Desalination xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Desalination

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

Performance evaluation of co-extruded microporous dual-layer hollow fiber membranes using a hybrid membrane photoreactor

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HIGHLIGHTS

- The work aims to study the effect on PEG in the inner layer as pore forming agent.
- The membrane comprised of dual layers, inner is PVDF/PEG while outer is PVDF/TiO_2.
- PEG leached out from the membrane during phase inversion and thus created microvoid.
- The addition of PEG enhanced NP solution flux due to the macrovoid formation.

ARTICLE INFO

Article history:
Received 30 September 2015
Received in revised form 22 May 2016
Accepted 29 May 2016
Available online xxxx

Keywords:
Dual layer hollow fiber membranes
Polyethyleneglycol
Titanium dioxide
Finger-like voids
Co-extrusion technique

ABSTRACT

Hybrid systems with immobilized TiO_2 within dual-layer hollow fiber membranes are the most promising set-up for photocatalytic applications because they possess advantages in both the degradation and separation processes. The performance of dual-layer hollow fiber membranes may be maximized using a functional material of high performance as the selective layer. This paper reports the influence of polyethyleneglycol (PEG) as a pore forming agent on the structure and performance of dual layer hollow fiber membranes. Titanium dioxide (TiO_2) was used as a photocatalyst in the outer layer of dual layer hollow fiber (DLHF) membranes. DLHF membranes were fabricated via a single step co-extrusion technique and characterized in terms of surface roughness, membrane porosity, hydrophilicity, and cross-sectional and surface morphology. Nonylphenol (NP) photocatalytic degradation and filtration were evaluated using a hybrid membrane photoreactor. The experimental results revealed that DL-PEG/TiO_2 membrane increases the NP solution flux, while decreasing the incidence of membrane fouling and allowing for a smoother and more hydrophilic membrane surface. The findings show that the addition of PEG in the inner layer of DLHF membranes may enhance flux performance in the photocatalytic process.

1. Introduction

A hybrid membrane reactor has been chosen as an alternative method for wastewater treatment process in order to achieve both separation and photocatalysis in a single system. Such a hybrid membrane reactor system may mitigate membrane fouling issues due to the simultaneous actions of pollutant degradation and separation [1].

Titanium dioxide (TiO_2) nanoparticles have been widely used as photocatalysts to degrade pollutants in water system due to excellent catalytic activity, high availability, and good antifouling abilities [2]. Several studies have reported that TiO_2 suspended in a reactor system showed better performance than when deposited on the membrane system [3–6]. However, the suspended catalyst reactor requires additional process to separate catalyst from the treated water. This additional process can be eliminated by immobilizing the TiO_2 photocatalyst in the membrane matrix. However, this immobilization approach would lead to a reduction in the surface area available for photocatalytic reaction. Proper distribution of TiO_2 nanoparticles within the membrane may also be achieved using a single-step co-extrusion process, allowing for a higher likelihood that TiO_2 nanoparticles would be exposed to UV light and allow photocatalytic action to take place [7]. Tahiri et al. suggests that the reaction kinetics rely a great deal on the kinetics of product transport through the porosity and pore size of the composite membrane [8], indicating that higher porosity and bigger pore size in the membrane structure are more favorable for the photocatalytic process.

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http://dx.doi.org/10.1016/j.desal.2016.05.029
0011-9164/

Nowadays, the dual layer hollow fiber (DLHF) membrane has attracted many researchers due to its advantages, including: (1) low material cost; (2) elimination of complex post treatment process; and (3) optimized membrane performance via a high-performance functional material in the selective layer. As mentioned by Dzinun et al. [9], DLHF membranes exhibited superior photocatalytic performance in comparison to single-layer hollow fiber membranes due to better dispersion of TiO_2 on the outer membrane surface.

Ma et al. suggested that high water flux can be achieved by increasing the length of the finger-like structures in membrane morphology with the addition of additives in the dope solutions [10]. Polyethylene glycol (PEG) is one such additive able to promote such a structure [11–14]. PEG with an increased molecular weight may enhance membrane porosity and permeation flux but reduce mechanical strength [10]. Zuo et al. [14] discussed the effects of increasing PEG molecular weight on macrovoid growth. When the molecular weight of PEG additive increased from 200 to 6000 Da, the affinity between casting solutions and PEG became poorer, inducing casting solutions to phase separation and the PEG separate casting solutions to enter into the nuclei of the lean polymer phase. Consequently, the casting solution in front of the nuclei became stable and led the nuclei to expand into the larger finger-like pores [15].

Moreover, the different loading of PEG in dope solution has different effects on the resulting structures and properties of the membrane [16–18]. As demonstrated by Garcia et al., when PEG concentration increased up to 4.5 wt%, macrovoids formation and membrane porosity also increased, leading to high pure water flux values and lower PEG rejection [18].

Therefore, the objective of this study is to investigate the performance of DLHF membranes with microporous structure with to the addition of PEG 6000 in the inner dope solution. In this membrane design, the outer layer is comprised of polyvinylidene fluoride (PVDF)/titanium dioxide (TiO_2), while the inner layer was PVDF/PEG. Photocatalytic degradation and filtration performance using dual-layer hollow fiber membranes were evaluated using a submerged membrane photoreactor. In this study, nonylphenol (NP) was chosen as the target pollutant due to greater tendency to bioaccumulate their toxicity in aquatic life [19]. Although NP is toxic to biota, detailed studies on the role played by NP in the environment remain lacking. Precise measurement of NP degradation rates in the environment is important.

2. Materials and methods

2.1. Materials

Polymer solutions were prepared using polyvinylidene fluoride (PVDF, Solef MW6012 grade in powder form, Solvay Specialty Polymers France) as polymer material and dimethylacetamide (DMAc) (Q-Rec) as a solvent to dissolve the PVDF for an outer dope solution. Titanium dioxide (TiO_2) supplied by Johnson Matthey (UK) was used as received. Meanwhile, polyethyleneglycols (PEG) with 6000 Da of molecular weight were specifically selected in order to determine the effects of the organic nature on the membrane performance. Nonylphenol was purchased from Sigma-Aldrich (CAS 84852-15-3) and used without further purification. Ethanol was used as a solvent for post-treatment in membrane fabrication.

2.2. Preparation of dual-layer hollow fiber membranes

The preparation and fabrication of dual-layer hollow fiber membranes have been described by Dzinun et al. [7]. Several spinning dope solutions for the outer and inner layers with different dope solutions were prepared. 3 wt% of TiO_2 nanoparticles and 5 wt% of PEG 6000 were added to the outer and inner dope solutions, respectively. Various compositions of dope solutions are listed in Table 1. The prepared solutions were degassed overnight using an ultrasonic bath system at ambient temperature before being subject to the spinning process. Then, the spinning dope mixture was extruded using a triple orifice spinneret to form DLHF membranes, as previously described in detail [20].

Table 1
Dope composition of the dual layer hollow fiber membranes.

Membrane identification code	Dope composition					
	Outer layer			Inner layer		
	PVDF (wt%)	TiO_2 (wt%)	DMAc (wt%)	PVDF (wt%)	PEG (wt%)	DMAc (wt%)
DL-TiO_2	15.0	–	85.0	18.0	5.0	77.0
DL-PEG/TiO_2	15.0	3.0	82.0	18.0	5.0	77.0

2.3. Membrane characterizations

2.3.1. Morphology study by SEM and EDX

Scanning electron microscopy (SEM, Model: TM 3000, Hitachi) and energy dispersion of x-ray (EDX, S250, EDAX), respectively, were used to examine the structural morphology of the membranes and measure the outer layer thickness by referring to the TiO_2 distribution within the membranes. To prepare the samples, the membranes were immersed in liquid nitrogen for 10 min and then fractured to reveal their cross sectional morphology. The samples were then positioned on a metal holder and sputter-coated with gold under vacuum for 3 min. Micrographs of their cross sectional and surface morphologies were taken and inspected under various magnifications. An EDX line scan was randomly drawn across the sample surfaces to profile the TiO_2 nanoparticle distribution.

2.3.2. Contact angle measurement

Contact angle measurements on the membranes were taken using a contact angle goniometer (Model: OCA 15EC, Dataphysics) with deionized water as its contact droplets. A 2 μL droplet was slowly placed on the membrane surfaces. Average and standard deviations for least 10 independent measurements were obtained at different spots for each sample.

2.3.3. Surface roughness characterization

The membrane surface roughness of the membranes was investigated by Atomic Force Microscopy (AFM) (Model: SPA-300HV, Seiko). The procedure used for measurement of surface roughness has been described elsewhere [21].

2.3.4. Fourier transform infrared spectroscopy (FTIR) analysis

FTIR (Thermo-electron Corporation, Nicolet 5700) was employed to detect and analyze the functional groups within the molecules of the polymer-based structure in the dual-layer hollow fiber membranes. All FTIR spectra were recorded using attenuated total reflection (ATR) technique with a resolution between 4000 cm^{-1} and 500 cm^{-1}.

2.4. Pure water flux performance

Pure water flux experiments were conducted using a U-like membrane module filtration apparatus. A bundle of 20 hollow fiber membranes with approximate lengths of 23.5 cm each (total effective membrane area: 248 cm^2) was potted into a PVC tube using epoxy resin (E-30CL Loctite® Corporation, USA). The module was then left at room temperature until the epoxy hardened before its protruding parts were cut and fixed into a PVC adaptor to complete the module preparation. It was then assembled into the filtration module. Pure water flux experiments were performed in a cross flow mode with a shell-bore configuration. Each membrane sample was tested and their fluxes were measured at different operating pressures to calculate their permeability.

Please cite this article as: H. Dzinun, et al., Performance evaluation of co-extruded microporous dual-layer hollow fiber membranes using a hybrid membrane photoreactor, Desalination (2016), http://dx.doi.org/10.1016/j.desal.2016.05.029