Regular Article

Versatile polyvinylidene fluoride hybrid ultrafiltration membranes with superior antifouling, antibacterial and self-cleaning properties for water treatment

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Graphical abstract

Article info

Article history:
Received 27 March 2017
Revised 23 May 2017
Accepted 23 May 2017
Available online 24 May 2017

Keywords:
N-halamine
Siloxane
multi-walled carbon nanotubes (MWNTs)
Antibacterial
Self-cleaning

Abstract

Novel ultrafiltration membranes with both superior antibacterial and self-cleaning properties were fabricated. By using a non-solvent induced phase separation method (NIPS), N-halamine epoxide and siloxane were grafted onto the multi-walled carbon nanotubes (N-Si-MWNTs) to fabricate polyvinylidene fluoride (PVDF) hybrid membranes. The membrane morphology was observed under a field emission scanning electron microscopy. The results demonstrated that the PVDF hybrid membranes had an asymmetrical structure, and their hydraulic permeability was evidently enhanced with the addition of modified MWNTs. When compared with the primitive PVDF membrane, the hybrid membranes presented improved surface hydrophilicity. After three ultrafiltration–regeneration cycles with bovine serum albumin as model biofoulant and pure water as detergent, the PVDF hybrid membranes exhibited a high flux recovery ratio (FRR). Furthermore, when compared with other membranes, the membrane containing N-Si-MWNTs displayed the highest FRR value of above 96.5% after the entire fouling and cleaning experiment. The fabricated PVDF/N-Si-MWNTs hybrid membranes had excellent antibacterial efficacy, presenting maximum antibacterial efficacy of 98.0% and 95.6% against Staphylococcus aureus and Escherichia coli, respectively. Thus, the PVDF/N-Si-MWNTs membranes fabricated in this study are environment-friendly with both benign antibacterial and self-cleaning properties.

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1. Introduction

Ultrafiltration technology has been widely used as an effective approach for applications in drinking water treatment and waste water drainage and reuse treatment. However, membrane fouling, including biofouling and organic fouling, decreases the ultrafiltration efficiency and shortens membrane life. Therefore, membrane surfaces with both superior antibacterial and self-cleaning properties are the most attractive owing to their long-standing diverse functions. Moreover, fabrication of novel membranes based on these features would promote surface-governed or surface-based technologies for industrial, medical, environmental, and marine applications. The key to achieve superior antibacterial and self-cleaning properties is to design rational material and prepare applications. The key to achieve superior antibacterial and self-cleaning properties is to design rational material and prepare applications. The key to achieve superior antibacterial and self-cleaning properties is to design rational material and prepare applications.

Various approaches have been employed to fabricate anti-fouling and self-cleaning membranes. For example, zwitterionic monomer ([3-(methacryloyl)amino]propyl)-dimethyl(3-sulfopropyl) ammonium hydroxide inner salt), and side-chain fluorinated methacrylate monomer with sodium dodecyl sulfate (SDS) as emulsifier were used to prepare amphiphilic copolymers via aqueous phase emulsion polymerization, and the product was used as an additive to fabricate antifouling and self-cleaning membranes. The permeation flux recovery of the resultant membranes reached nearly 100% [6]. In another study, hydrophilic poly (ethylene oxide) (PEO) and polydimethylsiloxane (PDMS) segments were constructed via free-radical polymerization. The resultant fabricated membranes presented antifouling and self-cleaning properties, and also exhibited a visible decline in irreversible and reversible flux and complete retention of permeation flux recovery [7].

Nowadays, polyvinylidene fluoride (PVDF) is widely used for the development of ultrafiltration membrane owing to its good chemical resistance, thermal and hydrolytic stability, and mechanical strength. However, its hydrophobicity often leads to organic fouling and biofouling. Several nanofillers such as aluminum oxide, titanium dioxide nanoparticles, zinc oxide, silicon oxide, and silver nanoparticles have been utilized to modify PVDF membranes [8–16], and have presented positive effects on membrane properties.

In recent years, MWNTs have been considerably used in modifying membranes because of their outstanding properties such as high specific area, prominent mechanical properties, and workability [17–20]. Nevertheless, crude MWNTs are difficult to disperse in casting solution owing to electrostatic influence, and opportune chemical modifications have been used to overcome this limitation. Strong acid has been commonly utilized to oxidize MWNTs and increase their dispersion and workability [21–24].

Current metal ions, quaternary ammonium salts, and N-halamines are widely employed to fabricate antimicrobial membranes. Among them, N-halamines are outstanding antibacterial agents owing to their excellent stability, biocidal efficacy, low toxicity, low corrosion of surfaces, and relatively economical properties [25–28]. Several tethering, grafting, and polymerization methods have been employed to anchor the antibacterial N-halamine moiety to membrane surfaces [4]. In general, chemical cleaning is commonly used to regenerate fouled membranes. Although chemical cleaning usually achieves a relatively high pure water flux recovery ratio (FRR), it destroys membrane properties and structure. Membrane cleaning with pure water alone may not achieve the desired FRR, and low surface energy architecture is generally employed in self-cleaning surfaces. For instance, hydrophobic polymers such as silicone-based and fluorinated polymers have been widely used through coating or grafting [29–31]. The mechanism of self-cleaning is to prevent the deposition and adsorption of foulants. As low surface energy architecture could decrease the interaction between membrane surfaces and foulants, the foulants could be rinsed using low water pressure, which has been generally recorded as fouling release [32,33]. Some of the recent representative studies on antifouling, self-cleaning, or antibacterial membranes are summarized in Table 1.

In the present study, novel PVDF ultrafiltration membranes simultaneously possessing antifouling, antibacterial, and self-cleaning properties were fabricated. In brief, MWNTs were oxidized by nitric acid steam (O-MWNTs), grafted with N-halamine and siloxane (N-Si-MWNTs), and used as nanofillers to fabricate PVDF hybrid membranes by non-solvent induced phase separation method (NIPS). Addition of N-halamine (derived from 5, 5-dimethylhydantoin) and siloxane ensured both antibacterial and self-cleaning properties. The effects of N-Si-MWNTs addition on the morphology, permeation, antibacterial performance, and self-cleaning efficiency of the final fabricated membranes were studied. To confirm the self-cleaning property of the resultant membranes, deionized water was used to rinse the fouled membranes. The bacteriostatic rates of the fabricated membranes were evaluated.
against Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli*.

2. Materials and methods

2.1. Materials

Commercial grade PVDF powder (FR904) used as membrane material was obtained from Shanghai 3F New Material Co. Ltd. (China). 1-methyl-2-pyrrolidone (NMP) and polyvinyl pyrrolidone (PVP, M<sub>n</sub> = 24,000 Da) were purchased from Shanghai Aladdin Chemical Agent Co. Ltd. (China). 3-chloropropyltriethoxysilane and sodium hypochlorite with 6–14% active chlorine content was purchased from Shanghai Aladdin Chemical Agent Co. Ltd. (China). 5,5-dimethylhydantoin used as a template was obtained in a two-step process (Scheme 1) [39]. Briefly, 0.05 mol 5,5-dimethylhydantoin and 0.05 mol NaOH were dissolved in 50 mL of acetone and isopropyl alcohol and stirred for 12 h at 70 °C. Next, the crude 5,5-dimethylhydantoin epoxide was dissolved in 50 mL of acetone and isopropyl alcohol and stirred for 12 h at 70 °C. The obtained 3-glycidyl-5,5-dimethylhydantoin was obtained as an oil.

2.4. Preparation of N-Si-MWNTs

N-Halamine-containing MWNTs (N-MWNTs) were prepared from O-MWNTs as follows. First, the O-MWNTs were dispersed in 10% 3-glycidyl-5,5-dimethylhydantoin solution with 1% NaOH for 30 min at 60 °C and sequentially cured at 60 °C for 1 h and 150 °C for 10 min. The subsequent procedure for N-MWNTs synthesis was similar to that illustrated in Scheme 1. The obtained N-MWNTs were soaked in 6 wt% 3-chloropropyltrithoxyxilane aqueous solution for 15 min and cured for 1 h at 90 °C (Scheme 2) to achieve the final functionalized MWNTs (denoted as N-Si-MWNTs).

2.5. Preparation of PVDF hybrid membranes

The casting solutions were prepared with 16 wt% PVDF, 2 wt% PVP, and 0.3 wt% various functionalized MWNTs (O-MWNTs/N-MWNTs/N-Si-MWNTs) (Table 2), and the residual was balanced with NMP solvent. Homogeneous casting solutions were obtained by stirring for 12 h at 70 °C, followed by degassing for at least 6 h. The PVDF hybrid membranes were fabricated at 25 ± 1 °C via NIPS. A casting knife with a clearance of 200 μm was used to spread the casting solution, and the crude films were immediately immersed in coagulation liquid (deionized water) at 25 ± 1 °C. All the fabricated membranes were immersed in deionized water for 24 h to remove the residual solvent.

<table>
<thead>
<tr>
<th>Refs</th>
<th>Year</th>
<th>Material</th>
<th>Pure water flux (L m&lt;sup&gt;-2&lt;/sup&gt; h&lt;sup&gt;-1&lt;/sup&gt; bar&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>FRR (%)</th>
<th>Rejection ratios (%)</th>
<th>Antibacterial rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liu [34]</td>
<td>2013</td>
<td>PVDF graft amphiphilic copolymer</td>
<td>126.6</td>
<td>89.2</td>
<td>93.8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>/</td>
</tr>
<tr>
<td>Duan [35]</td>
<td>2015</td>
<td>PES/Cu NPs @HNTs</td>
<td>212</td>
<td>/</td>
<td>&gt;80&lt;sup&gt;b&lt;/sup&gt;</td>
<td>94.5 (E.coli)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Li [36]</td>
<td>2014</td>
<td>PES-g-HPG</td>
<td>/</td>
<td>&gt;94</td>
<td>/</td>
<td>93.7 (E.coli)</td>
</tr>
<tr>
<td>Li [37]</td>
<td>2011</td>
<td>PES-PDA</td>
<td>81.6</td>
<td>94.5</td>
<td>76.7&lt;sup&gt;c&lt;/sup&gt;</td>
<td>/</td>
</tr>
<tr>
<td>Chen [38]</td>
<td>2013</td>
<td>PES/HNTs-CS@Ag</td>
<td>375.6</td>
<td>87.6</td>
<td>/</td>
<td>94 (E.coli)</td>
</tr>
<tr>
<td>Zhao [6]</td>
<td>2013</td>
<td>PVDF/P(HFBM-SPP)</td>
<td>-92</td>
<td>-100</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Kang [3]</td>
<td>2016</td>
<td>PVDF/MWNTs-g-CDDAC</td>
<td>94.7</td>
<td>93.6</td>
<td>97.8</td>
<td>92.7 (E.coli)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Bovine serum albumin (BSA) rejection;  
<sup>b</sup> Polyethylene glycol (M<sub>n</sub> = 20,000 Da) rejection;  
<sup>c</sup> Orange GII rejection;  
<sup>d</sup> E. coli;  
<sup>e</sup> S. aureus;  
<sup>f</sup> Staphylococcus aureus.
under non-contact mode. In brief, the prepared membranes were cut into small squares, stuck on a glass substrate, and the roughness parameters of the membranes were quantified from the topography images with a scan size of 5 × 5 μm. The hydrophilicity of the PVDF hybrid membranes was measured by using sessile drop method on the outer surfaces with a contact angle analyzer (KRUS DSA30, Hamburg, Germany). The contact angle experiments were conducted using a 3.0-μL droplet at ambient temperature. The initial contact angle was used to illustrate the surface hydrophilicity of the membranes. The membrane porosity ε (%) was calculated by using gravimetric method [40] as follows:

\[
\varepsilon = \frac{w_d - w_l}{a \times l \times L} \times 100\%
\]  

where \(w_d\) and \(w_l\) are the weights of wet and dry membrane samples, respectively, \(a\) is the membrane effective area (m²), \(l\) is the membrane thickness (m), and \(d_w\) is the water density (0.998 g/cm³).

The BSA rejections of the membranes were measured using an indigenous ultrafiltration system [24–42]. The fabricated membranes were pre-pressured with deionized water for 30 min at 2.0 bar to obtain a stable permeation flux before the analysis. After measuring the pure water permeability, the permeation and rejections for 500-ppm BSA aqueous solution were determined. The permeation flux for BSA aqueous solution was recorded as \(J_{BSA}\). The rejections were calculated using Eq. (2). The pure water permeability, the permeation and rejection were calculated using Eqs. (6)–(9).

The BSA concentrations in the feed and permeate flows were determined by ultraviolet and visible spectrophotometer (UV–Vis) at 280 nm. The rejections were calculated using Eq. (2). The pure water permeability, the permeation and rejection were calculated using Eqs. (6)–(9).

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

\[
J_w = \frac{Q}{a \times l} \times 100\%
\]  

\[
\text{FRR}(\%) = \frac{J_w}{J_{BSA}} \times 100\%
\]

where \(R\) is the solute rejection, \(C_p\) and \(C_f\) are the concentrations of permeate and feed solutions, respectively, \(Q\) is the volumetric flow rate (m³/s), \(a\) is the valid membrane area (m²), \(J_w\) is the water flux of cleaned membrane after each cycle (m/s), and \(J_{BSA}\) is the initial pure water flux (m/s).

2.6.3. Resistance analysis

Darcy’s Law was used to analyze mass transfer resistances during the ultrafiltration process, which can be expressed using Eq. (5) [43–45].

\[
J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu (R_m + R_r + R_t)}
\]

where \(J\) is the membrane permeation flux in the filtration process (m/s), \(\Delta P\) is the transmembrane pressure (bar), \(\mu\) is the filtrate viscosity (Pa S), \(R_t\) is the total permeation resistance of membrane (m⁻¹), \(R_m\) is the intrinsic membrane resistance, \(R_r\) is the reversible resistance (m⁻¹), and \(R_i\) is the irreversible resistance (m⁻¹). Each resistance was calculated using Eqs. (6)–(9).

\[
R_m = \frac{\Delta P}{J_{BSA}}
\]

\[
R_r = \frac{\Delta P}{J_{BSA}}
\]

\[
R_i = \frac{\Delta P}{J_w} - R_m
\]

\[
R_e = R_i - R_r - R_m
\]

2.6.4. Oxidative chlorine content and antibacterial ability measurements

The standard iodometric/thiosulfate titration procedure was used to measure the immobilized oxidative chlorine on the mem-

Table 2

<table>
<thead>
<tr>
<th>Membrane no.</th>
<th>PVDF</th>
<th>PVP</th>
<th>O-MWNTs</th>
<th>N-MWNTs</th>
<th>N-Si-MWNTs</th>
<th>NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-0</td>
<td>16.0</td>
<td>2.0</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>82.0</td>
</tr>
<tr>
<td>M-1</td>
<td>16.0</td>
<td>2.0</td>
<td>0.3</td>
<td>/</td>
<td>/</td>
<td>81.7</td>
</tr>
<tr>
<td>M-2</td>
<td>16.0</td>
<td>2.0</td>
<td>/</td>
<td>0.3</td>
<td>/</td>
<td>81.7</td>
</tr>
<tr>
<td>M-3</td>
<td>16.0</td>
<td>2.0</td>
<td>/</td>
<td>/</td>
<td>0.3</td>
<td>81.7</td>
</tr>
</tbody>
</table>

Scheme 1. Synthetic route of N-MWNTs.

Scheme 2. Synthetic route of N-Si-MWNTs.

The standard iodometric/thiosulfate titration procedure was used to measure the immobilized oxidative chlorine on the mem-

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<image>
brane samples [46]. The membrane samples were immersed in 0.5% NaClO solution and the pH was adjusted to 7 using HCl solution. After 45 min, the membrane samples were rinsed with deionized water and dried naturally at ambient temperature. Subsequently, about 1.0 g of the membrane sample was cut into pieces and immersed in 150 mL of sulfuric acid solution (0.04 mol/L) containing 0.5 g of potassium iodide and 0.4 mL of starch solution (0.5 wt%, acted as an indicator). Then, the mixture was titrated with sodium hyposulfite (0.01 mol/L) until the color transformed from blue to transparent. The positive chlorines (Cl\(^+\)) content of the membrane sample was calculated using Eq. (10):

\[
Cl^+ = \frac{35.45 \times N \times V}{2 \times W} \times 100\%
\]  

where \(N\) is the normality (eq/L) of the consumed NaS\(_2\)O\(_3\) in titration, \(V\) is the volume (L), and \(W\) is the weight of the sample.

The bacteriostatic efficiencies of the membranes were determined by using spread-plate method [47–49]. The optical density of the nutrient broth at 600 nm was measured to test the variation in the bacterial concentration after the sample was placed in a shake flask for 24 h. E. coli and S. aureus were respectively inoculated into Luria-Bertani (LB) growth medium and incubated overnight under agitation (250 rpm) at 37 °C. The optical densities of the two bacterial cultures at 600 nm (OD\(_{600}\)) were determined and adjusted to 0.6 using normal saline. Then, the E. coli and S. aureus cultures were diluted to 10\(^4\) and 10\(^5\) CFU/mL, respectively. For antibacterial assay, 1 mL of the bacterial culture was spread onto the sample membrane surface. After different periods of contact time, the membrane samples were cut into pieces and suspended in Eppendorf tubes containing 9 mL of normal saline. Then, 0.1 mL of the suspension was dispersed onto LB agar plates and incubated at 37 °C for 24 h. After incubation, the bacterial colonies on the plates were enumerated, and the sterilization ratio was calculated using Eq. (11):

\[
E = \frac{(B - A)}{B} \times 100\%
\]  

where \(E\) is the sterilization ratio, \(A\) is the number of visible bacterial colonies with membrane contact, and \(B\) is the number of visible bacterial colonies without membrane contact.

3. Results and discussion

3.1. Characterizations of functionalized MWNTs

Fig. 1(a) shows the FTIR spectra of MWNTs, O-MWNTs, and N-Si-MWNTs. As shown in the figure, the shoulder at 1728 cm\(^{-1}\) and absorption peak at 1581 cm\(^{-1}\) for O-MWNTs corresponded to the vibrations of the –COOH groups, confirming that MWNTs were successfully oxidized [23]. The absorption peaks at 1718 cm\(^{-1}\) and 1766 cm\(^{-1}\) for N-Si-MWNTs corresponded to the carbonyl groups [50,51], and the bands at 1032 cm\(^{-1}\) could be attributed to Si–O, implying that the MWNTs were successfully functionalized with N-halamine and siloxane.

Fig. 1(b) illustrates the dispersion of MWNTs, O-MWNTs, and N-Si-MWNTs in deionized water for 7 days. Owing to high surface energy and nano size, the MWNTs tended to aggregate and completely settle at the bottom of the flasks [52]. On the contrary, the O-MWNTs and N-Si-MWNTs were well dispersed in deionized water. This could be owing to the interactions between water and hydrophilic group as well as formation of a protective layer of carboxyl and hydroxyl groups preventing direct aggregation in the case of O-MWNTs [23], and existence of halamine group that enhances dispersion in water in the case of N-Si-MWNTs.

The TGA curves shown in Fig. 2 indicate the thermal stability of MWNTs, O-MWNTs, and N-Si-MWNTs. MWNTs exhibited the best thermal stability and a decline in the TGA curve occurred at above 600 °C. With regard to O-MWNTs, the decline in the TGA curve could be divided into two sections. The first section below 250 °C could be attributed to the loss of adsorbed water and free water.
in O-MWNTs, and the second section above 450 °C with a rapid decline could be attributed to the thermolysis of O-MWNTs. In the case of N-Si-MWNTs, the weight showed a downward trend from the beginning. The first section of the TGA curve below 250 °C corresponded to the loss of adsorbed water and free water in N-Si-MWNTs, and the second section of the curve could be ascribed to the thermolysis of hydantoin group. Furthermore, the decline in the TGA curve above 530 °C could be ascribed to the decomposition of carbon nanotubes. When compared with the TGA curves of MWNTs and O-MWNTs, that of N-Si-MWNTs presented an obvious decline trend, implying that the MWNTs surfaces were successfully grafted with functional groups [3].

3.2. Morphologies of PVDF hybrid membranes

The FESEM images of the top surfaces, bottom surfaces, and cross-sections of the PVDF hybrid membranes are presented in Fig. 3. No distinct variations in the top surfaces were observed, and the top surfaces of all the membranes appeared smooth and flat. Owing to strong non-solvent effect, the phase separation process immediately occurred on the top surfaces when the cast films were immersed in coagulation liquid (water). The bottom surfaces of the membranes were porous. As a result, the bottom surfaces adhered onto the glass, thus delaying the phase separation process when immersed in coagulation liquid. The demixing behavior resulted from the finger-like holes through the entire cross-section, which produced asymmetrical structure. The cross-sections of the membranes could be roughly segmented into three layers: skin layer, finger-like porous sub-layer, and macrovoid layer.

The top surfaces of the membranes were examined by AFM, as shown in Fig. 4. The antifouling ability of the membranes was associated with surface roughness, and the corresponding roughness parameters are presented in Table 3. The decrease in the $R_a$ value from 9.79 nm (M-0) to 7.3 nm (M-1), 5.38 nm (M-2), and 4.49 nm (M-3) could be ascribed to the improved exchange of non-solvents and solvents during the phase inversion process owing to the addition of functionalized MWNTs [53]. It is generally accepted that membranes with flat surfaces possess higher antifouling ability [54]. The lower surface roughness could weaken the interaction between foulant and membranes. The $R_q$ values of the membranes evidently decreased with the introduction of modified MWNTs. Surface skewness ($R_{sk}$) is the evaluation of symmetry of high distribution. For M-1 and M-2, the negative $R_{sk}$ values corresponded to the dominance of valleys, whereas the positive skew values for M-0 and M-3 indicated that the peaks manage the surfaces. Surface kurtosis ($R_{ku}$) is a measure of the sharpness of height distribution. The $R_{ku}$ values below 3 for M-3 indicated a repetitive and smooth surface, while those greater than 3 for M-0, M-1, and M-2 suggested a sharp height distribution [55].

3.3. The initial water contact angle and porosity of membranes

It is well known that surface hydrophilicity distinctly influences the permeability and antifouling ability of membranes. Fig. 5 shows the water contact angles of the top surfaces of the membranes. M-0 exhibited the largest water contact angle, demonstrating that raw PVDF membrane without the addition of modified MWNTs displayed the highest hydrophobicity. In comparison, the contact angles of membranes with modified MWNTs evidently decreased, establishing that the hydrophilicity of the hybrid membranes was increased. Both M-1 and M-2 presented similar water contact angles and best surface hydrophilicity among all the membranes owing to the addition of O-MWNTs and N-MWNTs, which resulted in interactions between the hydrophilic moieties (such as $-\text{COOH}$, $-\text{R}_2\text{NH}$) of the modified MWNTs and water molecules.

![Fig. 3. The FESEM images top surfaces, cross sections and bottom surfaces of PVDF hybrid membranes.](image-url)
When compared with M-1 and M-2, the surface contact angle of M-3 was slightly increased owing to the introduction of silane groups with low surface energy in Si-N-MWNTs. The porosity of the PVDF hybrid membranes is presented in Fig. 6. It can be seen from the figure that the porosity increased with the addition of modified MWNTs as a result of enhanced precipitation rate, which was conducive for the formation of porous membrane matrix and surfaces [41].

### 3.4. Permeation and self-cleaning properties of PVDF hybrid membranes

Fig. 7 shows the permeation fluxes of the PVDF hybrid membranes. The pure water permeation flux of raw PVDF membrane (M-0) was 126.3 L·m⁻²·h⁻¹·bar⁻¹. When compared with M-0, the other three membranes presented higher fluxes (161.8, 165.8, 176.0 L·m⁻²·h⁻¹·bar⁻¹) for M-1, M-2, and M-3, respectively. The self-cleaning properties of the membranes were evaluated using the initial contact angle test, as shown in Fig. 5. The surface roughness parameters of the top surfaces of the PVDF hybrid membranes are listed in Table 3. The roughness parameters include the arithmetic mean roughness (Ra), surface skewness (Rq), and surface kurtosis (Rsk). The results show that the roughness parameters decreased with the addition of modified MWNTs, indicating improved self-cleaning properties.
and 173.7 L·m⁻²·h⁻¹·bar⁻¹ for M-1, M-2, and M-3, respectively) owing to the introduction of functionalized MWNTs in the membrane matrix. The lowest pure water permeation flux of M-0 could be attributed to the lowest surface hydrophilicity (Fig. 5) and lowest porosity (Fig. 6). Interestingly, the other membranes containing functionalized MWNTs presented similar pure water permeation fluxes varying from 161.8 to 173.7 L·m⁻²·h⁻¹·bar⁻¹. In general, the pure water permeation flux, BSA aqueous solution permeation flux, and recuperative pure water permeation flux presented an increase trend, which could be attributed to the addition of modified MWNTs.

The ultrafiltration–regeneration cycles of the PVDF hybrid membranes are illustrated in Fig. 8. After the filtration of BSA aqueous solution for a specific time period, the permeation fluxes of all the membranes sharply decreased owing to concentration polarization and membrane fouling. The FRRs of the membranes are listed in Table 4. When compared with the FRR value for M-3, those for M-0, M-1, and M-2 were much lower, especially in the third cycle. Besides, the FRR values for M-0, M-1, and M-2 gradually decreased in the three cycles, which were evidently different from those for M-3. M-3 exhibited the highest FRR value of above 96.5% after the entire ultrafiltration–regeneration cycles, which confirmed that the self-cleaning property of the PVDF/N-Si-MWNT membranes (M-3) evidently improved with the addition of N-Si-MWNTs owing to decreased adhesion, resulting in easy removal of foulants. From Table 5, it can be noted that all the membranes examined possessed high BSA rejections, suggesting that the addition of MWNTs had no effect on BSA rejection.

The filtration resistances of the PVDF hybrid membranes were used to illustrate the underlying mechanism, and were calculated using Eqs. (6)–(9) (Fig. 9). As shown in Fig. 9, the presence of modified MWNTs in the PVDF hybrid membranes significantly reduced the permeation resistances. When compared with the permeation resistance of M-0, the observably reduced permeation resistances of M-3 could be ascribed to the addition of N-Si-MWNTs that enhanced the hydrophilicity and porosity of the membranes, ensuring water flux. Besides, siloxane prevented the adsorption of foulants, thus providing the membrane with self-cleaning ability.

A structural model was proposed (Fig. 10) to elucidate the antifouling and self-cleaning mechanism of PVDF/N-Si-MWNTs hybrid membranes. The PVDF/N-Si-MWNTs membrane surfaces presented optimal hydration energy and surface free energy, owing to the presence of hydrophilic groups (oxygen-containing functional groups and halamine groups), as well as low surface energy brushes. As shown in Fig. 10, the protective hydration layer on the surface of the PVDF hybrid membranes effectively prevented direct interaction between foulants and membrane surfaces comprising hydrogen bonds. However, as indicated in Fig. 10(b), removal of some intractable adsorption of irresistible fouling on the membrane surface by rinsing with water was difficult, which was further ameliorated by convective flow-through membranes. Incorporation of low surface energy fouling-release moieties on membrane surfaces could offer the possibility of fabricating a superior antifouling surface. The final chemical structure could decrease the entropic and enthalpic driving forces for the adsorption of foulants and promote removal of the adsorbed foulants from the surfaces at moderate shear rate (Fig. 10(d)). These desired fouling-release properties could reduce both reversible and irreversible fouling and achieve high FRR with water rinsing [7].

3.5. Oxidative chlorine content and antibacterial measurement

The release of Cl⁻ from N-halamine in N-MWNTs and N-Si-MWNTs contributed to the antibacterial ability of the membranes [56,57]. The Cl⁻ contents in PVDF membranes are presented in Table 4. It can be observed from the table that the Cl⁻ contents in M-2 and M-3 were 0.17 and 0.20 wt% with the addition of N-MWNTs and N-Si-MWNTs, respectively, which contributed to the bacteriostatic efficiency of the membranes.

The antibacterial efficacies of the PVDF hybrid membranes were determined using the spread-plate method. As shown in Fig. 11, the bacterial colonies of M-0 (Fig. 11(a) and (c)) occupied a large area of the Petri dish, suggesting that the raw PVDF membrane possessed no antibacterial effect against S. aureus and E. coli. In contrast, the hybrid membrane M-3 containing N-Si-MWNTs presented a dramatic decline in S. aureus and E. coli colonies, with
98.0% and 95.6% antibacterial efficacy, respectively, demonstrating the antibacterial properties of PVDF/N-Si-MWNTs membranes against both Gram-positive and Gram-negative bacteria. Based on the two antibacterial tests, it can be concluded that the PVDF/N-Si-MWNTs hybrid membranes presented excellent antibacterial efficiency against *S. aureus* and *E. coli*.

### Table 5
The BSA rejection and the contents of Cl\(^-\) of PVDF hybrid membranes.

<table>
<thead>
<tr>
<th>Membrane no.</th>
<th>BSA rejection/%</th>
<th>Cl(^-) wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st</td>
<td>2nd</td>
</tr>
<tr>
<td>M-0</td>
<td>95.5 ± 3.5</td>
<td>96.1 ± 1.1</td>
</tr>
<tr>
<td>M-1</td>
<td>94.1 ± 2.1</td>
<td>96.2 ± 2.4</td>
</tr>
<tr>
<td>M-2</td>
<td>94.5 ± 2.5</td>
<td>95.0 ± 1.0</td>
</tr>
<tr>
<td>M-3</td>
<td>95.7 ± 3.4</td>
<td>96.8 ± 0.2</td>
</tr>
</tbody>
</table>

### 4. Conclusions

In the present study, novel versatile PVDF ultrafiltration membranes possessing both antibacterial and self-cleaning properties were fabricated. First, the MWNTs were modified with 3-glycidyl-5, 5-dimethylhydantoin and siloxane (N-Si-MWNTs), and then introduced onto the PVDF ultrafiltration membranes. The introduced modified MWNTs evidently enhanced the permeability, hydrophilicity, antibacterial property, and antifouling ability of the PVDF hybrid membranes. The hydraulic permeability of the membranes increased from 126.3 to 173.7 L·M\(^{-2}\)·h\(^{-1}\)·bar\(^{-1}\). During the BSA aqueous solution ultrafiltration–regeneration cycles, the PVDF/N-Si-MWNTs membranes showed an excellent FRR value above 96.5% even after three cycles, thus confirming the superior self-cleaning ability of these membranes. Furthermore, the fabricated PVDF/N-Si-MWNTs membranes presented outstanding antibacterial ability, with bacteriostatic efficacy reaching 98% and 95.6% against *S. aureus* and *E. coli*, respectively. The integrated properties including FRR values and bacteriostatic efficacy are evidently improved in comparison with the previous ultrafiltration membranes [34–38]. In conclusion, versatile PVDF ultrafiltration membranes with antibacterial, antifouling, and self-cleaning properties were successfully fabricated in this study, thus contributing to the field of membrane technology. The future study should be devoted to verifying the stability in antibacterial, antifouling and self-cleaning properties, and practical applications in water treatments.
Fig. 11. The antibacterial efficiency against S. aureus (a, b) and E. coli (c, d) of PVDF/N-Si-MWNTs membranes.

References


