Construction of antifouling lumen surface on a poly(vinylidene fluoride) hollow fiber membrane via a zwitterionic graft copolymerization strategy

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ABSTRACT

Construction of PVDF hollow fiber membranes with antifouling lumen surfaces is of great interest and significance for many industrial applications because the inside-out filtration mode allows good control over module hydrodynamics. For the first time, a zwitterionic polymer was immobilized on the lumen surface of a PVDF hollow fiber membrane via thermal-induced graft copolymerization with an objective to render the PVDF membrane antifouling. The graft copolymerization consists of two steps: ozone-assisted surface pre-activation and grafting of sulfobetaine methacrylate (SBMA). The grafting density and chain length were systematically optimized by manipulating the operational parameters, e.g. ozone treatment and grafting duration. The resultant membranes were studied with respect to their structure, morphology, ultrafiltration (UF) performance, while their fouling behaviors were evaluated by flux recovery ratio and the resistance-in-series model. In comparison to the pristine one, the composite membranes exhibited superior fouling resistance for a 2-h filtration of a 2.0 wt% bovine serum albumin (BSA) solution. Especially, the irreversible fouling-induced resistance was prominently reduced from 53% to 15% due to the outstanding hydration capacity of the polySBMA polymer. Consequently, the flux recovery ratio (FRR) increased significantly from 47% to 85%, suggesting the promising prospect of the zwitterion-grafted PVDF hollow fiber membranes for their antifouling properties. Most importantly, the improvement in antifouling was achieved without sacrificing flux or rejection efficiency. This work may provide useful insights about lumen surface nano-structuring of the inner-selective hollow fiber membranes.

1. Introduction

Despite of various operational controls, fouling is still an inevitable issue hampering membrane applications in a variety of separation processes, e.g. ultrafiltration, nanofiltration and osmosis processes [1–3]. The accumulated fouling layer would gradually degrade separation capacities and consequently demand more energy, higher clean-up frequency and more frequent replacement of membranes [1–4]. Fouling on polyvinylidene fluoride (PVDF) membranes has been particularly highlighted due to their ubiquitous applications in various industries [5]. Regardless of their excellent properties such as superior processability, mechanical strength and chemical resistance, PVDF membranes are largely incapacitated by their inherent nature of low surface energy and hydrophobicity which accounts for easy adhesion of organic foulants and microbes [5,6]. Design of non-fouling or low-fouling PVDF membranes is imperative in order to prolong their life span and reduce operational costs.

Surface hydrophilization of PVDF membranes were widely studied in order to tackle fouling issues [5,6]. The increase in surface hydrophilicity offers better fouling resistance as the formation of a hydration layer on membrane surface would alleviate foulant adsorption. It has been demonstrated that water molecules would be attracted towards the hydrophilic surface to form a bonded water layer which shields the membrane from foulant adhesion [7–9]. Strong hydrogen-bonding interactions between the pendant hydrophilic moieties and water clusters may facilitate this process. To implement this mechanism, researchers have developed different physical and chemical methods for surface modifications of hydrophobic membranes, e.g. surface coating and grafting.
Surface grafting is considered to be an effective way for construction of durable hydrophilic surfaces with its versatility in chemical structure and geometry controls. In comparison to bulky grafting [17,18], surface grafting makes it possible to modify the surface of commercially available membranes, without sacrificing the outstanding physical and chemical properties of PVDF membranes [5,6]. Due to their chemically-inert nature, PVDF membranes need to be pre-activated to introduce the reactive groups onto their surfaces. Extensive studies have unveiled that the activation process lies on chemical initiators [19–21] or high-energy radiation by different energy sources, e.g. UV [10], plasma [12,22], electron beam [13] and ozone [14–16], etc.

Zwitterionic polymers, on the other hand, are a group of macromolecules that bear an equal number of homogenously distributed anionic and cationic moieties [23,24]. Due to their electrostatically induced hydration capacity, these polymers possess superhydrophilicity and strong resistance to nonspecific protein adsorption [25]. Construction of a zwitterionic layer on the surface of PVDF membranes seems to be a promising strategy towards antifouling. Various approaches have been explored to this end [26]. Chemical-initiated atom transfer radical polymerization (ATRP) was the mostly employed method. For example, Li et al. [19] used azo-bis-isobutyrylimidazole (AIBN) as the initiator to graft poly(sulfobetaine methacrylate) (polySBMA) on the surface of a flat PVDF membrane via a physisorbed free radical polymerization method. Meanwhile, Wang and his co-workers [20] successfully grafted a zwitterionic polymer, poly(3-(methacryloyloxy)propyl-dimethyl- (3-sulfopropyl) ammonium hydroxide) (poly-MPDSAH), onto the surface of a PVDF hollow fiber membrane via a two-step polymerization. The membrane surface was chemically pre-activated by grafting of the poly(2-hydroxyethylmethacrylate) (polyHEMA).

Surface activation via different high-energy radiations were also reported [12,15,22]. An examples was the atmospheric argon plasma-induced surface copolymerization of polySBMA on a PVDF membrane surface to achieve effective blood compatibility [12]. The plasma treatment was believed to generate free radicals which could initiate the crosslinking reactions [11,12,22]. Another example of SBMA grafting was due to the ozone-induced surface activation [15]. Peroxide groups were formed on the surface of the PVDF membrane, which provided initiation sites for the subsequent grafting of polyzwitterions. In addition, directly coating polyzwitterions on membrane surface was also investigated. Jiang and co-workers [27,28] invented a universal coating method to attach poly(carboxybetaine methacrylate) (polyCBMA) on both hydrophobic and hydrophilic surfaces with the aid of dopamine. A CBMA polymer with a catechol chain end was synthesized via ATRP and mixed with dopamine to realize the direct attachment of polyCBMA onto the surface in one step. Moreover, a hydrophobic-driven self-assembling method was reported for an effective zwitterion modification [29]. An amphiphilic diblock copolymer with hydrophobic propylene oxide (PPO) and hydrophilic SBMA blocks was synthesized. The PPO moiety acted as an anchorage group to hook up this copolymer to the PVDF surface via hydrophobic-hydrophobic interactions.

The aforementioned zwitterion-grafted PVDF membranes have demonstrated excellent antifouling behaviors in various solutions. The link between the Zwitterionic layer and the substrate played the key role for these successful polyzwitterion attachments. Since ozone pretreatment is a very effective and facile method and to the best of our knowledge, the ozone-induced zwitterion grafting has not been reported to modify the lumen surface of hollow fiber membranes, we are motivated to explore the feasibility of designing antifouling PVDF hollow fiber membranes via an ozone-assisted graft copolymerization of SBMA on the lumen surface. Construction of PVDF membranes with an antifouling lumen surface is of great interest and significance for many industrial applications because the inside-out filtration mode offers much more uniform flow distribution and higher flow shear rate compared to the outside-in mode. The inner-selective PVDF membrane could be an alternative to the PES membrane in this type of configuration. To lower the risks of interfering the bulky properties of the PVDF hollow fibers during the grafting, key parameters for ozone pre-treatment and grafting reaction would be systematically investigated in order to achieve the optimal grafting density and polymer chain length. The morphology and ultrafiltration (UF) performance of the resultant PVDF composite membranes would be examined and their antifouling properties in a BSA solution would be evaluated by the resistance-in-series model. This work may provide useful insights for the modification of PVDF membranes with an antifouling lumen surface for various liquid and protein separations.
2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF), Kynar® HSV 900, was kindly supplied by Arkema Inc. The [2-((methacryloyloxy)ethyl)]dimethyl-(3-sulfopropyl)ammonium hydroxide (sulfobetaine methacrylate, SBMA) monomer was purchased from Sigma-Aldrich. Polyvinyl pyrrolidone (PVP, Luvitec® K17) supplied by BASF SE and LiCl obtained from Sigma-Aldrich were used as additives in the polymer dope solutions. N-methyl-2-pyrrolidone (NMP) was purchased from Merck. Polyethylene oxide (PEO) with a molecular weight of 100 kDa was employed as a model solute to evaluate the molecular weight cut-off (MWCO) of the membranes. Bovine serum albumin (BSA) was purchased from VWR international Ltd. All the chemicals were used as received.

2.2. Dope preparation and hollow fiber spinning

The polymer dope solution was prepared in a three-neck round-bottom flask with vigorous stirring. Prior to hollow fiber spinning, the dope solution was degassed for overnight in a syringe pump. The inner-selective PVDF hollow fiber membranes were fabricated via dry-jet wet-spinning process [7,30,31] with the aid of a dual layer spinneret. The spinning parameters were tabulated in Table 1. The as-spun hollow fibers were rinsed in a water bath for two days to ensure complete removal of the residual solvent. Afterwards, two post-treatment protocols were adopted. The fibers were either immersed in a glycerol/water (50/50 wt%) solution for another two days and then air dried at ambient conditions prior to module fabrication or directly dried using a freeze dryer for characterization purpose.

2.3. Surface graft copolymerization of polySBMA

The graft copolymerization was carried out on the lumen surface of the PVDF hollow fiber membrane. A laboratory-scale module with three pieces of hollow fibers was firstly prepared. The effective surface area was 8.14 cm². The module was washed with DI water for at least 2 h to remove any residual organic carbon. Afterwards, with the shell side of the hollow fibers filled with DI water, the module was purged consecutively with argon for 2 min and then an O₃/O₂ mixture for a determined duration, ranging from 3 to 30 min (Fig. 1(a)). The O₃/O₂ mixture was supplied from a ozone generator (L10G by Faraday Instrument) with an ozone concentration of 0.055 g L⁻¹ and a flow rate of 3 L min⁻¹ at ambient temperature. After the ozone pre-activation, the module was immediately incubated in argon atmosphere for about 5 min in order to remove the excessive ozone and protect the peroxide functional groups.

Concurrently, a 2 wt% SBMA solution was prepared in a flask reactor. After 15 min of argon purging, the SBMA solution was circulated along the lumen of the hollow fibers. Fig. 1(b) illustrates the schematic of the reaction system. The reaction time was varied from 0.5 to 12 h while the reaction temperature was constant. The overall reaction scheme was illustrated in Fig. 1(c). In order to make a fair comparison of the fouling behaviors between the composite hollow fibers and the pristine one, a control module was also prepared by adopting the same procedures except that the O₃/O₂ mixture was replaced by argon gas while the SBMA solution replaced by DI water.

2.4. Membrane evaluation

The PVDF composite hollow fiber membranes were evaluated with regard to their pure water permeability (PWP) and molecular weight cut-off (MWCO). A laboratory-scale cross-flow UF system was employed to carry out the experiments at a transmembrane pressure (TMP) of 1.0 bar and an ambient temperature of 23 ± 2 °C. Its schematic diagram was shown in Fig. 2. Prior to PWP measurements, the hollow fiber modules were washed with DI water on the UF system for about 2 h in order to remove the soluble organic carbon residuals and stabilize the membranes [7,32]. The real-time mass of permeate was measured by an electronic balance (EK-4100i, A&D Company, Ltd., Japan) and recorded by a Labview program (National Instruments, Austin, TX) as a function of time. The PWP (L m⁻² h⁻¹ bar⁻¹) was calculated by the following equation:

\[
PWP = \frac{Q}{\rho A} \times \frac{1}{\text{TMP}}
\]

where \(Q\) is the slope of the mass-time curve (kg h⁻¹), \(A\) is the effective inner surface area of hollow fibers in a module (m²) and \(\rho\) is the permeate density (kg L⁻¹). To evaluate the molecular weight cut-off (MWCO) of the membrane, PEO solutions with a concentration of 200 ppm were used. The feed solution and permeate samples were collected at an interval of 30 min after conditioning for 1 h. The PEO content of the samples were then analyzed by a total organic carbon (TOC) analyzer. Thus, the solute rejection \(R\) was attained:

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

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

2.5. Fouling evaluation

Fouling behaviors of the PVDF composite membranes were assessed by using a 2.0 wt% BSA aqueous solution. The filtration experiments were carried out using the same UF system as shown in Fig. 2. The filtration was carried out at a constant TMP of 1.0 bar and at an average flow rate of 0.15–0.20 L min⁻¹. The experiments were designed to examine different fouling-induced resistances according to the resistance-in-series model and flux recovery ratio (FRR). It should be noted that the resistances were represented by the flux losses as reported elsewhere [33]. Prior to the BSA solution, DI water was employed to obtain the initial pure water flux, referred as \(J_{w,1}\). Permeation flux \(J\) was calculated by:

\[
J = \frac{Q}{\rho A}
\]

The BSA solution filtration was subsequently carried out for 2 h to measure the permeation flux, \(J_p\), and the rejection to BSA. The total fouling-induced resistance, \(R_t\), can be determined:

\[
R_t(\%) = \left(1 - \frac{J_p}{J_{w,1}}\right) \times 100
\]
The rejection to BSA was calculated according to Eq. (2). Afterwards, backwashing with DI water was performed for 10 min to remove loosely attached protein molecules. The cleaned membrane was subsequently re-tested using DI water to attain another water flux, $J_{w2}$. The reversible fouling-induced resistance, $R_r$, irreversible fouling-induced resistance $R_{ir}$ and FRR can be represented by the following equations.

$$\text{FRR} = \left( \frac{J_{w2} - J_p}{J_{w1}} \right) \times 100$$

**Fig. 1.** Schematic illustrations of (a) the ozone treatment system, (b) the system for graft copolymerization of zwitterions and (c) reaction scheme of the graft copolymerization on the PVDF hollow fiber membrane.

**Fig. 2.** Schematic illustration of the laboratory-scale cross-flow UF system.
temperature and water flux is observed, which is consistent with PEO rejection. A negative relationship between the treatment temperature and duration. The reaction temperature and duration exert considerable influences on the decomposition of peroxide groups and generate reactive radicals. The relation between peroxide half-life and reaction temperature has been demonstrated [43,44]. Since a higher temperature is not preferred because it may compromise membrane performance as aforementioned, we tend to carry out the reaction at a temperature as low as possible without sacrificing the reactivity. Based on previous reported data [43,44], the half-life is estimated to be about 1.2 h at 45 °C. Thus, the reaction was carried out at a constant temperature of 45 °C with various reaction times in this work. In summary, by isolating the grafting time and the ozone treatment time, it is possible to attain an optimal chain length and grafting density required for high fouling resistance. Table 2 summarizes the different experimental conditions for zwitterion graft copolymerization and their respective membrane IDs. A control sample without ozone treatment and SBMA grafting was also performed for fair comparison.

3.2. Determination of reaction conditions for graft copolymerization The key factors manipulating the antifouling characteristics of the composite membranes are chain length, grafting density and chain conformation of the grafted zwitterionic polymer [41]. The chain length was mainly determined by the grafting kinetics, while the grafting density was vastly susceptible to the ozone treatment conditions [42]. A variety of operational variables can be adjusted in order to form a decent zwitterionic layer. Generally, the peroxide content introduced by ozone activation lies on the ozone concentration, treatment temperature and time. Regulating the ozone treatment time may be the simplest approach. Thus, in this work, the ozone concentration and treatment temperature were kept constant while the ozone treatment time was varied. It should be noted that an excessive ozone dosage may degrade the polymer chains [17,42].

Given the certain reactive sites on membrane surface, the chain length can be adjusted by zwitterion concentration, reaction temperature and duration. The reaction temperature and duration exert considerable influences on the decomposition of peroxide groups and generate reactive radicals. The relation between peroxide half-life and reaction temperature has been demonstrated [43,44]. Since a higher temperature is not preferred because it may compromise membrane performance as aforementioned, we tend to carry out the reaction at a temperature as low as possible without sacrificing the reactivity. Based on previous reported data [43,44], the half-life is estimated to be about 1.2 h at 45 °C. Thus, the reaction was carried out at a constant temperature of 45 °C with various reaction times in this work. In summary, by isolating the grafting time and the ozone treatment time, it is possible to attain an optimal chain length and grafting density required for high fouling resistance. Table 2 summarizes the different experimental conditions for zwitterion graft copolymerization and their respective membrane IDs. A control sample without ozone treatment and SBMA grafting was also performed for fair comparison.

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3. XPS analyses of the composite hollow fiber membranes

Fig. 5 summarizes the XPS wide scanned spectra of the pristine and composite hollow fiber membranes. The upper-right inset clearly shows the S2p peaks in the spectra of the composite hollow fibers, which may evidence the occurrence of the desired reaction. In addition to those of the composite hollow fibers, the N1s and O1s peaks are also observed in the spectra of the pristine hollow fiber, probably reflecting the residuals of the PVP additive.

Core-level spectra of C1s, N 1s and O 1s and their deconvolution results were plotted in Figs. 6 and 7. The C1s spectrum of the pristine hollow fiber was deconvoluted into four peaks at the binding energies of approximately 285.0, 286.2, 287.5 and 290.6 eV, corresponding to the C–H, C–C, C=O and C–F bond, respectively. The carbonyl group is probably from the PVP polymer. After graft copolymerization, two more peaks in the C1s spectra show up at 285.7 and 289.1 eV, suggesting the existence of quaternary ammonium cations and ester groups. The displacement of the peak at 286.2 eV of the pristine hollow fiber to 286.9 eV is probably due to two reasons: the partial scission of the C–F bond during ozone treatment and the emergence of the ether groups. Thus, a peak shift towards higher binding energy takes place.
Deconvolution of the O1s and N1s core-level spectra of the pristine hollow fiber corroborates that the oxygen and nitrogen are due to the amide group of the PVP polymer. The O1s spectra of the composite hollow fibers were fitted into four peaks, attributed to the sulfonate group, ether group and ester group. Interestingly, the peak at 534.5 eV is ascribed to CF2A\(\text{-O}\text{-CF}_2\), implying that a side reaction to crosslink the PVDF polymer chains may take place simultaneously. In addition, the N1s spectra of the composite hollow fibers conspicuously signify the presence of quaternary ammonium cations. Collectively, the XPS analyses produce a strong evidence for the successful graft copolymerization of zwitterions on the inner surface of the PVDF hollow fiber membrane.

3.4. Fouling behavior of the composite hollow fiber membranes

3.4.1. Effects of chain length on surface morphology and protein fouling

Fig. 8 compares the separation performance and fouling behaviors of the four PVDF composite hollow fiber membranes, mPVDF-1, mPVDF-2, mPVDF-3 and mPVDF-4. These membranes were prepared under the same conditions except different grafting durations. The PWP in Fig. 8(a) shows a slight down-and-up trend with an increase in grafting time. The decrease in PWP is expected since the increase in chain length may lead to partial blockage of surface pores. Fig. 9(a) shows a logarithmic trend of the sulfur-to-fluorine (S/F) ratio as a function of grafting time. The S/F ratio to the sulfonate group, ether group and ester group.

### Table 2

<table>
<thead>
<tr>
<th>Fiber ID</th>
<th>Ozone treatment time (min)</th>
<th>Zwitterion concentration (wt%)</th>
<th>Grafting temperature (°C)</th>
<th>Grafting time (h)</th>
<th>BSA rejection</th>
</tr>
</thead>
<tbody>
<tr>
<td>mPVDF-1</td>
<td>15</td>
<td>2.0</td>
<td>45</td>
<td>0.5</td>
<td>99.8</td>
</tr>
<tr>
<td>mPVDF-2</td>
<td>15</td>
<td>2.0</td>
<td>45</td>
<td>2</td>
<td>99.7</td>
</tr>
<tr>
<td>mPVDF-3</td>
<td>15</td>
<td>2.0</td>
<td>45</td>
<td>4</td>
<td>99.5</td>
</tr>
<tr>
<td>mPVDF-4</td>
<td>15</td>
<td>2.0</td>
<td>45</td>
<td>12</td>
<td>97.7</td>
</tr>
<tr>
<td>mPVDF-5</td>
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<td>2.0</td>
<td>45</td>
<td>2</td>
<td>99.2</td>
</tr>
<tr>
<td>mPVDF-6</td>
<td>5</td>
<td>2.0</td>
<td>45</td>
<td>2</td>
<td>99.4</td>
</tr>
<tr>
<td>mPVDF-7</td>
<td>30</td>
<td>2.0</td>
<td>45</td>
<td>2 (DI water)</td>
<td>98.5</td>
</tr>
<tr>
<td>Pristine PVDF</td>
<td>5 (Argon)</td>
<td>2.0</td>
<td></td>
<td></td>
<td>98.8</td>
</tr>
</tbody>
</table>
can be a precise cursor to determine the content of the grafted polySBMA polymer [29]. A substantial increase in sulfur content is observed in the first few hours. It continues to increase by about 30% from 4 h to 12 h, implying a much longer chain is accomplished. Notwithstanding, the grafting of zwitterionic polymer generally does not contribute much to the membrane resistance.

In order to examine the fouling behaviors of the four composite membranes in protein solutions, ultrafiltration experiments were carried out to get the time-dependent flux curves as depicted in Fig. 8(b). The fouling-induced resistances were calculated and compared in Fig. 8(c). Several observations can be made from these results. First of all, the irreversible fouling-induced resistance, $R_w$,
exhibits a significant decrease from mPVDF-1 to mPVDF-2. This is probably due to the insufficient grafting of mPVDF-1 as evidenced by its low S/F ratio in Fig. 9. However, the $R_r$ value of mPVDF-4 is abnormally high. Despite its higher S/F ratio, mPVDF-4 may suffer from some physical deformation during the grafting of SBMA on its surface [39,40]. As shown in Fig. 10, the surface of mPVDF-4 displays more ridges and valleys as well as bigger pores, which further illustrates the compromise of the surface structure. As a result,
some cracks may be created so that the pore plugging is magnified in this case. The lower BSA rejection in Table 2 also supports this conclusion.

Secondly, the reversible fouling-induced resistance, $R_r$, shows no significant change from mPVDF-1 to mPVDF-3, while a tremendous increase is observed for mPVDF-4. It has been reported that reversible fouling may be more sensitive to the surface structure, e.g. surface roughness and pore size, because it is originally derived from concentration polarization [7]. The troughs of a rougher surface would trap more foulants regardless of physical or chemical interactions. The surface roughness in Fig. 8(d) exhibits the same trend as $R_r$, suggesting a dominant role of surface structure on the reversible fouling.

As a result, the total fouling resistance, $R_t$, follows a down-and-up trend with grafting time. An increase in grafting time is probably associated with an increase in surface hydrophilicity, which consequently leads to higher hydration capacity. The decline in $R_t$ value, as witnessed by mPVDF-1, mPVDF-2, and mPVDF-3, agrees well with this hypothesis. The improvement in surface hydrophilicity leads to better fouling resistance given a constant surface roughness. Consequently, $FRR$ displays an exactly opposite trend to $R_t$. mPVDF-2 and mPVDF-3 exhibit the best flux recovery performance, about 70%. This is probably due to their higher hydrophilicity and lower roughness of the membrane surfaces. Therefore, the grafting time of 2 h was chosen for further studies.

### 3.4.2. Effects of grafting density on surface morphology and protein fouling

Grafting density is correlated to how many peroxides can be created during the ozone treatment. As discussed earlier, the number of peroxides, or called reactive sites, are determined by ozone treatment conditions. In order to yield a decent anti-fouling membrane, effects of ozone treatment time were investigated by comparing mPVDF-5, mPVDF-6, mPVDF-2 and mPVDF-7. A control fiber without zwitterionic grafting was also included for comparison. Fig. 11 summarizes the separation performance, fouling-induced resistances and surface roughness of the five membranes.

As can be observed in Fig. 11(a), mPVDF-5 and the control have very similar PWP values, while PWP drops slightly with further increase in ozone treatment time, suggesting that the zwitterionic grafting produces a minimal addition to the membrane resistance. The variations in the permeation flux of the BSA solution as a function of time were plotted in Fig. 11(b). The pristine hollow fiber shows the lowest permeation flux in the BSA solution. Fig. 11(c) compares their fouling-induced resistances. $R_t$ essentially remains consistent at about 20%, except for a marginally higher value for mPVDF-5. As aforementioned, surface roughness is a crucial factor for the formation of reversible fouling. This conclusion is once again confirmed by the similar surface roughness data in Fig. 11(d). On the other hand, $R_t$ dramatically decreases to a minimum from the pristine one to mPVDF-6. This is owing to the
Fig. 11. (a) PWP, (b) Membrane fouling behaviors in BSA solutions, (c) Calculated membrane resistances and (d) Surface roughness of the pristine and composite hollow fiber membranes as a function of ozone treatment duration.

Fig. 12. Inner surface morphology of (a) Pristine PVDF, (b) mPVDF-5, (c) mPVDF-6, (d) mPVDF-2, (e) mPVDF-7 hollow fiber membranes.
formation of a hydration layer on membrane surface that provides better resistance against protein adsorption and minimises pore plugging. Insufficient grafting may occur for mPVDF-5. The ozone treatment time is probably too short to form enough peroxides. Thus, the grafting of zwitterions is substantially limited, as can be evidenced by its low S/F ratio in Fig. 9. On the other hand, a longer ozone treatment time seems to deteriorate the antifouling properties, especially for mPVDF-7 with a Rf value up to 33%. This is due to the degradation of the polymer chains in an oxidized ozone environment [17,42]. As a result, the integrity of the membrane surface may be deteriorated. Fig. 12 illustrates the inner surface morphology of the pristine and composite hollow fibers. More visible pores can be found on the surface of mPVDF-7, which renders the membrane more susceptible to pore plugging of foultants. Due to the same reasons, the BSA rejection of mPVDF-7 becomes lower than the others as shown in Table 2.

The total fouling resistance, Rf, shows a minimum value at the optimized ozone treatment time of 5 min. It is 50% lower than that of the pristine hollow fiber. Accordingly, the mPVDF-6 exhibits the highest FRR, about 85%, which is a substantial improvement to the pristine hollow fiber membrane. These results collectively suggest that protein fouling of the inner-selective PVDF hollow fiber can be substantially suppressed via the graft copolymerization of SBMA zwitterions under an appropriate grafting strategy.

4. Conclusions

With the imminent demands and great interest to immobilize zwitterionic polymers on the lumen surface of PVDF hollow fiber membranes, we have systematically studied the key parameters in order to manipulate the grafting density and chain length during graft copolymerization of polySBMA. The content of the grafted polySBMA on PVDF membranes exhibits logarithmic relations to the grafting time and ozone treatment time, respectively. Even though a higher grafting content may result in a higher hydration capacity, and hence, lower fouling tendency, the fouling-induced resistance shows a maximum trend as a function of grafting duration and collapse of membrane bulky structure. As a result, accented surface endows the membrane with a higher susceptibility to protein fouling. The effects of ozone treatment time display similar trend on fouling activities because excessive ozone renders PVDF degradation and creates large pores, which compromises the antifouling properties due to pore plugging of foultants. It was found that 5-min ozone pre-activation and 2-h SBMA graft copolymerization produce the optimal anti-fouling hollow fiber membrane without sacrificing its separation performance. The FRR increases by 84.7% in comparison to the pristine PVDF hollow fiber membrane.

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References


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