A novel salt-responsive TFC RO membrane having superior antifouling and easy-cleaning properties

Jianqiang Meng *, Zhen Cao, Lei Ni, Yufeng Zhang, Xiaoyan Wang, Xin Zhang, Enhua Liu

State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, Tianjin 300387, China

ARTICLE INFO

Article history:
Received 20 December 2013
Received in revised form 7 March 2014
Accepted 9 March 2014
Available online 16 March 2014

Keywords:
Stimuli-responsive
Thin-film composite (TFC) membrane
Surface-initiated graft polymerization
Antifouling
Zwitterionic polymer

ABSTRACT

A novel salt-responsive thin-film composite (TFC) reverse osmosis (RO) membrane was prepared by tethering a zwitterionic polymer poly [4-(2-sulfoethyl)-1-(4-vinylbenzyl) pyridinium betaine] (PSVBP) onto a commercial RO membrane. The graft polymerization was conducted by surface-initiated free radical polymerization of SVBP initiated by a K2S2O8–NaHSO3 redox system. The membrane surface before and after graft polymerization was investigated in detail using ATR-FTIR, XPS, zeta potential, water contact angle and SEM. The change on surface chemical composition demonstrated successful grafting of PSVBP onto the RO membrane surface. The PSVBP grafting added negative charge onto the membrane surface and significantly improved membrane surface hydrophilicity. The RO test indicates that PSVBP grafting can increase the rejection from 98.0% to 99.7% with the trade-off 20% of the permeation flux. A cross-flow protein fouling test as long as 100 h indicates that the resulted PA-g-PSVBP membrane had superior antifouling property in the short term but lost the advantage for long-term operation. In spite of the long-term fouling, the PA-g-PSVBP membrane can restore 90% of the initial flux by rinsing with brine. The salt-responsive property of the PSVBP brush is believed to provide a driving force for the release of protein foulants.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

With the population growth and industrialization across the world, the problem of water shortage became more and more serious. Today, many countries face chronic water shortages due to intense population growth and increased water pollution. Reverse osmosis (RO) is considered as a reliable and economic technology to solve the water crisis and has been widely used in seawater and brackish water desalination, waste water reclamation, pure water fabrication etc. [1,2]. The mainstream reverse osmosis membranes commercially available are polyamide thin-film composite membranes (PA TFC). The PA TFC membrane was made by interfacial polymerization of an aromatic polyamine (for example m-phenylenediamine (MPD)) with one or more aromatic polyacyl halides (for example trimesoyl chloride (TMC)) over a porous polysulphone support membrane [3]. It has several advantages such as high water permeability and ion rejection, resistance to pressure compaction, wide operation temperature and pH ranges. However, membrane fouling has limited the applications of RO because it leads to deteriorated membrane performance, shortened membrane service life and increased system cost [4].

Significant amount of work has been dedicated to membrane surface modification for improved anti-fouling performance. The most frequently used strategy is to build a fouling-resistant and hydrated layer on the membrane surface. Usually the obtained membrane was fouled less and slower than the unmodified membranes or commercial membranes [5]. However, fouling still occurs, which means that membrane cleaning is inevitable. Currently, the fouled RO membranes are routinely cleaned by specialized chemicals to restore its performance. The chemical cleaning often leads to continuous membrane degradation and chemical waste, resulting in the second pollution.

Alternatively, a more realistic and efficient solution to membrane fouling is to develop membranes having self-cleaning or easy-cleaning properties. Following this clue, Madaeni and coworkers attempted to modify the RO membrane with nano-TiO2 by a self-assembly method [6]. The modified membranes showed improved water flux and antifouling performance due to the obvious improvement of membrane surface hydrophilicity. But there remains a question whether TiO2 particles and UV irradiation can degrade the membrane itself. Shi and coworkers immobilized trypsin onto PMAA-g-PES membranes [7]. The results suggested that the enzyme-resided membrane had desirable anti-fouling and
self-cleaning properties, but the long-term stability of the trypsin on the membrane surface may be questionable. Zhao et al. designed membrane surfaces covered with hydrophilic and low surface energy brushes. The obtained membranes were demonstrated to have superior antifouling and self-cleaning abilities [8].

Stimuli-responsive polymers are capable of translating changes in their local environment to changes in their physical/chemical properties. This allows stimuli-responsive polymers to be used for a wide range of applications and to draw intensive attention in recent years [9,10]. Stimuli-responsive membranes have also drawn great attention, with the focus on responsiveness of the membrane permeability and selectivity to environmental stimuli. In fact, the abrupt switch between hydrophobicity and hydrophilicity together with the conformation change of the polymer chains responsive to environmental stimuli endows the stimuli-responsive polymer tunable ability to release the foulants, i.e., self-cleaning properties [11]. Yu and coworkers modified TFC polyamide membranes by depositing P (NIPAM-co-Am) on the membrane surface [12,13]. It was found that the application of PNIPAm layer improved the fouling resistance and cleaning ability of the membrane. However, in spite of the encouraging results, modulating the temperature of the RO feed will be hard to implement in the system, if considering the energy cooling down or heating up tons of the feed solution.

Zwitterionic polymers have been the focus as an excellent material for fouling control of membranes very recently [14–16]. However, their salt-responsive conformation change and adsorption properties have been rarely visited for membrane applications [17]. As one of the typical zwitterionic polymer, poly (4-(2-sulfoethyl)-1-(4-vinylbenzyl) pyridinium betaine) (PSVB) exhibits salt-responsive properties. It is insoluble in pure water but readily soluble in the presence of halide salt. In this work, PSVB was synthesized according to a method reported in the literature [18]. The deionized water (DI water) with a conductivity of less than 1 μS/cm was obtained from a Millipore Milli-Q Advantage A10 water purification system having a stable effluent pH of 6.8–6.9 (18.2 MΩ cm–1 at 25 °C, 1.2 µg/L TOC, Billerica, MA, USA) and was used as the solvent for preparing aqueous solution as well as for soaking and rinsing the membranes. The membrane coupons were soaked in DI water for 24 h with the water changed every 6 h to remove the membrane additives.

2.2. Synthesis of the PA-g-PSVB membrane

The PA-g-PSVB membrane was synthesized by free radical graft polymerization of SVBP from the XLE membrane surface initiated by the K₂S₂O₈–NaHSO₃ redox system. For a typical operation, the XLE membranes were split into 20 cm × 5 cm and immersed in aqueous solution containing SVBP (2 mmol L⁻¹), K₂S₂O₈ (1 mmol L⁻¹) and NaHSO₃ (1 mmol L⁻¹). After purging with pure nitrogen for 20 min to remove all of the dissolved oxygen, the reaction vessel was sealed and put into a water bath thermostate at 25 °C. After keeping the reaction for a prescribed time, the obtained membranes were thoroughly washed with DI water for 24 h to remove the residual reactant and homopolymer.

2.3. Membrane surface characterization

ATR-FTIR spectra of the membrane surface were determined using a Vector 22 FTIR spectrometer (Bruker, Germany). The membrane samples were entirely rinsed with DI-water and then dried at 25 °C in a vacuum oven overnight before analysis. ATR-FTIR spectra of the membranes were recorded in wave number of 600–4000 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher K-alpha X-ray photoelectron spectrometer (Thermo Scientific, USA) with a monochromatic Al-Kα X-ray source (hv = 1486.6 eV). Survey XPS spectra were obtained by sweeping over 0–1000 eV electron binding energy with a resolution of 1 eV. Each survey spectrum was the average of five survey scans. Scanning electron microscopy (SEM) images were taken on a field emission SEM (Quanta 200, FEI, USA). Imaging was carried out at 3 kV with a working distance of 7.7 mm. The dry membrane samples were mounted on aluminum stubs, using aluminum tape and Au coated before imaging. The water contact angles of pristine and modified membrane surfaces were measured by the circle-fitting method using a Drop Shape Analysis System DSA 100 (Krüss, Switzerland) at 25 °C and 60% relative humidity. Droplets of distilled water (2 μL) were placed at different spots of the membrane surface. The obtained value is an average of 5 measurements. The zeta potentials were calculated based on the streaming potential method reported previously [19,20]. A Teflon gasket was placed as a spacer between the

![Scheme 1. Synthesis of the salt-responsive TFC RO membrane having antifouling and easy-cleaning properties.](image-url)
thin film layer surfaces of a pair of RO membrane samples, forming a streaming channel. The normal passage of permeate was blocked so that the electrolyte solution could only flow through this channel. Reversible Ag/AgCl electrodes were placed at the channel entrance and exit. The streaming potential was surveyed by a digital electro- 

meter (UT30B, Shenzhen Uni-Trend Electronics Co., Ltd., China) when the electrolyte flows across the stationary charged membrane surface. Measurements are carried out with 1 mmol L⁻¹ KCl at 25 °C and the pH adjusted in the range of 3–11. The membrane samples were conditioned for at least 24 h in 1 mmol L⁻¹ of KCl solution before the test. The zeta potential was calculated from the streaming potential measurements based on the Helmholtz-Smoluchowski equation and Fairbrother–Mastin approach [21]. Results shown were averages of three measurements taken at each pH value.

2.4. Membrane flux and rejection measurements

All reverse osmosis experiments were conducted using a crossflow filtration system described previously [19]. The membrane samples were pressurized for 1 h before any data were collected. The membrane RO performance in terms of permeate water flux and salt rejection was measured using 2 g/L of sodium chloride (NaCl) aqueous solution at 1.5 MPa, 25 °C and pH 6.8. The permeate water flux was determined by measuring the permeate volume collected over a certain period and calculated through the following equation:

\[ J = \frac{Q}{A \Delta t} \]  

where \( J \) is the permeate water flux, \( A \) is the effective area of the membrane for permeation, and \( Q \) is the volume of permeation over a time interval \( \Delta t \). The salt rejection \( R(\%) \) was calculated by the following equation:

\[ R(\%) = \left( 1 - \frac{C_p}{C_f} \right) 100\% \]  

where \( C_p \) and \( C_f \) are the concentrations of salt in the permeate and feed solutions, respectively. The salt concentration was determined by measuring the electrical conductivity of the salt solution using a conductivity meter. The obtained flux and salt rejection values are averaged values from at least three samples for each membrane type.

2.5. Fouling experiments

Membrane fouling experiments were performed via crossflow filtration of an aqueous solution containing 100 mg/L of bovine serum albumin (BSA) and 2000 mg/L of NaCl. The antifouling property of the membrane was evaluated by monitoring the permeation flux as a function of time. For the experimental protocol, the membrane was first stabilized by filtrating a BSA-free NaCl solution of 0.2 g/L at 1.5 MPa for 12 h until the permeate flux was stabilized. After that, the BSA/NaCl solution, which was newly prepared according to the prescribed concentration, was added into the feed tank. Permeate flux was continuously monitored during the testing period. The obtained flux profile was used to analyze the BSA fouling behavior of the modified and pristine TFC membranes.

2.6. Cleaning experiments

In order to evaluate the easy-cleaning property of the PA-g-PSVBP membrane, the fouled membranes were cleaned via 2 h of rinsing using DI water and then 2 h of cycled DI water/brine rinsing. The membrane flux data were collected using 2000 mg/L NaCl solution at 1.5 MPa both following the DI water rinsing and following the cycled DI water/brine rinsing. The typical operation of the cycled DI water/brine rinsing is: (1) rinsing with DI water for 30 min; (2) washing with 1.5 mol/L NaCl solution for 30 min; (3) repeat steps (1) and (2). The rinsing process was conducted in line at 25 °C and 0.2 Mpa.

3. Results and discussion

3.1. Chemical composition of the membrane surface

ATR-FTIR was used to verify the presence of PSVBP on the membrane surface following the surface grafting. Fig. 1 shows the ATR-FTIR spectra of the XLE and PA-g-PSVBP membranes. The IR penetration depth in the ATR technique is typically over 1 μm, while the thickness of the active layer of the XLE membrane is below 1 μm. Therefore, both the adsorptions of the polyamide layer and the polysulphone support should appear in the spectra. The peaks at about 1660 cm⁻¹, 1610 cm⁻¹ and 1540 cm⁻¹ correspond to amide I stretching, hydrogen bonded amide II in-plane bending, respectively. They are characteristics of the aromatic polyamide barrier layer. The bands at about 1585 cm⁻¹ and 1490 cm⁻¹ are characteristics of the polysulphone support layer [22,23]. The adsorptions at 1080 cm⁻¹, 1105 cm⁻¹, 1150 cm⁻¹ and 1170 cm⁻¹ are attributed to the C–C stretch of the aromatic rings [24]. The PA-g-PSVBP membranes have very similar spectra to the XLE membrane. The adsorption profiles are the same except for a “signature” peak at 1047 cm⁻¹, which is induced by the symmetric stretching vibration of the sulfonate groups. This observation illustrates the successful graft polymerization of PSVBP on the membrane surface.

The chemical composition of the membrane surfaces was further investigated by the XPS analysis. Fig. 2 shows the XPS survey spectra of the XLE and PA-g-PSVBP RO membranes. For the pristine XLE membrane, there are three major emissions at 284.6 eV, 532.0 eV and 400.0 eV assigned to the binding energy of C 1s, O 1s and N 1s. The PA-g-PSVBP membranes have two new emissions at 164.0 eV and 229.0 eV, which can be ascribed to the binding energy of C 1s and O 1s originated from the grafted PSVBP. The element content of membrane surfaces is presented in Table 1. Table 1 shows obvious increase in the S atom content and decrease in N atom content after the graft polymerization of SVBP. The S/C atomic ratio increased from 0.007 to 0.029, and N/C atomic ratio decreased from 0.161 to 0.124. This is due to the higher S content and lower N content of PSVBP versus the original XLE membrane. The XPS results confirmed the successful grafting of PSVBP onto the XLE membrane surface.

3.2. Effects of surface modification on desalination performance of the membrane

The desalination performance of the RO membranes in terms of permeation flux and salt rejection was evaluated by cross-flow
both of which are lower than the reported values (72 L m\(^{-2}\) h\(^{-1}\)). Here XLE membrane samples were also tested at manufacturers’ rejection of PA-g-PSVBP membrane is 99.7%. It should be noted XLE membrane has a NaCl rejection of about 98% while the highest polymerization time show more prominent effects. The original permeation performance is shown in Fig. 3. It is apparent that the PSVBP grafting on membrane performance. The resulting membrane perfor-
tion time and temperature were varied to optimize the PA-g-
PSVBP membrane. In spite of that, the results are comparable.

Table 1
Elemental surface composition of XLE and PA-g-PSVBP membranes determined from XPS.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Atomic percent (mol%)</th>
<th>Atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>XLE</td>
<td>71.42</td>
<td>16.60</td>
</tr>
<tr>
<td>PA-g-PSVBP</td>
<td>73.58</td>
<td>15.11</td>
</tr>
<tr>
<td>PSVBP(^a)</td>
<td>67.10</td>
<td>16.76</td>
</tr>
</tbody>
</table>

\(^a\) The values of SVBP are calculated theoretically.

Fig. 3. Effects of grafting time on membrane water flux and salt rejection. (Membrane performance was tested under 1.5 MPa with 2 g/L NaCl solution at 25 °C.)

The increased salt rejection can be mainly explained as the result of plugging of minute surface defects in the polyamide membrane by PSVBP. Moreover, the addition of negative charge benefits Donnan exclusion of ions, which also contributes to the increased salt rejection [26–30]. The loss of the permeation flux can be related to the increased diffusion hindrance caused by the grafted PSVBP layer. It can also be seen that PSVBP grafting significantly alters the membrane performance at the very initial period of the polymerization. When the polymerization time was over 10 h for PSVBP grafting at 60 °C or over 14 h for PSVBP grafting at room temperature, the benefits of PSVBP grafting on membrane rejection were minimal but the flux loss was continuous. Compared with the membrane modified at 60 °C, the membrane modified at room temperature is easier to prepare and consumes less energy. Therefore, we selected two membranes for further study, the membrane grafted with PSVBP for 10 h at 60 °C and the membrane grafted with PSVBP for 14 h at room temperature, which are defined as PA-g-PSVBP\(_{60}\) and PA-g-PSVBP\(_{14}\), respectively.

3.3. Effects of surface modification on membrane surface charge and hydrophilicity

The surface charge of the membranes was studied by the streaming potential measurement over the pH range of 3.0–11.0. The membrane surface zeta potential as a function of pH is illustrated in Fig. 4. The data of original XLE membrane are in the range of values reported in the literature [31]. The membrane has a typical amphoteric surface of polyamide membrane with the isoelectric point at pH of slightly over 3. The evolution of its zeta potential with the environment pH is well documented in the literature and is attributed to the protonation and deprotonation of residue carboxylic and amine groups on the membrane surface [31–33]. It can also be seen that the zeta potential dramatically shifted to the negative charge direction after PSVBP grafting. Both PA-g-PSVBP\(_{14}\) and PA-g-PSVBP\(_{60}\) membranes are negatively charged under the full pH testing range, with PA-g-PSVBP\(_{14}\) membrane starting from –8 mV at pH 3 to –21 mV at pH 10 and PA-g-PSVBP\(_{60}\) membrane from –12.5 mV at pH 3 to –27 mV at pH 10. This is attributed to the presence of a large amount of sulfonic groups on the PA-g-PSVBP membrane surface.

Water contact angle is the most convenient method evaluating membrane surface hydrophilicity [34–39]; Fig. 5 shows the water contact angles measured by the circle-fitting method. It can be seen that the water contact angle significantly decreases after PSVBP grafting, indicating that the membrane surface hydrophilicity was significantly improved. This is believed to be able to suppress the deposition and accumulation of hydrophobic filtration of synthetic salt solutions. The membrane was tested at standard brackish water reverse osmosis (BWRO) conditions, i.e., 2000 mg/L of NaCl at 1.5 MPa and 25 °C. The grafting polymerization time and temperature were varied to optimize the PA-g-PSVBP membrane performance. The resulting membrane performance is shown in Fig. 3. It is apparent that the PSVBP grafting significantly increases the salt rejection with the trade off some permeation flux. Higher polymerization temperature and longer polymerization time show more prominent effects. The original XLE membrane has a NaCl rejection of about 98% while the highest rejection of PA-g-PSVBP membrane is 99.7%. It should be noted here XLE membrane samples were also tested at manufacturers’ specified conditions (\(\Delta P = 1.03\) Mpa, 0.2 g/L NaCl, pH ~8). The average flux is 67 L m\(^{-2}\) h\(^{-1}\) and the average NaCl rejection is 98%, both of which are lower than the reported values (72 L m\(^{-2}\) h\(^{-1}\) and 98.5%) [25]. The difference can be due to the variance of membrane samples, feed composition and other testing conditions. In spite of that, the results are comparable.

The surface charge of the membranes was studied by the streaming potential measurement over the pH range of 3.0–11.0. The membrane surface zeta potential as a function of pH is illustrated in Fig. 4. The data of original XLE membrane are in the range of values reported in the literature [31]. The membrane has a typical amphoteric surface of polyamide membrane with the isoelectric point at pH of slightly over 3. The evolution of its zeta potential with the environment pH is well documented in the literature [31–33]. It can also be seen that the zeta potential dramatically shifted to the negative charge direction after PSVBP grafting. Both PA-g-PSVBP\(_{14}\) and PA-g-PSVBP\(_{60}\) membranes are negatively charged under the full pH testing range, with PA-g-PSVBP\(_{14}\) membrane starting from –8 mV at pH 3 to –21 mV at pH 10 and PA-g-PSVBP\(_{60}\) membrane from –12.5 mV at pH 3 to –27 mV at pH 10. This is attributed to the presence of a large amount of sulfonic groups on the PA-g-PSVBP membrane surface.

Water contact angle is the most convenient method evaluating membrane surface hydrophilicity [34–39]; Fig. 5 shows the water contact angles measured by the circle-fitting method. It can be seen that the water contact angle significantly decreases after PSVBP grafting, indicating that the membrane surface hydrophilicity was significantly improved. This is believed to be able to suppress the deposition and accumulation of hydrophobic
foulants. It can also be seen that the water contact angle gradually decreased with the drop age. This is due to the absorption of water into the membrane surface and the continuous spreading of the water on the surface and hence enhanced evaporation. In addition, PA-g-PSVBP membranes show slightly quicker contact angle drop, with the final value after 180 s of aging reduced to only 7.2°. This indicates good wettability of the PA-g-PSVBP membrane, which is believed to enhance antifouling and foulant release properties of the membrane.

3.4. Effect of surface modification on membrane surface morphologies

Effect of PSVBP grafting on membrane morphology was studied by using FESEM. Representative SEM images of the XLE membrane and PA-g-PSVBP membranes are provided in Fig. 6. Obviously, the pristine XLE membrane shows a typical PA membrane morphology known as the “ridge-and-valley” structure [40]. The “ridge” part actually shows a lamellar structure and looks brighter under SEM than the “valley” part underneath. After PSVBP grafting, the PA-g-PSVBP membrane became brighter and the lamellar structure became thicker. This is due to the valley part being filled by the grafted PSVBP and the growth of PSVBP from the lamella. The decrease on surface roughness can lead to decreased effective surface area, which can also explain the loss of membrane flux from PSVBP grafting.

3.5. Fouling resistance and flux recovery in fouling tests

The fouling behavior of the XLE and PA-g-SVBP membranes was studied via crossflow filtration of aqueous solution containing
0.1 g/L of BSA and 0.2 g/L of NaCl at pH of 6.8 and 25 °C. It was found that 12 h of pre-filtration is enough for the membrane to reach a steady flux before BSA solution filtration. It is noteworthy that most protein fouling studies were performed for relatively short durations. In order to push the experimental conditions more approaching to the real condition, we tested the protein flux behavior at a much longer term. Fig. 7 shows the evolution of the flux within the filtration time of 100 h. It can be seen that the permeation flux dropped very quickly in the initial 10 h. This happened to both the XLE and PA-g-PSVBP membranes. However, much lesser fouling occurred with the PA-g-PSVBP membrane. It lost about 5% of the initial flux while the original XLE membrane lost almost 15% of the initial flux. This is attributed to the more hydrophilic surface built by the PSVBP and the electronic repulsion between the negatively charged membrane surface and BSA under the testing pH. After that, the membrane flux came to a plateau and decreased very slowly until 60 h of filtration was reached. This possibly indicates a temporary equilibrium of BSA adsorption/desorption on the membrane surface. Again, the PA-g-PSVBP membrane maintained about 90% of the initial flux, indicating a lesser amount of deposited BSA. In spite of that, when the testing time is prolonged over 60 h, there is a clear tendency that three flux plots were converging and the flux decline accelerated. Similar observation has been reported by others [41,42]. It is believed that during the early stages of fouling, BSA–surface interactions dominate the adsorption of BSA on the membrane surface. But as the fouling progresses, the membrane surface becomes less accessible, BSA–BSA interactions become dominant. These interactions may be expected to be independent of the membrane surface properties [43]. In fact, this may raise the concern on the effectiveness of building a hydrophilic hydrogel layer on the membrane surface to alleviate the fouling problem, either by chemical grafting or by coating, although this has been a prevalent methodology for membrane chemists.

We ran the cleaning experiments after 100 h of BSA filtration using DI water rinsing and then cycled DI water/brine rinsing. The flux recovery rates of the cleaned membranes are also shown in Fig.7. It is clear that the flux increased for the PA-g-PSVBP membrane after cleaning with DI water, whereas the flux of the XLE membrane has no obvious change. The high cleaning efficiency of the PA-g-PSVBP membrane is believed to be related to the protein repellent nature of the zwitterionic brush and better wettability of the PA-g-PSVBP membrane surface. However, it is obvious that the DI water rinsing itself is not sufficient and only 80% flux recovery was achieved. The following cleaning with brine further confirms the easy-cleaning property of PA-g-PSVBP membrane. After cleaning, the PA-g-PSVBP membranes recovered their lost water flux to over 90%. On the contrary, the flux of the pristine XLE membrane dramatically decreased to about 57% of the initial. This should be due to the protein dehydration at high salinity conditions, which leads to aggregation and precipitation of protein molecules, forming a dense layer that significantly hindered the water through the membrane. This result actually corresponds to the literature reports that the fouling due to hydrophobic–hydrophobic interaction will be more severe at high salinities [44].

We believe that the enhanced cleaning efficiency for the PA-g-PSVBP membrane is attributed to the phase transition and conformation change of the grafted PSVBP on the membrane surface, and as a result the deposited BSA layer loosen and collapse, leading to release of the foulants. However, it should be noted that the PA-g-PSVBP membrane still lost 10% of the initial flux. The reason behind this can be complex. Firstly, the dehydration of the BSA layer may lead to the compression of the fouling layer, which may actually prevent the “salt-in” process of PSVBP and discounts the effectiveness of this salt-responsive method. Secondly, the long-term protein filtration may lead to the irreversibility of BSA adsorption because the protein can slowly change the conformation and denature on the membrane surface. Lastly, the effectiveness of the PSVBP regulating protein adsorptions depends on several other factors, such as thickness of the grafted PSVBP layer, the size and flexibility of the protein molecules. Obviously, there is still appreciable space to improve the efficiency of this method.

4. Conclusion

The redox initiated surface graft polymerization method was employed to graft PSVBP onto the surfaces of commercial reverse osmosis membranes. A salt-responsive zwitterionic polymer PSVBP was grafted to impart the membrane improved antifouling and foulants release properties regulated by salt concentrations. The results of ATR-FTIR and XPS analysis verified the successful graft polymerizations of PSVBP onto the membrane surface. The PSVBP grafting was found to significantly increase the membrane rejection with only 20% loss of the permeation flux. Measurements of zeta potential and contact angle revealed that the surface of the TFC polyamide RO membrane became more hydrophilic and more negatively charged after graft polymerization of PSVBP. This is believed to improve the anti fouling property of the membrane because the hydrophobic–hydrophobic interaction was suppressed and most organic foulants in surface water are negatively charged. This assumption has been verified by short-term protein filtration performance. However, the PA-g-PSVBP membrane lost this superiority in the long-term test. Therefore, although it is quite prevalent to make anti fouling membranes by building a hydration layer on the membrane surface, its long-term efficiency can be

---

**Fig. 7.** (a) Normalized permeation flux and (b) flux recovery rates of XLE and PA-g-PSVBP membranes.
questionable when the foulant–foulant interaction dominates. Despite this, the severely fouled PA-g-PSVBP membrane can restore 90% of the initial flux by rinsing with the method adapted to its salt-responsive properties. It is noted here that in a full-scale RO system the brine can be ejected out of the drain using pure water after the rinse. In that case, the brine can be re-collected for cycled use.

The improved cleaning efficiency for the PA-g-PSVBP membrane was attributed to the state transition of the salt-responsive polymer, which would facilitate the removal of foulants located on the membrane surface, and thereby enhance the cleaning efficiency of the fouled membrane. Of course this method has not been able to retain the flux recovery to 100%, but since many factors, including surface coverage, density, molecular weight of the grafted stimuli-polymers and substrate–polymer interaction, can affect the responsiveness, there is appreciable space for this method to be optimized. We believe this method provides an alternative but effective way for alleviating fouling problems.

Acknowledgments

We gratefully thank the National Natural Science Foundation of China (Grant no. 21274108) and the National High Technology Research and Development Program of China (Grant no. 2012AA03A602) for financial support.

References


