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Mitigated membrane fouling in an SMBR by surface modification

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Abstract

Fouling is a major obstacle in membrane processes applied in membrane bioreactor. To improve the antifouling characteristics of polypropylene hollow fiber microporous membranes (PPHFMMs) in a submerged membrane bioreactor (SMBR), the PPHFMMs were surface modified by NH_3, CO_2 plasma treatment, photoinduced graft polymerization of acrylamide and acrylic acid. The structural and morphological changes on the membrane surface were characterized by X-ray photoelectron spectroscopy (XPS), attenuated total reflection-Fourier transform infrared spectroscopy (FT-IR/ATR) and field emission scanning electron microscopy (FE-SEM). The change of surface wettability was monitored by contact angle measurements. The results of XPS and FT-IR/ATR clearly indicated the successful modification on the membrane surface. The static water contact angle of the modified membrane reduced obviously. The antifouling characteristics of the modified membranes in an SMBR were evaluated. The modified membranes showed better filtration performances in the submerged membrane bioreactor than the unmodified one, and the acrylic acid-grafted membrane presented the best antifouling characteristics. The results demonstrated that (1) the surface carboxyl-containing membranes were better than the surface amido-containing membranes; (2) surface-grafted membranes were better than the plasma-treated membranes.

Keywords: Antifouling characteristics; Polypropylene hollow fiber microporous membrane; Submerged membrane bioreactor; Surface modification; Wastewater treatment

1. Introduction

Membrane fouling due to the interactions between solute and membrane surface are the object of intensive studies. Concerning to the membranes, the surface chemical and physical properties, including molecular weight cut off (MWCO) (or pore size), surface wettability, surface charge and surface acidic/basic character play dominant roles in determining the antifouling characteristics.

A mechanistic model [1] was developed to show how a dynamic secondary membrane formed by large particles is able to capture small particles and thereby slow the rate at which the latter foul the primary membrane. The relative size of the membrane pores and the particles are directly related to membrane fouling.

Hydrophilic membranes are better than the hydrophobic ones in the antifouling characteristics [2,3]; significant reductions in fouling behavior have been reported about membranes with modified hydrophilic surfaces. Six different hydrophilic membranes were evaluated for their ability to reduce fouling by natural organic matters [4]. The monomers included the neutral, the weakly acidic and the strongly acidic. The weakly acidic monomer, acrylic acid, produced the lowest fouling membrane.

Membrane surface charge also plays an important role in membrane fouling, specially when both protein molecules and membrane surface bear the same charge due to static electric repulsion [5].

Among various surface modification methods, grafting polymerization is widely used for its superior comprehensive properties [6–8]. The grafting chain length and grafting density have important roles in membrane permeate properties and antifouling characteristics [9–11]. Jeon [12,13] found that protein adsorption on surface was closely related to the balance between the attractive forces (van der Waals force and hydrophobic force) and the steric repulsion. The repulsion force increases with the increase of grafting chain density. The longer grafting chains can provide bigger repulsion force, and have higher mobility than the shorter ones, which makes higher hydrophilic layer between protein molecule and membrane surface.

With the increase of the grafting degree, the membrane permeability may decrease [14], there should be an optimal value

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of grafting chain length and grafting density for membranes permeability and membrane antifouling characteristics.

Membrane bioreactor process has been deemed to be a promising technology for wastewater treatment and water reclamation [15–17]. However, membrane fouling is still a major limitation to the large-scale application of the MBR process [18–20]. Thus, it is necessary to obtain the membranes with better performances for fouling control in MBR applications. In our previous studies, PPHFMMs were surface modified by NH_3 [21] and CO_2 [22] plasma treatment, photoinduced grafting polymerization of AAm [23] and AAc [24], the antifouling characteristic in SMBRs have been improved to some extent. Because the MBR system includes living microorganisms and their metabolites, the biomass biological characteristics and the physico-chemical properties of the suspension change with the change of operating conditions, the fouling mechanism is even more complex than that of any membrane separation processes. As a result, the effects of the membrane surface modifications on membrane fouling were discussed separately in our previous work.

In this work, surface modification of PPHFMMs by NH_3 and CO_2 plasma treatment, and photoinduced grafting polymerization of AAm and AAc were carried out; the antifouling characteristics for the surface-modified membranes by different methods in an SMBR were investigated combinedly, the surface chemical and physical properties which affect the membrane fouling mostly were discussed.

2. Materials and methods

2.1. Materials

Polypropylene hollow fiber microporous membrane (PPHFMM) 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. The inner and outer diameters of PPHFMM are 240 and 290 μm, respectively. In this study, U-shaped PPHFMM modules were carefully fabricated by hand. There were 100 bundles of hollow fibers within each module; the total area of a module was about 100 cm^2. Other commercially available chemicals were AR grade and used without further purification.

2.2. Surface modification

Before surface modification, polypropylene microporous membranes were 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.

2.2.1. Membrane surface modification by plasma treatment

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 the plasma gas was introduced. This process was repeated for several times to insure that the chamber was degassed. The plasma gas atmosphere in the chamber was kept at 40 Pa by a pressure regulator. After that, plasma was generated for 4 min. Finally, the membrane was taken out of the chamber, washed with acetone to remove the deposition of polymer fragments formed by the gas used and/or by the volatile products produced from the etched surface, and then stored in water to prevent “hydrophobic recovery” [25].

2.2.2. Membrane surface modification by photoinduced graft polymerization

An UV illumination system equipped with two high-pressure mercury lamps (2× 300 W with a wavelength range of 232–500 nm) was used [26]. The sequential photoinduced graft polymerization method was used in the present work. First, preweighed membranes (at least two samples per batch) were presoaked for 60 min in 50 mL solution of 10 mM benzophenone (BP) in heptane. UV irradiation was carried out for 5 min. Thereafter, the samples were taken out, washed with acetone and dried completely. Then the samples were immersed in acetone for 1 min, wiped with filter paper to remove the adhering solvent, and then immediately immersed into quartz glass tube containing 50 mL 100 g/L monomer solution in water. After 5 min of equilibration, UV irradiation for a given time followed under argon atmosphere. Finally, the samples were taken out of the reaction chamber and washed with pure water in a shaking water bath at 30 °C for 24 h, then dried completely in vacuum oven.

The grafting degree was calculated according to the following equation:

$$\text{grafting degree (wt.\%)} = \frac{w_a - w_b}{w_b} \times 100 \qquad (1)$$

where w_b and w_a are the weight of a membrane before and after surface modification, respectively.

2.3. Characterization of the membrane surface

The chemical composition of the PPHFMM surface was analyzed by X-ray photoelectron spectroscopy (XPS) with a PHI 5000c XPS spectrometer (Perkin-Elmer Instruments, USA). All the results presented here corresponded to the use of the Al Kα radiation (1486.6 eV). The background pressure was 1×10^{-5} Pa. Pass energy of 150 eV was used to obtain the wide scan spectra, while 25 eV pass energy and 45° take-off angle were used for the high-resolution spectra of C 1s, N 1s and O 1s signals, respectively. The signal of C 1s, 284.7 eV, was selected for energy calibration. The C 1s, N 1s and O 1s envelopes were analyzed and peak-fitted after subtraction of a Shirley background using a Gaussian–Lorentzian peak shapes obtained from the Casa XPS software package.

FT-IR/ATR spectra were recorded on an infrared spectrometer (Brucker Vector 22 FT-IR, Switzerland). The ATR accessory