Characterization and anti-fouling performance of nano-Al$_2$O$_3$/PVDF membrane for Songhua River raw water filtration

S. L. Yu, W. X. Shi, Y. Lu and J. X. Yang

ABSTRACT

Polyvinylidene fluoride (PVDF) flat ultrafiltration membranes modified by nano-sized alumina (Al$_2$O$_3$) particles were prepared by phase inversion process and their properties and anti-fouling performances were examined. The influence of three types of natural organic matters on the modified membrane fouling was also studied. Raw water was taken from two different locations, i.e., Harbin and Zhaoyuan, of Songhua River. Dissolved organic compounds in the raw water were fractionated using XAD resins into three fractions, i.e., hydrophobic fraction, transphilic fraction, and hydrophilic fraction (HPI). The three adsorbed compounds were further eluted and dissolved into distilled water respectively to prepare the feed for the fouling tests. All solutions were adjusted to a concentration of 10.6 mg C/L, which equals to the total organic carbon (TOC) of the raw water. Results show that the addition of nano-Al$_2$O$_3$ particulars did not affect the inherent traits of the PVDF membranes, however, its surface hydrophilic properties were improved significantly with the addition of nanoparticles and anti-fouling performance was enhanced as well. The HPIs in the Songhua River were the main foulant, causing more fouling to membrane than hydrophobic and transphilic matters.

Key words | anti-fouling, modified membrane, nano-Al$_2$O$_3$, organic pollutants, PVDF, ultrafiltration

INTRODUCTION

Ultrafiltration has been used extensively in many membrane separation processes. The membrane plays an important role in the separation processes. Polyvinylidene fluoride (PVDF) has become an important separation membrane material, as it possesses many good physical and chemical characteristics such as thermally stable and resistant to corrosion by most chemicals and organic compounds as well as easy processing. However, the inherent hydrophobicity of PVDF due to its structure leads to a low membrane flux and poor anti-fouling properties, as indicated by the contact angle as high as 83.64°, which have a great impact on its application and useful life.

Efforts have focused on increasing PVDF hydrophilicity either by chemical or physical modifications, such as physical blending, chemical grafting, and surface modifications. Of the aforementioned methods, blending with inorganic materials, especially nanoparticles, has attracted much interest due to their convenient operation and mild conditions. Several types of inorganic materials have been blended with PVDF such as silica (Bottino et al. 2001), zirconium dioxide (ZrO$_2$) (Bottino et al. 2002), Al$_2$O$_3$ (Lu et al. 2006). Lu et al. (2006) had reported effects of nano-Al$_2$O$_3$ addition on PVDF ultrafiltration membrane performance and indicated that Al$_2$O$_3$-PVDF composite membranes exhibit significant differences in surface properties and intrinsic properties due to nanoparticles addition. However, the anti-fouling performance of this novel membrane for raw surface water filtration is still poorly understood.

Natural organic matters (NOMs) in water represents abroad range of structural complex compounds such as humic and fulvic acids which derive from the degradation of plants and micro-organisms (Zularisam et al. 2007). NOM, which can be separated into hydrophobic fraction (HPO), hydrophilic fraction (HPI) and transphilic fraction (TPI) (Malcolm & MacCarthy 1992), is often recognized as major foulant of membrane systems (Nilson & DiGiano...
1996; Fan et al. 2001; Kimura et al. 2004). It has been suggested that NOM was the most important foulant due to its possible interaction between membrane surface and NOM. While the effects of different NOM fractions on the modified membrane anti-fouling performance is still kept unknown.

This research aimed to prepare Al2O3–PVDF composite membranes using the phase inversion method and to study the performance and properties of the modified membrane. The prepared membranes were also applied to filtration of raw water taken from Songhua River to investigate its anti-fouling performance to different NOMs fractions.

MATERIAL AND METHODS

Materials

The PVDF used was a commercial product (FR904). Dimethylacetamide (DMAC; >99%) was employed as the solvent. Alumina (Al2O3) particles (10 nm in size) were added to PVDF solutions. The other additives were sodiumhexad-phosphate and polyvinyl pyrrolidone (PVP). A mixture of distilled water and ethanol was used as the nonsolvents for the polymer precipitation.

Membrane preparation

PVDF was dissolved in the solvent DMAC to get 19% (m/m) casting dopes, which were further mixed with PVP and sodiumhexad-phosphate. Nano-Al2O3 was mixed with the casting dopes under stirring. To obtain optimal dispersions of the particles in the polymer solutions, agitation was required for at least 24 h. The casting solutions were then kept in the dark for 2–3 days to remove air bubbles. An appropriate amount of the dope was dispersed uniformly on a glass plate by the method of phase-inversion. After 1 min exposure to air, the glass plate was immersed in a bath filled with distilled water and ethanol for 24 h. The membranes formed were washed with distilled water and stock in distilled water for further application.

Characterization of membrane

The membrane permeation were tested in a UF (ultrafiltration) laboratory unit (effective area = 32.3 cm2) fed with distilled water at different transmembrane pressures (0.1–0.4 MPa). New membranes were used in each independent experiment to avoid unnecessary disturbances exerted by possible residual organic matter. The same unit was fed with proteins of different molecular weights (MWs), i.e., cell pigment C (MW12400), pepsin (MW35000), and bovine serum albumin (MW67000) to obtain the molecular-weight cut-off values of membranes. The membrane porosities were measured using dry–wet weight method. The contact angle between water and the membrane surface was measured with a contact-angle measurement apparatus (DSA10, American, needle point size = 1.5 mm) according to the sessile-drop method. The membrane surface morphology, in terms of the mean surface roughness (Ra), was studied by atomic-force microscopy (AFM, BioScopeTM, USA) using the tapping mode. Ra was defined as the average value of the surface relative to the center plane for which the volumes enclosed by the images above and below the plane were equal.

NOM fraction

NOM were fractionated into HPO, HP, and TPI according to organic matter hydrophilicity measured by a DAX-8 (Sigma-Aldrich) and XAD-4 resin. The resin clean-up procedure has been described by Leenheer (1981) and the fractionation operation has been described by other authors (Nilson & DiGiano 1996; Fan et al. 2001; Kimura et al. 2004). Briefly, raw water was first filtered by 0.45 μm membrane to remove particles and then its pH value was adjusted to 2 with HCl (1 mol/L) before the fractionation operation procedure. The filtered raw water was then forced through the DAX-8 and XAD-4 resin in turn. HPO was absorbed by DAX-8 and TPI was absorbed by Amberlite XAD-4. HPI passed through the two resins without any adsorption. NaOH (0.1 mol/L) was used to desorb organic matter from the two resins.

Analytical methods

Dissolved organic carbon (DOC) was measured by a TOC analyzer (TOCVPCH, Shimadzu). UV254 was determined by a UV spectrophotometer (UV755B, Shanghai 3rd Analytical Instruments). Foulants on the membrane surface were desorbed by NaOH (0.1 mol/L). The membranes were soaked in NaOH solution and stirred periodically for 1 day to desorb and dissolve the foulant components from the membranes. It was assumed that all the organic matters were desorbed and dissolved in NaOH when the membrane was in contact with NaOH solution for 24 h (Lee et al. 2001; Shon et al. 2006). By measuring the TOC of eluate, the mass of foulant could be known.
Table 1 | Water quality of raw water

<table>
<thead>
<tr>
<th>Parameters</th>
<th>HRB</th>
<th>ZY</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg L(^{-1}))</td>
<td>9.7</td>
<td>10.6</td>
</tr>
<tr>
<td>UVA(_{254}) (cm(^{-1}))</td>
<td>0.108</td>
<td>0.157</td>
</tr>
<tr>
<td>SUVA (m(^{-1}) mg(^{-1}))</td>
<td>1.11</td>
<td>1.29</td>
</tr>
</tbody>
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**Raw water pretreatment**

Raw water was collected from two sites, near Zhao Yuan (ZY) and Harbin (HRB) along Songhua River. The distance between the two sites is 195 km. Raw water was prefiltered through a 0.45 \(\mu\)m membrane to remove particles before using as feed to the UF unit. The raw water quality parameters are listed in Table 1.

**RESULTS AND DISCUSSION**

**Membrane characterization**

An original PVDF (PVDF-O) and a PVDF membrane modified by nano-Al\(_2\)O\(_3\) particles (PVDF-M) were used in this study. The properties of the membranes are listed in Table 2. As shown in the table, adding of nano-Al\(_2\)O\(_3\) caused a decrease of the contact angle from 83.64° to 57.42°, implying the improvement of the surface hydrophilicity of PVDF-M membrane. While the porosity, rejection, and MWCO (molecular weight cut-off) were not affected by the modification. The fluxes of PVDF-M were always higher than those of unmodified membranes PVDF-O, which was also attributed to the membrane hydrophilicity improvement due to the addition of nano-Al\(_2\)O\(_3\) into the PVDF. Stable flux of the PVDF-M membrane is 120 L m\(^{-2}\) h\(^{-1}\), which is much higher than that of the PVDF-O membrane, 38 L m\(^{-2}\) h\(^{-1}\). All these indicate that the permeability and anti-fouling performances of modified membrane are improved significantly.

**Figure 1** displays 3-D AFM images of the membrane surfaces. The surface roughness of PVDF-M was apparently higher than that of PVDF-O. In the scanned areas of 10 \(\mu\)m \(\times\) 10 \(\mu\)m, the Ra of the modified and unmodified membranes was 114.0 and 64.4 nm, respectively. Higher roughness commonly led to two changes in the modified membrane: an increase of efficient filtration area and a decrease of the anti-fouling performance. The enlarged efficient filtration area increases the membrane flux directly. The membrane-fouling trend increases with roughness owing to contaminants accumulating in the ‘valleys’ of the rough membrane surface. However, if the increase of roughness was caused by the accumulation of hydrophilic nano-Al\(_2\)O\(_3\), it can improve the membrane surface hydrophilicity and reduces the interaction between the contaminants and the membrane surface, and further the increased membrane hydrophilicity can enhance the anti-fouling performance and the permeate flux.

**Flux decline in ultrafiltration experiments**

**Figure 2** shows the relative flux of tests with raw water filtered by the PVDF-O and PVDF-M membranes. Flux of the PVDF-O membrane declined rapidly when raw water (HRB) was filtered. After 5 min of the test running, the flux was drop to 60% of the initial value, which was further decreased with the test lasting. While the flux declining rate of PVDF-M was much lower than that of the PVDF-O membrane; the flux declined to 60% of the original flux after 30 min running, implying the good anti-fouling performance of the modified membrane. Similar phenomenon was discovered when raw water (ZY) was filtered. The results revealed that the presence of nano-Al\(_2\)O\(_3\) enhanced the anti-fouling capability of PVDF-M, which might be due to the increase of membrane surface roughness and hydrophilicity.
The flux declined much faster in the tests with water (ZY) than the tests with water (HRB) at the beginning of the tests, implying that water (ZY) has a higher fouling potential than water (HRB). This might be due to the difference of the DOC content between those two water samples. Firstly, a high HPI DOC content might exhibit a high fouling potential (Amy 2008). Indeed, HPI fraction in ZY raw water account for 67% DOC, while for 63% in HRB raw water. Secondly, the large molecular weight fraction of NOM, which may have access to the inner structure of membrane pores and cause membrane fouling, contributed more to the formation of a fouling layer (Lee et al. 2004). In our previous research (Yang et al. 2009), we found the difference of molecular weight distribution in ZY and HRB raw water samples: DOC fraction with large molecular weight (≥30 kDa) only accounted for 5% of the total DOC in HRB water sample, while the percentage of this fraction in ZY water sample was as high as 15%, which might explain why ZY water caused more membrane fouling.

Anti-fouling performance of PVDF-M on different NOM fractions

NOM extracted by resins were dissolved into distilled water to prepare the feed for the fouling tests. For purpose of comparison and analysis, TOC in the prepared feed was adjusted to 10.6 mg/L, TOC concentration of raw water (ZY). As can be seen in Figure 3, HPI showed the highest fouling potential when PVDF-M was employed, as the flux dropped rapidly to 40% of original flux during the first 5 min. Then the flux continued to decline with a smooth trend and relative flux which finally stabilized at 0.3 after 30 min (Figure 3(a)). In another case in which feed was prepared by HPO fraction, the relative flux gradually declined to 0.5, while the flux declined with the lowest rate when TPI was applied. A similar phenomenon was discovered when PVDF-O was employed in ultrafiltration experiments (Figure 3(b)). It was clear that HPI possessed of the highest membrane fouling capability followed by HPO and TPI. This result is consistent with other reports that polysaccharide matter, a fatty compound characterized by low/no charge or low SUVA aromaticity, belongs to HPI, which could lead to long term flux decline (Cho et al. 1998, 2000).

A static charge exclusion force played a role in preventing hydrophobic and transphilic organic matter to precipitate on the PVDF-M membrane surface. The low/no-charged property of hydrophilic organic matter created a less static charge exclusion force. Therefore hydrophilic organic matter showed a bigger fouling potential. The
PVDF-M membrane’s zeta potential (−17.2 mV) was higher than that of the PVDF-O membrane (−8.3 mV). Thus, a strong static exclusion force might partly explain why the HPO did not easily foul the PVDF-M membrane, which is consistent with Amy (2008) that a greater (negative) charge reduced UF fouling. Though the concentration of HPO was much more than other two fractions in the water samples (HPI:HPO:TPI = 63:29:8), it contributed less to PVDF-M membrane fouling.

It can also be seen from Figure 2 that no matter which kind of feed used, PVDF-M showed better anti-fouling performance. These results verified again that anti-fouling capability of PVDF-M ultrafiltration membrane was enhanced by the presence of nano-Al2O3.

Amount of foulant on membrane surface

When the UF experiments fed with water synthesized by DOC fractions were finished, the mass of foulant on the membrane surface was measured. More hydrophilic matters were desorbed from the PVDF-M membrane surface than that from PVDF-O membrane (Figure 4), revealing the increase of membrane hydrophilicity could lead to more hydrophilic NOM adsorption. Similar phenomenon had also been reported by Violleau et al. (2005). The difference of membrane contact angle between PVDF-O and PVDF-M might partly explain the difference of adsorption potential of the three fractions.

Even though the mass of HPO and TPI desorbed from membrane surface is less that of HPI, fouling caused by the adsorption of hydrophobic and transphilic matter on the membrane surface could still not be neglected, because NOM with higher hydrophobicity has an also bigger capability to be adsorbed on the hydrophobic membrane surface (Kimura et al. 2006). Although the presence of nanoparticles can change the contact angle from 83.64° to 57.42°, the surface of the modified membrane is still thought to be hydrophobic, according to Cho et al. (2000) that only membrane with contact angle less than 50° was considered to be hydrophilic.

Contaminants analyses

Figure 5 shows the results of GC/MS analyses of contaminants desorbed from PVDF-O and PVDF-M which were used for filtration of raw water taken from Songhua River. As shown in this figure, number of peaks, which means kinds of contaminations desorbed from the membrane PVDF-M and PVDF-O, are more or less the same. However, by calculating adsorption peak areas, one can find that modified membrane PVDF-M was 16% less than unmodified membrane PVDF-O, implying that amounts of contaminants adsorbed on the modified membrane was reduced to some extent. All these owed to hydrophilicity improvement of the modified membrane.

CONCLUSIONS

The presence of nanoparticles in the composite membrane decreased the contact angle and increased the surface hydrophilicity of the modified membrane, and further enhanced the anti-fouling capability of PVDF-M membrane, while other properties of the membrane were not affected by the modification. The HPIs in the Songhua River were the...
main foulant, causing more fouling to membrane than hydrophobic and transphilic matters.

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