Membrane Water Treatment, Vol. 1, No. 1 (2010) 83-92
DOI: http://dx.doi.org/10.12989/mwt.2010.1.1.083

Surface modification of polypropylene membrane to improve antifouling characteristics in a submerged membrane-bioreactor: Ar plasma treatment

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(Received August 7, 2009, Accepted October 28, 2009)

Abstract. To improve the antifouling characteristics of polypropylene hollow fiber microporous membranes in a submerged membrane-bioreactor for wastewater treatment, the surface-modification was conducted by Ar plasma treatment. Surface hydrophilicity was assessed by water contact angle measurements. The advancing and receding water contact angles reduced after the surface modification, and hysteresis between the advancing and receding water contact angles was enlarged after Ar plasma treatment due to the increased surface roughness after surface plasma treatment. After continuous operation in a submerged membrane-bioreactor for about 55 h, the flux recovery after water cleaning and the flux ratio after fouling were improved by 20.0 and 143.0%, while the reduction of flux was reduced by 28.6% for the surface modified membrane after 1 min Ar plasma treatment, compared to those of the unmodified membrane. Morphological observations showed that the mean membrane pore size after Ar plasma treatment reduced as a result of the deposition of the etched species; after it was used in the submerged membrane-bioreactor, the further decline of the mean membrane pore size was caused by the deposition of foulants. X-ray photoelectron spectroscopy and infrared spectroscopy confirmed that proteins and polysaccharide-like substances were the main foulants in the precipitate.

Keywords: antifouling characteristics; polypropylene microporous membrane; Ar plasma treatment; submerged membrane-bioreactor; membrane surface modification; wastewater treatment.

1. Introduction

Membrane-bioreactor (MBR) is a combination of biological wastewater treatment process and physical membrane filtration process. Therefore the gravitational settling tank in the conventional activated sludge process is not needed. In an MBR, biomass is strictly separated by a membrane, as a result, MBR system offers several advantages over the conventional activated sludge process, including a small footprint, high quality effluent, a low sludge production rate and easy manipulation of the sludge retention time. With effective biomass-effluent separation by membrane filtration, the MBR process is expected to lead the next generation of biological wastewater technologies. However, MBR process is reliable in terms of perfect capture of solids in the system, membrane fouling has restricted its practical application and increased operational costs (Le-Clech, *et al*. 2007, Wang and Li 2008).

Polypropylene microporous membrane are comprehensively applied as micro- and ultra- filtration

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because of their high void volume, well-controlled porosity, high thermal and chemical stability, and low cost. Membrane fouling is caused by the deposition of soluble and particulate materials onto the membrane surface and/or into the membrane pores, which is attributed to the interactions between activated sludge components and the membrane. Physical rinsing and chemical cleaning have to be applied frequently in the operation of an MBR, which increases the operation cost and shortens the life of the membrane. Thus, it is necessary to obtain membranes with better antifouling characteristics for fouling control in MBR applications.

It is well known that the antifouling characteristics of hydrophilic membranes are usually better than those of the hydrophobic ones (Kim, *et al*. 2004). Various methods, such as surfactant coating, UV irradiation (Hu, *et al*. 2006), plasma treatment (Buonomenna, *et al*. 2007), gamma ray irradiation, and chemical reaction, have been employed to improve the antifouling characteristics of the membranes. Amongst these methods, surface plasma modification is considerably important in both technology and science. This method has been successfully utilized to improve the hydrophilicity, biocompatibility and adhesion of membrane surface. Plasma treatment of membrane surfaces not only produces modification during the plasma exposure, but also leaves active sites on the surfaces, which are subject to post-reactions. Polar functional groups can be introduced on the polypropylene membrane surface after breaking C-C, C-H bond by using the plasma treatment of membrane surface without altering the bulk properties. Its content and effect on the material surface depend on the composition of the gas in the discharge, the composition of the treated sample, and the process parameters. From a single material, various surfaces can be obtained by changing plasma gas or parameters. In our previous work, H_2O (Yu, *et al*. 2008), N_2 (Yu, *et al*. 2007a), NH_3 (Yu, *et al*. 2005a) and CO_2 (Yu, *et al*. 2005b) have been changed for plasma to modify the membrane surface, antifouling characteristics have been improved to some extent. Argon plasma treatment has been employed to improve surface hydrophilicity, biocompatibility and proton conductivity (Zhu, *et al*. 2005). However, the effect of Argon plasma treatment on the antifouling characteristics of the membranes in an MBR has not been investigated.

This study aims to investigate the effects of Ar 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 about 0.07 μm were prepared in our laboratory (Yu, *et al*. 2006b). The inner and outer diameters of PPHFMM are 240 and 290 μm respectively. U-shape PPHFMM modules were carefully fabricated by hand. There were 100 bundles of hollow fibers within each module. The surface area of each membrane module is about 100 cm^2.

2.2. Membrane surface modification and characterization

Membrane surface modification was conducted by Ar plasma treatment for 1 min according to the literatures (Yu, *et al*. 2008). The surface hydrophilicity was performed in detail (Gu, *et al*. 2009).

Surface morphologies of the unmodified and modified PPMMs were observed by field emission scanning electron microscope (FE-SEM) with a Hitachi 4800 (Hitach, Japan) 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. To prevent surface charging, a thin film (5 nm) of Au was sputtered onto all samples before imaging.

FE-SEM images were afterwards treated with image analysis software (Image-Pro plus 6.0) for information on mean membrane pore size (Gu, *et al*. 2009).

The sludge particle size distributions of sludge suspension were determined by laser particle sizer (GSL-101BI, Liaoling Institute of Instruments Co. Ltd., China).

Cake was assessed by X-ray photoelectron spectroscopy (Gu, *et al*. 2009) and infrared spectroscopy (IR). The IR spectra was recorded on an infrared spectrometer (Brucker Vector 22 FT-IR, Switzerland) by using KBr as the matrix.

2.3. Filtration and antifouling properties measurements

Each membrane was first pre-compacted for 30 min at 60 kPa with the flow from-out-to-in. Then, the de-ionized water flux ($J_{0,u}$) was obtained at 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 (SMBR), the experimental set-up and the operation conditions have been described in detail elsewhere (Yu, *et al*. 2007b). All membrane modules were installed into the SMBR at the same time (Chang, *et al*. 2001) to eliminate the differences on the filtration performance caused by different physiological states of the activated sludge suspension.

Permeability was continuously removed by a suction pump at 40 KPa for about 55 h. The permeation flux was designated as J_p when 5 recording values differed by less than 2% (1 h for each record). After being used in the SMBR for about 55 h, the membranes were taken out and cleaned with de-ionized water, and then the de-ionized water flux (J_1) was measured.

The volumetric fluxes, such as $J_{0,u}$, $J_{0,m}$, J_p and J_1 were determined through the timed collection of permeate, adjusted to a reference temperature of 20°C by accounting for the viscosity change of water (Chang, *et al*. 2001). All these fluxes were normalized (divided by $J_{0,u}$) to eliminate the differences that exist between the original flux.

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

$$\text{Reduction from initial water flux} = (1 - J_p/J_{0,u}) \times 100\% \quad (1)$$

$$\text{Flux ratio after fouling} = J_{p,m}/J_{p,u} \quad (2)$$

$$\text{Flux recovery after water cleaning} = J_1/J_{0,u} \times 100\% \quad (3)$$

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

3. Results and discussion

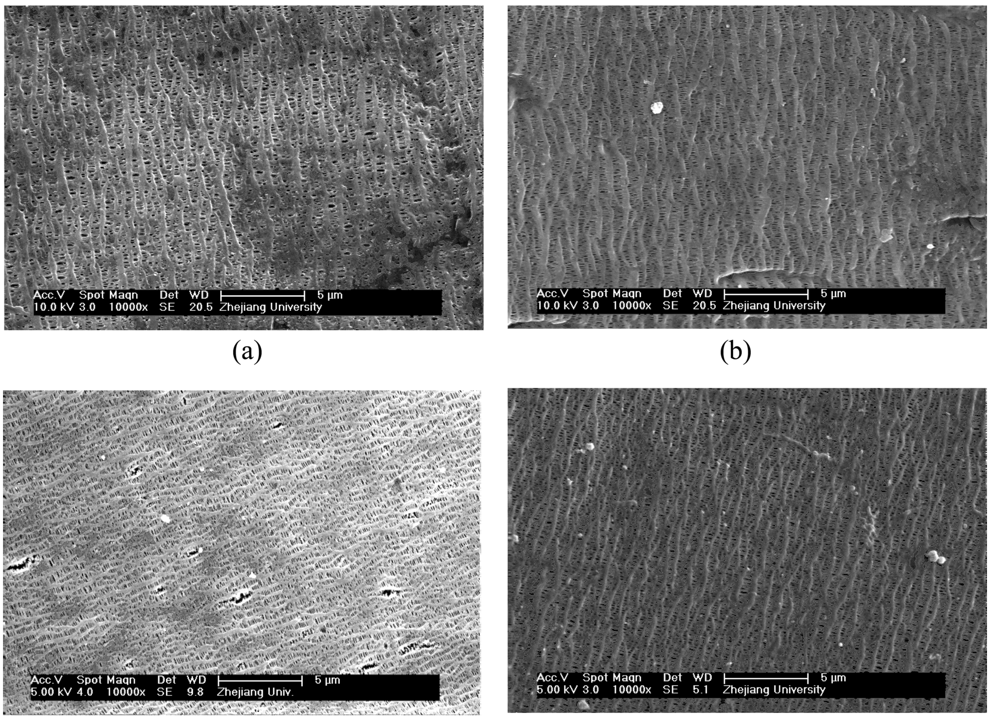
3.1. Characterization

The surface morphologies of the virgin and modified PPHFMMs were observed by FE-SEM.

Typical images are shown in Fig. 1. It can be found that after 1 min plasma treatment, PPHFMMs seem to be damaged, and the membrane pore size and porosity reduce. Etching and deposition of the etched species would take place during the plasma treatment. The former will result in the increase of pore diameter and porosity, produce cracks on the membrane surface; while the latter will result in the decrease of pore diameter and porosity, which will be discussed below. As a result, the reduction of the mean membrane pore sizes is caused by the deposition of the species produced during the plasma treatment (Yu, *et al*. 2005a, 2005b). It also can be found some cracks appear on the surface, which may be due to the bombardment of the ions with high energies on the surface (Bodas and Khan-Malek 2007). The red circles were drawn by the image analysis software (Image-Pro plus 6.0) for calculating the membrane pore size.

FE-SEM images were afterwards treated with image analysis software (Image-Pro plus 6.0) to obtain information on the mean membrane pore size (Table 1). The mean membrane pore sizes are 0.071 μm and 0.056 μm for the nascent membrane before and after used in the SMBR; the mean membrane pore sizes are 0.059 μm and 0.049 μm for the Ar plasma treated PPHFMM before and after used in the SMBR. The reduction of the mean membrane pore sizes were caused by the deposition of the foulants within the membrane pores, leading to serious irreversible membrane fouling, which can not be easily removed by water cleaning. These results are in good consistence with the FE-SEM observations.

Advancing and receding water contact angles on the unmodified and Ar plasma treated membrane



(c) (d)

Fig. 1 FE-SEM images of the PPHFMMs. (a) Nascent PPHFMM; (c) The surface modified PPHFMM after 1 min Ar plasma treatment; (b) Nascent PPHFMM used in the SMBR; (d) Ar plasma treated PPHFMM used in the SMBR, respectively

Table 1 Pore size of the nascent and modified PPHFMMs before and after used in the SMBR. The used membranes were followed by water and caustic cleaning

Different membranes	Average pore size and standard deviation (μm)
Nascent	0.071 ± 1.13
Nascent PPHFMM used in the SMBR	0.059 ± 1.008
1 min Ar plasma treated PPHFMM	0.056 ± 0.846
1 min Ar plasma treated PPHFMM used in the SMBR	0.049 ± 0.0757

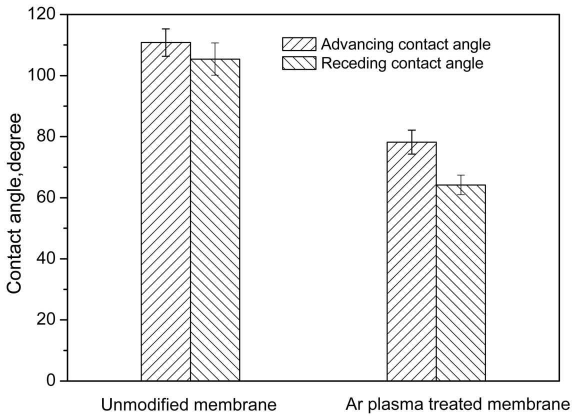


Fig. 2 Advancing and receding water contact angles on the unmodified and modified membrane surface

are depicted in Fig. 2. It can be found that after the surface plasma treatment, both of the advancing and receding water contact angles reduce, which may be attributed to the hydrophilization effect of Ar plasma treatment. There is an obvious hysteresis between the advancing contact angle and receding contact angle for the unmodified and modified membranes. The hysteresises are 5.4^{o} and 14^{o} for the unmodified and modified membranes, respectively. The increase of contact angle hysteresis is attributed to the roughening membrane surface caused by plasma treatment (Wei, *et al*. 2007). The differences of contact angles are very small and insignificant. However, compared with our previous work, the advancing contact angle would significantly affect the hydrophilicity of membranes (Yu, *et al*. 2006a).

3.2. Filtration and antifouling properties of the PPHFMMs

To study the effect of Ar plasma treatment on the performance of the membrane, the filtration of activated sludge in a submerged aerobic MBR were carried out for about 55 h, which is shown in Fig. 3. Fig. 3 shows that J_p for the modified membrane is lower than that for the unmodified membrane throughout the process, which indicates that membrane surface modification by the Ar plasma treatment can improve the membrane filtration performances.

The antifouling characteristics of the studied membranes, such as the reduction from initial water flux, the flux recovery after water cleaning and the flux ratio after fouling, are shown in Table 2. It can be seen that the surface modified membranes show better performance, i.e. lower reduction of

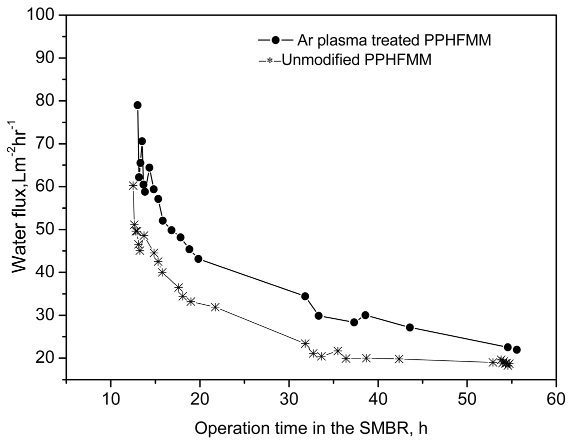


Fig. 3 Change of flux with operation time in the SMBR

Table 2 Changes of water fluxes and the antifouling characteristics for the unmodified and modified membranes

Different PPHFMMs	Unmodified	1 min Ar plasma treated
J_0 or $J_{0,m}$	400.0 ± 15.0	452.0 ± 22.0
J_p	20.0 ± 1.0	48.6 ± 2.4
J_1(water washed)	32.0 ± 1.6	52.0 ± 2.5
Flux ratio, $J_{p,m}$ / $J_{p,u}$	1.00	2.43
Reduction of flux, %	80.0	51.4
Flux recovery after water cleaning, %	8.0	13.0

flux, higher flux recovery and flux ratio after fouling than those of the nascent PPHFMM. After continuous operation in a submerged membrane-bioreactor for about 55 h, the flux recovery after water cleaning and the flux ratio after fouling are improved by 20.0 and 143.0%, while reduction of flux decreases by 28.6% for the surface modified membrane after 1 min Ar plasma treatment. The results indicate that the surface modification of PPHFMM could improve the antifouling characteristics for this hydrophobic membrane.

3.3. Foulants characteristics

After a long-time operation in the SMBR, a thick biomass cake layer, which consolidated with the inorganic precipitate, was found in the membrane surface. The analytical methods such as XPS and IR were employed to verify the chemical composition of the observed biomass cake layer (foulant).

The existence of protein- and polysaccharide-like substances is obvious, as evidenced by infrared spectroscopy (Fig. 4). The IR spectra reveals possible separate bands for the various constituents of the foulants: O-H stretching in the 3400 cm^{-1}; peptide peaks from proteins are observed at 1546 cm^{-1} and 1660 cm^{-1}, which are the characteristic of amide I and amide II respectively, the amide I at 1660 cm^{-1} is the stretching vibration bands associated primarily with the peptide carbonyls (C=O), and the amide II bands at 1546 cm^{-1} is attributed to the interaction between the N-H bonding and the C-N stretching of the C-N-H group; there was a broad peak at 1080 cm^{-1}, which is due to C-O

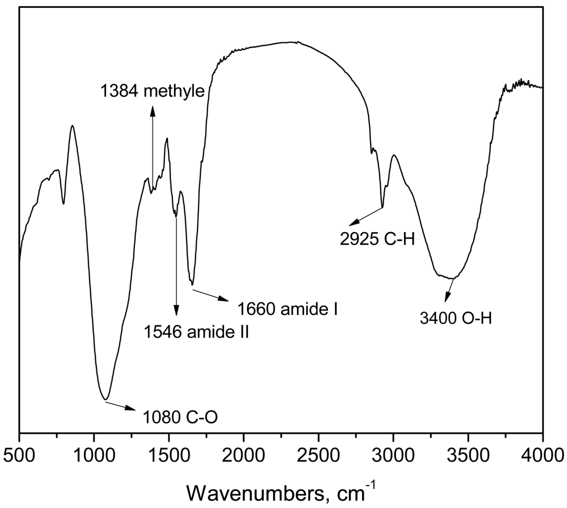


Fig. 4 FT-IR spectra of the cake

bonds and is associated with alcohols, ethers and polysaccharides, indicating the presence of polysaccharides or polysaccharide-like substances; the peak at 1380 cm^{-1} appears, suggesting the presence of lipids in the membrane foulants (Meng, *et al*. 2008). These results show that protein- and polysaccharide-like substances deposited on the fouled membrane surface (Her, *et al*. 2007). However, the presence of the sensitive carbonate band was not shown by IR spectroscopy, suggesting that carbonate dose not exist in the precipitate (Kwon, *et al*. 2005).

The XPS spectrum shows peaks of C, N, O, and Si elements (Fig. 5). The major composition of the inorganic foulant was identified as $MgNH_4PO_4{\cdot}6H_2O$ (struvite) in many literatures (Choo, *et al*. 2000, Kang, *et al*. 2002, Yoon, *et al*. 1999). However, P and Mg were not detected in the XPS spectra, indicating that the struvite was not found in the cake layer, which was reported as the major inorganic foulants in the membrane-bioreactors (Choo and Lee 1996). Based on this analysis, proteins and polysaccharide-like substances could be the possible foulants in the precipitate.

Particle size distribution of the suspended solids is an important parameter affecting the characteristics of the cake formed by the rejected solids, thereby influencing the antifouling characteristics (Satyawali and Balakrishnan 2009). Suspended solids were collected in the middle of the reactor and characterized, as shown in Fig. 6. It can be seen that the range of mean particle size for the membrane-bioreactor operated for different time is of 0-250 μm with most of them in the range of 50-200 μm. This result also indicates that it is a relative homogeneous system. The MLSS would remain unchanged in a short operation time (0-30 d), consequently, it didn’t change. For the 25 d operation time, there is a sharp peak in the range of 0-50 μm, suggesting that most of the small particles distributed in the size less than 50 μm. The aeration was stopped for several hours before the particle size distribution measurement, accordingly the particle size distribution result was mainly caused by the supernatant. With respect to the operation time of 15 d, there are two significant peaks at 60 μm and 140 μm, suggesting there were two classes of particles or macromolecule solutes in the supernatant (Meng, *et al*. 2008). As has been confirmed by the recent researches that the aeration intensity has a very important impact on the particle size and its distribution, which may play an important role on the membrane antifouling characteristics (Liu, *et al*. 2003).

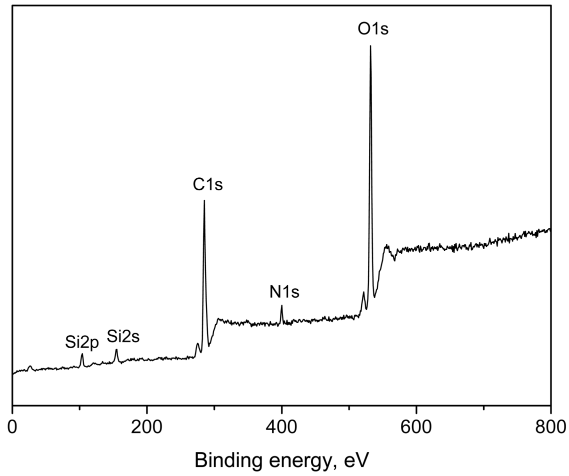


Fig. 5 XPS spectra of the cake

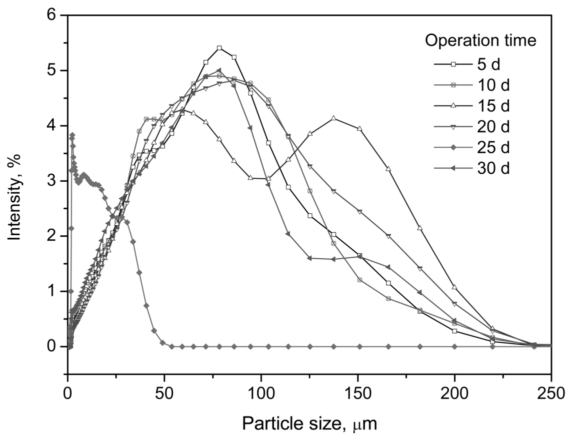


Fig. 6 Particle size distribution of the sludge in the SMBR

4. Conclusions

Hydropholic surface modification of polypropylene microporous membranes were performed by Ar plasma treatment. The effect of the surface modification and the antifouling characteristics of the modified membranes in the submerged membrane-bioreactor were summarized as follows.

(1) The pore size of the membranes reduced after Ar plasma treatment, and it also dropped after used in the submerged membrane-bioreactor; the advancing and receding contact angles declined, while the hysteresis between them was enlarged after Ar plasma treatment due to the surface roughness increasing.

(2) The modified membranes showed better filtration performances in the submerged membrane-bioreactor than the unmodified membrane. It was substantiated that Ar plasma treatment could reduce the surface water contact angle, improve the filtration performance, and make fouling less troublesome and membrane regeneration more efficient.

(3) With the reduction of membrane price, membrane-bioreactor will be widely used due to its advantages. However, membrane fouling remains the major obstacle in the present time, the improvement of its antifouling characteristics by plasma treatment seems to be the most favorable method for its convenience.

Acknowledgements

Financial support from the National Natural Science Foundation of China (No. 20871003) is gratefully acknowledged.

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