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Composite hollow fiber membranes with different poly (dimethylsiloxane) intrusions into substrate for phenol removal via extractive membrane bioreactor

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ABSTRACT

Due to its toxicity to ecosystem, phenol removal from industrial wastewater before discharge is a priority concern. Extractive membrane bioreactor (EMBR), a novel wastewater treatment process combining aqueous–aqueous extractive membrane process and biodegradation, has shown potential in treating phenol in wastewater. In this paper, composite hollow fiber membranes with different levels of poly (dimethylsiloxane) (PDMS) intrusion were prepared by coating a layer of PDMS on a Polyetherimide (PEI) hollow fiber substrate. Their applicability to EMBR for phenol removal was studied. The prepared membranes were characterized by microscopy and gas permeation test, and their performances were evaluated in aqueous–aqueous extractive membrane processes and EMBR process. The overall mass transfer coefficient for phenol, or k_0, was found to be significantly affected by the level of PDMS intrusion in the composite membranes. This is because the penetration of PDMS into the porous substrate results in a denser membrane structure, which consequently increases the membrane resistance. A slight penetration of PDMS into the substrate was found to be necessary for the composite membranes to achieve high k_0 while maintaining low inorganic flux across the membranes. Wilson-plot analysis suggests that membrane resistance dominated over liquid boundary layer resistances. After more than 250 h of EMBR operation, significant biofilm growth was observed on the composite membranes and the k_0 was dropped but stabilized at around 7.5×10^{-7} m/s. This k_0 was 7.5 times higher than commercial PDMS tubular membranes (without biofilm development) reported in previous studies, confirming the superiority of thin film composite membranes prepared in this work. It was also found that process optimization to control biofilm thickness is important in order to enhance phenol removal rate in EMBR.

1. Introduction

Phenol is an organic that often presents in wastewater of many industries such as chemical, pharmaceutical, petrochemical, and paint production industries [1]. Due to its toxicity to human and ecosystem even at low concentration, phenol and phenolic compounds are listed as a priority pollutant by United States Environmental Protection Agency [2]. Therefore, it is essential to remove phenol from wastewater before discharge using reliable and economically feasible technologies. Currently, methods used for phenol removal include traditional techniques such as steam distillation [3], liquid–liquid extraction [4], adsorption [5], wet air oxidation [6], and biodegradation [7], as well as advanced techniques such as electro-chemical oxidation [8], photo-oxidation [9] and membrane extraction [10]. Among these, biodegradation offers some advantages such as low cost and high energy efficiency. However, microorganisms can be inhibited by the toxicity of phenol at high concentration, making biodegradation suitable only for treating wastewater with low phenol concentration.

Extractive membrane bioreactor (EMBR), first proposed by Livingston, is a novel wastewater treatment process combining aqueous–aqueous extractive membrane process and biodegradation [11]. In EMBR, target organic pollutants transport through a non-porous membrane from the feed solution to the receiving solution by solution-diffusion mechanism, driven by the concentration gradient across the membrane; the organic pollutants are then biodegraded by specific microorganisms at the receiving side. Wastewater with inhibitory compounds and harsh conditions such as extreme pH and high salt concentration can be treated by

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this process as the bioreactor is separated with the feed solution by the membrane. In addition, the ongoing biodegradation helps to maintain low (or zero) organic concentration at the receiving side, maintaining the organic concentration gradient across the membrane as the driving force.

The membranes used in EMBR should have a high organic flux while being effectively impermeable to inorganics and water. Most commonly used membrane materials for this application are silicon-based rubbers such as poly(dimethylsiloxane) (PDMS) and poly(vinylmethylsiloxane) (PVMS) [12,13]. The Si–O units that comprise the PDMS backbone make it a highly flexible polymer and thus small molecules are able to transport through the free volume of PDMS. In addition, PDMS exhibits hydrophobicity and organophilicity, making it highly permeable for organic compounds [14,15]. However, phenol transfer rate across PDMS membranes has been found to be much lower compared with those of other aromatic compounds such as toluene, benzene, and monochlorobenzene [16,17]. This is due to the relatively hydrophilic nature of phenol that causes phenol to have a lower affinity to PDMS. Therefore, membrane resistance was reported to always dominate over liquid boundary layer resistances in the case of phenol extraction [11]. In most of the previously reported studies on EMBR, commercial silicon rubber tubes which had a thickness of at least 0.2 mm were used as the membranes for phenol extraction [11,12,17]. The large thickness of silicon tubes further increased membrane resistance to phenol transfer and thus limited the feasibility of removing phenol via EMBR.

A strategy to reduce the membrane resistance to phenol transfer is to prepare thin film composite membranes, which consist of a thin PDMS film as the selective layer and a porous substrate as the mechanical support. The use of PDMS composite membranes have been reported to significantly enhance organic transfer in other organic extraction applications such as aqueous–aqueous extractive membrane process and membrane aromatic recovery system [18,19]. However, the use of composite membrane and its systematic performance study in EMBR have not been reported so far. Therefore, for the first time, this paper discusses the preparation of thin film composite hollow fiber membranes to address the issue of low phenol transfer in EMBR.

When doing coating of PDMS on a porous substrate, one issue that often arises is the intrusion of PDMS into the pores of the substrate. While PDMS intrusion may help in enhancing the adhesion between the coating layer and the substrate, it also increases the membrane resistance. It has been reported that the mass transfer resistance of a composite membrane increases linearly with the PDMS intrusion depth [20]. Therefore, PDMS intrusion is normally undesirable and hence various techniques, such as pre-wetting of substrate pores by liquid and use of high-viscosity coating solution, have been employed to minimize it during coating [20,21]. In this work, PDMS was coated on Polyetherimide (PEI) hollow fiber substrate to prepare composite membranes, while membranes with different levels of PDMS intrusion were prepared for comparison. Through various characterization methods including microscopy, gas permeation test, and performance evaluation in aqueous–aqueous extractive processes, the efficiency for phenol transfer, structural integrity, long-term stability, and significance of membrane resistance/liquid boundary layer resistances of the resultant composite membranes were examined. Finally, selected membranes were subjected to EMBR operation. By carrying out the abovementioned studies, this paper aims to demonstrate the applicability of composite hollow fiber membranes to EMBR process and the importance of membrane optimization to enhance phenol removal while maintaining minimum salt and water flux.

2. Experimental

2.1. Materials and chemicals

Polyetherimide (PEI) (Ultems® 1000, M_n=12,000, GE Plastics) was used as the hollow fiber membrane material. A silicon elastomer and a curing agent were dissolved in an appropriate solvent to prepare the coating solution. Phenol (pK_a in water=9.95) was obtained from Sigma-Aldrich while NaCl, HCl (37%), and NaOH were purchased from Merck. $MgSO_4 \cdot 7H_2O$, KH_2PO_4, KH_2PO_4, $FeCl_3$, $CaCl_2 \cdot 2H_2O$, and NH_4Cl from Merck were used as the nutrients for biomedium, All the reagents were used as received. Deionized water (DI water) was produced from a Milli-Q® water purification system. High-purity gases including O_2 and N_2 were supplied by Singapore Oxygen Air Liquide (SOXAL). For experimental setups involving phenol solution, tubings and fittings made of Viton®, polytetrafluoroethylene (PTFE), or polypropylene (PP) were used to prevent phenol absorption.

2.2. Preparation of PDMS–PEI composite membranes

PEI hollow fiber membranes were prepared via dry-jet wet spinning technique as described elsewhere [22,23], and the membrane characteristics are listed in Table 1. Lab-scale hollow fiber modules were made by sealing 5 pieces of 20-cm-length hollow fibers in plastic tubing. Coating solution was then injected through the lumen side of the hollow fibers to create a PDMS layer on the PEI substrate. Different levels of PDMS intrusion were achieved on the composite membranes by changing coating conditions. The codes of prepared composite membranes (CI, PI-a, PI-b, and PI-c) were listed in Table 2.

2.3. Membrane characterizations

The cross-sectional and surface morphologies of hollow fiber membranes were observed using a field emission scanning electron microscope (FESEM) (JSM-7600F, JEOL). The membranes were broken in liquid nitrogen and sputtered with platinum prior to the test. The PDMS intrusion in the composite membranes was characterized by examining the distribution of silicon element at different locations along the membrane cross-section using Energy-dispersive X-ray spectroscopy (EDX) (coupled with FESEM). The contact angle of hollow fibers was measured based on the procedure mentioned in previous studies [24,25]. The contact angle for shell surface was measured by sealing the lumen using epoxy glue.

2.4. Gas permeation test

O_2/N_2 selectivity can serve as an indicator to check if the composite membranes are defect free. The setup for gas permeation test was similar to that described in the literature [26]. Feed gas flowed through the lumen of hollow fibers while the gas flow rate (100 mL/min) was controlled by a mass flow controller (Model 32907-63, Cole Parmer). The feed pressure was adjusted to 0.5 bar

Table 1
Characteristics of PEI hollow fiber substrate.

Parameter	Value
OD (μm)	1020 ± 8
ID (μm)	740 ± 9
Thickness (μm)	140 ± 4
Pore size (μm)	0.05 ± 0.01
Overall Porosity (%)	82 ± 1
Contact angle (deg)	77 ± 3