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Surface modification of polypropylene microporous membrane to improve its antifouling property in MBR: CO_2 plasma treatment

Hai-Yin Yu[a,b], Ya-Jie Xie[c], Meng-Xin Hu[a], Jian-Li Wang[d], Shu-Yuan Wang[a], Zhi-Kang Xu[a,*]

[a] *Institute of Polymer Science, Zhejiang University, Hangzhou 310027, China*
[b] *School of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, China*
[c] *College of Biochemical Engineering, Jiaxing University, Jiaxing 314001, China*
[d] *Department of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310027, China*

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Abstract

To improve the antifouling property of polypropylene hollow fiber microporous membranes (PPHFMMs) in a membrane-bioreactor (MBR) for wastewater treatment, the PPHFMMs were subjected to surface modification by CO_2 plasma treatment. Structural and morphological changes on the membrane surface were characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Water contact angle, which reflects the hydrophilicity of the membrane surface, was measured by the sessile drop method. Results of XPS clearly indicated that the plasma treatment introduced oxygen containing polar groups on the membrane surface. The static water contact angle of the modified membrane reduced obviously at first and then kept almost constant with the increase of CO_2 plasma treatment time. To assess the relation between the plasma treatment and the membrane fouling in a MBR, filtration for activated sludge was carried out using synthetic wastewater. The PPHFMMs after CO_2 plasma treatment showed better flux recovery after cleaning than that of the unmodified membrane. Fouling index (FI) for the CO_2 plasma treated PPHFMMs was lower than that of the unmodified PPHFMM.

Keywords: Membrane-bioreactor; Wastewater treatment; Antifouling property; Surface modification; Polypropylene hollow fiber microporous membrane; Plasma treatment

1. Introduction

Increasingly the shortage of water is a serious problem all over the world because of the population growth and the expansion of industry activities. Therefore, there is a growing impetus for wastewater recycle and reuse. Interests in the membrane-bioreactor (MBR) technology for wastewater treatment have continually increased [1–10]. The advantages offered by MBR over conventional treatment technologies are well known and the main of them are given below [11]: (1) complete removal of solid; (2) effluent disinfections; (3) separation of hydraulic retention time (HRT) and sludge retention time (SRT); (4) higher loading rate capability and longer SRT; (5) lower/zero sludge production; (6) rapid start-up; (7) more compact size; (8) lower energy consumption. Negative aspects, however, include membrane fouling and concentration polarization (which are to some extent exacerbated by membrane fouling) [11–15]. When membrane fouling occurs, a thick gel layer (which can be both biological or abiotic in composition) is formed onto the membrane surface and into the membrane pores, which causes the permeate flux to decline quickly. There have been many investigations concerning the mechanisms of membrane fouling [16–20] and the processes to restrict fouling and to enhance flux [21,22]. A series of methods, such as pretreatment of feed solution [23], using air sparging [24], unsteady flow [22], limiting the

* Corresponding author. Tel.: +86 571 8795 2605; fax: +86 571 8795 1773.
E-mail address: xuzk@ipsm.zju.edu.cn (Z.-K. Xu).

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flux and flushing by big bubbles [21], adding activated carbon [25], suitable design of membrane modules [8], back washing and cleaning [26], have been described in the literatures.

In general, membrane fouling occurs more seriously on hydrophobic membranes than hydrophilic ones because of hydrophobic interaction between solutes, microbial cells, and membrane materials. Membrane fouling can also be attributed to the adsorption of organic species, the precipitation of less soluble inorganic species, and the adhesion of microbial cells at the membrane surface. It is widely accepted that membrane fouling is less troublesome for the hydrophilic membranes than for the hydrophobic ones [12]. As a result, much attention has been made to reduce membrane fouling by modifying hydrophobic materials to relative hydrophilic [27–30]. In our previous work [31–34], it was found that grafting hydrophilic polymers on the membrane surface can enhance the resistant property of protein adsorption for polypropylene microporous membranes. This result indicates that the static antifouling property of polypropylene microporous membrane can be improved by surface modification. However, to our knowledge, few results [35,36] have been reported to describe the effect of surface modification on the dynamic antifouling property of a polymeric membrane in MBR for wastewater treatment. Therefore, the primary objective of this study is to investigate the effects of CO_2-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) and polypropylene flat microporous membrane (PPFMM) with a porosity of 45–50% and an average pore diameter of 0.10 μm were prepared with a melt-extruded/cold-stretched method in our laboratory [31]. The inner and outer diameters of PPHFMM are 240 and 290 μm, respectively. The area of each membrane module is about 91 cm^2. All other chemicals were AR grade and used without further purification.

2.2. Surface modification of PPHFMM by CO_2-plasma

Before plasma treatment, the PPHFMM was washed with acetone to remove any chemicals and wetting agents absorbed on the membrane surface, 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. These two electrodes were powered through a matching network by a 13.56 MHz radio-frequency generator. On the basis of systematic experiments considering surface etching and modification induced by plasma, 30 W was chosen as the applied rf power for all the experiments described here. The membrane was fixed in the center of the plasma reactor chamber. Then, the chamber was vacuumed and CO_2 was introduced. This process was repeated for several times to insure that air in the chamber was degassed. The CO_2 atmosphere in the chamber was kept at 10 Pa by a pressure regulator. After that, plasma was generated for a given time. Finally, the membrane was taken out of the chamber and used for characterization and/or filtration measurement.

2.3. Characterization of the membrane surface

Chemical composition of the PPHFMM surface was analyzed by X-ray photoelectron spectroscopy (XPS) with a PHI 5000c XPS spectrometer (Perkin-Elmer Instruments, USA). As a phonon source, Al Kα radiation (1486.6 eV) was used. The energy scale of the spectrometer was calibrated using the lowest BE component present in the superficial layer.

Surface morphology of the nascent and modified PPHFMMs were observed by scanning electron microscope (SEM) with a S-570 system (Hitachi, Japan). The morphological changes of these PPHFMMs after used in a MBR followed by water and NaOH solution cleaning respectively were also characterized with a Sirion FEG-SEM (FEI, USA).

To evaluate the hydrophilicity changes of the membrane surface, polypropylene flat microporous membrane (PPFMM) with almost similar average pore size and porosity was treated by CO_2-plasma at the same condition. Water contact angle on the membrane surface was measured by the sessile drop method using a DATA Physics System (OCA20, Germany) in which a droplet of water on the surface was imaged by a precision video camera and displayed on a monitor. Calculation of the contact angle was made directly from the monitor screen with a software. A minimum of seven contact angle measurements were obtained for each membrane, and five values besides the maximum and minimum values were used for the calculation of an average value. The standard deviation was about 0–3°.

An Autoscan 3310X Porosimeter (Porous Materials Inc.) was used to measure the pore diameter and porosity of the studied membranes. The apparatus has an available pressure range of 0–22770 × 10^3 Pa (0–3300 psi) (absolute). A weighted amount of hollow fiber membrane was introduced into the chamber filled with mercury. When the maximum pressure is achieved, the extrusion curve starts by slowly reducing the applied pressure. From the data, on intruded volume versus applied pressures, the porosity and pore size can be obtained according to a procedure outlined elsewhere [37].

A versatile materials experimental instrument (RG2000-10, Shenzhen, China) was used to estimate the mechanical properties after CO_2 plasma treatment, at least 10 measurements were made to calculate the mean values.

2.4. Filtration and antifouling properties measurements

A submerged MBR (Fig. 1) was designed to characterize the filtration performance of the unmodified and modi-