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

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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 polydimethylsiloxane (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.

Keywords: superhydrophobic; superhydrophilic; electrospinning; nanofibrous composite membranes; extractive membrane bioreactors

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 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 biomedium 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.

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

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 polydimethylsiloxane (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.

2. Experiments

2.1 Materials and chemicals

Commercial polymer polyvinylidene fluoride (PVDF, Kynar HSV 900) was purchased from Arkema to fabricate membrane substrates. Anhydrous lithium chloride (LiCl, Merck chemical) was used as an additive in the polymer dopes. N, N-Dimethylformamide (DMF) and acetone were provided by Merck as solvents. A silicon elastomer and a curing agent (Sylgard 184) were supplied by Dow Corning for PDMS fabrication. Dopamine hydrochloride, tris(hydroxymethyl) aminomethane (Tris), poly(ethylene glycol) methyl ether thiol (mPEG-SH, Mn 800), copper(II) sulphate pentahydrate and H₂O₂ were ordered from Sigma-Aldrich to modify the membranes. Isopropyl alcohol (IPA) with analytical grade (Merck), glycerol (80% aqueous solution, Merck), and deionized water (DI water, purified by a Milli-Q system, Millipore Co. Singapore) were used as pre-wetting agents for membrane substrates. In extractive membrane tests, phenol and NaCl were obtained from Sigma-Aldrich. MgSO₄·7H₂O, KH₂PO₄, FeCl₃, CaCl₂·H₂O and NH₄Cl from Merck were used as the nutrients for biomedium in the bioreactors. All reagents were used as received. Polyethylene terephthalate (PET) nonwoven (Grade 3233) was purchased from Ahlstrom Filtration.

2.2 Electrospinning of a nanofibrous substrate with a tiered structure

The detailed electrospun parameters of the composite nanofibrous substrate used in this work are summarized in **Table S1**. The electrospun PVDF substrate, composed of a top ultrafine nanofibrous layer (feed side), a coarse nanofibrous intermediate layer, a non-woven mechanical support, and a micro/nano-beaded bottom layer (receiving side) was fabricated by tuning the dope solutions. Briefly, a coarse

nanofibrous layer was firstly electrospun onto the non-woven support by an 8 wt % PVDF dope, on top of which an ultrafine nanofibrous layer was prepared by electrospinning a 3 wt% PVDF dope. The dual-layer nanofibrous membrane with a non-woven mechanical support was then heat-pressed under 155 °C and 2 bar for 30 min to guarantee the membrane integrity and mechanical strength. After that, a micro/nano-beaded layer was electrospun on the non-woven surface of the nanofibrous substrate (receiving side) using a 4 wt% PVDF solution, in which 8 wt% modified silica nanoparticles were blended. The method to modify silica nanoparticles has been reported in our previous work [23, 24]. The resultant PVDF composite substrate was pre-wetted by a mixture of DI water and glycerol (1:1) prior to the PDMS coating. The 50 wt% glycerol aqueous solution was demonstrated as an effective pre-wetting agent to fill the substrate pores and mitigate PDMS intrusion [8, 9].

2.3 Preparation of PDMS-coated nanofibrous composite membranes by spray-coating

A 5 wt% PDMS coating solution was prepared by mixing the base polymer and curing agent in a mass ratio of 10:1 in *n*-hexane. The pre-wetted substrates with a length of 23 cm and a width of 13 cm were pasted onto a clean glass plate vertically aligned, perpendicular to the spraying cone. The excess pre-wetting solutions on the substrate surface were removed by a rubber roller. The PDMS layer was manually sprayed onto the membrane surfaces in a zigzag motion, which consumed 50 mL coating solution. The spraying pressure was 70 kPa. The coated membrane was then cured in an oven at 80 °C for 2 days to cross-link PDMS completely. The as-prepared PDMS-coated nanofibrous composite membrane is denoted as NC.

2.4 Membrane modification

As shown in **Fig. 2**, the nanofibrous composite membrane NC was immersed in an aqueous dopamine solution (2 mg/mL dopamine, 10 mM tris, pH:8.5) for 20 min to form a thin poly-dopamine (PDA) coating layer on the membrane. Small amounts of CuSO₄ and H₂O₂ (CuSO₄: 5 mM; H₂O₂: 19.6 mM) were added to the aqueous solution to accelerate the dopamine polymerization as triggers [25]. Grafting of an additional layer onto the PDA-coated NC (PDA-NC) was accomplished through immersing it in a 1 g/L mPEG-SH aqueous solution for 30 min. The nanofibrous composite membrane modified by mPEG-SH is coded as M-NC.

Fig. 2. Schematic illustration of preparing PEG-modified nanofibrous composite membrane M-NC.

2.5 Membrane characterization

To accurately analyse the chemical compositions on the membrane surface, X-ray photoelectron spectroscopy (XPS) tests were conducted using a Theta Probe XPS provided by Thermo Fisher Scientific (Singapore). The surface morphologies of membranes were observed by a field emission scanning electron microscope (FESEM, JSM-7200F, JEOL Asia Pte Ltd, Japan). The water contact angles of the membranes were measured using a goniometer (Contact Angle System OCA, Data Physics Instruments GmbH, Singapore). The pore size of the substrate was determined by a capillary flow porometer (CFP 1500A, Porous Material. Inc. (PMI),

Singapore). The mechanical properties of the membranes were measured using a Zwick/Roell testing machine at a constant elongation velocity of 50 mm/min at room temperature (23 ± 2 °C). The surface charges of the membranes were determined using an electro-kinetic analyzer (SurPASSTM 3, Anton Paar) based on the streaming potential measurements.

2.6 An aqueous-aqueous extractive test

An aqueous-aqueous phenol extractive test was conducted to measure the phenol extractive performance of as-prepared nanofibrous composite membranes NC and M-NC, which was repeated for three times for each membrane [8, 9]. The feed solution (1L) was synthetic wastewater containing 1 g/L phenol and 5 g/L NaCl while the receiving solution was DI water (1L). Both feed and receiving solutions were recycled through a flat-sheet membrane cell with an effective membrane area of 36 cm² at a cross-flow velocity of 8.3 cm/s in a counter-current mode. The phenol mass transfer was characterized by overall mass transfer coefficient (OMTC) k_o (m/s) as detailed in [9]:

$$k_o = \left(\frac{dC_r}{dt} V_r \right) / \{A(C_f - C_r)\} \quad (1)$$

where C_f and C_r (g/m³) are the phenol concentrations at the feed and receiving sides, respectively, at the time t (s); V_r (m³) is the receiving solution volume; A (m²) is the effective membrane area.

NaCl flux was measured to examine the rejections of water and inorganic salts by the nanofibrous composite membranes, which was determined by the equation:

$$J_s = \Delta c V / (\Delta t A) \quad (2)$$

where J_s (mg/m²h) is the NaCl flux, Δc (mg/L) is the variation of NaCl concentration in the receiving solution with volume V (L) during time interval Δt (h).

2.7 Extractive membrane bioreactors

The nanofibrous composite membranes were examined in both cross-flow EMBR (CF-EMBR) and submerged EMBR (S-EMBR) processes. In both configurations, the feed solution (1L) was 1 g/L phenol with 5 g/L NaCl; the phenol concentration in the feed was maintained by periodically adding concentrated phenol solution. The receiving side was 4L biomedium comprising of phenol-acclimated seed sludge and essential inorganic nutrients [10]. The pH in the bioreactor was maintained at 6.9 ± 0.4 throughout the experiments while the conductivity remained at 4.7 ± 0.4 mS/cm, indicating negligible salt flux across the membranes from the feed side. In the CF-EMBR (**Fig. S1A**), both feed and biomedium receiving solutions were recycled through a flat sheet membrane cell with an effective membrane area of 36 cm² with a cross-flow velocity of 8.3 cm/s in a counter-current mode. As shown in **Fig. S1B**, in the S-EMBR system, two flat sheet nanofibrous composite membranes with an effective membrane area of 238 cm² were placed in the centre of the bioreactor, between which the feed was circulated with a flow rate of 200 mL/min. To assist in controlling the biofilm thickness, air bubbling was applied to scour the membrane surface as this has been successfully used in the S-EMBR with hollow fiber membranes [10].

The organic concentration in the feed solution was monitored by high-performance liquid chromatography (HPLC). Routine sampling of phenol concentration in the

biomedium showed that it was below detectable limits, indicating complete biodegradation of phenol. As such, the Eq. (1) was modified as follows:

$$k_0 = \frac{V_f}{At} \ln \frac{C_f^t}{C_f^0} \quad (3)$$

where C_f^t is the phenol concentration at time t and C_f^0 is the phenol concentration in the feed. Before using biomedium in the receiving sides, the initial (control) k_0 values of composite nanofibrous membranes were tested using DI water as the receiving solutions in both CF-EMBR and S-EMBR processes, which were recorded as the k_0 values at the day 0. Analysis of biofilms, including total suspended solids (TSS), polysaccharides and protein amounts, on the membrane surfaces were conducted following the methodologies reported in our previous work [10].

2.8 Continuous stirred-tank reactor (CSTR) in series model

A pilot S-EMBR with a CSTR-in-series arrangement was designed and commissioned in this study. As shown in **Fig. S2**, three submerged flat-sheet modules with the same design used in section 2.7 were installed in series while the industrial wastewater was circulated in each stage with an influent flow rate of 3.6 ± 1.4 L/day through the feed sides of membrane modules in sequence. The industrial wastewater was obtained from an integrated water treatment plant treating wastewaters from chemical and petrochemical companies. The pH of wastewater is 7.5 ± 0.4 while the conductivity is 5.1 ± 0.4 mS/cm. It has a total organic carbon (TOC) of 571 ± 50 ppm and a phenol concentration of 120 ± 2 ppm. As the current study focuses on the feasibility of as-developed composite nanofibrous membranes in removing phenol from actual industrial wastewaters via EMBR, the compositions of other pollutants and nutrients in this wastewater have not been defined at this stage.

3. Results and discussion

3.1 Membrane characterizations

3.1.1 An electrospun composite substrate with a tiered structure

The FESEM images (**Fig. 3**) show cross-sectional and surface morphologies of the electrospun composite substrate with a multilayered structure. As shown in **Figs. 3A** and **3B**, the PVDF composite substrate exhibited a tiered structure composed of a top ultrafine PVDF nanofibrous layer with a thickness of $0.5 \pm 0.1 \mu\text{m}$, an intermediate coarse PVDF nanofibrous layer with a thickness of $5.4 \pm 0.3 \mu\text{m}$, a non-woven mechanical support with a thickness of $45.0 \pm 4.0 \mu\text{m}$ and a micro/nano-beaded layer with a thickness of $3.8 \pm 1.0 \mu\text{m}$ on the bottom.

Fig. 3. (A, B) Cross-sectional morphologies of the electrospun composite substrate. The surface morphologies of each layer of this substrate: (C) ultrafine and (D) coarse PVDF nanofibrous layers on the feed side; (E) the electrospun micro/nano-beaded layer on the receiving side.

As shown in **Fig. 3C**, the feed side surface of the as-developed substrate presented a continuous arrangement of nanofibers with an average diameter of 55 ± 1 nm. Compared to the PVDF nanofibers with a diameter of 129 ± 10 nm in the intermediate layer (**Fig. 3D**), the ultrafine nanofibers were obtained due to the polymer dope having a lower concentration and a higher conductivity. The highly conductive polymeric solution is unstable in the presence of strong electric fields, leading to significant decrease in nanofibers diameter [26]. This ultrafine PVDF layer was developed to effectively support a thin and defect-free PDMS selective layer and mitigate PDMS penetration [8]. Whereas, the coarse bottom nanofibrous layer was tailored to provide sufficient mechanical support for the ultrafine nanofibrous layer, enhance porosity and reduce the mass transfer resistance of the substrate. The nanofibrous surface possessed a water contact angle of $116 \pm 2^\circ$ (**Table 1**). It is worth pointing out that the strong adhesion at the interfaces between the two nanofibrous layers and between the coarse nanofibrous layer and non-woven support are ensured by heat-press post-treatment [27].

According to **Fig. 3E**, the substrate surface at the receiving side (facing the biomedium) showed a rough topology with a large amount of protrusions and valleys, which provided superhydrophobicity indicated by a water contact angle of $155 \pm 3^\circ$ (**Table 1**). These micro/nano-beads were created due to the present of the modified silica particles [23, 24]. As illustrated in our previous study [24], the PVDF-silica composite materials are able to intrude and wrap the non-woven fibers, which guarantee membrane integrity.

Table 1. Thickness, water contact angles at feed and receiving sides, mechanical properties and zeta potential at the receiving side (pH=6.9) of the substrate and nanofibrous composite membranes.

Membrane	Thickness (μm)	Water contact angle ($^{\circ}$)		Mechanical properties			Zeta potential (mV) Receiving side (pH=6.9)
		Feed side	Receiving side	Tensile modulus (MPa)	Tensile at break (MPa)	Strain at break (%)	
Substrate	50 ± 2	116 ± 2	155 ± 3	422 ± 48	14 ± 2	34 ± 8	
NC	57 ± 3	118 ± 2	156 ± 2	351 ± 79	14 ± 3	29 ± 8	-31.1 ± 0.3
M-NC	62 ± 4	58 ± 8	0	354 ± 20	12 ± 1	41 ± 6	-32.8 ± 0.5

3.1.2 Nanofibrous composite membranes before and after modification

The FESEM images of nanofibrous composite membrane NC fabricated by spray-coating a PDMS selective layer on the electrospun substrate are shown in **Figs. 4A-4C**. The cross-sectional morphology of NC (**Fig. 4A**) demonstrates that a dense PDMS layer with a thickness of $12 \pm 1 \mu\text{m}$ has been successfully fabricated on the substrate surface by spray-coating. The cross-linked PDMS top layer showed a smooth and defect-free morphology (**Fig. 4B**) with a water contact angle of $118 \pm 2^\circ$ (**Table 1**). As discussed above, the membrane NC possessed a superhydrophobic surface on the receiving side with a water contact angle of $156 \pm 2^\circ$ (**Table 1**) due to the hierarchical structure of the substrate (**Fig. 4C**).

As shown in **Figs. 4D-4F**, the morphologies of the M-NC showed no significant changes after PDA and PEG modifications. However, the water contact angle of the PDMS surface on the feed side reduced from $118 \pm 2^\circ$ to $58 \pm 8^\circ$ after the chemical modifications (**Table 1**). The apparent water contact angle of the receiving side surface reduced from $156 \pm 2^\circ$ to 0° . Thus, a superhydrophilic surface has been obtained successfully due to the combination of surface roughness and the hydrophilic nature of PEG.

Fig. 4. Cross-sectional morphologies, the PDMS selective layers facing the feed side and the micro/nano-beaded layers facing the receiving side of (A-C) unmodified membrane NC and (D-F) PEG-modified membrane M-NC.

The possible reaction pathways for PDA and PEG modifications are shown in **Fig. S3**. In the first step, the pristine membrane NC was treated by dopamine. During the dopamine oxidative self-polymerization, the catechols of dopamine were oxidized to quinone forms, followed by polymerization in a manner of melanin formation (**Fig. S3A**) [28]. Small amounts of CuSO_4 and H_2O_2 were added to the aqueous dopamine reaction solution as triggers to strongly enhance the deposition rate of PDA coatings on the composite substrate. It has been demonstrated that Cu^{2+} and H_2O_2 can produce reactive oxygen species, such as $\text{O}_2^{\cdot-}$, $\text{HO}_2^{\cdot}$ and $\text{OH}^{\cdot}$, in an alkaline medium, which are critical to improve the deposition rate of PDA coating [25]. The PDA coating is able to act as an intermediate layer for further facile functionalization of the membrane surface. Antifouling surfaces can be constructed by covalently grafting thiol-terminated PEG via Michael addition as shown in **Fig. S3B** [28].

To demonstrate the successful grafting of PDA and PEG on the membrane surface, the surface compositions on the receiving sides of NC, PDA-NC and M-NC membranes were characterized via XPS measurements. As shown in **Fig. 5A**, the C 1s core-level spectrum of the receiving side surface of NC can be curve-fitted with four peak components, one at a binding energy (BE) of 285.0 eV for the carbon bonded to hydrogen and carbon (C-H/C-C) and one at a BE of 291.0 eV for a single carbon bonded to fluorine (C-F₂) due to existence of PVDF, O-CH₂-C at 286.6 eV and -CO-N- at 287.9 eV attributed to the chemical structure of modified silica [23, 29]. The distinct differences in the C 1s core level line shapes between NC and PDA-NC (**Fig. 5B**) are the presence of additional C-N at 286.0 eV and C=O at 288.9 eV [25, 30]. These additional peaks were detected due to the emitted photoelectrons from the PDA layer on the membrane surface. Furthermore, the result that C-F₂ peaks associated with PVDF persisting in the C 1s spectrum of the PDA-NC confirms that the thickness of the deposited PDA layer was below the probing depth of the XPS technique (< 10 nm). As shown in **Fig. 5C**, the appearance of ether carbon (C-O at 286.5 eV) in the C 1s spectra of M-NC demonstrates the successful grafting of PEG on the membrane surfaces [31]. In addition, the disappearance of groups associated with the PDA layer including C-N, C-H₂-O, -CO-N- and C=O illustrates that the PEG layer exhibited a thickness more than 10 nm, which shielded the electron signals from the PDA layer.

Fig. 5. The XPS C 1s core level spectra of (A) NC, (B) PDA-NC and (C) M-NC.

The effects of surface modification on the mechanical properties of membranes including tensile modulus, tensile at break and strain at break are summarized in **Table 1**. The PVDF composite substrate exhibited a 7 times higher tensile modulus, a 4 times higher tensile at break and a lower strain at break compared with other reported PVDF membranes prepared via phase inversion [32, 33]. This robust mechanical property can be attributed to effective combination between the composite layers and the non-woven mechanical support. After PDMS spray-coating, the overall mechanical properties, especially the tensile moduli of NC and M-NC, decreased because of the soft PDMS layer. However, their tensile moduli were still significantly better than that of reported PVDF membranes developed via phase inversion [32, 33]. There is no significant difference in the mechanical properties of NC and M-NC, which indicates that the modifications did not alter the membrane structure.

3.2 Aqueous-aqueous extractive processes

The k_o 's and salt fluxes of both NC and M-NC are shown in **Fig.6**. NC possessed a k_o of $10.4 \pm 0.1 \times 10^{-7}$ m/s, which was an order of magnitude higher than that of the commercial silicon tubing (1.0×10^{-7} m/s) [34]. The significantly higher k_o should be attributed to a thinner PDMS selective layer as well as a highly porous substrate. The k_o of M-NC was slightly enhanced to $12.0 \pm 0.1 \times 10^{-7}$ m/s due to the superhydrophilic modification. The PEG modification may have accelerated the diffusion of phenol across the hydrophilic substrate and thus enhanced phenol transfer efficiency. In addition, salt fluxes were maintained at less than 20 mg/m²h for both nanofibrous composite membranes (**Fig. 6**), indicating that the membranes effectively restrain salt diffusion through the membranes during the aqueous-aqueous extractive process.

Fig. 6. The k_0 and salt fluxes of NC and M-NC in an aqueous-aqueous cross-flow membrane extractive process.

To examine the stability of the nanofibrous composite membranes, NC was continuously operated in the aqueous-aqueous extractive process for 14 days. As shown in **Fig. 7A**, the membrane NC showed a stable k_0 over the testing period while the salt flux was less than $20 \text{ mg/m}^2\text{h}$. After the long-term testing, no delamination could be observed between each layer (**Fig. 7B**). A uniform PDMS layer observed on the membrane surface at the feed side (**Fig. 7C**) and micro/nano-beaded topology with valleys and protrusions on the membrane surface at the receiving side (**Fig. 7D**) demonstrate the outstanding membrane stability.

Fig. 7. (A) Long-term performance of NC in an aqueous-aqueous extractive process; the morphologies of NC after 14-days operation: (B) cross-section and surface of (C) PDMS selective layer and (D) the mico/nano-beaded layer.

3.3 Performance of nanofibrous composite membranes in EMBRs

According to **Fig. 8A**, decreases of k_o values were observed for both NC and M-NC within the first three days of CF-EMBR operation due to rapid biofilm growth on the membrane surfaces at the receiving side. The stabilized k_o values were similar for both membranes at around $4.0 \times 10^{-7} \text{ m/s}$ after 12 days of operation, which were 38% of initial values. Nevertheless, the stabilized k_o values remained 10 times higher than that of commercial PDMS tubular membrane in our previous CF-EMBR study [10]. Periodic samplings from the bioreactors illustrated that the phenol concentrations in the bioreactors remained at zero, demonstrating that the active biofilms on the membrane surfaces and microorganisms in the

bioreactors had biotransformed all phenol diffused from the feed to the receiving side. Conductivity in both bioreactors remained at 4.7 ± 0.4 mS/cm, indicating negligible salt flux from the feed solutions. Membrane autopsy data in **Fig. 8B** shows that the amounts of protein, polysaccharide and TSS deposited on the NC were 0.52 ± 0.09 mg/cm², 0.24 ± 0.06 mg/cm² and 7.35 ± 0.75 mg/cm², respectively. The concentrations of protein, polysaccharide and TSS accumulated on the M-NC surface were 0.23 ± 0.01 mg/cm², 0.34 ± 0.03 mg/cm² and 5.85 ± 0.61 mg/cm², respectively. The protein and TSS concentrations on the NC surface were higher than that of M-NC while the polysaccharide amount on NC surface was lower than that of M-NC. Overall, the slight differences in the biofilm components and amounts did not affect the stabilized k_o values after 12 days of CF-EMBR operation. Visual inspection of the membrane surfaces, shown in **Fig. 8C**, display that at the first day the bacterial flocs had started to accumulate on both membranes surface. The complete coverage of both membrane surfaces by a thick biofilm layer could be observed after 12 days of CF-EMBR operation. The 62% decreases in k_o demonstrate that biofilm resistance become the dominant mass transfer resistance in the CF-EMBR.

Fig. 8. (A) Long-term performance of NC and M-NC in a cross-flow extractive membrane bioreactor (CF-EMBR); (B) membranes autopsies after 12 days of CF-EMBR operation; (C) photographs of membrane surfaces at the receiving side during CF-EMBR operation.

To reduce the mass transfer resistance associated with excessive biofilms on membrane surface, both NC and M-NC were operated in the S-EMBR configuration that incorporated bubbling for biofilm control. As shown in **Fig. 9A**, the normalized k_0 's decreased to 65% for NC and 40% for M-NC after 12 days of operation. Compared to the 38% normalized k_0 obtained for NC in the CF-EMBR after stabilization, the normalized k_0 of NC in the S-EMBR was 27% higher. The stabilized k_0 after 12-days S-EMBR operation were 5.7×10^{-7} m/s and 5.0×10^{-7} m/s for NC and M-NC, respectively. These values were higher than k_0 of both membranes in the CF-EMBR system, indicating that membrane scouring through aeration is effective in controlling biofilms in the S-EMBR. Interestingly, the k_0 of NC

increased by 5% on the first day. Similar phenomenon has been reported in a previous study [35]. At the beginning of S-EMBR operation, the biofilm on the membrane surface was thin and porous, which conferred negligible organic transfer resistance yet was able to biodegrade phenol rapidly at the receiving side. Thus, the thin and porous biofilm was able to maximize phenol concentration gradient across the membrane and thus enhance the overall mass transfer efficiency. However, as the test proceeded, the biofilm became thicker and denser, which increased organic transfer resistance dramatically. The phenomenon of k_o increasing at the beginning was not observed for M-NC, which could be due to a faster biofilm accumulation rate on the PEG-modified surface of M-NC.

As shown in **Fig. 9B**, the concentrations of protein, polysaccharide and TSS detected on the receiving side surface of the NC were $0.21 \pm 0.07 \text{ mg/cm}^2$, $0.05 \pm 0.01 \text{ mg/cm}^2$ and $1.67 \pm 0.02 \text{ mg/cm}^2$, which were significantly lower than the amounts on the same membrane after long-term CF-EMBR operation. Analogously, the protein, polysaccharide and TSS amounts on M-NC surface after prolonged S-EMBR testing were lower than that of M-NC after 12 days of CF-EMBR testing, which were $0.15 \pm 0.01 \text{ mg/cm}^2$, $0.08 \pm 0.01 \text{ mg/cm}^2$ and $1.83 \pm 0.19 \text{ mg/cm}^2$, respectively.

According to the images shown in **Fig. 9C**, the biofilm was not clearly observed on either membrane surface in the first two days, which suggests that it is more challenging for the biofilm to accumulate on the membrane surfaces in the S-EMBR operation. After two days of operation, a thin biofilm layer could be observed on the M-NC surface while the unmodified NC with a superhydrophobic surface still exhibited a clean surface. At the end

of the testing, a relatively thin and yellow biofilm layer was attached on the NC surface while a relatively thick and white biofilm layer was developed on the M-NC surface.

Fig. 9. (A) Long-term performance of NC and M-NC in the submerged extractive membrane bioreactor (S-EMBR); (B) membranes autopsies after 12 days of S-EMBR operation; (C) Photographs of membrane surfaces at the receiving side during the S-EMBR operation.

3.4 Understanding the biofilm attachment on different membrane surfaces in the EMBRs

According to the classical Derjaguin-Landua-Verwey-Overbeek (DLVO) and thermodynamic theories, the bacterial attachment on the ‘conditioned’ membrane surface includes two steps: firstly, bacteria are attracted and weakly bonded to the membrane surface

as inert colloidal particles by physicochemical interactions; secondly, bacteria overcome the repulsion and stabilize the biofilm matrix by means of extracellular bacteria structures such as flagella, pili and fimbriae, which strongly bridge the bacteria to membrane surface [17]. The hydrodynamic conditions, and the chemical properties and physical topology of the membrane surface directly relate to the biofilm attachment.

In the S-EMBR configuration, the upward bubble flow is able to create a bubble-induced hydrodynamic shear near the membrane surface that can scout biofilm deposits from the membrane surface [36]. The bubble-induced hydrodynamic shear is absent in the CF-EMBR, which may account for the higher amount of biofilm deposition and higher k_o decline observed in the CF-EMBR system.

Moreover, membrane surface properties, including surface charge, surface roughness and chemistry may also influence microbial attachment and biofilm development. The surface charges of NC and M-NC at operational pH of 6.9 were examined as shown in **Table 1**. No significant difference can be observed. Since that PEG-modified membrane M-NC possessed the same micro/nano-beaded topology on the receiving side as the unmodified membrane NC, it is elucidated that the different performance of these membranes in the S-EMBR should be mainly attributed to the chemical groups on the membrane surface.

As reported in the literature, fluoropolymer is one of the polymeric materials possessing good fouling release properties, which is related to its hydrophobicity and low surface energy ($25 \text{ mJ} \cdot \text{m}^{-2}$ for PVDF) [37]. The nonpolar and nonreactive surfaces covered with fluoropolymer discourage the bio-adhesive interactions between bacteria and membrane

surfaces. The micro-foulants can be released from the fluoropolymer surface under suitable hydrodynamic shear stress. On the other hand, PEG surfaces are known for their resistance to protein adsorption and cell adhesion, despite a relatively higher surface energy ($>43 \text{ mJ}\cdot\text{m}^{-2}$). Their resistance to fouling organisms adhesion was reported to rely on a steric repulsion of the adhesive molecules from the hydrated PEG [38]. Therefore, both unmodified membrane NC, with a superhydrophobic fluoropolymer surface facing the bioreactor, and modified membrane M-NC with a superhydrophilic PEG surface facing the bioreactor, should possess mechanisms to limit biofilm attachment.

In both CF-EMBR and S-EMBR operations, a greater amount of protein was attached on the hydrophobic NC surface while a greater amount of polysaccharides was observed on the hydrophilic M-NC surface. The possible reasons are that more proteins were attached on the superhydrophobic surface of NC due to the intrinsic hydrophobicity of proteins while the more polysaccharides on the superhydrophilic surface of M-NC could be due to the intrinsic hydrophilic property of polysaccharides (**Figs. 8B and 9B**) [39]. The extracellular polysaccharides are known as bio-glues, which facilitate cell-to-cell interaction and strengthen microbial structures through formation of a sticky polymeric matrix. A greater amount of polysaccharides in the deposit on the hydrophilic M-NC surface could result in a more adhesive strength between the membrane surface and the biofilm layer, which prevents the biofilm from being removed by scouring and form a 'less permeable' biofilm with greater mass transfer resistance [39].

To demonstrate the different adhesive forces between the biofilm and membranes surface, the k_o recoveries of both membranes after physical cleaning were evaluated (**Fig. 10**). After

attaining steady state by 20 days of S-EMBR operation, the biofilm layers on both NC and M-NC surfaces were physically removed by flushing with DI water. The biofilm on the hydrophobic NC surface was fluffier and easier to remove, and an almost 100% k_o recovery was achieved for NC. However, since the biofilm layer developed on the M-NC surface was stickier, the k_o of the M-NC could only be recovered to 80% of the initial value after cleaning. These results demonstrate that the fluoro-polymeric superhydrophobic surface exhibits a better fouling releasing property than the PEG-coated superhydrophilic surface in the S-EMBR operation.

Fig. 10. Performance recoveries of NC and M-NC in S-EMBR after flushing with DI water

3.5 Long-term performance in a pilot S-EMBR treating industrial wastewater

To further explore the membrane performance in a real industrial application, a pilot S-EMBR with a three-module CSTR design was operated using industrial wastewater as feed. The k_o decreased by about 50% from 13.0×10^{-7} m/s to the steady state of 6.5×10^{-7} m/s in 14 days of operation as shown in **Fig. 11A**: the stable period was from day 7. The initial

value and decline trend of k_0 are comparable to those observed for synthetic phenol feed solution in S-EMBR configuration, indicating that the mixed organic matrix in the industrial wastewater did not compromise the phenol extraction efficiency of the nanofibrous composite membrane. According to **Fig. 11B**, the amounts of protein, polysaccharides and TSS of each module were lower than that of the same membrane operated in the S-EMBR using the synthetic phenol aqueous solution. This could be due to a lower organic carbon loading to the bioprocess and hence less biofilm formation. In addition, the biodegradation of unknown organics which had been extracted from the industrial wastewater could have impacts on the biofilm development and composition. For now, the competitive performance of the NC membrane in removing phenol from industrial wastewater has demonstrated the potential of as-developed nanofibrous composite membranes in practical wastewater treatment.

Fig. 11. (A) Long-term performance of NC treating actual industrial wastewater in a pilot S-EMBR with a three-modules CSTR design, (B) the membrane autopsies of each membrane cell after 14 days of S-EMBR operation.

3.6 Comparison of phenol extractive performance of various membranes

The phenol mass transfer coefficients of as-developed nanofibrous composite membranes NC and M-NC are compared with other reported PDMS composite membranes in **Table 2**. In contrast with the commercial PDMS tubular membranes, a noticeable flux enhancement has been achieved for both NC and M-NC membranes, which should be attributed to the high porosity and open structure of nanofibrous substrates and thinner PDMS selective layers [10, 12]. The nanofibrous composite membranes developed in this work exhibited similar performance as our previous membranes operated in CF-EMBR process, but outperformed in the S-EMBR configuration [8]. This should be attributed to an effective biofilm control in the S-EMBR process.

Table 2. Phenol mass transfer coefficients of different membranes in EMBRs.

Membrane	EMBR process	Feed Side	Receiving side	Operation Time (h)	Stable k_0 (x 10^{-7} m/s)	Reference
PDMS tube	S-EMBR	1000 ppm phenol, 1 M HCl, 50 g/L NaCl		70	2.1	[12]
PDMS tube	CF-EMBR	2000 ppm phenol		336	0.5	[10]
	S-EMBR			336	0.8	
PDMS-PVDF nanofibrous composite membrane	CF-EMBR	1000 ppm phenol, 1 M HCl, 50 g/L NaCl		336	4.1	[8]
			Biomedium			
NC	CF-EMBR	1000 ppm phenol, 5 g/L NaCl		288	4.0	This work
	S-EMBR			288	5.7	
		Industrial wastewater		744	6.5	
M-NC	CF-EMBR	1000 ppm phenol,		288	4.0	
	S-EMBR	5 g/L NaCl		288	5.0	

4. Conclusions

In this work, novel nanofibrous composite membranes NC, with a superhydrophobic surface at the receiving side, and M-NC, with a superhydrophilic surface at the receiving side, have been designed and developed for phenol removal in EMBRs. The findings are as follows:

- (1) The unmodified membrane NC exhibited a k_o of $10.4 \pm 0.1 \times 10^{-7}$ m/s while the PEG-modified membrane M-NC showed a k_o of $12.0 \pm 0.1 \times 10^{-7}$ m/s in aqueous-aqueous membrane extractive processes, which are 10 times higher than the commercial PDMS tubular membrane.
- (2) The k_o values of both membranes decreased by 65% after 12 days of CF-EMBR operations, and suffered from excessive biofilm attachment. However, the stabilized k_o of 4.0×10^{-7} m/s was still 10 times higher than that of the commercial PDMS tubular membrane operated in the same CF-EMBR process.
- (3) In comparison to CF-EMBR, the S-EMBR configuration could effectively control the accumulation of biofilms on both membrane surfaces probably due to the beneficial shear and presence of surface scouring via air bubbles.
- (4) Compared to the fluoro-polymeric superhydrophobic surface of NC, a sticker and thicker biofilm layer was developed on the PEG-modified superhydrophilic surface of M-NC. This appears to be due to more polysaccharides accumulated on the M-NC surface which strengthened the biofilm attachment.
- (5) Physical cleaning could effectively remove the biofilm from the NC surface and fully recover k_o to the initial value while M-NC only achieved an 80% recovery. Because of its better performance, the NC has been operated in a pilot S-EMBR with a three-module CSTR design to treat industrial wastewater for 14 days. It exhibited

a stabilized k_o of 6.5×10^{-7} m/s, confirming the feasibility of nanofibrous composite membranes fabricated in this work for practical industrial wastewater treatment.

The presence of biofilm is critical for EMBRs, but achieving an optimum biofilm thickness on the membrane surface is challenging. In order to control the biofilm precisely, the mechanism of how the extracellular polymeric substances interact with the different membrane surfaces and how this interaction relates to biofilm structure, strength and resistance to membrane scouring need to be studied at a more fundamental and systematic level. In addition, more work is required to design air bubble delivery to the membrane surface, the use of chemical agents and biofilm quorum-sensing disruptors to control the biofilms, which should be guided by experience with conventional MBRs. Moreover, the effects of the industrial wastewater properties, including chemical oxygen demand (COD), TOC, presence of complex pollutants and nutrients, on membrane extractive efficiency and biofilm formation in the EMBR processes should be investigated. Finally, assessment of the EMBR capital costs, life expectancy and reliability could bring the technology closer to real industrial applications for difficult organic wastewater treatment.

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