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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.

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]. Ampheric 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

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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. CO_2 [20] and NH_3 [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 cm^2.

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 ($h\nu$ = 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-