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Chain-length dependence of the antifouling characteristics of the glycopolymer-modified polypropylene membrane in an SMBR

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ABSTRACT

Membrane-bioreactor processes have increased considerably in recent years. However, the natural disadvantages of common membrane materials, such as hydrophobic surface, cause membrane fouling and cumber further extensive applications. In this work, hydrophilic surface modification of polypropylene microporous membranes was carried out by the sequential photoinduced graft polymerization of D-gluconamidoethyl methacrylate (GAMA) to meet the requirements of wastewater treatment and water reclamation applications. The grafting density and grafting chain length were controlled independently in the first and second step, respectively. Attenuated total reflection–Fourier transform infrared spectroscopy (FT-IR/ATR) and X-ray photoelectron spectroscopy (XPS) were employed to confirm the surface modification on the membranes. Water contact angle was measured by the sessile drop method. Results of FT-IR/ATR and XPS clearly indicated that GAMA was grafted on the membrane surface. It was found that the grafting chain length increased reasonably with the increase of the UV irradiation time. Water contact angle on the modified membrane decreased with the increase of the grafting chain length, and showed a minimum value of 43.2°, approximately 51.8° lower than that of the unmodified membrane. The pure water fluxes for the modified membranes increased systematically with the increase of the grafting chain length. The effect of the grafting chain length on the antifouling characteristics in a submerged membrane-bioreactor for synthetic wastewater treatment was investigated. After continuous operation in the submerged membrane-bioreactor for about 70 h, reduction from pure water flux was 90.7% for the virgin PPHFMM, and ranged from 80.8 to 87.2% for the modified membranes, increasing with increasing chain length. The flux of the virgin PPHFMM membrane after fouling and subsequent washing was 31.5% of the pure water flux through the unfouled membrane; for the modified membranes this ranged from 27.8 to 16.3%, decreasing with increasing chain length. These results demonstrated that the antifouling characteristics for the glucopolymer-modified membranes were improved with an increase in GAMA chain length.

1. Introduction

In recent years, membrane-bioreactor (MBR), as a novel and powerful technique for wastewater treatment and water reclamation, has received tremendous attention due to the increasingly shortage of water worldwide [1,2]. However, a frequently encountered bottleneck is serious membrane fouling [3–6].

The negative effects on membrane performance due to the fouling are basically known. However, the actual mechanism of the fouling, especially in an MBR system, is not well understood. Because the MBR system includes living microorganisms and their metabolites, the biomass biological characteristics and the physico-chemical properties of the suspension, change with time, the fouling mechanism is more complex than that of any membrane separation processes.

It has been widely accepted that the effective strategy to suppress membrane fouling especially is to increase hydrophilicity of membrane surface by incorporating hydrophilic macromolecule modifiers [7–9]. As a result, much work has been done to reduce membrane fouling by modifying hydrophobic materials to relative hydrophilic. Different methods including physical coating and chemical reacting have been employed to modify the membrane surface [8,10].

Among them, the grafting of hydrophilic monomers on the membrane surface shows some promises [11–13]. Using hydrophilic materials, this technique can increase the hydrophilicity of the membrane, resulting in the enhancement of membrane performance properties while simultaneously reducing the foul-

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ing. However, grafting polymerizations induced by radical, plasma, electron-bean, γ-radiation and ultraviolet may result in significant disadvantages of these free radical techniques. The homopolymerization of the monomer always occurs to some extent, producing a product, which is a mixture of graft polymer and homopolymer. Moreover, backbone degradation and gel formation can occur as a result of uncontrolled free radical production. In most of the cases, the grafting density (mole of surface initiators per area) and grafting chain length (repeating units per chain) cannot be determined independently, much less controlled.

UV-assisted graft polymerization is a powerful and highly attractive technology with a number of desirable properties [14]. Firstly, prior modification of a surface is unnecessary. Secondly, a high concentration of active species can be produced locally at the substrate surface; as a result, the homopolymerization of the monomer can be significantly reduced. Thirdly, the procedure is relatively simple, energy-efficient, and cost-effective. Fourthly, photoinduced polymerization is well suited to produce desired surface chemistry changes in well-defined two-dimensional regions on a surface. Finally, the grafting density and grafting chain length can be controlled independently in the first and second step by the method of sequential photoinduced graft polymerization, which cannot be readily controlled by other methods [15].

Chain length and grafting density play important roles in membrane fouling and membrane permeability [16]. Grafting short polymer chains may be one method of maintaining more of the unmodified membrane permeability after modification. However, a high grafting chain density and long grafting chain length may be essential to impart the necessary surface hydrophilicity to decrease membrane fouling, especially irreversible fouling. Therefore, the grafting chain density and grafting chain length should be optimized to impart the necessary surface hydrophilicity and maintain the permeability as high as possible. Jeon et al. [17] also reported that protein adsorption on surface was reduced with the increase of grafting chain density and the grafting chain length. The longer grafting chains can produce bigger repulsion force and have higher mobility than the shorter ones.

Glycopolymers have been noted in the last decade because of their various functions. Also, these polymers are potential surface modifiers for development of interface properties. However, few works have been concerned for membrane surface modification with the graft polymerization of the sugar-containing monomer. In our previous study, α-allyl glucoside (AG) was tethered on a polypropylene microporous membrane (PPMM) by plasma treatment and some promising results were obtained [18]. On the other hand, vinyl sugars with an open-chain structure were more efficient in improving the hydrophilicity of the polymeric material surface than those with cyclic ones [19].

In the present work, a linear sugar, GAMA was grafted onto the surface for the hydrophilic modification of polypropylene hollow fiber microporous membrane (PPHFMM) by the sequential photoinduced graft polymerization. The antifouling characteristics for the unmodified and the modified PPHFMMs during the membrane filtration of activated sludge in an aerobic submerged membrane-bioreactor (SMBR) for synthetic wastewater treatment were investigated, and the effect of the grafting chain length on the membrane performance was also studied.

2. Materials and methods

2.1. Materials

PPHFMM (for the filtration experiment, the average inner and outer diameters are 240 and 290 μm, respectively) and non-porous polypropylene films (for water contact angle measurement) were used. Glycopolymer, D-gluconamidoethyl methacrylate (GAMA) was synthesized according to the literature [20]. Benzophenone (BP) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and recrystallized twice from ethanol and used as photosensitizer. In this study, U-shaped PPHFMM modules were carefully fabricated by hand. There were 100 bundles (50 fibers) of hollow fibers within each module, and the total area of the membrane module was about 100 cm^2.

2.2. Photoinduced graft of GAMA

An UV illumination system (self-made) equipped with two high-pressure mercury lamps (2×300 W with a wavelength range of 232–500 nm, an intensity of 13.08 ± 2.08 mW cm^{-2} and providing homogenous illumination up to 200 cm^2) was used. 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 BP solution in heptane. UV irradiation was carried out for predetermined time. Thereafter, the samples were taken out, washed with acetone and dried completely. Then the samples were immersed in acetone for 1 min, and then immersed into quartz glass tube containing 50 mL GAMA solution in water. After 5 min of equilibration, UV irradiation for a given time followed. Finally, the samples were taken out and washed with water vigorously using a vibrator. After drying in a vacuum oven at 40 °C to constant weight, the grafting density and grafting chain length were calculated as follows according to Ma et al. [15]:

$$\text{Grafting density of BP on PPMM, } \sigma = \frac{(W_1 - W_0)/\mathrm{MW_{BP}}}{S} \quad (1)$$

$$\text{Grafting chain length of PGAMA on PPMM, } \gamma = \frac{W_2 - W_0}{\mathrm{MW_{GAMA}}} \quad (2)$$

where σ is the grafting density, mol cm^{-2}; γ the grafting chain length of GAMA on the membrane surface, repeating units per chain; W_0 is the weight of the blank membrane, W_1 and W_2 are the weights of the membrane after the first and the second step; S is the surface area of the membrane; $\mathrm{MW_{BP}}$ (182.22 g/mol), $\mathrm{MW_{GAMA}}$ (307.30 g/mol) are the molecular weights of BP and GAMA, respectively.

2.3. Characterization of the membrane surface

X-ray photoelectron spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (PerkinElmer) 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) were 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).

FT-IR/ATR spectra were recorded on an infrared spectrometer (FT-IR 8900, Shimadzu, Japan). The ATR accessory contained a ZnSe crystal at a nominal incident angle of 45°, the FT-IR/ATR penetration for this incident angle was 0.1–1 μm [21]. All spectra (40 scans at 4.0 cm^{-1} resolution and ratio to the appropriate background spectra) were recorded at 25 °C.