Applied Surface Science 330 (2015) 351–357

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effect of membrane polymeric materials on relationship between surface pore size and membrane fouling in membrane bioreactors

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ARTICLE INFO

Article history:
Received 6 November 2014
Received in revised form
24 December 2014
Accepted 4 January 2015
Available online 9 January 2015

Keywords:
Membrane fouling
Membrane polymeric materials
Pore size
Membrane bioreactor (MBR)
Polyvinylidene fluoride (PVDF)

ABSTRACT

We investigated the effect of different membrane polymeric materials on the relationship between membrane pore size and development of membrane fouling in a membrane bioreactor (MBR). Membranes with different pore sizes were prepared using three different polymeric materials, cellulose acetate butyrate (CAB), polyvinyl butyral (PVB), and polyvinylidene fluoride (PVDF), and the development of membrane fouling in each membrane was evaluated by batch filtration tests using a mixed liquor suspension obtained from a laboratory-scale MBR. The results revealed that the optimal membrane pore size to mitigate membrane fouling differed depending on membrane polymeric material. For PVDF membranes, the degree of membrane fouling decreased as membrane pore size increased. In contrast, CAB membranes with smaller pores had less fouling propensity than those with larger ones. Such difference can be attributed to the difference in major membrane foulants in each membrane; in PVDF, they were small colloids or dissolved organics in which proteins are abundant, and in CAB, microbial flocs. The results obtained in this study strongly suggested that optimum operating conditions of MBRs differ depending on the characteristics of the used membrane.

1. Introduction

Membrane bioreactors (MBRs) have many advantages over conventional wastewater treatment technologies, including high quality of treated water, small footprint, and ease of operation [1,2], and are becoming increasingly popular for wastewater treatment [3]. However, high operation and maintenance costs that can mainly be attributed to the development of membrane fouling (deterioration of membrane permeability) are obstacles that limit the widespread application of this technology. To use MBRs more efficiently, strategies to control membrane fouling need to be established.

Membrane fouling in MBRs has therefore been a hot research topic and numerous papers on this subject have been published [4,5]. Attention has been paid to various design and operating parameters such as membrane flux [6–10], solid retention time (SRT) [11–13], and food-to-microorganism (F/M) ratio [14–16]. In addition to these factors, it is widely accepted that the membranes used also greatly influence the development of membrane fouling in MBRs [17–22]. These previous studies suggested that the development of membrane fouling in MBRs could be substantially suppressed by using an appropriate membrane. At present, however, a clear consensus on the characteristics of membranes with low fouling propensity has not been established.

Generally, membranes with smooth surface morphology are thought to be desirable for preventing membrane fouling [18,20,21]. However, Choi et al. [19] reported that pore structure has a greater influence on the development of membrane fouling than the roughness of membrane surfaces. The effect of pore size on the development of membrane fouling is also complicated. While some researchers reported that membranes with larger pore sizes are more susceptible to membrane fouling [20], the opposite result has also been published [22]. The effect of pore size

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http://dx.doi.org/10.1016/j.apsusc.2015.01.018
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Table 1
Preparation conditions of hollow fiber membranes.

	CAB			PVB			PVDF		
	0.2 μm	0.05 μm	0.04 μm	0.15 μm	0.1 μm	0.02 μm	0.4 μm	0.25 μm	0.02 μm
Polymer solution		CAB-TEG			PVB-PEG			PVDF-DEP	
Polymer concentration (wt%)	12	15	20	15	18	20	25	28	35
Solution temperature (K)		443			443			463	
Flow rate of polymeric solution (g/s)	0.65	0.45	0.44	0.22	0.18	0.17	0.18	0.15	0.13
Flow rate of diluent (g/s)	0.10	0.10	0.088	0.10	0.10	0.097	0.097	0.10	0.10
Take-up speed (m/s)	0.39	0.37	0.37	0.26	0.26	0.24	0.11	0.14	0.14
Air gap (mm)		2			0			5	
Batch composition		Water			Water			Water	
Batch temperature (K)		313			313			273	

on membrane fouling strongly depends on the pure water permeability (PWP) of a membrane. Membranes with higher PWP are generally believed to have lower fouling propensity [18,19,21]. It is still open for discussion whether the hydrophobicity of a membrane affects the development of membrane fouling or not. Although van der Marel et al. [22] reported that hydrophobic membrane was fouled more severely than hydrophilic one by comparison of polyvinyl fluoride (PVDF) membranes with different hydrophobicity (other membrane properties were basically the same), other researchers have reported that the effect of membrane hydrophobicity on the development of membrane fouling was not significant compared with other indexes representing membrane properties [18,19,21]. Hydrophilic membranes may be capable of mitigating the development of membrane fouling to some extent, but the influence of membrane hydrophobicity on the development of membrane fouling is likely to be less important than those of other membrane properties such as PWP or pore structure.

As summarized above, many contradictory results regarding the properties of membranes that affect fouling formation have been reported. One possible reason for these discrepancies might be the difficulty in controlling membrane properties to solely evaluate the effect of a particular membrane property on the development of membrane fouling. For example, membranes with high porosity tend to have high PWP. This means that sufficient information cannot be obtained when small number of membranes are examined. On this basis, here we comprehensively investigated which of membrane properties affect on the development of membrane fouling in MBRs. Membranes with different pore sizes were prepared using three different membrane polymeric materials, cellulose acetate butyrate (CAB), polyvinyl butyral (PVB), and PVDF, and the development of membrane fouling in each membrane was evaluated by batch filtration testing using mixed liquor suspensions obtained from a laboratory-scale MBR. On the basis of the results obtained in this study, the effect of membrane pore size on the development of membrane fouling caused by the difference in membrane polymeric materials was discussed.

2. Materials and methods

2.1. Materials

PVDF (M_w = 322,000, Solvay Specialty Polymers Japan K.K., Tokyo, Japan), PVB (M_w = 135,000, Denki Kagaku Kogyo K.K., Tokyo, Japan), and CAB (M_w = 65,000, Daicel Chemical Industries, Osaka, Japan) were used as membrane polymeric materials. Diethyl phthalate (DEP, Wako Pure Chemical Industries, Osaka, Japan), triethylene glycol (TEG, Nacalai Tesque Inc., Kyoto, Japan), and polyethylene glycol 200 (PEG 200, Wako Pure Chemical Industries) were used as diluents for membrane preparation via thermally induced phase separation (TIPS). A Pierce BCA Protein Assay kit was purchased from Thermo Scientific. All chemicals were used without further purification.

2.2. Membrane preparation

All hollow fiber membranes used in this study were prepared using a batch-type extruder (BA-0, Imoto Co., Kyoto, Japan) by TIPS [23]. The preparation conditions are summarized in Table 1. Membranes with different pore sizes were prepared by changing the polymer concentration and air gap. Detailed protocols of membrane preparation have been reported elsewhere [24].

To evaluate the pore size of the prepared membranes, filtration experiments were carried out. Solution of monodisperse polystyrene latex particles with diameters of 20, 50, 100 and 300 nm (Thermo Fisher Scientific, MA, USA) containing 0.1 wt% Triton X-100 (Wako Pure Chemical Industries) were used as the feed solution. The particle rejection was determined by measuring the solute concentration in the feed and filtrate solutions using an ultraviolet–visible spectrophotometer (U-200, Hitachi, Ltd., Tokyo, Japan) to measure absorption at 380 nm. We used the particle diameter when the rejection was 90% as the pore size of each membrane. Refer to our previous report for details [25]. Although not shown here, observation of the pores for membranes with small pore size and recognition of the difference in pore size for diferent membranes based on the SEM images was difficult and not accurate enough. Thus, for current study membranes pore size was determined by polystyrene latex particles filtration experiment.

To evaluate the hydrophobicity of the prepared membranes, the water contact angle of the film surface was measured using a contact angle meter (DM-300; Kyowa Interface Science, Saitama, Japan).

2.3. Operation of a laboratory-scale MBR

A laboratory-scale MBR was operated continuously. Two hollow fiber membrane modules where the effective membrane surface area of each module was 0.015 m^2 were simultaneously submerged in the same MBR tank (10 L) and filtered the same mixed liquor suspension side by side. The MBR tank was initially filled by the wastewater supplied from industrial wastewater treatment plant at Shizuka prefecture, Japan. These membrane modules were operated under a constant membrane flux of 0.23 m^3/m^2/day (9.6 L/m^2/h). Hydraulic retention time (HRT) and SRT were set at 35 h and 90 days, respectively. In this study, two separate continuous operations (Runs 1 and 2) were carried out. In Run 1, the MBR was fed with synthetic wastewater composed of 525 mg/L skimmed milk and 175 mg/L bonito extract (Kyokuto Pharmaceutical Industrial, Japan). The composition of synthetic wastewater used in Run 2 was 1.37 g/L sucrose, 0.27 g/L acetic acid, 0.32 g/L ammonium sulfate, and 0.062 g/L disodium hydrogen phosphate. The mixed-liquor suspended solids (MLSS) concentration was approximately 15 g/L in both the runs.