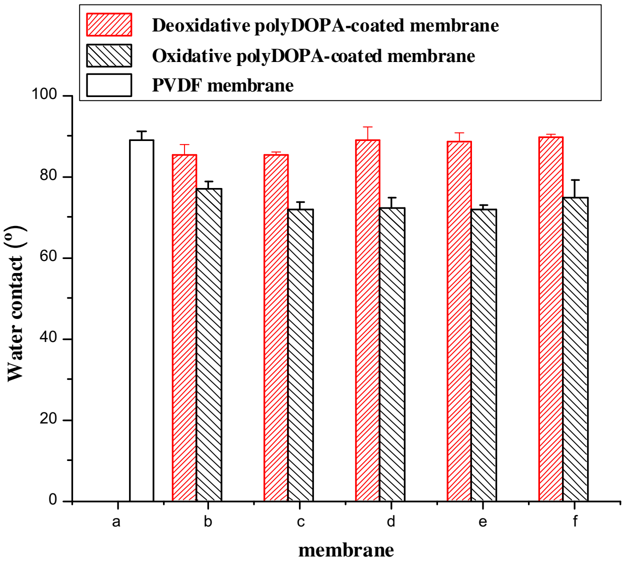

Fig. 10. Contact angles for PVDF pristine membrane (a), oxidized polyDOPA-coated membrane and deoxidized polyDOPA-coated membrane (b), oxidized polyDOPA-coated membrane, and deoxidized polyDOPA-coated membrane after durability experience at pH = 1.45 (c), pH = 4.75 (d), pH = 9.25 (e), and pH = 11.5 (f), respectively.

hydroxyl groups on deoxidized polyDOPA coating occurs in the dry process.

3.5. Protein adsorption resistance

Resistance to protein adsorption is another important parameter to evaluate the effect of the membrane surface anti-fouling. In this paper, BSA (IEp = 4.8) is used as model protein. The amount of adsorbed BSA from 1 g/L BSA solution (pH = 7.4) is 60 μg/cm^2 for the original PVDF membrane which is soaked thoroughly by ethanol and PBS (pH = 7.4) solution before BSA adsorption. For all the polyDOPA-coated films which are fully soaked by PBS solution, the effective reduction in the amounts of adsorbed BSA is probably attributed to the residence of more phenolic hydroxyl groups after outer layer desorption. The amounts of adsorbed BSA on the oxidized polyDOPA-coated membranes decrease with the increase of the pH value of the desorption solution. When pH = 11.5, the amounts of adsorbed BSA decrease to zero. The pH of the desorption solution decreases from 11.5 to about 8.5, which is possibly the most stable pH for the oxidized polyDOPA under marine environment, showing an almost complete shielding of the surface to BSA protein adsorption. For the deoxidized polyDOPA-coated membranes, the amounts of adsorbed BSA increase with pH increase of the desorption solution due to the oxidation of a little phenolic hydroxyl groups in the base solution. When using strong base sodium hydroxide (pH = 13) as the soaking solution, the amounts of adsorbed BSA all increase. There is only a small increase of the amounts of adsorbed BSA for all the oxidized polyDOPA-adsorbed films, indicating the hydroxyl groups on this film are relative stable in strong acid and alkali environments. However for the deoxidized polyDOPA-adsorbed films, the amounts of adsorbed BSA increase significantly and the color of the membranes surface turns pale pink except at pH = 1.45, which is the typical color of benzoquinone. When pH value of the desorption solution is 1.45, the amount of BSA adsorption is dropped dramatically to 6.02 μg/cm^2 shown in Table 2. It maybe ascribed to the high contents of phenolic hydroxyl groups in acid solution.

3.6. Permeation properties and flux recovery ratio

Ultrafiltration experiments were carried out to investigate the separation performance of pristine and coating membranes. All the membranes were kept wet until use. The BSA solution is prepared to 1 g/l in PBS solution (pH = 7.4). Table 3 summarizes the pure water flux and BSA rejection ratio of pristine and coating membranes. All the coating membranes exhibit a dramatically higher pure water flux than the pristine membrane due to the increased hydrophilicity of membrane surface. However, the coating membranes have lower BSA rejection ratio than pristine membranes. It is probably because DOPA is biocompatible

Table 3
Pure water and BSA permeation flux and rejection of BSA

Membrane	Pure water flux (L/m^2 h)	BSA flux (L/m^2 h)	Rejection of BSA (%)
PVDF pristine membrane	40.02 ± 0.80	14.13 ± 0.80	87.31 ± 5.93
Oxidized polyDOPA-coated membrane	72.84 ± 7.06	21.82 ± 3.04	81.43 ± 6.94
Deoxidized polyDOPA-coated membrane	80.01 ± 5.43	29.44 ± 0.63	78.18 ± 5.69

Table 2
BSA adsorption of coating membrane before and after durability experiment

No.	BSA adsorption before durability experiment (μg/cm^2)	BSA adsorption after durability experiment (μg/cm^2)			
		pH = 1.45	pH = 4.75	pH = 9.25	pH = 11.5
a	52.89 ± 2.14	37.06 ± 1.35	16.76 ± 1.48	15.14 ± 1.17	0
b	–	52.62 ± 2.38	56.95 ± 2.18	16.81 ± 1.67	19.27 ± 1.07
c	49.31 ± 1.55	6.02 ± 0.81	9.46 ± 0.72	12.46 ± 1.25	27.62 ± 1.69
d	–	7.40 ± 0.47	378.54 ± 1.24	418.17 ± 9.56	443.74 ± 13.7

Notes: (a) Oxidized polyDOPA-coated membrane soaked by ethanol and PBS (pH = 7.4) solution, respectively before BSA adsorption. (b) Oxidized polyDOPA-coated membrane soaked by ethanol and NaOH (pH = 13) solution, respectively. (c) Deoxidized polyDOPA-coated membrane soaked by ethanol and PBS solution. (d) Deoxidized polyDOPA-coated membrane soaked by ethanol and NaOH solution.

and part of unstable DOPA molecular is smaller than the pore sizes, then it easily passes through the membrane pores without blocking under strong hydraulic filtration and cleaning conditions (especially the unstable adsorption of phenolic hydroxyl on the outer layer of deoxidized polyDOPA-coated membranes). This also causes a decline in BSA retention.

The biofouling characteristics of the coating PVDF membranes are evaluated by cyclic filtration tests. Fig. 11 presents time-dependent flux during ultrafiltration operation. The first half hour in the curve is referred to pure water ultrafiltration. Then the feed is switched from pure water to BSA solution. After 1 h ultrafiltration of BSA solution, the membrane is refreshed by a simple membrane flushing using pure water and the pure water flux is measured again for another half an hour. In the initial stage of protein ultrafiltration, the permeation flux of BSA solution declines rapidly. The initial fouling in this system is caused by the convective deposition of protein aggregates onto the membrane surface. Native (non-aggregated) BSA only fouls the membrane by chemical attachment to an existing protein deposit via the formation of intermolecular disulfide linkages [20]. However, the concentration polarization is minimized because of the rigorous flushing near the membrane surface. Therefore, we would conjecture that the flux decline of the membranes is mostly caused by membrane fouling. Protein molecules may be entrapped in the large pores and block the channels, which can not be removed by hydraulic cleaning for hydrophobic membranes. Water flux after cleaning can not completely resume to the initial value. In the subsequent ultrafiltration, the channels are restricted for BSA molecules to intrude in. The water flux recoveries for pristine and oxidized polyDOPA-coated membranes are 44.75 and 50.27% in the successive three ultrafiltration cycles, respectively. The percentage of unrecoverable flux results from the irreversible fouling of persistent protein adsorption.

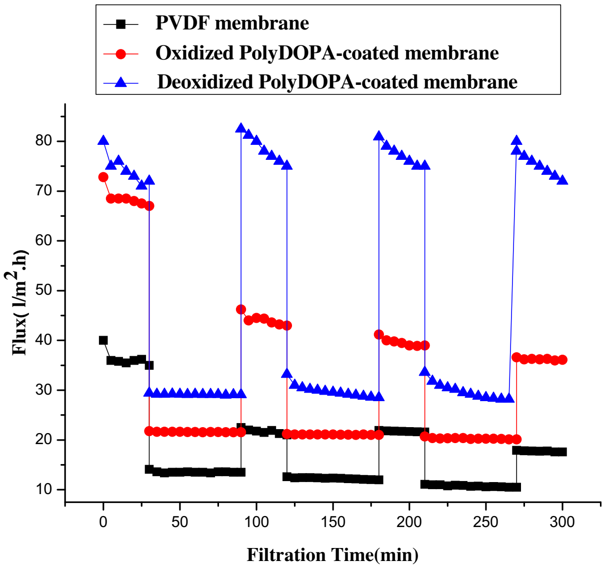

Fig. 11. Time-dependent flux of PVDF pristine membrane and polyDOPA-coated membrane operated with three cycles of BSA solution ultrafiltration.

The water flux recovery value of the first-cycle could reach 100% for deoxidized polyDOPA-coated membranes, and the value of three-cycle is also higher than 95%. The higher flux recoverable rate indicates lower total flux loss, corresponding to less protein adsorption on the membrane surface. Deoxidized polyDOPA-coated membrane has better protein adsorption resistance, higher hydrophilic properties, and consequently higher water flux in the successive recycles than unmodified PVDF membrane. In general, the protein layer permeability is determined by the balance between the compressive pressure associated with the filtration and the electrostatic repulsion between the negatively charged proteins in the deposit [21]. Coated membranes with phenolic hydroxyl groups and dipole-ions (carboxylic and amino groups) are capable of binding a significant amount of "free water" which is similar to water. When protein contacts the membrane surface, the protein is excluded from the hydrophilic layer to avoid the substantial entropy loss which is caused by the entrance of large protein molecules into the highly hydrophobic layer. Therefore, less protein will adsorb at the interface of the membrane surface, which rendered the membranes "easy to clean" [22,23].

In summary, the excellent flux recovery of DOPA-based modified membrane indicates that the coated membranes could be reused for prolonged time. Most important of all is to seek more optimizing fabrication conditions to obtain a more suitable coating membrane, which can be realized by adjusting the reaction time, DOPA concentration and washing thoroughly in acid and base solutions. Further study will be carried out in the later work.

4. Conclusions

Hydrophobic PVDF ultrafiltration membranes are facilely modified by coating polyDOPA layer under oxidation and deoxidation conditions. The oxidized and deoxidized polyDOPA not only coats on membrane surface, but also on membrane pore walls. The PVDF ultrafiltration membranes become smoother after introducing polyDOPA coating. The hydrophilicity of PVDF membranes with polyDOPA coating was significantly improved. Although the phenolic hydroxyl groups on the deoxidized polyDOPA-coated membranes are easily oxidized into quinone-based carbonyl groups under strong base environment or dehydrated in dry state, the antifouling effect of deoxidized polyDOPA-coated membranes is better than that of oxidized polyDOPA-coated membranes due to the residence of double phenolic hydroxyl groups and dipole-ions (carboxylic and amino groups). However, the stability of the oxidized polyDOPA-coated membranes are excellent than that of deoxidized polyDOPA-coated membranes, because the phenolic hydroxyl group and quinone carbonyl group can coexist on the oxidized polyDOPA-coated membranes. This research offers a new way to improve the hydrophilicity of PVDF membrane by polyDOPA modification.

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