Surface modification of polypropylene microporous membrane to improve its antifouling characteristics in an SMBR: Air plasma treatment

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Abstract

Polypropylene hollow fiber microporous membranes (PPHFMMs) were surface-modified by air plasma treatment. Morphological changes on the membrane surface were characterized by field emission scanning electron microscopy (FE-SEM). The change of surface wettability was monitored by contact angle measurements. The static water contact angle of the modified membrane reduced obviously with the increase of plasma treatment time. The relative pure water flux for the modified membranes increased with plasma treatment time up to 2 min, and then it decreased with further increase of plasma treatment time. Decreases in the tensile strength and the rate of tensile elongation at break of the modified membranes were also observed. The antifouling characteristics of the membranes in a submerged membrane-bioreactor (SMBR) for wastewater treatment were investigated. After continuous operation in the SMBR for about 110 h, flux recoveries after water and caustic cleaning are 11.66 and 34.99% higher for the 4 and 2 min air plasma treated membrane than those of the unmodified membrane. Result indicated that reversible fouling was only weakly dependent on membrane surface chemistry; in contrast, irreversible fouling exhibited a marked dependence on surface chemistry.

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Keywords: Air plasma treatment; Antifouling characteristics; Polypropylene hollow fiber microporous membrane; Submerged membrane-bioreactor; Surface modification

1. Introduction

Polypropylene microporous membranes exhibit high potentials for comprehensive application due to their high void volume, well-controlled porosity, high thermal and chemical stability, and low cost. However, the low energy surface and relatively high hydrophobicity probably lead to membrane fouling [1,2]. In an attempt to improve the antifouling characteristics of these membranes, the modification of commonly used membranes such as polypropylene microporous membranes is very important. Different methods such as UV irradiation, plasma treatment, gamma irradiation, and chemical reaction have been employed to modify the membrane surface [3–5].

Among the various surface-modification techniques, plasma treatment is regarded as the most advantageous one [6,7], the active species generated in plasma can activate the upper molecular layers on the surface, thus improving wettability, adhesion and biocompatibility without affecting the bulk of the polymer [8–10]. From a single material, by changing plasma gas or parameters, surfaces with various characters can be obtained. Many kinds of gases can be used as plasma gases, such as argon, helium, hydrogen, nitrogen, ammonia, nitrous oxide, oxygen, carbon dioxide, sulfur dioxide, water and tetrafluoromethane. Chemical nature of the plasma gases has strong influences on surface modification reactions. For example, air plasma is very effective in hydrophilic modification accompanied by extensive etching and by the implantation of both oxygen- and nitrogen-containing polar groups [11,12]. Amperic character may be obtained, which is connected to degrees of ionization of amino and carboxyl groups at different pH values [13].

The combination of membrane separation with the process of biological reactor is called membrane bioreactor (MBR) [14]. Studies on MBRs have received considerable attention due to the deterioration of the water environment all over the world [15,16] and due to the advantages of MBRs compared with conventional activated sludge process. However, membrane fouling is still the major limitation to the large-scale application of an MBR process, which causes a decline in flux over time. Therefore many
researches have been done for its enhancement [17,18]. Physical rinsing and chemical cleaning have also to be applied frequently in the operation of an MBR, which increases the operation cost and shortens the life of the membrane [19].

The characteristics of membrane surface, such as surface wettability, surface charge and surface acidic/basic character play dominant roles in determining the antifouling characteristics. CO₂ [20] and NH₃ [21] plasma treated membranes have been conducted in our previous work, the surface characters were more acidic and basic due to the introduction of carboxyl and amino groups [22]. The antifouling characteristics in a submerged membrane-bioreactor (SMBR) increased to some extent.

As mentioned above, modification by air plasma treatment may introduce ampheric character onto the membrane surface, which may have some effects on the antifouling characteristics of the membrane. Based on the previous studied and such an expectation, the primary objective of this study is to investigate the effects of air plasma treatment on the membrane fouling during the filtration of activated sludge in a submerged aerobic MBR.

2. Experimental

2.1. Materials

Polypropylene hollow fiber microporous membrane (PPHFMM) with a porosity of 45–50% and an average pore diameter of 0.10 µm was prepared with melt-extrusion/cold-stretch in our laboratory. The average inner and outer diameters of PPHFMM are 240 and 290 µm, respectively; deionized water was obtained by using a Milli-Q UF Plus (Bedford, MA) system at 18 MΩ resistance; and U-shape PPHFMM modules were carefully fabricated by hand. There were 100 bundles of hollow fibers within each module, and the total area of the membrane module was about 100 cm².

2.2. Surface modification of PPHFMM by air plasma treatment

Before plasma treatment, the PPHFMM was washed with acetone to remove any chemicals and wetting agents absorbed on the membrane surface, then dried in a vacuum oven at room temperature for 24 h, and stored in a desiccator.

A plasma generator from Peking KEEN Co. Ltd. (China) was used. Tubular type Pyrex reactor (10 cm × 150 cm) was rounded with a pair of copper electrodes, which were powered through a matching network by a 13.56 MHz radio-frequency generator. The surface modification depends on plasma treatment duration and plasma parameters such as density, power and gas type. Higher powers result in plasma-induced damage to the membranes [23]. On the basis of considering surface etching, 30 W was chosen as the applied rf power for all the experiments described here. U-shaped membrane modules were fully stretched out in a rectangular frame with rubber bands, which was put in the center of the plasma reactor chamber. The chamber was vacuumed; and then plasma was generated at 10 Pa for a given time (0–8 min). Finally, the membrane was taken out of the chamber.

2.3. Characterization

X-ray photoelectron spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with Al Kα radiation (hv = 1486.6 eV). In general, the X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54°. The pass energy was fixed at 23.5, 46.95 or 93.90 eV to ensure sufficient resolution and sensitivity. The base pressure of the analyzer chamber was about 5 × 10⁻⁸ Pa. The sample was directly pressed to a self-supported disk (10 mm × 10 mm) and mounted on a sample holder then transferred into the analyzer chamber. The whole spectra (0–1100 (1200) eV) and the narrow spectra of all the elements with much high resolution were both recorded by using RBD 147 interface (RBD Enterprises, USA) through the AugerScan 3.21 software. Binding energies were calibrated by using the containment carbon (C1s = 284.7 eV). The C1s, O1s and N1s envelopes were analyzed and peak-fitted after subtraction of a Shirley background using a Gaussian–Lorenzian peak shapes obtained from the Casa XPS software package.

Surface morphologies of the unmodified and modified PPHFMMs were observed by field emission scanning electron microscope (FE-SEM) with a Sirion FEG-SEM (FEI, USA) operating with an accelerating voltage of 5 keV. Prior to FE-SEM analysis, the membrane was affixed to a standard sample stub by double-sided carbon conductive tape (Ted-Pella). To prevent surface charging, a thin film (5 nm) of Au was sputtered onto all samples by an Anatech sputter coater prior to imaging.

Image analysis was carried out by means of an interactive and computerized system (Image-pro Plus, IPP, version 6.0), adequately calibrated [24–26]. Each photograph was digitalized with a resolution of 766 × 510 pixels, assigning to each one a grey level ranging from 0 to 255 (white). Thereafter, each image field was filtered and smoothed in order to improve contrast and definition, eliminating some parasite images due to unequal illumination and other noise-generating causes. Then the images were redefined according to an assigned grey threshold level under which every pixel was assigned to 1 and the rest to 0. Then the background was improved by scraping isolated pixels in such a way that all the remaining 1’s in the matrix were assumed to belong to a pore. Finally the pore borders were smoothed in order to reduce the influence of the finite size of pixels and low definition.

Water contact angle on the membrane surface was measured by the sessile drop method using a DATA Physics System (OCA20, Germany). The contact angle was measured at a constant temperature (25 °C). The liquid drop of 1 µl was placed onto the membrane surface by a micro-syringe. The drop image was recorded by video camera and digitalized. The average value was obtained from at least 10 measurements tested for each membrane. The standard deviation was about 1–3°.

A versatile material experimental instrument (RG2000-10, Shenzhen, China) was used to estimate the mechanical proper-
ties after air plasma treatment, at least 10 measurements were made to calculate the mean values.

2.4. Filtration and antifouling characteristics measurements

Each membrane was first pre-compacted for 30 min at a transmembrane pressure (TMP) of 60 kPa with the flow from-out-to-in [27]. Then, the de-ionized water flux \( J_{0,u} \) was obtained at a TMP of 40 kPa. After surface modification, the de-ionized water flux \( J_{0,m} \) was also obtained by the same procedure.

U-shaped hollow fiber membrane modules were used in the submerged membrane-bioreactor, the experimental set-up and the operation conditions have been described in details elsewhere [20]. All membrane modules were installed into the SMBR at the same time [28,29] to eliminate the differences on the filtration performance caused by different physiological states of the activated sludge suspension.

Permeate was continuously removed by a suction pump at 40 kPa for about 110 h, and then was registered again. The permeation flux was designated as \( J_p \) when five recording values differed by less than 2% (1 h for each record). After being used in the SMBR, the membranes were taken out from the SMBR and cleaned with de-ionized water, and then the de-ionized water flux \( J_1 \) was measured. The membrane was further cleaned with 5% NaOH solution for 4 h and the pure water flux \( J_2 \) was measured again.

The volumetric fluxes, such as \( J_{0,u} \), \( J_{0,m} \), \( J_p \), \( J_1 \) and \( J_2 \) were determined through the timed collection of permeate, and adjusted to a reference temperature of 20°C by accounting for the viscosity change of water [28]. All the above fluxes were adjusted to a relative value by divided by \( J_{0,u} \) to eliminate the differences that exist between the original flux.

The antifouling characteristics, such as reduction from pure water flux and flux ratio after fouling, flux recovery after water and caustic cleaning, were described by the following equations:

- Reduction from pure water flux \( = \left( 1 - \frac{J_p}{J_{0,u}} \right) \times 100\% \) (1)
- Flux ratio after fouling \( = \frac{J_{p,m}}{J_{p,u}} \) (2)
- Flux recovery after water cleaning \( = \frac{J_1}{J_{0,u}} \times 100\% \) (3)
- Flux recovery after caustic cleaning \( = \frac{J_2}{J_{0,u}} \times 100\% \) (4)

where the subscripts m and u refer to the modified and unmodified membrane.

Statistical analysis was carried out by univariate linear correlation analysis to identify major factors affecting membrane fouling by using the statistics package of social science (SPSS, Version 11.5).

3. Results and discussion

3.1. Air plasma treatment and characterization of PPHFMMs

The chemical changes occurred in the membranes were ascertained by XPS analysis (Fig. 1). Compared with the virgin membrane (Fig. 1(1)), it can be clearly seen that after air plasma treatment (Fig. 1(2)), two obvious peaks, namely the peak at 531.6 eV corresponding to O1s and the peak at 402.3 eV corresponding to N1s, appear. The N1s peak can be designated to the nitrogen-containing groups present in the air plasma treatment [12].

Information concerning the manner in which oxygen and nitrogen were implanted on the membrane surface during the air plasma treatment can be obtained from the deconvolution of XPS signals. As shown in Fig. 2, the binding energies referenced for curve fitting are 284.7 eV for C=C/C=H, 286.7 eV for C=O, C=N, 287.9 eV for C=O and C=CONH, 289.1 eV for O=C for the plasma treated membrane appeared (Fig. 2(a)) [30]. Peaks at 531.5 and 532.2 eV are found, which correspond to O=C and O=O groups (Fig. 2(b)) [31], respectively. N1s spectrum for the air plasma treated membrane (Fig. 2(c)) has peaks assigned to N=C/H (402.1 eV) and N=O (404.2 eV) [22].

The elemental composition of the untreated and the air plasma treated membrane for 4 and 8 min is shown in Table 1. The O/C ratio of the unmodified membrane is 2.8 mol.%, which means that the untreated membrane appears to contain some contamination or more probably low-level surface oxidation [32]. The atomic ratio of O/C increases from 2.8 to 14.9 mol.%, N/C...
increases from 0 to 0.9 mol.% with the increase of plasma treatment time from 0 to 8 min. These results indicate that prolonged plasma treatment time will introduce more O and N onto the membrane.

The surface morphologies of the virgin and modified PPHFMMs were observed by FE-SEM. Typical images are shown in Fig. 3. Before 1 min of plasma treatment, the membrane seems to be undamaged and the surface quite uniform (Fig. 3(a–c)). When treated in air plasma for a longer time (2–4 min), the membrane structure is severely affected, numerous cracks can be seen on the surface (Fig. 3(d and e)), due to the etching action taking place during plasma treatment [22,33,34].

In the case of a porous membrane, plasma can change pore size essentially. Depending on plasma gas and process parameters, increase or decrease of pore size can be observed [35,36]. In this work, FE-SEM images were afterwards treated with image analysis software (Image-Pro plus 6.0) to obtain useful information on pore size. Typical results are shown in Table 2. It is found that the pore size increases with increasing plasma treatment time up to 2 min; which may be the effect of plasma etching. Then the pore size decreases gradually with the further increase of plasma treatment time. Because more aggressive plasma causes freeing large amounts of degraded species that, in turn, deposited on the membrane surface and probably also inside the pores [37].

The hydrophilicity or hydrophobicity of each membrane can be easily obtained by water contact angle measurement, though it is difficult to definitely interpret the surface property for porous membranes [23,38,39]. Water contact angles on the unmodified and modified membrane surfaces are shown in Fig. 4. It indicates that the static water contact angle decreases evidently from about

<table>
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<th>Air plasma treatment time (min)</th>
<th>Average pore size (μm)</th>
<th>Standard deviation (μm)</th>
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<tbody>
<tr>
<td>0</td>
<td>0.10</td>
<td>0.02</td>
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<tr>
<td>0.5</td>
<td>0.10</td>
<td>0.03</td>
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<tr>
<td>1</td>
<td>0.11</td>
<td>0.03</td>
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<tr>
<td>2</td>
<td>0.13</td>
<td>0.04</td>
</tr>
<tr>
<td>4</td>
<td>0.12</td>
<td>0.04</td>
</tr>
<tr>
<td>8</td>
<td>0.09</td>
<td>0.02</td>
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128.5° to 35.0° with the increase of air plasma treatment time from 0 to 8 min. As discussed above, the element content of O and N increase with the increase of plasma treatment time. The reduction in water contact angle may be ascribed to the increase of hydrophilicity on account of the introduction of polar groups by air plasma treatment [12,40]. It can also be found that a sharp decrease in water contact angle during the first minute of plasma treatment, prolonged excitation did not cause further changes. This means that most of the surface reactions changing its character occurs during the first moment of plasma treatment [41].

The change of mechanical properties after plasma treatment is also an important factor in practical membrane application processes such as backwashing and chemical cleaning. Therefore, the mechanical properties (tensile strength and rate of elongation at break) of the virgin and air plasma treated PPHFMMs were measured as a function of plasma treatment time. The results are shown in Fig. 5. It can be seen that both the tensile strength and the rate of elongation decrease quickly with the increase of plasma treatment time to 1 min, then slowly with prolonged plasma treatment time. It can be confirmed by the FE-SEM observations (Fig. 1), the surface morphologies remained nearly unchanged before 1 min air plasma treatment. However, scission of the polymer chain due to ablation and etching mainly took place after 1 min plasma treatment, some cracks appear on the membrane surface. The decrease of tensile strength and the rate of elongation at break can be attributed to the scission of the molecular chains [34] on the membrane surface. This is a negative result attributed to the surface-etching phenomenon of plasma treatment.

3.2. Filtration and antifouling properties of the PPHFMMs

In this study, relative pure water flux through the membrane was measured as a function of air plasma treatment time (Fig. 6). A maximum value is observed for a plasma treated PPHFMM for 2 min. The relative pure water fluxes for all the air plasma treated PPHFMMs are higher than that for the untreated PPHFMM. However, after 2 min plasma treatment, the relative pure water flux decreases continuously. Membrane pore size/porosity and surface hydrophilicity/hydrophobicity are two major factors affecting water flux [20,42]. As mentioned
above (Fig. 3 and Table 2), the membrane pores are enlarged up to 2 min, and the hydrophilicity increases continuously, as a result, the water flux increases; after 2 min of plasma treatment, membrane pores are blocked to some extent, which play a dominant role in the water flux, leading to the decrease of water flux. Furthermore, in the present work, the membranes were damaged during plasma treatment; the membrane damage may also contribute to the enhancement of the pure water permeability.

To study the effect of the plasma treatment on the antifouling characteristics of the membrane, filtration experiments of activated sludge in an SMBR were carried out. The flux curves of the unmodified and the modified PPHFMMs are shown in Fig. 7, which indicates that the flux curve for each membrane possesses the same trend, and the water fluxes decrease with the increase of operation time. Flux decline was a result of the increase of membrane resistance to the permeate flow, which was caused by membrane fouling or particle deposition onto the membrane surface or into the membrane pores [43,44]. However, except for the plasma treated PPHFMM for 0.5 min, the water fluxes for the modified PPHFMMs are lower than that of the unmodified one. This can be attributed to the fact that hydrophilic surface decreases the overall resistance, causing an increase in flow rate, resulting in significant cake formation and compaction. Cake formation and compaction on the membrane surface increases (porosity decreases), causing the resistance to increase, which results in a decrease of the flow rate. This result confirms that if the membrane surface is more hydrophilic, the cake thickness increases and thus cake resistance increases, causing the decrease in the flow rate [45].

To compare the permeation properties of the studied membranes, ultra pure water and mixed liquid of activated sludge filtration experiments were carried out. After being used in the SMBR, the membranes were washed with pure water and 5 wt.% NaOH solution, then the corresponding water fluxes were obtained. Typical results for the permeation fluxes, $J_{0,\text{im}}, J_p, J_1$ and $J_2$ through the original and plasma surface modified PPHFMMs are depicted in Fig. 8. It can be seen that, $J_1$ and $J_2$ increase greatly for the plasma surface modified membranes after water and caustic cleaning. However, it also shows the low-
Fig. 8. Permeation fluxes, \( J_{0\text{un}}, J_p, J_1 \) and \( J_2 \) through the original and plasma surface modified PPHFMMs.

It can be seen that the plasma surface modified membranes show higher flux recoveries after cleaning, but higher reduction from pure water flux and flux ratio after fouling than those of the unmodified one (except for the 0.5 min plasma treated membrane). After continuous operation in the SMBR for about 110 h, flux recoveries after water and caustic cleaning are 11.66 and 34.99% higher for the 4 and 2 min air plasma treated membrane than those of the unmodified membrane. This is due to that the foulant was less adherent to the more hydrophilic membrane surface and could be more easily washed off from the surface. These results indicate that the plasma surface modification of PPHFMM can improve the regeneration characteristics for this hydrophobic membrane. Flux recoveries after water and caustic cleaning are much high for the long time plasma treated membranes. While the flux recovery after water cleaning for all tested membranes are very small. These results also indicate that reversible fouling resulting from cake formation (which can be washed off by water from the membrane surface) was only weakly dependent on membrane surface chemistry; in contrast, irreversible fouling (which is due to irreversible adsorption and pore plugging, and cannot be washed off by water from the membrane surface) exhibited a marked dependence on surface chemistry [48]. Significant improvements in the antifouling characteristics would be obtained during the automatic backwashing cycle of an SMBR, which is typically performed in the range of 10 min, if surface was modified.

It is known that surface wettability and average membrane pore size play important roles in the antifouling characteristics. To find out which is the major factor affecting the antifouling characteristics in the SMBR, the Pearson correlations of water contact angle, average membrane pore size with reduction from pure water flux, relative flux ratio after fouling, flux recoveries after water and caustic cleaning were calculated by SPSS software according to Ref. [49] (Table 3). Results demonstrate that between the two factors, water contact angle and average membrane pore size, water contact angle plays more important role in determining the antifouling characteristics. The Pearson correlation between water contact angle and reduction from pure water flux is negative, which confirms the conclusions discussed above. The Pearson correlation between water contact angle and the flux recovery after water cleaning is negative, which indicates that the lower the water contact angle, the better the generation characteristics. The Pearson correlation of average membrane pore size with the reduction of pure water flux is positive, while the Pearson correlation of average membrane pore size with the relative flux ratio after fouling is negative, which means that the membrane with small average membrane pore size would possess better antifouling characteristics, similar result were also obtained [40,50].

The flux recoveries after water cleaning were 37, 12.3 and 23%, the relative flux ratios after fouling were 1.58, 1.50 and 1.17 for the CO\(_2\) [20], O\(_2\) [51] and NH\(_3\) [21] plasma treatment membranes. While the flux recovery after water cleaning and the relative flux ratio after fouling for the 30 s air plasma treated membrane are 22.69 and 1.35%, respectively. These

<table>
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<th>Water contact angle</th>
<th>Average membrane pore size</th>
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<tr>
<td>Reduction from pure water flux</td>
<td>−0.747</td>
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<tr>
<td>Relative flux ratio after fouling</td>
<td>0.745</td>
</tr>
<tr>
<td>Flux recovery after water cleaning</td>
<td>−0.468</td>
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<tr>
<td>Flux recovery after caustic cleaning</td>
<td>−0.721</td>
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Table 3 Pearson correlations of water contact angle, average membrane pore size with reduction from pure water flux, relative flux ratio after fouling, flux recoveries after water and caustic cleaning.
results demonstrate that CO₂ plasma treated membrane possesses the best antifouling characteristics among these plasma treated membranes, and the surface character plays an important role in the antifouling characteristics. Georges Belfort also found that the membrane with weakly acidic surface produced the lowest fouling when treat natural organic matter [48]. This may be due to that the nature colloids molecules and membrane surface were negatively charged at pH 7.0 [52,53], as a result, the foulant cannot reach the membrane surface because of electric repulsion. In our previous work, it was also found that the surface carboxyl-containing membranes were better than the surface amido-containing membranes [54].

4. Conclusions

Hydrophobic polypropylene microporous membranes were surface modified by air plasma treatment. The water contact angles for the plasma surface modified membranes decreased evidently from about 128.5° to 35.0° with the increase of air plasma treatment time from 0 to 8 min. The antifouling characteristics of the modified membranes in the submerged membrane-bioreactor were investigated. The modified membranes showed better filtration behaviors in the submerged membrane-bioreactor than the unmodified membrane. After continuous operation in the SMBR for about 110 h, flux recoveries after water and caustic cleaning are 11.66 and 34.99% higher for the 4 and 2 min air plasma treated membrane than those of the unmodified membrane. The results demonstrated that reversible fouling was only weakly dependent on membrane surface chemistry; in contrast, irreversible fouling exhibited a marked dependence on surface chemistry.

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