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Effects of internal concentration polarization and membrane roughness on phenol removal in extractive membrane bioreactor

Yuan Liao ^{a,1}, Miao Tian ^{a,1}, Shuwen Goh ^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

*Corresponding author at: School of Civil and Environmental Engineering,
Nanyang Technological University, 639798 Singapore,
Singapore. Tel.: +65 6790 5327; fax: +65 6791 0676.

E-mail address: rwang@ntu.edu.sg (R. Wang).

¹ These authors contributed equally to this work.

Abstract

Recent studies have proved the advantages of novel composite membranes in the extractive membrane bioreactor (EMBR) for recalcitrant organic wastewater treatment. However, more systematic research into membrane properties and mass transfer effects are required. This study investigates the role of internal concentration polarization (ICP), including concentrated and diluted ICP, in an aqueous-aqueous extractive process, and the coupled effects of membrane roughness and hydrodynamic conditions on membrane performance in both cross-flow EMBR (CF-EMBR) and submerged EMBR (S-EMBR) processes. To study these factors, a nanofibrous composite membrane with a four-tiered structure, consisting of a dense polydimethylsiloxane (PDMS) selective layer, a polyvinylidene fluoride (PVDF) nanofibrous sublayer, a non-woven mechanical support and a rough micro/nano-beaded layer, has been developed for the EMBR by electrospinning and spray-coating.

A diluted ICP, which occurred when the selective layer faces receiving water (SL-R_w), was less severe than a concentrated ICP in the selective layer facing feed (SL-F) orientation. It resulted in higher overall membrane mass transfer coefficients (k_o 's) in the SL-R_w mode during the aqueous-aqueous extractive tests. In addition, less biofilm was observed on the smooth PDMS surface after 14-days CF-EMBR and S-EMBR operations in the selective layer facing biomedium (SL-R_{bio}) mode. In contrast, in the SL-F mode during EMBR operations, the ridges and valleys on the membrane surface were able to provide a more favourable micro-environment for microorganisms and protect them from external stresses. The mature micro-colonies that developed in the SL-F mode clogged the membrane support and enhanced concentrated ICP, resulting in a significant reduction of

k_0 's by more than 58%. Moreover, as the shear force on the membrane surface due to up-flow of air bubbles in the S-EMBR could mitigate the biofilm attachment, the most effective biofilm control strategy found in this study was to operate the nanofibrous composite membrane in the S-EMBR configuration with a smooth selective layer facing the biomedium. This effectively decreased the amounts of protein by 86%, polysaccharides by 88% and total suspended solids (TSS) by 89% in the biofilms on membrane surface, and achieved the highest stable k_0 of 7.0×10^{-7} m/s.

Keywords: Extractive membrane bioreactor (EMBR); Nanofibrous composite membrane; Internal concentration polarization (ICP); Biofilm; Membrane orientation; Membrane roughness

1. Introduction

The extractive membrane bioreactor (EMBR) is a membrane process in which toxic organic contaminations (e.g. phenolic compounds) diffuse across a non-porous membrane from a feed solution of higher organic concentration to a receiving solution of biomedium [1, 2]. The acclimatized biomedium is able to biodegrade the contaminations and maintain the organic concentration of the receiving solution at close to zero [1, 2]. This concentration-driven membrane process separates highly inhibitory wastewaters (e.g. highly caustic or acidic, highly saline and *etc.*) from acclimatized biomedium by a semi-permeable membrane, which is highly permeable to the target organics and effectively impermeable to inorganics and water [3]. The EMBR process eliminates the demands of pretreatment (such as pH neutralization and dilution) for wastewaters with inhibitory compounds and harsh conditions, thus providing an economically feasible route for treating difficult waste streams directly. It also exhibits advantages over conventional techniques (e.g. steam distillation and adsorption) for hostile chemicals removal [4]. For instance, the entire process is operated at atmospheric temperature and pressure [5]. The organic retention time (ORT) and cell residence time can be optimized for better removal of less-readily biodegradable organics [6]. Additionally, as EMBR produces a small waste stream, it diminishes the requirements of complicated post-treatments and waste disposal [7].

The growing interest in the EMBR for recalcitrant or difficult organic wastewater treatment calls for fundamental and systematic investigations that can lead to a better understanding of the process and further advance this technology [8, 9]. Efforts have been made to demonstrate its success with the treatment of a diverse range of compounds,

including hydrophobic and hydrophilic chemicals, volatile and less volatile organics, and metal-containing wastewaters in hostile conditions [10-13]. In addition, the influence of membrane module design on extraction efficiency has been studied [14]. Pilot scale trials have demonstrated that the EMBR is a robust technique to treat difficult industrial emissions [7]. However, many of these studies had been conducted over a decade ago. At that time, one of the main obstacles impeding progress of the EMBR was the absence of specially designed membranes with high efficiency and robustness.

Recently, our group has developed highly efficient composite membranes for the EMBR by coating a thin layer of poly(dimethylsiloxane) (PDMS) on electrospun nanofibrous (flat sheet) or hollow fiber substrates [3, 15]. In contrast to commercial PDMS tubes with a thickness of 0.1 mm, the composite membranes can significantly enhance organic transfer efficiency due to a thin and permeable selective layer and a highly porous support. Moreover, to further enhance the phenol extraction efficiency in the extractive process, dense PDMS membranes with different micromolecular architectures have been developed and evaluated in our recent work [16]. It was found that the condensation-cured PDMS membrane with network architecture exhibited higher phenol transport efficiency than the hydrosilylation-cured PDMS membranes with linear and branch architectures, which could be attributed to the four-armed quaternary-siloxy linkages formed in the three-dimensional network structure.

In addition to the development of novel composite membranes, one notable research area which has not been studied in the EMBR is the effects of internal concentration polarization (ICP) due to the porous membrane support. The primary reason for this

oversight is the fact that most previous studies utilized commercial dense PDMS membranes. The asymmetric composite membranes have been developed for the EMBR only recently. Analogous to the osmotic driven membrane processes, ICP could occur within the support layer of the composite EMBR membranes, such that the organic concentration at the internal boundary between the selective layer and support differs significantly from the bulk solutions [17, 18]. In the osmotically driven membrane processes, ICP results in a reduction of the effective concentration difference and a corresponding significant decrease in water flux. As ICP cannot be mitigated by optimizing hydrodynamic conditions, it has been identified as a primary obstacle for using asymmetric membranes for osmotic driven processes and has resulted in design of ‘tailored’ membrane structures [17]. However, the influences of ICP on the behavior of composite membranes in the EMBR processes have not been reported yet. There is an urgent demand to address this knowledge gap.

Furthermore, it has been observed that excessive biofilm accumulation on the membrane surface is one of the key issues hindering EMBR applications at the industrial scale, because it leads to the significant increase of overall organic mass transfer resistance [11, 19]. A mathematical model of membrane-attached biofilm behavior in a single-tube EMBR has been developed to predict the trends in EMBR systems, including biofilm thickness, organic flux across the membrane and suspended biomass [20]. Nitrate has been used as the electron acceptor instead of oxygen to prevent the formation of inactive biofilms [21]. In our recent work, it was found that strategies involving reduction of the inorganic loading rate and scouring the membrane surface *via* air bubbles were capable of effectively controlling the biofilm thickness on the membrane surface, and enhance the

overall mass transfer efficiency of membranes in a prolonged submerged EMBR (S-EMBR) process [1]. Furthermore, as polysaccharides prefer to accumulate on the hydrophilic surface rather than hydrophobic surface, this appears to strengthen the biofilm matrix against detachment by membrane scouring, resulting in greater biofilm accumulation on hydrophilic surfaces [22]. Compared to the hydrophobic and hydrophilic properties, some studies suggested that membrane roughness maybe a more critical factor affecting the accumulation of foulants on membrane surface [23, 24]. To date, however, it is still not clear how the membrane roughness influences biofilm accumulation on the membrane surface in the EMBR processes.

Therefore, the key objectives of this study are to understand the effects of ICP and membrane surface roughness on the phenol extractive performance by the nanofibrous composite membrane applied in the EMBR processes. In this work, a PDMS-coated nanofibrous composite membrane was developed by electrospinning and spray-coating as reported in our previous study [22]. A highly porous composite substrate exhibiting a three-tiered structure was fabricated by electrospinning, which was composed of a poly(vinylidene fluoride) (PVDF) nanofibrous layer, a non-woven mechanical support and a micro/nano-beaded hierarchical layer. A thin PDMS layer was spray-coated and cross-linked on the surface of the nanofibrous layer. The effects of ICP on the composite membrane performance in an aqueous-aqueous extractive process were examined by testing the membrane in different orientations, including selective layer facing feed (SL-F) and selective layer facing receiving water (SL-R_w) orientations. Additionally, the influences of membrane roughness on its performance in cross-flow EMBR (CF-EMBR) and S-EMBR processes were investigated. Moreover, the effects of different

hydrodynamic conditions in CF-EMBR and S-EMBR systems on the biofilm development on membrane surface and resultant membrane efficiency were studied. It is hoped that our observations and discussion would provide new insights into the membrane design and operation for the EMBR.

2. Materials and methods

2.1 Materials and chemicals

Poly(vinylidene fluoride) (PVDF, Kynar HSV 900, Arkema) as a substrate material, anhydrous lithium chloride (LiCl, Merck) as an additive and N, N-Dimethylformamide (DMF, Merck) as a solvent were purchased to electrospin a membrane substrate. Fluorinated silica nanoparticles were obtained by the method reported in our previous works [25, 26]. A silicon elastomer and a curing agent (Sylgard 184) were ordered from Dow Corning for poly(dimethylsiloxane) (PDMS) coating. Isopropyl alcohol (IPA, Merck) with analytical grade, glycerol (80% aqueous solution, Merck), and deionized water (DI water) purified by a Milli-Q system (Millipore Co.) were used as pre-wetting agents for the electrospun substrate. In the aqueous-aqueous extractive test and EMBR processes, the feed solutions contained phenol and NaCl purchased from Sigma-Aldrich. The nutrients for biomedium in the bioreactors, including $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, KH_2PO_4 , FeCl_3 , $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ and NH_4Cl were ordered from Merck. All reagents were used as received. The Polyethylene terephthalate (PET, Grade 3233) non-woven mechanical support was purchased from Ahlstrom Filtration.

2.2 Development of a nanofibrous composite membrane for EMBR

2.2.1 Preparation of a nanofibrous composite substrate by electrospinning

The nanofibrous composite substrate was fabricated by electrospinning different dope solutions. Firstly, a coarse nanofibrous layer was developed on the non-woven support by electrospinning an 8 wt % PVDF dope. Then, an ultrafine nanofibrous layer was electrospun on the coarse layer *via* a 3 wt% PVDF dope [15]. In order to enhance membrane integrity and mechanical strength, this dual-layer nanofibrous membrane with a non-woven mechanical support was post-treated by heat-pressing at 155 °C and 2 bar for 30 min. After the post-treatment, a micro/nano-beaded layer was fabricated on the non-woven surface of the nanofibrous substrate by electrospinning a modified silica/PVDF blended dope. In all electrospun processes, the applied voltage was set as 30 kV, the working distance between the spinnerets and grounded collector was 15 cm, and the relative humidity was maintained around $70 \pm 2\%$. The surrounding temperature was at $23 \pm 2^\circ\text{C}$. To ensure that the electrospun composite substrate was wetted thoroughly, it was immersed in IPA overnight. Then the substrate was pre-wetted by a mixture of DI water and glycerol (1:1) prior to PDMS spray-coating. This pre-wetting solution was effective to mitigate PDMS intrusion as proved in our previous studies [3].

2.2.2 Preparation of a PDMS-coated nanofibrous composite membrane

The pre-wetted substrate was attached on a clean glass plate and positioned perpendicular to a spraying nozzle. The excessive pre-wetting solution on the nanofibrous surface of the substrate was wiped off by a rubber roller. A 5 wt% PDMS solution, which contained a base polymer and a curing agent with a mass ratio of 10:1 in *n*-hexane, was then sprayed on the nanofibrous surface fabricated by electrospinning PVDF dopes. The spraying pressure was set as 70 kPa. An

electrospun substrate with a surface area of 300 cm² consumed 50 mL coating solution. The PDMS-sprayed membrane was subsequently cured at 80 °C for 2 days. The as-prepared nanofibrous composite membrane is denoted as PDMS-PVDF. The PDMS-PVDF membrane was immersed in IPA overnight and washed by DI water before testing in the EMBR processes to ensure the complete wetting of the composite membrane.

2.3 Membrane characterizations

2.3.1 Characterizations of membrane morphologies and properties

The surface morphologies and cross-sectional structures of the nanofibrous composite membrane PDMS-PVDF were examined by a field emission scanning electron microscope (FESEM, JSM-7200F, JEOL Asia Pte Ltd, Japan) at 5 kV. The topologies of the composite membrane surfaces on both sides were observed by atomic-force microscopy (AFM, XE-100, Park System, Korea) operated in the non-contact mode. The water contact angles of the membrane surfaces on both sides were measured using a goniometer (Contact Angle System OCA, Data Physics Instruments GmbH, Singapore). The zeta potentials of PDMS-PVDF surfaces were determined using an electro-kinetic analyzer (SurPASSTM 3, Anton Paar) based on the streaming potential measurements. A 1 mM KCl aqueous solution was prepared as the background electrolyte solution while 0.05 M HCl and NaOH aqueous solutions were used for pH titration. Each membrane sample was measured at least three times and average values were provided.

2.3.2 Membrane performance in an aqueous-aqueous extractive process

As the PDMS-PVDF has an asymmetric structure, its overall mass transfer coefficients k_0 's (m/s) at different membrane orientations were examined in a bench-scale aqueous-aqueous phenol extractive process as depicted in our previous works [3, 22]. The composite membrane was placed in a flat-sheet membrane cell with an effective membrane area of 36 cm². When the membrane selective layer (PDMS) was placed against the feed solution, this orientation is referred to as 'selective layer facing feed' (SL-F) mode. Analogously, when the PDMS layer was against the receiving solution (DI water in this test), it is denoted as selective layer facing receiving water (SL-R_w) mode. In the aqueous-aqueous extractive process, the feed solution (1L) consisted of 1 g/L phenol and 5 g/L NaCl while the receiving solution was 1L DI water. The phenol concentration in the feed solution was monitored using high-performance liquid chromatography (HPLC, Shimadzu). Both feed and receiving solutions were recycled through the flat-sheet membrane module in a counter-current mode with a membrane surface velocity of 8.3 cm/s. The overall mass transfer efficiency (k_0 , m/s) of the membrane can be determined as follows [22]:

$$k_0 = \left(\frac{dC_r}{dt} V_r \right) / \{A(C_F - C_R)\} \quad (1)$$

where C_F and C_R (mg/L) are the phenol concentrations at the feed and receiving sides at time t (s); A (m²) is the effective membrane area; V_r (mL) is the volume of receiving solution.

NaCl flux (J_s , mg/m²h) was measured to examine the membrane rejections of water and inorganic salts, which was calculated by the equation:

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

where Δc (mg/L) is the variation of NaCl concentrations in the receiving solution during time interval Δt (h). The NaCl concentrations in the receiving solutions were monitored by an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer Optima 8000, USA).

2.3.3 Evaluation of membrane performance in EMBR

The phenol removal performance of nanofibrous composite membrane PDMS-PVDF was evaluated in both CF-EMBR and S-EMBR configurations. The design of CF-EMBR and S-EMBR processes was described in our previous study [22]. The k_0 's of the membrane in the two orientations, including SL-F and selective layer facing biomedium (SL-R_{bio}) modes, were tested in both EMBR configurations. The feed solution (1L) in the EMBRs was composed of 1 g/L phenol and 5 g/L NaCl. The phenol concentration in feed was topped up to 1 g/L after one day operation by adding a certain amount of 25 g/L phenol solution calculated based on HPLC results. Before using biomedium in the receiving sides, the control k_0 's 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 's at the day 0. Then the receiving solution was changed to 4L biomedium solutions with phenol-acclimated seed sludge and essential inorganic nutrients [1]. The pH in the bioreactors was maintained at 6.9 ± 0.4 throughout the entire operations. Additionally, the conductivity in the bioreactors was around 4.7 ± 0.4 mS/cm, demonstrating that negligible salt diffused across the membrane from the feed side to the receiving side. In the CF-EMBR configuration, both feed and receiving solutions were cycled through the flat sheet membrane cell with a

membrane surface velocity of 8.3 cm/s in a counter-current mode. In the S-EMBR system, two PDMS-PVDF membranes with a total effective membrane area of 238 cm² were placed in the centre of the bioreactor, between which the phenol feed solution was circulated with a flow rate of 200 mL/min using a variable-speed peristaltic pump (Cole-Parmer). Meanwhile, the membrane surfaces were scoured by up-flow air bubbles in the S-EMBR configuration with an airflow rate of 5 m³/h per 1 m² membrane surface [22].

As the phenol concentrations in the bioreactors were below detectable limits due to complete digestion by the active sludge, the k_0 (m/s) across the membrane in EMBRs can be determined as follows:

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

where C_f^0 and C_f^t are the phenol concentrations in the feed at the beginning and at time t . Analysis of biofilms accumulated on the membrane surface after continuous EMBR operations were conducted as reported in our previous work [1].

3. Results and discussion

3.1 Characterizations of the nanofibrous composite membrane

According to the cross-sectional morphology of the nanofibrous composite membrane PDMS-PVDF shown in **Fig. 1A**, the membrane exhibits a four-tiered asymmetric structure consisting of a dense PDMS layer with a thickness of $11.6 \pm 0.6 \mu\text{m}$, a highly porous nanofibrous layer with a thickness of $6.5 \pm 0.4 \mu\text{m}$, a non-woven mechanical support with a thickness of $45.0 \pm 4.0 \mu\text{m}$ and a rough micro/nano-beaded layer with a thickness of $3.8 \pm 1.0 \mu\text{m}$. The surface morphologies on both sides of PDMS-PVDF are presented in **Figs. 1B** and **1C**. **Fig. 1B** reveals that a homogenous PDMS layer with an in-air water contact angle of $118 \pm 2^\circ$ was successfully coated on the nanofibrous surface. The image confirms that the nanofibrous sublayer is completely covered by PDMS without any defects. On the other side, a superhydrophobic surface (**Fig. 1C**) with an in-air water contact angle of $156 \pm 2^\circ$ was created by electro-spraying a PVDF/modified-silica blended dope on the non-woven mechanical support. This surface exhibits a hierarchically micro/nano-beaded structure with a large amount of ridges and valleys. This micro/nano-beads are constructed on the non-woven support due to a lower polymer concentration and a higher amount of modified silica nanoparticles in the electrospun dope [25-27].

Fig. 1. (A) Cross-sectional morphology of the nanofibrous composite membrane PDMS-PVDF; surface morphologies on both sides: (B) the PDMS selective layer and (C) the superhydrophobic micro/nano-beaded layer.

In order to further characterize the surface features of the nanofibrous composite membrane, the topologies of its surfaces on both sides were analyzed by AFM at non-contact mode as shown in **Fig. 2**. The three-dimension (3D) and two-dimension (2D) maps along with a one-dimension (1D) profile in a given location (red line in figures) are presented for each surface. A scan size of $5.0\ \mu\text{m} \times 5.0\ \mu\text{m}$ was examined to acquire enough bumps and sufficient resolution to achieve an accurate characterization. The roughness average (Ra), which is the arithmetic mean of the absolute height values on the surfaces, was measured to describe the surface feature [28].

Fig. 2. Surface height and flat maps along with 1D profiles in a given location of the surfaces of the nanofibrous composite membrane PDMS-PVDF on both sides: (A1, A2, A3) the PDMS selective layer; (B1, B2, B3) the rough micro/nano-beaded layer.

Significantly different topologies can be observed in the AFM images of the two surfaces. While the surface of PDMS selective layer (**Fig. 2A**) shows a smooth topology with a height variation of an order of a few nanometers ($Ra = 0.48 \pm 0.06$ nm), the surface of the composite micro/nano-beaded layer on the other side (**Fig. 2B**) exhibits a hierarchically rough architecture with a height variation of several hundred nanometers ($Ra = 164 \pm 77$ nm). Here, the topology images of the micro/nano-beaded surface clearly show that it is composed of beaded ridges separated by valleys. Each ridge is further composed of smaller nano-sized beads separated by shallow depressions. Air pocket formations due to the ridges and valleys on the hierarchically structured surface decrease the solid-liquid

contact area on the surface and thereby amplify the in-air water contact angle to above 150° [29].

In addition to the physical surface properties analyzed by FESEM and AFM, the zeta potentials of membrane surfaces on both sides versus pH were examined as shown in **Fig 3**. At the EMBR operating conditions ($\text{pH}=6.9 \pm 0.4$), the zeta potentials of both membrane surfaces are in the range of -30 to -35 mV. In general, the high negative zeta potential of the membrane surfaces should lead to limited and difficult attachment by negatively charged sludge species at the initial stage of EMBR operations [30, 31].

Fig. 3. Zeta potentials of PDMS-PVDF membrane surfaces on both sides against different pH.

3.2 Effects of membrane orientation in an aqueous-aqueous extractive process

The absence of external hydraulic pressure in both the aqueous-aqueous extractive process and the EMBR processes allows the nanofibrous composite membrane to be operated in two orientations. The effects of membrane orientation on the k_0 's of the nanofibrous composite membrane PDMS-PVDF in the aqueous-aqueous extractive process were examined as shown in **Fig. 4**. In the SL-F orientation (**Fig. 4A**), the membrane PDMS-PVDF possess k_0 's of $9.7 \pm 0.7 \times 10^{-7}$ m/s, $9.8 \pm 1.2 \times 10^{-7}$ m/s, $9.9 \pm 0.6 \times 10^{-7}$ m/s, and $9.8 \pm 1.4 \times 10^{-7}$ m/s against the phenol concentrations of 1 wt%, 2 wt%, 3 wt% and 4 wt% in the feed solutions, respectively. In the SL-R_w orientation (**Fig. 4B**), it exhibited k_0 's of $11.8 \pm 0.1 \times 10^{-7}$ m/s, $10.8 \pm 1.1 \times 10^{-7}$ m/s, $11.2 \pm 0.1 \times 10^{-7}$ m/s, and $11.2 \pm 1.6 \times 10^{-7}$ m/s when the phenol concentrations in feed were 1 wt%, 2 wt%, 3 wt% and 4 wt%, respectively. The similar k_0 values at different concentrations in a given orientation means that the phenol flux is proportional to the concentration gradient across the composite membrane and k_0 is independent of feed concentrations, which agrees with the classical solution diffusion theory [32]. In addition, the salt fluxes below 40 mg/m²h shown in **Fig. 4** demonstrate that the membrane remained defect-free and prevented transportation of salt and water across the membrane in both orientations.

Fig. 4. Experimental results of k_0 's and salt fluxes in an aqueous-aqueous extractive process as a function of phenol concentration in the feed: (A) PDMS selective layer facing feed (SL-F) orientation; (B) PDMS selective layer facing receiving water (SL-R_w) orientation.

However, it is worth noting that compared with an average k_0 of $9.8 \pm 0.1 \times 10^{-7}$ m/s in the SL-F orientation, the PDMS-PVDF exhibited a 15% higher average k_0 of $11.3 \pm 0.4 \times 10^{-7}$ m/s in the SL-R_w orientation, which could be attributed to the ICP occurring in this process. The phenomenon of ICP is due to the hindered diffusion, which causes the solute accumulation in a layer of the membrane adjacent to the separation layer, such as a supporting layer or a fouling layer [17]. As shown in **Fig. 5A**, in the SL-F mode, after the phenol transports through the free volume of dense PDMS from a feed solution, it needs to diffuse through the porous support layer to reach the bulk receiving water. The phenol would accumulate at the interior surface between the dense PDMS layer and the porous nanofibrous layer due to the diffusion resistance, which results in a phenol concentration ($C_{R,I}$) at the interior surface higher than that of the bulk receiving solution (C_R) and the surface layer on the support ($C_{R,S}$). This phenomenon is similar to the concentrated ICP

encountered in the forward osmosis (FO) process [33]. The stagnant phenol at the interface between the selective layer and the support layer can decrease the effective concentration difference (ΔC_{eff}) across the membrane, which consequently reduce the overall organic mass transfer efficiency in the extractive process. Similarly, ICP can also arise when the feed solution is placed against the porous support layer as shown in **Fig. 5B**. When the porous support layer of PDMS-PVDF is facing the high concentrated feed solution (SL- R_w mode), a dilute ICP can occur. After the steady state has been reached, the phenol concentration ($C_{F,I}$) at the interior surface between the nanofibrous support and the PDMS selective layer is lower than the phenol concentration of bulk feed solution (C_F) as well as the support surface ($C_{F,S}$). The diluted phenol concentration also reduces the effective concentration gradient (ΔC_{eff}) across the membrane, and influences the final overall mass transfer efficiency of the nanofibrous composite membrane.

Fig. 5. Schematic representation of internal concentration polarization (ICP) in (A) selective layer facing feed (SL-F) orientation and (B) selective layer facing receiving water (SL- R_w) orientation.

According to the Fick's first law [34],

$$J = -D \frac{dc}{dx} \quad (4)$$

where J is the diffusion flux ($\text{g/m}^2\text{s}$), D is the intrinsic diffusion coefficient (m^2/s), c is the concentration of solute (g/m^3) and x is the diffusion distance (m). The intrinsic diffusion coefficient depends on the temperature, viscosity of the fluid and the sizes of solute. In the case of constant diffusion coefficient, the diffusion flux of a solute is in direct proportion to the solute concentration difference. As shown in **Fig. 5**, as the feed solution possesses a much higher phenol concentration than the receiving solution ($C_{F,S} \gg C_{R,I}$), the diffusion flux of phenol within the nanofibrous support layer driven by $C_{F,S}$ in the SL- R_w mode should be much higher than the diffusion flux of phenol within the nanofibrous support layer driven by $C_{R,I}$ in the SL-F mode. The phenol concentration ($C_{F,I}$) at the interface layer in the SL- R_w mode could be replenished fast. Thus, the concentration loss ($C_{F,S}-C_{F,I}$) within the nanofibrous support in the SL- R_w mode seems to be less than the concentration loss ($C_{R,I}-C_{R,S}$) within the nanofibrous support in the CL-F mode. Consequently, the effective concentration difference in the SL- R_w mode ($C_{F,I}-C_{R,S}$) should be higher than that in the CL-F mode ($C_{F,S}-C_{R,I}$), which resulted in a higher average k_0 in the SL- R_w mode as shown in **Fig. 4**.

3.3 Evaluation of the nanofibrous composite membrane in EMBR

The targeted organics extracted from the feed solution need to be metabolized by the microorganisms in the receiving side of the EMBR. The biofilms developed on the downstream side of the membrane are critical to biotransform the organics and maintain the pollutant concentration in the receiving side at close to zero [35]. In this section, the

coupled effects of membrane roughness and hydrodynamic conditions on the biofilm growth and resultant membrane extraction efficiency in both CF-EMBR and S-EMBR configurations are discussed. In both EMBR processes, periodic sampling from the receiving biomedium showed that the phenol concentration in the bioreactors remained at zero, demonstrating that the biofilms accumulated on membrane surface and the acclimated biomedium in the bioreactors were capable of biotransforming the extracted phenol from the feed solutions. Moreover, non-observable feed volume change and the stable conductivity in the bioreactor (4.7 ± 0.4 mS/cm) imply negligible salt and water fluxes through the membranes. This demonstrated the stable structural integrity of the nanofibrous composite membrane PDMS-PVDF in long-term EMBR operations.

3.3.1 Effects of membrane orientations in a cross-flow EMBR (CF-EMBR)

According to **Fig. 6**, a sharp decrease in k_0 's can be observed within the first few days of CF-EMBR operations before approaching steady state after 7 days of operation. A similar declining trend can be observed in both SL-F and SL-R_{bio} orientations. The PDMS-PVDF not only exhibited higher initial mass transfer efficiency in the SL-R_{bio} mode, but also showed a less significant decrease of k_0 in this orientation. The stabilized k_0 's of the membrane after 14 days of CF-EMBR operation were $3.1 \pm 0.6 \times 10^{-7}$ m/s and $4.9 \pm 1.4 \times 10^{-7}$ m/s in SL-F and SL-R_{bio} modes, respectively, which were 32% and 42% of initial values. The significant reduction in k_0 's for both orientations illustrates that without controlling biofilm development, the excessive biofilms on the membrane surfaces would become the dominant mass transfer resistance in the CF-EMBR process. Nevertheless, the stabilized k_0 's in both orientations after 14 days of operation were still more than 3 times

higher than the k_0 exhibited by the commercial PDMS tubular membranes (1.0×10^{-7} m/s) [36].

Fig. 6. Long-term performance of the nanofibrous composite membrane PDMS-PVDF in the selective layer facing feed (SL-F) and selective layer facing receiving bioreactor (SL-R_{bio}) modes in the cross-flow EMBR (CF-EMBR) process: (A) overall mass transfer coefficients (k_0 's) and (B) normalized k_0 's.

Membrane autopsies illustrated that the composition of biomass accumulated on the rough micro/nano-beaded surface after 14 days of CF-EMBR operation in the SL-F mode was 0.29 ± 0.04 mg/cm² proteins, 0.08 ± 0.01 mg/cm² polysaccharides and 4.05 ± 0.31 mg/cm² total suspended solids (TSS). Meanwhile, the proteins, polysaccharides and TSS concentrations on the surface of PDMS selective layer after operated in the SL-R_{bio} mode for 14 days were 0.28 ± 0.02 mg/cm², 0.04 ± 0.01 mg/cm² and 3.91 ± 0.14 mg/cm², respectively. The polysaccharides amount was lower than that on the porous support layer surface.

Moreover, **Fig. 7** shows FESEM images of the membrane surfaces after removing the upper non-sticky suspended biofilms by manually shaking in DI water. As shown **Fig. 7A1**, a dense and thick biofilm layer consisting of cocci-shaped bacteria and extracellular polymeric substance (EPS) had fully covered the surface of the porous support layer. These coccus-shaped microorganisms which were firmly anchored on the surface created an interconnecting network structure connected *via* EPS (**Fig. 7A2**). The closer observation of these micro-clusters shown in **Fig. 7A3** indicates that these bacteria have pili or curli to promote the cell-to-cell, cell-to-EPS interactions and consequently promote their adhesion to the membrane surface. The dense biofilm matrix would result in greater mass transfer resistance in the SL-F mode. In contrast, **Fig. 7B1** clearly demonstrates that the number of micro-colonies on the smooth PDMS surface was significantly reduced. At high magnifications shown in **Figs. 7A2** and **7A3**, only few individual and small colonies of bacteria cells can be observed on the PDMS surface. The significant reduction of biofilm attachment in the SL-R_w orientation reduced the additional phenol mass transfer resistance from biofilms and enhanced the k_0 as shown in **Fig. 6**. This observation indicates that the membrane surface roughness is crucial for the biofilm accumulation in the CF-EMBR process.

Fig. 7. FESEM images of the membrane surfaces after 14 days of CF-EMBR operation: (A) mature biofilms composed of micro-colonies and EPS embedded on the porous support surface after operated in the SL-F mode; (B) individual cells and small colonies attached on the dense PDMS surface after operated in the SL-R_{bio} mode.

3.3.2 Effects of membrane orientation in a submerged EMBR (S-EMBR)

To control the biofilm accumulation on the membrane surface, the nanofibrous composite membrane PDMS-PVDF was operated in an S-EMBR configuration in both SL-F and SL-R_{bio} modes. The membrane surfaces in the S-EMBR system were continuously scoured by the up-flow of air bubbles. As shown in **Fig. 8**, the stabilized k_0 's in SL-F and SL-R_{bio} modes were $4.1 \pm 0.9 \times 10^{-7}$ m/s and $7.0 \pm 1.4 \times 10^{-7}$ m/s, which were 42% and 59% of the respective initial k_0 . Compared to the 32% and 42% normalized k_0 's obtained in the CF-EMBR, the k_0 's decline in the S-EMBR configuration is reduced by more than 10%,

indicating that the membrane scouring by air bubbles is effective in mitigating excessive biofilm development on membrane surfaces.

Fig. 8. Long-term performance of PDMS-PVDF in the S-EMBR process in both selective layer facing feed (SL-F) and selective layer facing receiving bioreactor (SL-R_{bio}) modes: (A) overall mass transfer coefficients (k_0 's) and (B) normalized k_0 's.

It is worth noting that the phenol mass transfer efficiencies of the nanofibrous composite membrane in the S-EMBR system increased in the first few days. A similar phenomenon has been observed in a single tube extractive membrane bioreactor and our previous work [22, 37]. The plausible reason is that at the beginning of S-EMBR operation, the extracted phenol solute needs to overcome the boundary layer resistance due to external concentration polarization (ECP), then diffuses to the biomedium in the bulk receiving solution. With the development of a thin, porous and active bacteria layer with negligible mass transfer resistance in the initial period of S-EMBR operation, the phenol extracted from the feed solution is able to rapidly biodegrade by the thin biofilm layer, which thus minimizes the boundary layer resistance across the membrane and enhance the overall

mass transfer efficiency. As the process proceeded, a thicker and denser biofilm layer gradually developed on the membrane surface, which resulted in greater mass transfer resistance and reduced the organic transfer efficiency significantly until reaching a steady state. As it is easier to control excessive biofilms on the surface of a smooth PDMS layer, a longer duration of higher k_o 's than the initial value was observed in the SL-R_{bio} orientation than for the SL-F orientation.

The amounts of proteins, polysaccharides and TSS on the membrane surfaces after 14 days operation of S-EMBR were examined. As a result of the effective biofilm control *via* membrane scouring, the proteins ($0.25 \pm 0.06 \text{ mg/cm}^2$), polysaccharides ($0.03 \pm 0.01 \text{ mg/cm}^2$) and TSS ($1.22 \pm 0.03 \text{ mg/cm}^2$) amounts on the composite support layer were significantly less than those on the same surface in the SL-R_w orientation after 14 days of CF-EMBR operation. Moreover, the concentrations of proteins, polysaccharides and TSS on the PDMS selective layer of the membrane after 14 days operation in SL-R_{bio} mode were significantly lower at $0.04 \pm 0.01 \text{ mg/cm}^2$, $0.01 \pm 0.004 \text{ mg/cm}^2$ and $0.43 \pm 0.15 \text{ mg/cm}^2$. Compared to the excessive biofilms deposited on the rough support surface after CF-EMBR operation, the combination of reduced membrane roughness and optimized hydrodynamic conditions have dramatically reduced the amount of protein by 86%, polysaccharides by 88% and TSS by 89%.

The surface morphologies of the nanofibrous composite membrane PDMS-PVDF after 14 days of S-EMBR operation were observed by FESEM as shown in **Fig. 9**. The mature bacterial micro-colonies consisting of multi-layer cells surrounded by EPS were developed on the porous support surface of the nanofibrous composite membrane operated in the SL-

F orientation as shown in **Fig. 9A**. In contrast, only individual bacterial cells were attached on the PDMS surface after operated in the SL-R_{bio} mode (**Fig. 9B**). Moreover, compared to the biofilm layer shown in **Fig. 7A**, a flat biofilm with more compacted bacterial cells were deposited on the support layer after S-EMBR operation (**Fig. 9A**). This might be attributed to the air bubbling, which had sheared off excessive biofilm from the membrane surface and resulted in a slightly more compact biofilm.

Fig. 9. FESEM images of the membrane surfaces after 14 days of S-EMBR operation: (A) micro-colonies with multi-layering cells and EPS on the porous surface after operated in the SL-F orientation; (B) Individual bacteria cells attached on the dense PDMS surface after operated in the SL-R_{bio} orientation.

3.3.3 Coupled effects of membrane roughness and operational conditions

The influences of membrane roughness and hydrodynamic forces on biofilms in both SL-F and SL-R_{bio} modes is conceptually illustrated in **Fig. 10**. The corresponding k_0 's and normalized k_0 's obtained in this study are also shown in this figure.

Fig. 10. Schematic illustration of the coupled influences of membrane roughness and hydrodynamic conditions on biofilm development in EMBR systems: (A) Accumulation of micro-colonies composed of multi-layering cells and EPS on the rough surface during the S-EMBR operation; (B) Attachment of individual cells on a smooth surface in the S-EMBR process; (C) Development of mature biofilms with micro-colonies embedded in a thick EPS matrix on a rough surface during the CF-EMBR operation; (D) Attachment of individual cells and small colonies with slime on a smooth surface during the CF-EMBR testing.

In general, the growth of biofilms on a membrane surface in the EMBR processes can be grouped into several key steps, including:

- (1) Formation of a conditioning film by an initial accumulation of physically adsorbed organic molecules, including proteins, polysaccharides and TSS;
- (2) With the assistance of conditioning film, a few pioneer individual bacteria cells settle and grow on the membrane surface and create a thin biofilm matrix. In this step, individual planktonic bacteria prefer to worm into cavities or valleys on a rough surface and create a secure mechanical lock by bio-adhesives (polysaccharides). The rougher a surface is, the easier it is to be adhered to by bacterial colonies. Thus, more biofilms tend to be developed on the rough and porous surfaces (**Figs. 10A and 10C**) than the smooth surfaces (**Figs. 10B and 10D**). Additionally, the anfractuositities on a rough surface are capable of protecting the microorganisms in these confined areas from external stresses, such as shear, abrasion and antimicrobial agents, thus making their removal extremely difficult. In contrast to the rough surface, it is more challenging for a biofilm matrix to stabilize on a smooth surface, which is demonstrated by the less biofilms and higher k_0 's of the nanofibrous composite membrane operated in the SL- R_{bio} orientation (**Figs. 10B and 10D**);
- (3) After primary colonization, the existence of a firmly attached microbial film provides sufficient nutrient and adequate environment to allow further propagation of secondary and tertiary colonization. In order to prolong their lives on a surface, the microorganisms could undergo a series of changes such as expression of a large quantity of EPS. The biofilms developed in this stage can exhibit complex 3D architectures. For instance, a network-shaped micro-colonies composed of bacteria

surrounded by a large amount of EPS matrix were observed on the support surface of the PDMS-PVDF after 14 days of CF-EMBR operation in the SL-F mode (**Fig. 7A** and **Fig. 10C**). Analogously, a relatively flat biofilm composed of compact bacterial cells embedded in EPS was developed on the support surface after 14 days of S-EMBR operation in the same mode (**Fig. 9A** and **Fig. 10A**);

- (4) After biofilm maturation, sessile cells are released into the planktonic state, which can spread and colonize on other surfaces. Many factors are responsible for the detachment of the mature biofilms, such as mechanical force and nutrient scarcity. The mechanism is cyclic as the liberal microbial cells attach to new surfaces and the same process continues. This biofilm disassembly was observed on the rough surfaces shown in **Figs. 7A** and **9A** during CF-EMBR and S-EMBR operations.

In addition to less mechanical interlocking due to a smooth and slippery surface of the PDMS selective layer, the silicone elastomer PDMS has been reported as an effective fouling release material [38]. It not only has a flexible backbone of Si-O to allow small organics (e.g. phenol) to diffuse through, but also possesses low surface energy side groups to minimize the adhesion between the microorganisms and its surface. Furthermore, due to a low elastic modulus of PDMS, the application of a mechanical/hydrodynamic force is able to deform the silicone surface and easily peel off the deposited biofilms from the surface [38]. Therefore, the biofilms deposited on the PDMS surface can be removed easily by the flow of biomedium solution during the CF-EMBR process or up-flow air bubbles during the S-EMBR operation.

Furthermore, in the SL-F mode, the severe internal clogging within the porous support by bacterial micro-colonies and EPS increased membrane resistance, exacerbated concentrated ICP, reduced effective concentration gradient across the membrane, and therefore resulted in the significant reduction of overall membrane mass transfer coefficients. This effect is akin to the fouling-enhanced ICP phenomenon encountered in the FO process [18].

3.4 Membrane comparison

The phenol mass transfer coefficients of the nanofibrous composite membrane PDMS-PVDF in the SL-R_{bio} mode are compared with other extractive membranes tested in the EMBR process in **Table 1**. In contrast to the commercial tubular PDMS membranes, a noticeable flux enhancement has been achieved, which should be attributed to a highly porous nanofibrous substrate and a thin PDMS selective layer [1, 6]. The membrane operated in SL-R_{bio} mode exhibited better performance than other reported nanofibrous composite membranes due to less biofilm accumulation on the surface of the PDMS selective layer [15, 22]. Thanks to the coupled effects of a smooth surface facing the bioreactor and a shear force on the membrane surface, a highest stable k_0 of 7.0×10^{-7} m/s in the S-EMBR process was obtained in this work.

Table 1. Phenol mass transfer coefficients of different membranes in EMBRs.

Membrane	EMBR process	Feed Side	Receiving side	Operation Time (h)	Stable k_0 ($\times 10^{-7}$ m/s)	Reference
PDMS tube	S-EMBR	1000 ppm phenol, 1 M HCl, 50 g/L NaCl		70	2.1	[6]
PDMS tube	CF-EMBR	2000 ppm phenol		336	0.5	[1]
	S-EMBR			336	0.8	
Nanofibrous composite membrane (SL-F)	CF-EMBR	1000 ppm phenol, 1 M HCl, 50 g/L NaCl		336	4.1	[15]
Superhydrophobic nanofibrous composite membrane (SL-F)	CF-EMBR	1000 ppm phenol, 5 g/L NaCl	Biomedium	288	3.9	[22]
	S-EMBR			288	5.7	
Superhydrophilic nanofibrous composite membrane (SL-F)	CF-EMBR			288	4.0	
	S-EMBR			288	5.0	
PDMS-PVDF (SL-R _{bio})	CF-EMBR	1000 ppm phenol, 5 g/L NaCl		336	5.2	This work
	S-EMBR			336	7.0	

4. Conclusions

The effects of ICP on phenol mass transfer efficiency of the nanofibrous composite membrane were investigated in this study. In the aqueous-aqueous extractive process, the membrane operated in the SL-R_w mode had a higher average overall mass transfer coefficient (k_0) of $11.3 \pm 0.4 \times 10^{-7}$ m/s attributed to less severe diluted ICP. In contrast, the same membrane operated in the SL-F orientation exhibited a lower k_0 of $9.8 \pm 0.1 \times 10^{-7}$ m/s at the expense of concentrated ICP. In addition, the biofilm development on membrane surface in the EMBR processes is strongly related with membrane surface roughness and hydrodynamic conditions. Autopsy data of the membrane after 14 days of EMBR operation indicated that mature biofilms prefer to develop on the rougher surface, since that the surface is able to afford more breeding ground for the bacterial population and protect them from external stresses. The excessive amount of biofilms clogged the support layer, exacerbated ICP and reduced membrane permeability, which consequently decreased membrane efficiency. Moreover, the scouring force from up-flow air bubbles in the S-EMBR configuration can effectively mitigate the biofilm amount deposited on the membrane surface. Therefore, the least amount of biofilms was observed on the smooth PDMS selective layer surface of the nanofibrous composite membrane operated in the S-EMBR system under the SL-R_{bio} mode, which achieved the highest stable k_0 of $7.0 \pm 1.4 \times 10^{-7}$ m/s.

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Abbreviations	
1D	one-dimension
2D	two-dimension
3D	three-dimension
AFM	atomic-force microscopy
CF-EMBR	cross-flow EMBR
DI water	deionized water
DMF	N, N-Dimethylformamide
ECP	external concentration polarization
EMBR	extractive membrane bioreactor
EPS	extracellular polymeric substance
FESEM	field emission scanning electron microscope
FO	forward osmosis
HPLC	high-performance liquid chromatography
ICP	internal concentration polarization
ICP-OES	inductively coupled plasma optical emission spectrometer
IPA	isopropyl alcohol
LiCl	lithium chloride
ORT	organic retention time
PDMS	polydimethylsiloxane
PET	polyethylene terephthalate
PVDF	polyvinylidene fluoride
S-EMBR	submerged EMBR
SL-F	selective layer facing feed
SL-R _{bio}	selective layer facing biomedium
SL-R _w	selective layer faces receiving water
TSS	total suspended solids

Nomenclature

A	effective membrane area (m^2)
C_f^0	phenol concentration in the feed at the beginning (mg/L)
C_f^t	phenol concentration in the feed at time t (mg/L)
C_F	phenol concentration of the bulk feed solution (mg/L)
$C_{F,S}$	phenol concentration at the membrane surface in the feed side (mg/L)
$C_{F,I}$	phenol concentration at the interior surface between the nanofibrous support and the PDMS selective layer in the SL-F mode (mg/L)
C_R	phenol concentration of the bulk receiving solution (mg/L)
$C_{R,S}$	phenol concentration at the membrane surface in the receiving side (mg/L)
$C_{R,I}$	phenol concentration at the interior surface between the nanofibrous support and the PDMS selective layer in the SL-R _w mode (mg/L)
J_s	NaCl flux ($\text{mg}/\text{m}^2\text{h}$)
k_0	phenol mass transfer coefficient (m/s)
R_a	surface roughness average (nm)
V_r	volume of receiving solution (mL)
Δc	variation of NaCl concentrations in the receiving solution (mg/L)
Δc_{eff}	effective phenol concentration difference across the membrane (mg/L)
Δt	time interval (h)