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Research article

Tackling membrane fouling in microalgae filtration using nylon 6,6 nanofiber membrane

M.R. Bilad[a], A.S. Azizo[a], M.D.H. Wirzal[a,*], L. Jia Jia[a], Z.A. Putra[a], N.A.H.M. Nordin[a], M.O. Mavukkandy[c], M.J.F. Jasni[b], A.R.M. Yusoff[b]

[a] Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610, Perak, Malaysia
[b] Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, 81310, Skudai, Johor, Malaysia
[c] Institute Center for Water and Environment (iWater), Department of Chemical and Environmental Engineering, Masdar Institute of Science and Technology, PO Box 54224, Abu Dhabi, United Arab Emirates

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ABSTRACT

Microalgae technology, if managed properly, has promising roles in solving food-water-energy nexus. The Achilles' heel is, however, to lower the costs associated with cultivation and harvesting. As a favorable technique, application of membrane process is strongly limited by membrane fouling. This study evaluates performance of nylon 6,6 nanofiber membrane (NFM) to a conventional polyvinylidene fluoride phase inverted membrane (PVDF PIM) for filtration of *Chlorella vulgaris*. Results show that nylon 6,6 NFM is superhydrophilic, has higher size of pore opening (0.22 vs 0.18 μm) and higher surface pore density (23 vs 18 pores/μm^2) leading to higher permeance (1018 vs 493 L/m^{2}hbar) and better fouling resistant. Such advantages help to outperform the filterability of PVDF PIM by showing much higher steady-state permeance (286 vs 120 L/m^{2}hbar), with comparable biomass retention. In addition, unlike for PVDF PIM, imposing longer relaxation cycles further enhances the performance of the NFM (i.e., 178 L/m^{2}hbar for 0.5 min and 236 L/m^{2}hbar for 5 min). Overall findings confirm the advantages of nylon 6,6 NFM over the PVDF PIM. Such advantages can help to reduce required membrane area and specific aeration demand by enabling higher flux and lowering aeration rate. Nevertheless, developments of nylon 6,6 NFM material with respect to its intrinsic properties, mechanical strength and operational conditions of the panel can still be explored to enhance its competitiveness as a promising fouling resistant membrane material for microalgae filtration.

1. Introduction

Biofuels from lipid derivation is sustainable alternative to fossil fuels. However, the use of food crops as feed-stock for biofuels is untenable, largely due to food-energy conundrum (Ho et al., 2014). Other sources of feed stocks from agricultural residues and domestic wastes offer a low sustainability (Rawat et al., 2013). Those constrains lead to emergence of microalgae biomass as a potential source of lipids.

Autotrophic microalgae acquire their carbon from inorganic carbon (such as in a form of dissolved CO_2) and use sun-light as energy source for their metabolisms. Microalgae are simple organisms that can grow rapidly even in harsh environments (Mata et al., 2010). They regenerate biomass more efficiently than most conventional food and non-food crops. They also have the ability to accumulate large amount of lipids (López et al., 2015). Microalgae are also promising due to their ability to grow on marginal lands at any time of the year even in wastewater as growth medium (Sheng et al., 2017; Hende et al., 2012).

Microalgae biomass have to be harvested from the cultivation broth and concentrated - an Achilles' heel of microalgae processing - before being processed as biofuel feedstock. Selection of harvesting technique is dictated by the characteristics of the microalgae species and process objectives (i.e., up to 25 wt% of biomass) (Laamanen et al., 2016). Harvesting microalgae biomass is challenging, particularly due to their density that is close to water and their small size (Bilad et al., 2014a,b).

Technological options for microalgae harvesting are centrifugation, sedimentation, flotation, flocculation and membrane filtration (Barros et al., 2015). Centrifugation is considered not only as an energy-intensive process, but also carries a risk of damaging the microalgae cell due to the excessive shear force, while gravity sedimentation is too time-consuming. In contrary, membrane filtration is seen as a promising technique due to its high biomass recovery, but also allows the separation of shear sensitive species, and -under optimum conditions- requires low energy (Bilad et al., 2013; Venault et al., 2016).

Polyvinyl fluoride phase inverted membranes (PVDF PIM) have

* Corresponding author.
E-mail address: mdzulhakim.wirzal@utp.edu.my (M.D.H. Wirzal).

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been widely used for microalgae harvesting (Marbelia et al., 2018). However, due to hydrophobic nature, plain PVDF PIMs are vulnerable from fouling, specifically from sorption, deposition and irreversible attachment of hydrophobic macro-molecules. Few strategies to reduce fouling propensity of polymeric membranes towards hydrophobic species (such as microalgae biomass) have been reported. Among them are hydrophilic coating, surface grafting, in situ polymerization of monomers and in situ dope blending with amphiphilic copolymers (Kang and Cao, 2014; Kochkodan and Hilal, 2015; Miller et al., 2016).

Attempts in tailoring PVDF membrane for microalgae harvesting have been reported. Most approaches explore membrane fabrication parameters or exploit the benefits of chemical additives (Bilad et al., 2013, 2012; Bilad et al., 2014a,b; Discart et al., 2015; Hwang et al., 2015; Venault et al., 2016). PEGylated PEI particles and pluronic F-127 as additives have been proven effective to improve PVDF PIM performance (Hwang et al., 2015). Venault et al. (2016) reported remarkably high flux of PVDF membrane prepared via vapor-induced phase separation after proper wetting, despite having high hydrophobicity. Membrane filtration can also be applied in a dynamic system to maximize throughput while still maintaining low energy foot-print (Bilad et al., 2013; Kanchanatip et al., 2016; Zhao et al., 2016a, 2016b, 2016c, 2017).

Advances in nanotechnology have prompted researchers to explore the potential of nanofiber membranes (NFM), including for water-based filtration processes (Ahmed et al., 2015; Feng et al., 2013; Mansour et al., 2017; Ray et al., 2016; Wang and Hsiao, 2016). The NFM has proven attractive as filter material for microalgae harvesting ascribed by its good structural morphology and surface chemistries (Azizo et al., 2017), and could help to tackle membrane fouling.

This study explores the potential of NFM to tackle membrane fouling in microalgae filtration. We applied nylon 6,6 mat, a proven material for NFM fabrication (Bilad et al., 2011; Huang et al., 2016; Huang and McCutcheon, 2014; Islam et al., 2016), for filtration of *C. vulgaris* broth and compared its performance with a traditional PVDF PIM. After materials characterization, the hydraulic performances of both membranes were first compared. Later, the effect of relaxation time was also evaluated for both membranes. Lastly, the performance of both membranes in a full-scale set-up was also projected and compared with established modules.

2. Materials and methods

2.1. Preparation of nylon 6,6 NFM and PVDF PIM

The dope solution for nanofiber mat preparation was prepared from 12.3 wt% of nylon 6,6 pellet in a mixture of equal volume acetic acid glacial (99.85%, HmbG Chemicals) and formic acid (> 98%, Merck). The solution was stirred overnight until homogeneous. The nylon 6,6 mat was fabricated using electrospinning set-up (Fanavaran Nano Meghyas). The dope solution was placed into a 10 ml syringe connected with a high precision pump. The syringe was equipped with a capillary tip of 0.6 mm inner diameter and was connected with high-voltage electrode (26 kV). The solution was injected at a constant rate of 0.4 mL/h.

The PVDF PIM was prepared via immersion precipitation using a dope solution containing 15 wt% of PVDF powder (Sigma-Aldrich, MW of 537 kDa) in dimethylacetamide (DMAC, Sigma-Aldrich) solvent. The bubble-free and homogeneous dope solution was cast at a wet casting thickness of 22 mm atop a non-woven support (Novatexx 2471), followed by immediate immersion into a bath containing deionized water. The PVDF PIM was then stored wet until usage.

2.2. Membrane characterization

The scanning electron microscopy (SEM) images were used to identify the microstructures of both membranes. The images were later processed with ImageJ (NIH software) to estimate surface porosity, pore size and pore density. The pore size and pore size distribution were also experimentally measured using capillary flow porosimetry. The contact angle (CA), fibers thickness and porosity were respectively measured using goniometer, micrometer and dry-wet method.

The filtration tests were conducted in a constant-pressure and in a submerged system. The tests were performed in parallel after the membranes were assembled into workable panels. The filtration flux (J) and permeance (L) were calculated using eqs.((1) and (2), respectively.

$$J = V/(At) \qquad (\mathrm{L/m^2h}) \tag{1}$$

$$L = J/\Delta P \qquad (L/\mathrm{m^2hbar}) \tag{2}$$

where V is volume of permeate (L), A effective membrane area (m^2), t filtration time (h) and ΔP trans-membrane pressure (bar). When involving relaxation, the net-permeance and net-flux were calculated by counting the relaxation time. All reported data are the net-permeance.

To determine the biomass retention (η, %), biomass concentration was measured using spectrophotometer (Hach Lange DR-2800). The η was calculated as in Eq. (3).

$$\eta = (\mathrm{OD_f} - \mathrm{OD_p})/\mathrm{OD_f} \qquad (100\%) \tag{3}$$

where $\mathrm{OD_f}$ and $\mathrm{OD_p}$ are the optical density of the feed and permeate, respectively.

2.3. Membrane panel assembly

After synthesis, both nylon 6,6 NFM mat and PVDF PIM sheet were assembled into filtration panels with an operative membrane area of 112 cm^2 (2 sided surface of 7 × 8 cm) (Fig. 1). To assemble the PVDF PIM, the sheet was fixed to the panel frame by gluing all edges using an epoxy glue (Hardex clear epoxy compound). A spacer was used in the interior side to separate the sheets and to allow space for permeate flow. In this panel system, the permeate passes through the membrane from outside to inside of the panel driven by a vacuum pressure. From panel interior, the permeate was then transferred into the collector tank through a 0.5 cm top hole.

The same protocol was applied for the nylon 6,6 NFM. However, the nanofiber mat was first fixed onto a Novatexx 2471 support (donated by Freudenberg-Filter, Germany) to enhance its physical strength and allow for module assembly, as suggested elsewhere (Bilad et al., 2011).

2.4. Filtration set-up

The membrane filterability was tested under constant-pressure operation in a submerged filtration system (Fig. 1). The filtrations were performed in parallel to ensure equal feed conditions for both panels. The vacuum, used to drive the filtration, was exerted from a vacuum pump and was set at −0.05, −0.075 or −0.1 bar, depending on the tests. The detail descriptions of the filtration system are available elsewhere (Eliseus et al., 2017). The permeate for each panel was collected semi-batch-wise for each filtration cycle (ranging from 10.5 to 15 min). After collected and measured, the permeate was returned back into the tank to maintain the liquid level and nearly constant feed. Part of permeate was also collected to be used for biomass rejection sample. Each panel was aeration at a constant flow rate of 1.8 L/min.

2.5. Filterability test

2.5.1. Effect of feeds

To assess the hydraulic performance of the PVDF PIM and nylon 6,6 NFM, three tests were performed by using a feed of 0.5 g/L *C. vulgaris* broth. Each test was performed at different ΔPs with filtration cycle of 15/0.5 min, comprising of 15 min filtration and 0.5 min relaxation. During the interval between filtration tests, the membranes were chemically cleaned by soaking the panels into 1 g/L of sodium hypochlorite