Journal of Membrane Science 551 (2018) 55–65

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Design, development and evaluation of nanofibrous composite membranes with opposing membrane wetting properties for extractive membrane bioreactors

Yuan Liao[a,1], Shuwen Goh[a,1], Miao Tian[a], Rong Wang[a,b,*], Anthony G. Fane[a]

[a] Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Singapore 637141, Singapore

[b] School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

ARTICLE INFO

Keywords:
Superhydrophobic
Superhydrophilic
Electrospinning
Nanofibrous composite membranes
Extractive membrane bioreactors

ABSTRACT

Extractive membrane bioreactors (EMBRs) are promising wastewater treatment processes combining an aqueous-aqueous extractive membrane process and biodegradation. The target contaminants diffuse through an extractive membrane and are metabolized by the active biofilm attached on the downstream membrane surface and microorganisms in the bioreactor. The benefit of EMBRs is that the biomass is not exposed to the potentially hostile feed conditions (high salinity, pH extremes etc.). The physicochemical properties of membrane surfaces on the receiving side facing the bioreactor are critical in controlling the extent and nature of the membrane-attached biofilm. In this work, novel nanofibrous composite membranes with a superhydrophobic surface (coded as NC) or a superhydrophilic surface (coded as M-NC) on the receiving side have been designed, developed and evaluated in EMBRs. Compared to commercial polydimethysiloxane (PDMS) tubular membranes, both NC and M-NC possessed 10 times higher phenol extraction efficiency in an aqueous-aqueous extractive membrane process. The uncontrolled biofilm growth on the membrane surface after 12 days of cross flow EMBR (CF-EMBR) operation resulted in 62% reductions of overall mass transfer coefficients (k_O) of both NC and M-NC. However, both membranes exhibited better performance in a submerged EMBR (S-EMBR) configuration due to the presence of air bubbles scouring on the membrane surface. Moreover, the fouling-releasing fluoro-polymeric surface of the hydrophobic NC was able to attenuate the tendency of microbial attachment and encourage biofilm scouring from the membrane surface in the S-EMBR. In contrast, more polysaccharides were present in the biofilm on the poly (ethylene glycol) (PEG)-modified M-NC surface, which acted as adhesives to tightly immobilize the biofilm on the membrane surface. Lastly, the NC which exhibited a higher stable k_O of 5.7×10^{-7} m/s in 12 days of S-EMBR operation, has been tested in a pilot S-EMBR to treat actual industrial wastewater. It showed a stable and competitive k_O of 6.5×10^{-7} m/s in 31 days operation, demonstrating its feasibility for hostile industrial wastewater treatment.

1. Introduction

Mixtures of toxic organic chemical compounds present in wastewaters from industries, such as oil refineries, coal conversion plants, petrochemicals, pharmaceutical chemistry, and etc., are hazardous to humans and the ecosystem even at a low concentration [1]. These wastewaters are difficult to treat in conventional activated sludge plants. In some cases, the toxic organics are in hostile feed solutions (high salinity, pH extremes and etc.) to typical biomass or themselves bioinhibitory except for acclimatized biomass. The phenolic compounds are inhibitory and among the most prevalent chemical pollutants in the industrial wastewaters [2,3]. Known as microbiocides, they cause changes in the lipid-to-lipid and lipid-to-protein ratios of the cell membranes as well changes in membrane permeability and activity, which thus inhibit cell growth [3]. Therefore, it is essential to remove these pollutants from wastewaters before discharge, preferably via an energy-efficient, environmentally friendly and reliable method. The traditional techniques available for phenol removal include distillation, liquid–liquid extraction, adsorption, wet-air oxidation, and biodegradation [4,5]. Among these conventional techniques, biodegradation is an attractive, cost-effective and energy-efficient technology that utilizes the metabolic potential of acclimatized microorganisms to

* Corresponding author at: School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Singapore.
E-mail address: rwang@ntu.edu.sg (R. Wang).

[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.memsci.2018.01.029
Received 19 November 2017; Received in revised form 29 December 2017; Accepted 15 January 2018

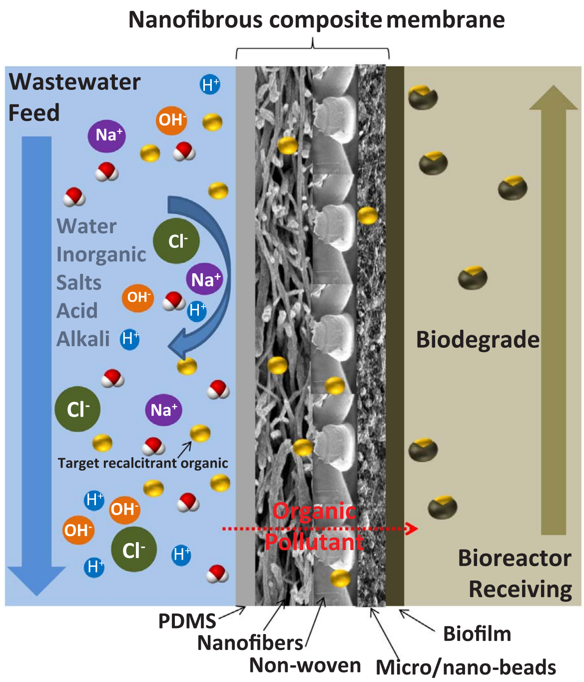

Fig. 1. Schematic illustration of an extractive membrane bioreactor (EMBR) and an as-designed nanofibrous composite membrane.

degrade the contaminants. However, the activity of these microorganisms can be restrained due to the toxicity of phenol at high concentration.

The extractive membrane bioreactor (EMBR) invented by Livingston, which combines an aqueous-aqueous extractive membrane process and biodegradation, is an attractive option to simultaneously separate and biodegrade organics from difficult wastewaters [6]. As shown in Fig. 1, the target organic pollutants, which maybe inhibitory to biological growth, are extracted from wastewaters through a non-porous membrane to a downstream bio-medium by the solution-diffusion mechanism, driven by the concentration gradient across the membrane. The organic pollutants are subsequently biodegraded by specific microorganisms. Thus, the organic concentration on the receiving side can be maintained at close to zero [7]. As the biomedium is protected from the hostile wastewater by the extractive membrane, EMBRs provide niche advantages over traditional bioprocesses, including simple pre-treatment (eg. pH adjustment) and direct treatment without diluting the waste stream [8]. Furthermore, the EMBRs can be operated under mild conditions (room temperature and atmospheric pressure), that are optimised for the biomass.

Despite their potential to address key issues surrounding ‘difficult’ organic treatment, the EMBRs have yet to progress significantly beyond conceptualization. The main obstacles impeding EMBRs include: (1) the lack of specially-designed extractive membranes with enhanced organic mass transport efficiency and excellent stability; (2) significant flux decline due to the accumulation of excessive biofilms onto the membranes; and related to this, (3) the lack of effective biofilm control strategies [7–10].

The main requirements of more effective extractive membranes for EMBRs are: (1) the membranes should be highly permeable to organics and impermeable to acid, caustic, inorganic salts and water; and (2) the membranes should be stable under harsh conditions in long-term usage [8]. Silicon rubbers such as polydimethysiloxane (PDMS) have been utilized in previous works as phenol can be transported through PDMS networks via hydrogen bonding between phenol and Si-O units [11]. However, commercially-available silicon rubber tubes usually exhibit substantial wall thickness (> 0.2 mm), and this increases membrane resistance significantly [11,12]. As shown in Fig. 1, a possible strategy to reduce membrane resistance is to develop nanofibrous composite membranes, which consist of a thin PDMS selective layer and a highly porous nanofibrous support. To radically improve mass transfer efficiency and ensure high selectivity, a thin and defect-free PDMS skin layer is critical. Although traditional technologies such as dip-coating and spin-coating have been conducted to prepare the PDMS selective layer, more facile techniques, which are easy to scale up, need to be developed [8,13]. In addition to a thin and defect-free selective layer, a highly porous support layer is essential for developing an effective composite membrane. Fortuitously, nanofibrous scaffolds produced by electrospinning have gained increasing attention in composite membrane fabrication [14,15]. The electrospun three-dimensional meshes constructed by over-lapped nanofibers exhibit an open, interconnected and highly porous structure, making them attractive for serving as substrates to fabricate nanofibrous composite membranes. However, few works have reported the preparation of nanofiber-supported extractive membranes [8].

As the sole, or major, carbon source for heterotrophic microorganisms in EMBRs is the target pollutant which diffuses across the membrane, a biofilm tends to develop excessively on the membrane surface and in the membrane pores on the receiving side, and this could increase the overall mass transfer resistance significantly [10]. Although the biofilm is beneficial to the process, it needs to be controlled. Although a few investigations [16,17] have been conducted to restrain the formation of excessive biofilms on the membrane surface in EMBRs by adjusting ionic balance, surfactants and bubbling in the bioreactor, more work is necessary. It is well-known that biofilm depositions, including several steps such as cell adhesion, protein and polysaccharide secretions and biofilm formation, are strongly associated with the topography, wettability and chemistry of membrane surface [18–21]. Consequently, it is likely that novel membrane surfaces, achieved by controlling surface topology and chemistry, could make a difference in the EMBRs. To the best of our knowledge, no research has been published to study the effects of membrane surface properties (superhydrophilicity and superhydrophobicity) on biofilm accumulation in EMBRs.

Therefore, in this work, novel PDMS-coated nanofibrous composite membranes with superhydrophobic or superhydrophilic surfaces on the receiving side were fabricated for EMBRs by electrospinning, spray-coating and chemical modifications as shown in Fig. 1. A highly porous poly(vinylidene fluoride) (PVDF) composite substrate with a tiered nanofibrous structure on the feed side and a micro/nano-beaded hierarchical surface on the receiving side were fabricated by electrospinning while the PDMS selective layer was synthesized in-situ on the nanofibrous surface by spray-coating. A highly uniform, defect-free and thin film can be rapidly obtained over a large membrane area by spray-coating [22]. To obtain a superhydrophilic surface on the receiving side, poly (ethylene glycol) (PEG) was grafted onto the micro/nano-beaded surface of a nanofibrous composite membrane via chemical modification. This is the first time that the phenol extraction performance of these novel nanofibrous composite membranes with superhydrophobic or superhydrophilic surfaces on the receiving side has been examined and evaluated in both an aqueous-aqueous extractive process and EMBRs. Additionally, the effectiveness of different EMBR configurations involving the cross-flow EMBR (CF-EMBR) and the submerged EMBR (S-EMBR) for controlling the biofilms was studied in this research. To the best of our knowledge, this is the first time that the nanofibrous composite membranes have been evaluated in an S-EMBR process. The phenol extraction efficiency, membrane stability and performance recovery of the resultant nanofibrous composite membranes were evaluated in long-term EMBR tests. To demonstrate the membrane feasibility in an industrial application, the membrane has been applied to treat real industrial wastewater in a pilot S-EMBR with a continuous stirred-tank reactor (CSTR) arrangement.