Preparation and characterization of fouling-resistant composite membranes based on layer-by-layer self-assembly technique

J. L. Duan, H. M. Zhang, C. C. Wang, H. Y. Li and F. L. Yang

ABSTRACT

This paper introduces a versatile approach for surface modification of 621-terylene filtration fabric (FF) self-assembled by a dynamic layer-by-layer technique. The hexadecyl trimethyl ammonium bromide (HTAB) and cross-linked polyvinyl alcohol microspheres (PVA-MS) were alternatively deposited on support membrane under a pressure of 0.01 MPa to modify FF. Morphological changes and hydrophilicity of the modified FF were characterized in detail by scanning electron micrograph and water contact angle measurements. Results revealed that PVA-MS could be adsorbed mainly on the surface of FF and water contact angle decreased with the increase of HTAB/PVA-MS bilayer numbers indicating an enhanced hydrophilicity for the modified FF. Backwash experiments of the modified FF exhibited much higher stability of PVA-MS. Protein adsorption experiments were conducted to evaluate the antifouling property of the modified FF. Results indicated that protein adsorption of the membrane surface could be obviously improved by modification, which exhibited superior antifouling property of the modified FF.

Key words | composite membranes, filtration fabric, fouling-resistant, modification, self-assembly

INTRODUCTION

The membrane bioreactor (MBR) system is a biological treatment process that coupled a membrane separation process in order to biologically treat wastewater and physically separate solid and liquid in an integrated step (Kornboonraksa & Lee 2009). The use of membrane filtration technology has been advancing at a rapid pace in replacing the conventional wastewater treatment processes to produce high quality treated water, and MBR is becoming an innovative and promising option for wastewater treatment and water reuse (Kim & Jang 2006; Tang et al. 2009). However, membrane fouling is a major obstacle to the wide application of MBRs. Additionally, large-scale use of MBRs in wastewater treatment will require a significant decrease in price of the membranes.

Membrane fouling is often caused by irreversible deposition of organics in the feed water on the hydrophobic membrane surface, which will result in water flux loss and solute selectivity change with time (Kwon et al. 2008). With respect to the prevention of membrane fouling, less hydrophobic membranes are normally favored, but hydrophilic membranes are susceptible to chemical and thermal impact in their application (Zhang et al. 2008). Recently, microporous membranes, microfiltration and ultrafiltration membranes are commonly employed in commercial MBR processes (Chang et al. 2007). However, the high cost of membrane materials limits its further applications. Less expensive filtration fabric (FF) with larger pores can be used as an alternative to microporous membranes. However, FF is relatively non-wettable with water, and the potential application in aqueous fluid is limited. Therefore, there is much interest in the modification of the FF surface to improve their hydrophilicity and functionalize membrane surface. To obtain a hydrophilic surface with anti-fouling property, several methods have been investigated including the dip coating process (Du & Zhao 2004), interfacial polymerization (Mohammad et al. 2003) and plasma-initiated polymerization (Aerts et al. 2006) etc., which can be divided into two classes: physical and chemical modifications. Compared with the above methods, the self-assembly polyelectrolyte on porous supports is a simple, versatile and environmental benign technique for making the composite membrane. Recent
studies have shown that the alternating layer-by-layer (LBL) adsorption of oppositely charged polyelectrolytes can be successfully applied to prepare ultrathin films of controlled thickness. In recent years, this technology has been applied to prepare composite membranes (Zhang et al. 2007; Ji et al. 2008).

The interactions between the membrane surface and charged foulants are affected by their electrostatic forces (Zhou et al. 2009). It is thus expected that electrostatic repulsion will help make the membrane less susceptible to fouling by foulants that have same charges as on the membrane surface. To improve their fouling resistance of membranes to negatively charged foulants of activated sludge (Choi et al. 2008), it is proposed to change charges on the membrane surface by electrostatic self-deposition of negatively charged polymer, so as to enhance the electrostatic repulsion between membranes and foulants. As the modified material, cross-linked polyvinyl alcohol microspheres (PVA-MS) with highly negative charges, which were self-made via an emulsion polymerization, showed highly anti-fouling characteristics in the MBR (Ye et al. 2007; Cui et al. 2008). In this paper, dynamic LBL technique instead of static LBL technique was used to assemble the polyelectrolyte composite membranes aiming to simplify the LBL procedure (Zhang et al. 2006). Different from the previous study, hexadecyl trimethyl ammonium bromide (HTAB) and PVA-MS were alternatively deposited on FF support membrane. The objective of this study was to characterize the anti-fouling property of the modified FF. The morphology and hydrophilicity of the modified FF were characterized by scanning electron microscopy (SEM) and contact angle goniometer, respectively. Stability of PVA-MS on the surface of self-assembly composite membranes was also studied. Protein adsorption experiments were conducted to evaluate the antifouling property of the modified FF.

**MATERIALS AND METHODS**

HTAB with the molecular weight of 364.36 was purchased from Tianjin Guangfu Fine Chemical Institute (China). PVA-MS with the average particle size and zeta potential of 412.16 nm and −58.6 mV were self-made via an emulsion polymerization. 621-Terylene FF was obtained from Zhejiang Lufeng Co. Ltd. (China) with the mean pore diameter of 18.19 μm. Bovine serum albumin (BSA) was obtained from Beijing Aoboxing Co. Ltd. (China) with molecular weight being 60,000.

**Composite membrane preparation by dynamic LBL process**

As shown in Figure 1, the preparation of multilayer membranes was carried out by using a 500 mL stirred dead-end filtration cell with ~19.6 cm² membrane area. Aqueous HTAB and PVA-MS solutions with the suitable concentration of 20 and 400 mg/L (Ye et al. 2008), respectively, were prepared by dissolving the polymer in distilled water and then ultrasonic dispersion until homogeneous. The modified FF membrane was accomplished by filtering the polycation HTAB and polyanion PVA-MS alternatively during a predetermined period of filtration. The following steps were orderly carried out: (a) HTAB solution was poured into the stirred cell in which a support membrane had been loaded, and was pressured through the membrane under a pressure of 0.01 MPa for 8 min. (b) The membrane was taken out, briefly rinsed with deionized water for ~10 min and dried in an oven at 55 °C for 30 min. (c) PVA-MS solution was poured into the stirred cell and pressured under a pressure of 0.01 MPa for 10 min. (d) The same way as (b). Steps (a)–(d) were repeated up to the predetermined times. Upon the formation of composite membranes, the preparation of multilayer membranes with different HTAB/PVA-MS bilayer numbers were stored for successive experiments.

**Membrane characterization**

**Morphology observation**

The morphologies of the surface of membranes were examined by a scanning electron microscope (Zhongke, KYKY-2800B, China). Image magnifications were 50× and 500× for surface views. All specimens were freeze-dried and coated with a thin layer of gold before observation.

**Contact angle measurement**

The dynamic contact angle between water and the membrane surface was measured to evaluate the membrane

![Figure 1](https://iwaponline.com/wst/article-pdf/64/11/2223/444126/2223.pdf)
hydrophilicity by Wilhelmy plate method, using a contact angle goniometer (Cahn, DCA-32, USA). Both the advancing and receding contact angles could be measured with it. The dipping time was 100 s and penetration depth was 4.0 mm. Prior to the measurements, the samples were dried under vacuum at 75 °C for 24 h. Each contact angle reported was the mean value of several measurements at different samples of membranes, and the standard deviation was within 5%.

**Zeta potential measurement**

The zeta potential measurements were performed using electrophoresis and streaming potential techniques. Zeta potential of the modified membranes were measured by self-made analyzer equipped with a plated sample cell. The detail of the experimental setup was shown in published reference (Ye et al. 2008). Membranes were cut circularly with the diameter of 5 cm. The measurements were carried out at 20 °C in KCl solution. Zeta potential measurements were obtained at pH 8 ± 0.2 and calculated using the Helmholtz–Smoluchowski equation.

**Membrane mean pore diameter determination**

Mean pore size measurements, which were measured by the extrusion flow porometry method (Jena & Gupta 2001), were conducted on a capillary flow porometer (Qixinghuachuang, 007-19BM, China) with nitrogen gas as a working gas. In each case a diameter of 5 cm long specimen was used after cleaning and drying.

**Membrane performances**

Membrane hydraulic permeability has got significance particularly for membranes used in pressure-driven separation processes. Membrane permeability was determined by allowing deionized water to pass through the compact membrane. Flux values of pure water at different transmembrane pressures (ranging 0–40 kPa) were measured under steady state condition using the following equation:

\[ J_w = \frac{Q}{AT} \]

where \( J_w \) is pure water flux (m³ m⁻² h⁻¹), \( Q \) is volume of water permeated (m³), \( A \) is effective membrane area (m²) and \( T \) is sampling time (h).

**Protein adsorption experiments**

BSA was used as a model protein to evaluate the fouling resistance of the membrane. A membrane of 5 cm in diameter was rinsed with phosphate-buffered solution (PBS), and then soaked in BSA solutions of 1.00 g/L at 30 °C for 24 h. pH was maintained at 6.9 with PBS (composed of 149.76 g NaCl, 4.02 g KCl, 4.56 g NaH₂PO₄ and 23.00 g Na₂HPO₄). Protein concentrations were determined spectroscopically at 280 nm using a UV/VIS spectrophotometer (Shimadzu, UV-2450, Japan). By comparing the initial and the later concentrations, the adsorption amounts could be calculated. The calibration curves and equations of absorbance versus BSA concentrations in fixed working conditions were obtained by linear fit.

**RESULTS AND DISCUSSION**

**Morphologies of composite membranes**

SEM images of composite membranes prepared with different HTAB/PVA-MS bilayer numbers are shown in Figure 2. A n amount of PVA-MS adsorbed on the outer surface and partly embedded on the pore surface of composite membranes compared with nascent FF. It could be seen that the structure of composite membranes was not obviously different with the increase of HTAB/PVA-MS bilayer numbers. Moreover, the higher PVA-MS content induced a slight aggregation phenomenon. As presented in Figure 2, the composite membrane had an unsymmetrical layered structure: a macroporous support layer and a porous active layer. The porous active layer is responsible for permeation and retention of solutes whereas the macroporous support layer acts as a mechanical support (Rahimpour et al. 2009). Therefore, composite membranes using HTAB/PVA-MS as active layer and FF as support layer were successfully self-assembled by a dynamic LBL technique.

**Enhancement of membrane surface hydrophilicity**

The nascent FF membrane is hydrophobic, and a hydrophilic membrane surface is desirable because not only it is better for water flux but also it could reduce fouling by various hydrophobic foulants. Therefore, surface hydrophilicity is one of most important factors to the filtration membrane and much attention has been paid to it (Li et al. 2009). In this study, hydrophilicity of the modified FF composite membrane was quantified by measuring the contact angle after modification. As a droplet of ultrapure water was used to measure the contact angle, smaller angles indicate greater hydrophilicity.
Mean values of contact angles obtained from these samples are presented in Figure 3. The modified FF with dynamic contact angle values ranging from 70.11° to 41.46° depended on the HTAB/PVA-MS bilayer number. These values were much lower than for the unmodified FF (116.4°). The increase in hydrophilicity of modified FF with more bilayer numbers was attributed to the increase of PVA-MS. This is due to the presence of PVA-MS which contain a great deal of hydroxyl groups, responsible for the hydrophilicity increase. The decrease of water contact angles clearly indicated that the introduction of PVA-MS could significantly enhance the hydrophilicity of FF.

Zeta potential of the composite membrane

As mentioned above, HTAB/PVA-MS composite membranes were prepared in order to enhance the electrostatic repulsion between the membrane and foulants. The zeta potential values of the unmodified and modified FF membranes were measured at pH 8 ± 0.2. As shown in Figure 4, the absolute values of negative surface charges increased significantly with the increase of bilayer numbers. And more bilayer numbers resulted in more PVA-MS adsorbing on surface of the composite membrane. Thus, it was plausible that PVA-MS with more hydroxyl groups increased negative surface charges of composite membranes. The substantial changes in the zeta potential of the modified membranes proved that membrane surface was significantly changed by modification.

Permeation properties of composite membranes

Pure water permeability as a function of various transmembrane pressures is plotted in Figure 5. Increasing transmembrane pressure resulted in enhanced water fluxes, which was a characteristic of micro-filtration membrane.
Meanwhile, pure water permeability was significantly decreased with the increase of bilayer numbers. These results were clearly in good agreement with the membrane structures observed by SEM images and mean pore diameter results. The mean pore size of the membrane was declined from 18.19 μm for nascent FF membrane to 7.27, 3.88 and 2.80 μm for composite membranes prepared with one, three and eight bilayers, respectively. Results indicated that the composite membrane with micro-structure in surface area was successfully formed by a dynamic LBL technique. For the modified membranes, the hydrophilicity and morphology which are two major variations in membrane characteristics affect the membrane performance in two different ways. The former enhances the flux due to increase membrane hydrophilicity and the latter diminishes the flux due to lower membrane pore size (Rahimpour et al. 2009). Based on the reasoning, the results obtaining from the above demonstrated that morphology predominated the membrane performance by PVA-MS modification.

### Short-term stability test of composite membranes

The stability of PVA-MS on the surface of the composite membrane is very important to keep hydrophilicity of self-assembly membranes. It is unavoidable that some of PVA-MS fall from membrane surface and the hydrophilicity is decreased during the filtration process. Backwash experiments of composite membranes were conducted to investigate the stability of PVA-MS on the membrane surface, and changes of flux and dynamic contact angle were measured. Table 1 presents pure water flux and dynamic contact angle changes of composite membranes before and after backwash experiments. No significant change in pure water flux or dynamic contact angle was observed even after two hours’ backwash at the trans-membrane pressure of 0.04 Mpa, which indicated an excellent stability of PVA-MS on the modified FF composite membranes.

### Static protein absorption property

BSA adsorption tests were conducted to find out the membrane fouling potential caused by the membrane surface-protein interaction. Figure 6 shows BSA absorption amount of composite membranes with different HTAB/PVA-MS bilayer numbers in the batch tests. For the nascent FF, a large amount of BSA was adsorbed on the surface. However, the BSA adsorption was suppressed after modification with PVA-MS. The amount of BSA adsorption on unit membrane surface area decreased sharply with the increase amount of PVA-MS. The modified FF obtained in this work had a small adsorption capacity for BSA. These results indicated that protein adsorption of FF could be improved obviously by the immobilization of PVA-MS, which might be attributed to the hydrophilicity and

![Figure 5](image5)  
**Figure 5** | Pure water flux of the unmodified and modified FF as a function of trans-membrane pressure.

![Figure 6](image6)  
**Figure 6** | BSA absorption amount of the unmodified and modified FF.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Short-term stability test of the modified FF composite membrane before and after backwash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bilayer number</td>
<td>Before backwash</td>
</tr>
<tr>
<td></td>
<td>$J_w$ (m$^3$ m$^{-2}$ h$^{-1}$)</td>
</tr>
<tr>
<td>1</td>
<td>10.23</td>
</tr>
<tr>
<td>3</td>
<td>5.36</td>
</tr>
<tr>
<td>8</td>
<td>2.97</td>
</tr>
</tbody>
</table>

*Pure water flux measured at 40 kPa.*
electronegativity of PVA-MS. Thus, the PVA-MS modified FF had an enhancing tendency toward anti-fouling property as the amount of PVA-MS increased. Although the immobilized PVA-MS might obstruct pores of FF and led to the decrease in both pore size and porosity, the immobilization of PVA-MS onto the FF surface produced a more hydrophilic and electronegative surface, which improved anti-fouling property of FF.

CONCLUSIONS

621-Terylene FF was modified by the dynamic LBL self-assembly method to immobilize PVA-MS on the surface. This study revealed that PVA-MS on the surface could significantly alter the surface properties of FF by changing surface physical and chemical characteristics. SEM pictures demonstrated that PVA-MS could be adsorbed mainly on the surface of FF. The modified FF with dynamic contact angle values ranging from 70.11 to 41.46° were much lower than for the unmodified FF (116.4°), indicating that the hydrophilicity of the modified FF was enhanced with the increase of HTAB/PVA-MS bilayer numbers. Backwash experiments of composite membranes exhibited much higher stability of PVA-MS. BSA adsorption experiments revealed that the modified FF composite membrane had a smaller adsorption capacity for BSA in comparison of the nascent FF. The amount of BSA static absorption on the modified FF with eight bilayers was decreased by 85.9%, which exhibited superior anti-fouling property of the modified FF.

ACKNOWLEDGEMENTS

Financial support from the Program for New Century Excellent Talents in University (NCET-07-0141) is gratefully acknowledged.

REFERENCES


First received 3 September 2009; accepted in revised form 21 January 2010