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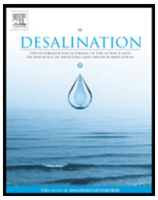

Effect of membrane pore morphology on microfiltration organic fouling: PTFE/PVDF blend membranes compared with PVDF membranes

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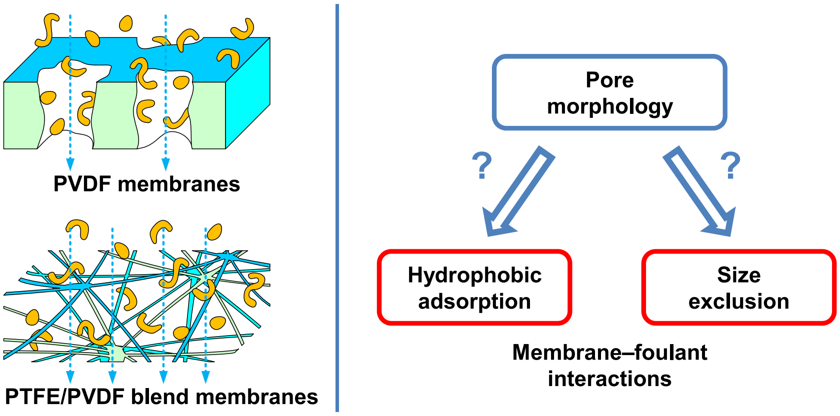
HIGHLIGHTS

- Pore morphology impacts on the interactions between membrane and foulant.
- Hydrophobic adsorption and size exclusion are key mechanisms promoting fouling.
- PVDF and PTFE/PVDF blend membranes were compared on morphology and fouling.
- Thread-like pore walls of the blend membranes discourage hydrophobic adsorption.
- High structural complexity of the blend membranes encourages size exclusion.

GRAPHICAL ABSTRACT



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ABSTRACT

This study provides an insight into the effect of membrane pore morphology on microfiltration organic fouling, by comparing the fouling behaviors of a series of polytetrafluoroethylene/polyvinylidene fluoride (PTFE/PVDF) blend membranes with those of PVDF membranes at varied hydrophobicity and pore size levels. Unlike the PVDF membrane pore morphology which resembled particulate bed, the PTFE/PVDF blend membrane morphology was characterized as fibrous network with thread-like pore walls and interconnected pore channels of high structural complexity. Fouling evolution rate and irreversibility of these membranes were assessed using batch filtration tests, with a membrane bioreactor supernatant employed as the foulant. Fouling of the PVDF membranes deteriorated significantly with increasing hydrophobicity and decreasing pore size. By comparison, all the blend membranes showed moderate fouling, much less sensitive to hydrophobicity and pore size. It was demonstrated that hydrophobicity and pore size pertain to hydrophobic adsorption and size exclusion respectively, which are fundamental membrane–foulant interactions for promoting fouling. Pore morphology may affect fouling by influencing these interactions. For the case of the blend membranes, it was inferred that the thread-like pore walls with limited adsorption area discouraged hydrophobic adsorption, while the high structural complexity encouraged size exclusion on the other hand.

1. Introduction

Microfiltration (MF) technology has attracted increasing attention in the recent years in the field of wastewater treatment and reclamation

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[1]. The growing application of MF owes much to the popularization of membrane bioreactor (MBR) [2], which has been increasingly used for pre-treatment of desalination for wastewater reclamation [1,3]. However, a major obstacle to the broadening application of MF lies in membrane fouling [2,4]. Organic fouling, as induced by attachment of colloidal and soluble organic matter to membrane, has been well reported to form a significant part of MF membrane fouling [5–7]. Membrane properties can have profound impact on fouling, because fouling essentially originates from the interaction between membrane and foulant [2]. In order to select or develop proper membranes to mitigate organic fouling, it is important that the effect of membrane properties be well understood.

Among the membrane properties that may influence MF fouling, membrane hydrophobicity and pore size have been the most extensively studied [8–10], owing to their direct relation to hydrophobic adsorption and size exclusion, which are two fundamental membrane–foulant interactions in the physicochemical and steric aspects respectively [11]. Also highlighted in the literature is the importance of pore morphology to fouling [4,12,13]. Pore morphology could differ widely according to membrane material or fabrication method. As a typical example, the well-applied polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) membranes have very different pore morphologies. PVDF membranes made via phase separation usually represent granular pore structure, while PTFE membranes made via controlled stretching usually represent fibrous network with interconnected pore channels [14–16]. Pore morphology might affect fouling directly, or indirectly by altering the effects of other factors. Despite its potential importance, the role of pore morphology in MF fouling has been studied by only a few researchers [17,18]. Especially, mechanisms of how pore morphology can affect the fundamental interactions of hydrophobic adsorption and size exclusion, has not yet been reported.

This study aimed to provide an insight into the effect of pore morphology on MF organic fouling, by systematically comparing the fouling behaviors of a series of PTFE/PVDF blend membranes with those of PVDF membranes. These two types of membranes had distinct pore morphologies. Each type included membranes with varied hydrophobicity and pore sizes, which would enable investigation into the role of pore morphology in hydrophobic adsorption and size exclusion for fouling. A typical MBR supernatant was employed as the foulant for the MF fouling experiments, which were conducted in a well-defined stirred dead-end filtration system [19]. Fouling evolution and fouling irreversibility during multi-cycle filtration of all the membranes were quantitatively analyzed. An in-depth discussion was then made about the mechanisms for the effect of pore morphology on MF organic fouling.

2. Materials and methods

2.1. Microfiltration membranes

Four PTFE/PVDF blend flat-sheet membranes (Minglie, China) and four PVDF flat-sheet membranes (Millipore, USA) were studied, including hydrophobic and hydrophilic ones with small pore size (~0.1 μm) and large pore size (~0.2 μm). Detailed information of the membranes is given in Table 1. Herein, the hydrophobic, hydrophilic, small-pore and large-pore membranes are denoted respectively as HOB, HIL, SP and LP. Prior to use, the hydrophobic membrane disks were washed by filtering 50 mL 95% (v/v) alcohol and 50 mL Milli-Q water successively, ensuring that the membranes were sufficiently wetted and degassed. All the hydrophilic as well as the wetted hydrophobic membrane disks were rinsed with Milli-Q water and soaked in 3 mM NaN_3 for 24 h to remove impurities or additives from the fabrication process.

2.2. Foulant solution

An MBR supernatant was employed as the foulant solution. The supernatant was separated from the mixed liquor of a full-scale MBR plant treating municipal wastewater in Beijing, China. The separation procedure consists of centrifugation at 3000 ×g and 4 °C for 5 min (CF16RX II, Hitachi, Japan), coarse filtration with filter paper, and fine filtration using 0.7 μm glass-fiber membranes (GF/F, Whatman, UK) with each membrane serving 200 mL of the liquid. The supernatant was then stored at 4 °C with the addition of 3 mM NaN_3 as a microbial inhibitor. The supernatant contained ~23 mg/L total organic carbon (TOC), with its chemical composition as well as the hydrophobic proportion and molecular weight distribution of each chemical species listed in Table 2.

2.3. Fouling tests

Fouling of the four PVDF membranes as well as the four blend membranes by the MBR supernatant was examined via multi-cycle MF tests conducted in a constant pressure stirred dead-end filtration system. A 50 mL filtration cell (Amicon 8050, Millipore, USA) with an effective filtration area of 13.4 cm^2 was employed, which was connected to a 1.5 L acrylic reservoir. Other details of the system were described previously [19]. The pressure applied to the cell was maintained at 10 kPa and the stirring rate at 300 rpm during the filtration.

The evolution of fouling during filtration was described by the curve of filtration resistance (R, m^{-1}) versus specific permeate volume (V, m^3-permeate/m^2-filtration area). R was calculated from filtration flux (J, m/s) according to Darcy's law:

$$R = \frac{\Delta P}{\mu J} = \frac{\Delta P}{\mu} \bigg/ \frac{dV}{dt} \tag{1}$$

where ΔP is the trans-membrane pressure (Pa), μ the dynamic viscosity of permeate (close to that of water) (Pa·s), and t the filtration time (s). Noting that the filtration flow was instantly unstable at the beginning of filtration (possibly due to the sudden opening of the permeate valve), we excluded the flux data at $V < 0.001\ m^3/m^2$ after the beginning of each filtration cycle from the calculation of R.

The rapidity of fouling evolution was then assessed by considering the stages of fouling. The evolution process of fouling by soluble and colloidal organics typically consists of the initial pore blocking stage and the subsequent gel layer growth and maturation stages [19]. The demarcating point between the first two stages is defined as the “critical point”, which could be determined by considering the constant-pressure filtration laws:

$$\frac{d^2t}{dV^2} = k_n\left(\frac{dt}{dV}\right)^n \quad \text{or equivalently} \quad \frac{dR}{dV} = k_nR^n \tag{2}$$

where k_n is a model parameter, and the exponent n is characteristic of fouling mode: $n = 0$ for gel layer growth and $n > 0$ for pore blocking (i.e. complete blocking, standard blocking, intermediate blocking, or a mixture of them) [19]. The “critical point” can therefore be determined as the point at which n becomes 0. The volume of permeate collected from the beginning of filtration till the “critical point” (denoted as V_{crit}) measures the length of the initial pore blocking stage, and hence can reflect the rapidity of fouling evolution in each filtration cycle.

The irreversibility of fouling was assessed by physical cleaning experiments performed at the end of each filtration cycle (when $R > 1.5 \times 10^{12}\ m^{-1}$). The fouled membrane was swept tenderly by hand to remove the external fouling layer, and backwashed at 20 kPa with 50 mL Milli-Q water. The filtration resistance was then measured by filtration (in the forward direction) of another 50 mL Milli-Q water at 10 kPa. The filtration resistance induced by physically irreversible fouling was calculated by subtracting the intrinsic resistance of the virgin membrane from the resistance remained after the physical cleaning.