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Improvement of the antifouling characteristics for polypropylene microporous membranes by the sequential photoinduced graft polymerization of acrylic acid

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Abstract

Surface modification of polypropylene hollow fiber microporous membranes (PPHFMMs) was performed by a sequential photoinduced graft polymerization of acrylic acid (AA) from water solution. Structural and morphological changes on the membrane surface were characterized by attenuated total reflection-Fourier transform infrared spectroscopy (ATR/FT-IR) and field emission scanning electron microscopy (FE-SEM). Water contact angles of the membrane surfaces were also measured by the sessile drop method. Results of ATR/FT-IR indicated the successful graft polymerization of AA onto the membrane surface. Water contact angle of the modified membrane decreased with the increase of the grafting degree (GD). It showed 68° for the grafted membrane with a GD of 45.8 wt.%, nearly 61° lower than that of the nascent one. The pure water fluxes of the studied membranes depending on GD and pH value were studied. It was found that the pure water flux increased with the increase of GD and the decrease of pH value. The antifouling characteristics for the PPHFMMs before and after surface modification were assessed by the filtration of activated sludge in a submerged membrane bioreactor for synthetic wastewater treatment. Results demonstrated that after continuous operation for about 85 h, the flux recovery was 13.7% and 25.4% while the flux ratio was 1.00 and 2.52 for the nascent and grafted PPHFMMs, respectively.

Keywords: Photoinduced graft polymerization; Polypropylene hollow fiber microporous membrane; Acrylic acid; Submerged membrane-bioreactor; Antifouling characteristics

1. Introduction

It is widely known that the chemistry of the membrane surface directly affects the performance in many applications, such as bioseparation [1–3] or membrane bioreactor [4–13]. In bioseparation using membrane technology, functionalizations are widely used to change the character of the membrane surface to decrease the adsorption of proteins or to introduce functional groups to obtain special permselective membranes or membrane adsorbers. Therefore, there is an increasing interest for the surface modification of membranes, and a variety of surface modification methods have been reported for a large number of different membranes [14–22]. Among several approaches, UV-assisted graft polymerization is a powerful technology, with low cost of operation and potentially reducing or even avoiding negative effects onto the bulk membranes. However, photoinduced polymerization will result in the production of significant amounts of homopolymer and crosslinked polymer if the initiator, normally benzophenone (BP), abstract hydrogens from monomers and/or reacted polymers. The undesired homopolymer wastes expensive starting materials, and cross-linked polymers are [23] detrimental to applications, such as membrane permeability. To avoid this, Ma and Ulbricht [23,24] described a two-step photoinitiated process for the graft functionalization of polypropylene membrane using BP as the photoinitiator: first (without monomer), BP was bound onto the membrane surface, yielding a semipinacol; second (with monomer), far-UV irradiation was used to cleave this bond again, and a “quasi-living” polymerization via the recombination and photocleavage of semipinacol was proposed. Furthermore, polymer brush layers

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will be especially suited for effectively shielding the base membrane at a minimum layer thickness, and it also has been demonstrated that functional brush layers can have a three-dimensional binding capacity for proteins. Among the two strategies toward covalently anchored polymer brush structures, "grafting to" and "grafting from", the latter using functional monomers was proven to be much flexible and versatile. Using heptane as an entrapping solvent, Ulbricht and Yang [24] described a rather simple and robust method to improve the efficiency of photoinitiation by controlling photoinitiator location (entrapping in the surface layer).

On the other hand, there is a growing impetus for wastewater recycle and reuse due to the shortage of water all over the world. Interest in the membrane-bioreactor (MBR) technology for wastewater treatment has increased because of the advantages offered by MBR over the conventional treatment technologies [25,26]. Negative aspects, however, include membrane fouling and concentration polarization (which are to some extent exacerbated by membrane fouling) [27,28]. In general, membrane fouling occurs more seriously on hydrophobic membranes than hydrophilic ones because of hydrophobic interactions between solutes, microbial cells and the membrane surfaces [29]. As a result, much attention has been made to reduce membrane fouling by modifying hydrophobic membranes to relative hydrophilic [30,31].

In our previous work, polypropylene microporous membrane were hydrophilized by ammonia and carbon dioxide plasma treatment [32,33], or by the tethering of sugar moieties induced with nitrogen plasma treatment [34], and the antifouling characteristics for polypropylene microporous membranes in an MBR were improved to some extent. Although the use of plasma treatment processes has many advantages, such as a very shallow modification depth compared to other surface modification techniques, it still has drawbacks. For examples, the chemical reactions in the discharge itself are rather complex, the control and ultimate analysis of the surface chemistry is limited and it is not convenient to extend its applications on large scale.

In this work, the surface modification of polypropylene hollow fiber microporous membranes was accomplished by a procedure including coating the membranes with BP using the entrapping method [25], and subsequent UV irradiation in aqueous acrylic acid solutions. The impacts of polymerization conditions on the grafting degree were analyzed, the modified membranes with poly(acrylic acid) brush layers were characterized with ATR/FT-IR and FE-SEM as well. Membrane permeabilities depending on the grafting degree and pH value were also studied. The antifouling characteristics in a submerged membrane bioreactor for synthetic wastewater treatment were assessed.

2. Materials and methods

2.1. Materials

Polypropylene hollow fiber microporous membrane (PPHFMM) and polypropylene flat microporous membrane with a porosity of 45.9 ± 3.1% and an average pore diameter of 0.10 ± 0.04 μm were prepared with a melt-extruded/cold-stretched method in our laboratory, the details were described as the following. Typically, fiber grade isotactic polypropylene (FY-4012) was pretreated at 250 °C in the spinning apparatus. The spinning temperature was set at 200 °C, and the melt-draw ratio was 1000%. The hollow fibers were subsequently annealed at 145 °C for 30 min to increase crystallinity. Then, to form microspores, the hollow fibers were cold-stretched at 60 and 110 °C with a cold-stretching ratio of 120% and 300%, respectively, and reannealed at 145 °C for 1 h. The inner and outer diameters of PPHFMM are 240 and 290 μm, respectively. PPFMM with a thickness of 100 ± 3.5 μm was prepared by a similar process from corresponding dense film. In this study, U-shape PPHFMM modules were carefully fabricated by hand. There were 100 bundles of hollow fibers within each module with an area of about 90 cm^2. Acrylic acid (AA, 99.9%) was purified under depressurized pressure to remove the inhibitor before use. Benzophenone (BP) was recrystallized twice from ethanol and used as photoinitiator.

2.2. Photoinduced graft polymerization

An UV illumination system equipped with one high pressure mercury lamp (500 W with a wavelength range of 232–500 nm) was used. The sequential photoinduced graft polymerization method was used in the present work. First, preweighed PPHFMMs (at least two samples per batch) were presoaked for 60 min in 50 mL solution of 10 mM 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 AA 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, dried completely in vacuum and used for characterization and/or filtration measurements.

The grafting degree (GD) was calculated according to the following equation:

$$\mathrm{GD(wt.\%)} = \frac{w_a - w_b}{w_b} \times 100 \quad (1)$$

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

2.3. Characterization of the membrane surface

ATR/FT-IR spectra were recorded on an infrared spectrometer (Brucker Vector 22 FT-IR, Switzerland). The ATR accessory contained a ZnSe crystal at a nominal incident angle of 45°, yielding about 12 internal reflections at the sample surface. All spectra (16 scans at 4.0 cm^{-1} resolution and ratio to the appropriate background spectra) were recorded at 25 °C.

Surface morphology for the nascent and modified PPHFMMs were observed by field emission scanning electron microscope (FE-SEM) with a Sirion FEG-SEM (FEI, USA).